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Safety and Accident Prevention in Chemical Operations

ETC 03013

Safety and Accident Prevention in Chemical Operations

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Dedicated to the memory of
Will A. Shearon, Jr.
(1915–1963)

in tribute to his deep insight into the safety problems of the chemical industry, his many contributions as an editor toward the dissemination of chemical safety knowledge, and his never-failing support of chemical accident prevention.

ETC 03016

Foreword

Realities in Accident Causation

The popular present day concept of an accident is:

To the victim and his family ultimate tragedy,
To the witness a profound and horrifying experience which in time becomes a conversation piece,
To his company a preventable and irreparable loss of an employee,
To the public a news item,
To the legal courts an "act of God,"
To the government a statistic, and
To the nation a tragic, unnecessary loss.

Despite all one hears concerning this modern age, accidents are as preventable today as they were in the dim past when man would roll a stone over his big toe while securing his cave for the night. The safety engineer, as with all professional men concerned with the preservation of life and limb, has no illusions about defining an accident. To him an accident is a series of coincidental events whose climax results in personal injury, property damage, or both. He holds that these series of events are within the scope of human control barring an "act of God."

The successful safety engineer is not permitted the luxury of loose thinking and glib generalizations in arriving at his definitions. He can have no part of the alibi psychosis which today has become so much a part of human behaviorism that it is almost autogenetic. When he speaks of an "act of God," he is referring to an accident

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whose cause analysis failed to show in the series of events a contributory act of commission or omission on the part of any person.

The "act of God" accidents are rare, and many safety engineers are hard pressed to cite one such accident, even after many years of experience. Their very scarcity demands a descriptive comparison here. If a man is walking down the road under a clear blue sky and because of some freak of nature beyond our understanding or control he is struck by lightning and killed, the cause analysis can truthfully read "an act of God." If the same man continues gauging and sampling steel tanks as a thunderstorm approaches and he is killed by lightning, to the safety engineer this is not an "act of God" because the deceased, through an act or omission of an act, has contributed to the cause of his own death.

Understandably, the rigid interpretive definitions of the safety engineer often do not receive general popular acceptance, either by management or personnel. To ignore or discourage the best thinking of the safety engineer is as asinine as a patient offering his doctor an additional fee for a more favorable diagnosis. Following fatal accidents there is sometimes a tendency for those concerned to seek the cover of an alibi or even a false alibi, but no alibi or group of alibis can explain away that pathetic occupant of the morgue slab.

The natural tendency of our ever-present, highly developed defense mechanisms to taint our definition with alibis is a violation of the basic law of self-preservation. Such violations often make possible the series of events whose climax consists of an accident. If we create these series of events, they are within the scope of our control. In the field of accident prevention to be inaccurate in definition is to turn away from today's error only to come face to face with tomorrow's tragedy.

Cause Analysis

The lessons taught the injured (if he survives) and others concerned are the only items that may be entered on the credit side of the ledger when an accident is experienced. Safe practices, codes, standards, and regulations have not been created from the known laws of physics, chemistry, and physiology alone.

All safety codes and regulations bear the unqualified endorsement of the ghostly hands of industry's early accident victims. No executive, regardless of scope of authority or vastness of organization, can acquire a sound accident prevention program by merely giving orders. He can only initiate, guide, and support it. Safety programs that

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yield constant low-frequency and severity rates are the results of the co-operative efforts of all, from executive management to the newest employee. A prerequisite to successful cooperation is the realization that *safety is efficiency*. We cannot have one without the other.

All groups that make up the people of industry agree on the worth and desirability of safety's objective, yet solidarity is often lost when enforcement is necessary to insure attainment of an accident-free plant. It is not enough for management to provide safe facilities and procedures. There must be a fair and equitable discipline to maintain safe working conditions.

When deliberate safety violations occur there should be no compromise in discipline for the sake of expediency. Any such doubtful benefits acquired are but temporary and in their passing sow the seeds of destruction in the form of accidents, just as fixing a traffic ticket may contribute in a small but important way to the death of the next child killed on the highway.

One of the most important and necessary weapons in the war against accidents is the cause analysis. To be effective the method of analyzing the causes of accidents must be accurate, thorough, logical, impersonal, simple, and readily understood by all parties concerned. The type of cause analysis known as "the immediate cause and contributing factor" most nearly meets all the above requirements.

Accident investigation is seldom simple, but the less complicated the method used the greater the chance of uncovering the true causes in an acceptable manner. Many times the cause of the injury is erroneously given as the cause of the accident. A caustic liquid splashing into the eye is cause of the injury, but whatever circumstance permitted the liquid to leave its proper containment is the cause of the accident.

If the analysis is to be of use in accident prevention, logic must prevail. It is not enough to say that "while injured was climbing the ladder he failed to keep a secure grip on the ladder rungs" especially when the contributing factors reveal that the injured was carrying a section of hose over his shoulder and a bucket in one hand while climbing the ladder.

Repetitive use of the expression "the injured failed to do" this or that indicates either dishonest reporting or the failure of supervision to carry out its mission. If every employee always followed orders, there would be 75% less foremen in industry. The very act of bestowing the title of foreman is recognition of leadership ability, the ability not only to receive and properly give orders, but to see that the orders are carried out efficiently.

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Chronic employee failure is supervision failure. If there is a general sense of justifiable pride in the maintenance of a good safety record, then there must be a general acceptance of responsibility for a bad record. The safety engineer abhors the title of expert, reluctantly accepts the title of specialist, and he of all persons must "practice what he preaches."

A safety engineer [the author] once investigated an accident where an employee suffered a serious injury from a fall while descending stairs from tank tops to the ground. All conditions at the accident site appeared normal, and the safety engineer submitted a smug report stating in part "the actions of the injured were the greatest contribution to the cause." The very next day at the very same time a second employee was injured under identical conditions. This time a more thorough investigation revealed an unannounced change in processing which released deadly hydrogen sulphide gas in the area. This lack of interdepartmental communication changed a normally safe operation into a potential death trap. The safety engineer, when constructing his second cause analysis, gave as one of the contributing factors, "Failure of the safety department to properly investigate the previous accident."

When a series of accidents arises from identical causes, then supervision must bear an increasing proportion of responsibility for each succeeding accident. The theory of calculated risk, so necessary to competitive progress, must be limited to dollars and cents. Any attempt by supervision or employee to apply this theory to life and limb can only end in eventual disaster. The preceding statement is generally accepted as a matter of principle, yet in the daily score of industrial accidents, many are the result of ignoring this principle.

The overextension of equipment and inadequate maintenance by supervision, the departure from safe practices and regulations (the so-called short cut) by the individual employee are more common forms of violating this principle. Calculated risk to life and limb would be a small problem if those who did the calculating were the only persons exposed to the risk. Just as the navigator must know where he has been in order to plot the course to his destination, so too must industry know through proper analysis what caused the accidents of yesterday, how to insure maximum safety today, and how to plan intelligent accident prevention of tomorrow.

The Specter of Monotony

There are certain types of accidents whose causes remain the same through the years; only the victims are new. These causes have noth-

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ing to do with modern processes and advanced technology. They are the same causes that brought injury and death to our fathers' and grandfathers' generations. The plasterer who lost the sight of an eye from contact with quicklime, and his son, who twenty years later lost an eye while carrying out an unguarded ether distillation, are equally handicapped. The fact that the father went as far as the sixth grade in school and the son was a college graduate seems to have little or no bearing on the cause of their accidents. The father had seen fellow workers blinded while committing the unsafe act that cost him his eye, and the son understood well the peroxide instability that brought about his permanent disability. *Education alone* is not complete protection against this type of accident.

An experienced operator can reprimand a helper for not wearing goggles while drawing acid from a drum and the next day suffer severe burns while "rodding" out a plugged line with the valve open. *Experience alone* is not complete protection against this type of accident. The superintendent of a gas works was awakened by his wife during the night because she had detected a strong odor of gas in the house. He berated his wife for having turned on the lights in the presence of gas. Having made this contribution to his wife's education, he turned out the lights and in doing so blew up the house. *Technical knowledge alone* is not complete protection against this type of accident.

The safety man readily admits that all cause analyses contain the element of error, but the term error implies that judgment has been exercised whereas in many accident causes judgment is lacking entirely. The term, negligence, cannot be used as an overall description. Negligence smacks of deliberate neglect or mental and physical laziness. The courts of the land use the term, negligence, as a yardstick to measure the degree of responsibility. The word carelessness is inept, bearing as it does the connotation of "couldn't care less."

In the area of chronic accident causes the only term that can be applied to behaviorism that is otherwise an insult to our intelligence is "mental lapse." Mental lapse is often the prime mover that sets in motion the series of events that end in disaster. The causes of mental lapses can be varied and complex, but they all have one thing in common. They flourish in an atmosphere of monotony.

The expression "another day, another dollar" is a familiar form of acknowledging the impact of monotony on our daily lives. Most of us have a remarkably short concentration span even under ideal conditions. Distraction, the antithesis of concentration, usually arises from two general sources: external, such as noise and motion, and internal, the never ending thought processes that are the price of in-

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tellect. Through experience acquired from practice we develop industrial skill to a high degree as an individual, as a department, as a plant, and as an industry. This skill, absolutely necessary for safe operation, is not static in the sense that once attained, perfection results automatically.

In the field of accident prevention it is paradoxical that the most skillful are in the greatest need of additional skills. If a safety engineer arrives at that "predisaster" stage knowing all the answers, he becomes the epitome of hazards.

The rubber mill operator who has developed sufficient mental and manual dexterity to meet his work quota and daydream at the same time has not necessarily acquired sufficient skill to afford protection against accidents. He has succumbed to the influence of monotony, and the slightest change in repetitive function, either human or mechanical, can bring him face to face with deadly peril, as the rotation of the rollers hypnotizes the thought processes. The psychological sins of accident causation are monotony and complacency. The most deadly is monotony.

Since the turn of the century, industry has made the greatest progress in the history of mankind. We have turned from splitting wood to splitting the atom, adding immeasurably to our store of knowledge. Whether this knowledge will result in a better or a shorter life for us all only the future can tell. We do know with certainty that we cannot relax our efforts in accident prevention, for as members of supervision we are the custodians of a sacred trust; that is, the protection of life and limb. Just as the surgeon or the lawyer cannot let the element of monotony interfere with his daily life and death struggles, so we too cannot permit accident prevention to become monotonous. In this work we are fortified and inspired by the highest of ideals, but there is also a selfish motivation. The mortuary is the abode of pure democracy, and the accident we fail to prevent may be our own.

Alfred J. Gorand

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Preface

It is perhaps significant that no one has heretofore collected under one cover a treatise on safety in the chemical industry. The diversity of problems has caused most of the outstanding men in the field of chemical safety to specialize to a considerable degree, thus few candidates would be qualified to write a book covering the whole subject. We, the editors, likewise felt our incompetence, and for this reason we have tried to collect some of the best thinking of leaders in their respective specialties. We feel that herein is reflected the distilled wisdom and judgment of practical men and women who have made some phase of accident prevention their life work, and who have demonstrated over and over in their daily endeavors, that accidents can be prevented and controlled. This book is highly experimental It certainly is far from perfect, and the editors consider it only a first attempt to provide a useful reference for people involved with chemical safety. Hopefully it will encourage research and publication of further, needed information on chemical safety—perhaps another book.

Since effective control of accidental injury and property damage in chemical operations is based on such a broad spectrum of knowledge, the scope of this book is necessarily quite wide. Chemical safety requires the study of man in his industrial environment, considers the properties of the materials involved, requires exhaustive analysis of the chemical reaction or operation, and also covers the final packaging and shipping of the product in an acceptable manner. At any place in this chain, loss of control may lead to injury: from mechanical forces, from fires, from explosives, or from toxicity. These accidents in addition to injuring the worker, possibly causing permanent injury or even death, also constitute a financial loss. They delay the process and reduce the contribution that the industry makes to society. Losses due to accidents can be materially reduced by application of the principles set forth in this book. Each chapter discusses a phase of chemical safety with direct application in many operations. In-

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cluded are numerous literature references which will enable the reader to make a more thorough study than is possible here.

Even if this book were perfect, we concede that it would still not prevent all accidents, for, as we have tried to emphasize, we do not completely understand the human being who works surrounded by the bewildering array of tanks, pipes, valves, vessels, and pumps used in chemical operations. The more nearly we approach, biologically and psychologically, an adequate understanding of man, the more nearly we will find success in accident control.

Many whose names do not appear in print have supported and encouraged us in the preparation of this book. To these behind-the-scenes friends, we extend our sincere appreciation and gratitude.

To the supervisors in the chemical industry, to the designers of chemical equipment, to the safety personnel involved with chemical operations, to the management of chemical and related industries, we submit this book in the sincere hope that it will be a useful tool in helping to prevent injuries and losses due to accidents in chemical operations.

HOWARD H. FAWCETT
WILLIAM S. WOOD

Washington, D.C.
West Chester, Pennsylvania
December, 1964

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Safety and Accident Prevention in Chemical Operations

ETC 03029

1

Why Safety?

H. H. *Fawcett*

The prime purpose of business is to make money. To achieve this basic objective, needed goods and services are offered to customers at prices the customers can afford to pay, while the business still realizes a profit. Unless it is sufficiently profitable, the business is unsafe in the economic sense (and often in the personal injury sense as well), for profits are the usual method of financing research, development, new facilities, and new employment opportunities, as well as the health, safety, and fire protection programs. Furthermore, profitable businesses provide the support for the desirable noneconomic institutions of our society, including schools, churches, government, and the arts.

In operating a business profitably, a careful balance must be maintained to insure that four groups are properly serviced, namely, the owners (investors or shareholders), the customers, the employees, and the suppliers. Any imbalance in the relations with any group can adversely affect the business health.

The chemical and related industries occupy a key position in the economic life of the nation. The wide variety of chemical compositions and their finished forms, ranging the periodic chart from hydrogen to transuranic, is available in literally hundreds of thousands of mixtures and compounds. This variety constitutes a major supply house from which the chemical industry and all other industries can easily obtain new and better substances, or improved properties in older, more familiar products. Whole new industries have grown and continue to

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grow from laboratory experiments, properly developed and backed with the required capital investment. The chemical industry supplies a wide spectrum of products, which find their way into a wide range of human activity. Even life itself may be considered in terms of a series of chemical reactions—certainly chemicals, in the form of air we breathe, water and other beverages we drink, and food we eat, are essential to sustain and promote life.

Since the chemical industry plays a vital role in our economic structure (even though much of this support is not obvious in the finished consumer product), the profitable performance of the chemical industry becomes of vital concern far beyond the industry itself, since the supply as well as the price of chemicals is involved. A chemical plant that suddenly becomes a pile of twisted rubble or a crater in the ground cannot produce on schedule. Any factor that is an unnecessary cost, or economic loss to the chemical industry, must be borne in higher costs, and hence higher prices, paid by the customers in many other industries. The full cost of accidents is never completely covered by insurance, and never absorbed directly into operating expenses—ultimately this cost raises the selling price and is passed on to consumers. For that reason, and many others, chemical safety can be an economic aid to a far wider field than chemical industry (Fig. 1.1).

As used in this book, safety will be defined as a positive, organized activity or program based on knowledge of the reaction between man and his working environment, which aids business enterprise by minimizing human, economic, and sociological losses caused by injuries, health impairment, fires, explosions, and other occupational accidents. It should be noted that this definition is both positive and dynamic, and does not depict safety as a passive obstructional activity that prevents constructive and profitable operations, but as an activity that aids them.

A second objective of business, which may be considered an adjunct to profitability, is efficiency. In the chemical industry, many operating and supervisory positions are both specialized and complicated, hence, requiring a high degree of training and experience to achieve the maximum production with safety. If an accident of any type occurs, in which a highly trained employee is injured, the equipment damaged, or the product rendered scrap or substandard, another employee must be trained and repairs made, but frequently at a price in operating efficiency. In the technical areas, specific formulations and scientific know-how of a chemist or technician may be vital to the efficient functioning of the enterprise, and serious losses may occur if he is incapacitated by injury or disease.

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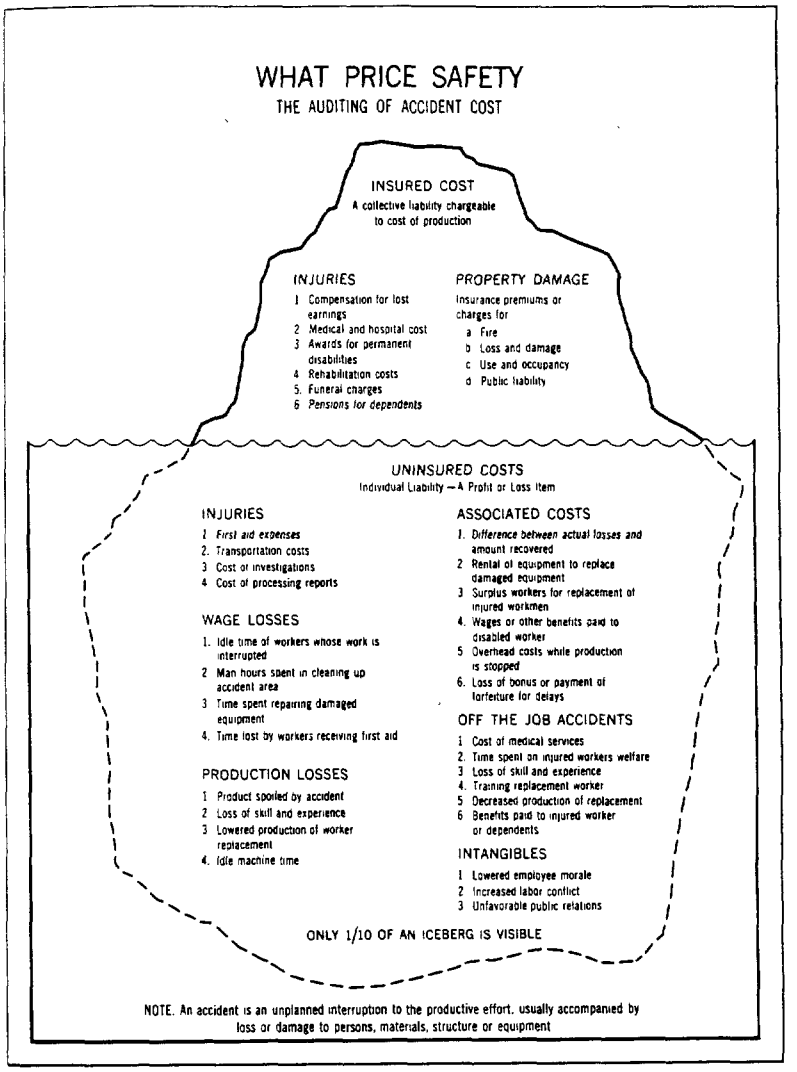

FIG. 1.1. Insurance often is only a partial answer. *Source:* Workmen's Compensation Board of British Columbia.

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A third factor, closely related to economics and efficiency, is the human aspect. An ethical business, whether large or small, must have a proper consideration and respect for its employees, or it will soon have high labor turnover, a bad injury experience (and hence excessive compensation and medical costs), and poor morale. If an organized union exists in the plant, it will become increasingly vocal in its demands for better conditions and job security, as well as higher wages. Business is not expected to be a benevolent fraternity, but it is not successful if run in the spirit of the "bull-of-the-woods" foremanship widely publicized a generation ago. Employees work best when they are led (not driven) by superiors in whom they have respect and trust, and who treat them with the dignity and understanding which is, after all, only a reflection of a human being. Regardless of the size of our income or the title of our job, each of us is responsive to proper treatment, and reflect it in the zeal, loyalty, and quality of our work.

Closely related to the human aspect is the public relations consideration. A company image, like company integrity or company stability, is the hallmark of a successful business. The public, which extends far beyond the neighbors who live on the opposite side of the plant property line to the residents of the county, the state, and the nation, eventually form an opinion as to whether the company is a "good place to work" or a "place to avoid." If frequent accidents result in ambulance calls to the plant, if fires and explosions light up the night sky, if the news media, barred from the plant during an emergency, flash radio, television, and newspaper reports that are inaccurate and misleading, the public relations will suffer, regardless of the subsequent favorable facts that might emerge. The public, unfortunately, quickly forgets publicity regarding safety awards (perhaps because it expects a business to run its affairs without injuries), but will note in all detail reports of accidents, injuries, fires, explosions, misplaced radioactive sources, tank cars that overflow or leak, or clouds of smoke, fumes, or dusts. Favorable public relations cannot be bought—it must be earned—and a safe operation, properly managed over the years, will greatly assist in earning it.

Another major reason for safety activity is in the legal area. An amazing number of laws, codes, edicts, and regulations have been enacted by all levels of government, from the town or city through the county, state, and federal. Some may have specific requirements in clear numerical terms, such as the regulation of the Federal Aviation Agency regarding a certain-wattage lamp in a special red globe atop a water tower or smokestack located a certain distance from an airport runway. Others are less obvious, as the parts per million of

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various substances permitted in an effluent discharging into a river or a bay (usually a state or local law). Many companies have legal consultants who can cite appropriate laws and the penalties for noncompliance.

Directly affecting chemical industry are the state workmen's compensation laws and the Walsh-Healy Public Contract Act.

Workmen's compensation laws have been enacted since 1911 in all fifty states, Puerto Rico, and the District of Columbia. In addition, there exists the Federal Employees' System and the Longshoremen's and Harbor Workers' Systems. These laws differ widely in their content and in methods of operation. The recent studies published from the Research Program of the Institute of Industrial Relations, University of California, have aired both the differences and the inadequacy of the various laws in achieving their original objectives. The present confusion that an injured employee must face when seeking economic recovery from work injuries is a strong argument for accident prevention, though it is seldom mentioned.[1, 2]

The Walsh-Healy Public Contract Act, Health and Safety Standards (41 CFR 50-204) are intended to improve the safety of the industrial environment for plants that have government contracts in amounts over $10,000. These physical control measures, which range from specification of the size of stair treads to the concentration of dusts, vapors, and gases permitted in the air, may be helpful in improving the safety of the physical facilities, but they are only one relatively small step forward, since they neither specify nor encourage any higher safety standards of performance by the *employee*, and they reward neither employer nor employee for superior or even perfect safety achievement. It is hoped that from the present discussions about these standards will evolve a better program of achieving the stated objective—namely, injury prevention—with more attention directed to the *human* and less to the *physical* aspects than reflected by the current regulations.

The chemical industry, as reflected by the injury rates reported in Fig. 1.2 by the National Safety Council, is one of the safer industrial groups, and its frequency and severity rates are much more favorable than the average for all industry.[3] When we consider the potential hazards in the manufacture of thousands of substances from high explosives and rocket propellants to newly synthesized esoteric compounds whose properties are unknown even to the research chemist who created them, the safety record is outstanding.[4]

This relatively favorable safety experience did not just happen. As shown in Table 1.1, during forty years the frequency rate in the chemical industry for all disabling injuries was reduced from 24 to slightly

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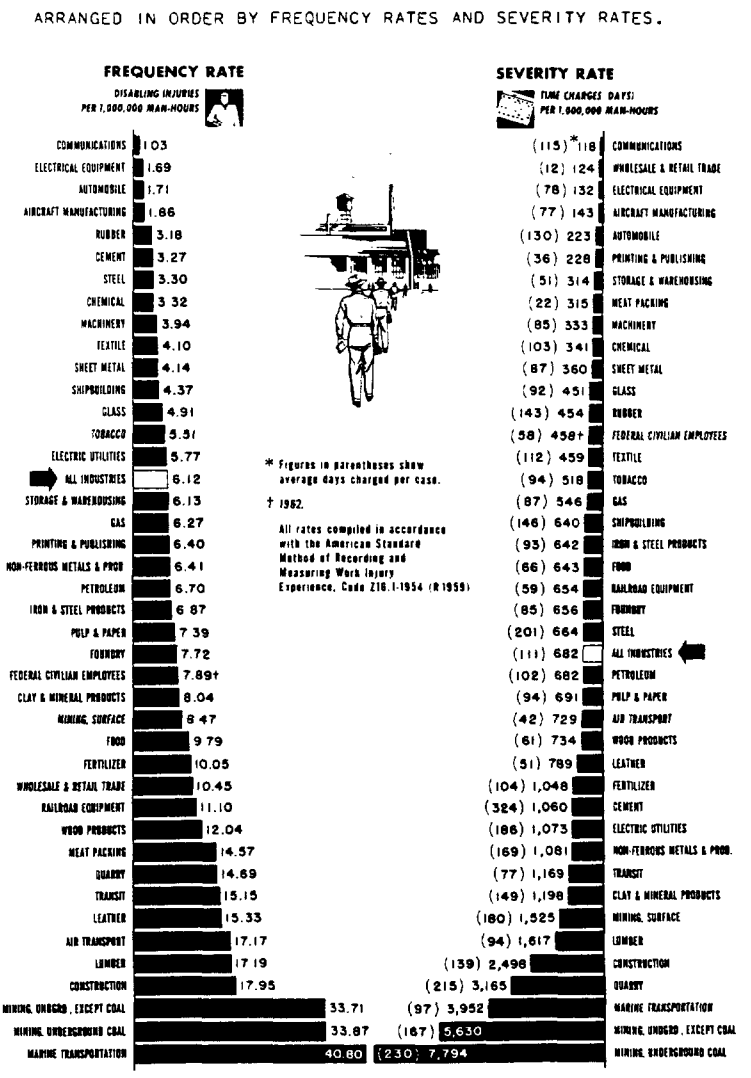

FIG. 1.2. 1963 Injury Rates, reporters to National Safety Council. *Source: Accident Facts,* 1964 Edition.

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TABLE 1.1. Chemical Industry Injury Rates

		Injury Rates					*Average Time Charges (Days) Per Case*		
		Frequency							
Year	*No. of Units*	*Fatal*	*Perm. Partial*	*Temporary Total*	*All Disab. Injuries*	*Severity*	*Perm. Partial*	*Temp. Total*	*All Injs.*
1923	13	.61	.55	23.39	24.55	4780	1425	14	195
1924	30	.33	1.30	24.50	26.13	3070	544	15	117
1925	65	.31	.69	19.91	20.91	2710	821	15	129
1926	108	.25	.72	17.29	18.26	2280	644	17	125
1927	143	.19	.61	16.38	17.18	1900	834	17	111
1928	162	.23	.64	18.78	19.65	2080	635	15	106
1929	172	.18	.68	16.64	17.50	1720	548	15	98
1930	211	.17	.88	14.45	15.50	1940	777	15	125
1931	238	.20	.72	11.73	12.65	1840	635	17	146
1932	266	.23	.65	9.65	10.53	1920	538	17	182
1933	245	.18	.64	9.64	10.46	1670	647	17	159
1934	254	.21	.66	9.43	10.30	1810	572	18	176
1935	282	.09	.68	8.76	9.53	1030	469	19	108
1936	305	.11	.57	9.55	10.23	1180	667	17	115
1937	323	.13	.61	9.49	10.23	1290	591	16	126
1938	307	.13	.51	7.29	7.93	1230	543	20	155
1939	417	.13	.56	6.79	7.48	1260	616	19	169
1940	419	.33	.57	8.25	9.15	2530	697	19	276
1941	434	.12	.63	8.73	9.48	1300	650	18	137
1942	475	.15	.48	9.27	9.90	1290	469	17	131
1943	575	.12	.47	9.48	10.07	1120	562	17	112
1944	551	.08	.52	9.64	10.24	910	454	18	89
1945	567	.10	.57	9.41	10.08	1060	482	21	105
1946	598	.07	.53	9.49	10.09	860	489	18	85
1947	563	.09	.44	8.33	8.86	920	441	19	104
1948	569	.09	.46	6.96	7.51	900	462	19	119
1949	545	.05	.48	5.19	5.72	600	433	23	106
1950	520	.08	.37	5.37	5.82	760	446	24	131
1951	573	.09	.32	5.07	5.48	850	654	24	155
1952	659	.04	.41	4.65	5.10	550	456	22	108
1953	851	.09	.33	4.11	4.53	810	465	25	179
1954	900	.05	.31	3.76	4.12	570	582	24	138
1955	953	.05	.31	2.85	3.77	604	445	26	163
1956	1000	.04	.27	3.07	3.38	462	450	25	137
1957	1005	.05	.33	3.17	3.55	536	367	28	151
1958	1024	.06	.26	3.24	3.56	552	428	28	155
1959	1025	.05	.22	3.05	3.32	495	387	29	149
1960	1073	.06	.25	3.40	3.71	538	384	30	145
1961	973	.03	.26	2.97	3.26	392	421	27	120
1962	974	.06	.24	3.01	3.31	532	309	28	161
1963	1056	.03	.25	3.04	3.32	341	273	27	103

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over 3; at the same time the severity rate was reduced from nearly 4800 to about 550. It is interesting to note that the number of units (plants, laboratories, and companies) reporting increased from 13 to nearly 1000—a reflection of the growing awareness and interest of the role of injury control in efficient operations. A sincere attempt to share experiences voluntarily, reflecting both favorable and unfavorable operation, has given the chemical industry an advantage over many industries where the knowledge is simply filed away and kept as classified data.[5]

This book reflects the spirit of sharing information about accident prevention. We hope this book will serve as a seed crystal to encourage even greater cooperation designed to achieve greater control of accidents.[6, 7]

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2

Who Makes Safety?

H. H. Fawcett

In addition to being a financial and legal problem, as noted in Chapter 1, safety (including health and fire prevention) is a very personal problem, and herein lies the all-too-often overlooked secret to accident prevention. Injuries occur to a *person,* and, regardless of the agency producing the injury (chemical, electrical, mechanical, radiological, or bacteriological), the method by which the agency acted, or the sequence of events, the one common denominator in all injury mathematics is one *person*—a human being—Homo sapiens.

To control injuries, then, we must resist the temptation to write a manual or set of safety rules, issue a statement signed by a corporate official or works manager supporting the safety effort, and then complacently and passively sit back to await the day that injuries stop so the payroll department can mail "lack of work" notices to the medical staff, and plant engineering can convert the dispensary or plant clinic into more productive facilities. Accident prevention is not that simple. If it were, injuries would have largely disappeared from the industrial scene years ago, for many companies, both large and small, have approached the problem with the viewpoint that they have established rules, and hence, have solved the problem of accidents for all times. One fundamental fact has been largely overlooked. The very person with the most to lose by injuries—a man—is the weak link in the chain of the safety movement.

The above paragraph should be construed in no way as casting doubt on the importance for safety to start at the top of the organization

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structure. Unless the chief executive officer, whatever his title, is convinced that injuries, fires, explosions, and impairment to health of employees and the public are not only undesirable but are subversive to the financial health of the company, and hence justify positive aggressive measures to control or eliminate these losses (which are never completely covered by insurance, no matter how comprehensive the insurance coverage might seem), it is futile to propose or promote accident prevention at the lower echelons of management. Furthermore, the chief executive officer must let it be known that he expects the same attention given to control of accidents that he expects in control of sales, budgets, scrap, overtime, absenteeism, and expense accounts; and that he will hold lower management responsible and accountable for adequate control of injuries, fires, explosions, and impairment of health. He expects the accident prevention activities to have more than lip-service or to be more than a gesture. A clear statement must be made, such as the Basic Rule of Responsibility of the United States Navy: "Safety is a command function. Responsibility for the safety of personnel is vested in the commanding officer. Because these safety precautions apply only to usual conditions, commanding officers or others in authority may find it necessary to issue special precautions to their commands to cover local conditions and unusual circumstances. In addition to the posting of appropriate precautions, careful instruction and indoctrination of all personnel are necessary to insure effective compliance with these precautions."

It is usually agreed that a safety policy should exist that offers clear-cut guidance for all members of a company, that expresses formally the company safety position and its safety program, and that specifies responsibility in accident prevention throughout the company.

The concept of organized cooperative safety, currently understood in the United States as organized control and prevention activity, began in 1912, when the National Safety Council was formed at a meeting in Milwaukee. The chemical section of the council was formed in 1916. The Safety Committee of the Manufacturing Chemists' Association held its first meeting in 1925. Individual chemical companies had long before instituted very effective and highly specialized approaches to safety. When the black powder mills were built on the banks of the Brandywine River in 1802, both workers and owners lived near the operations with their families, hence insuring a direct interest in safety for purely personal reasons. However, the fact is that the full impact of the safety movement has yet to be felt—in fact, it may be decades before the concept of accident prevention becomes both an industrial and a household reality. We may never fully achieve the ideal stated

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by Professor Albert Einstein, while addressing an audience at the California Institute of Technology in 1938:

> Concern for man himself and his fate must always form the chief interest of all technical endeavor. Never forget this in the midst of your diagrams and equations.

This does not suggest that we should be unrealistic in filling our obligations to society, and in achieving economic advantage for ourselves and our employers. It does, however, present a moral and ethical guide, without which both the economy, and ultimately our society, will destroy itself, both collectively and individually.

As suggested above, policies, edicts, rules, and procedures regarding safety will not prevent injuries by themselves. They must be the blueprint or pipeline that carries the vital thoughts to a man. We believe that *man*—as an individual—is the weak link, in spite of the obvious fact that it is man who has the most to lose by injuries. We have concluded:

1. Man, as a group or as a type, does not exist, except statistically. He exists only as a single person, one human wholly unique, different, and peculiar. His background, environment, education, drives, ambitions, and outlook establish his individual nature. He is not constant for more than a few seconds at a time, for he is continually changing his actions, his thoughts, his desires, and his objectives. His biology, as well as his emotions, range far wider than even he realizes. Sweeping generalizations about "man" will usually fall short when applied to a single person, for he will usually differ considerably from the norm or average. Statistics are useful tools or measuring devices, but the basis of the statistic must never be overlooked.

2. Man is not truly concerned about safety, *per se*. In the native preconditioned states, man cares little or nothing about the plant safety record or whether it wins an award for safety. He is not always primarily concerned about living forever or about self-preservation—two ideas frequently advanced as why man should be naturally interested in safety. There is adequate documentation of the fact that some injuries, both on and off the job, doubtlessly are motivated, inspired, or at least closely related to mental pressures that overwhelmed the person for the immediate moment. Each man, regardless of his social or economic station in life, has an Achilles heel, which is his personal mental breaking point, as the Communists have demonstrated with their "brain-washing" techniques, and as a study of suicides will suggest. Unless the accumulated pressures of life have some vent—and

the relief may be as simple as talking to a friend, either real or imaginary (as in *The Listener* by Taylor Caldwell)—man may be driven to highly irrational conduct which may be misinterpreted as an "accident." Doubtlessly the brain fails or "blacks out" at critical moments in industries, and elsewhere mental lapses or other forms of preoccupation may explain accidents which "should never have happened because he knew better."

3. Man is vitally concerned with his own self-interests, whatever they may be. The frank question, "What's in it for me?" cannot be ignored or glossed over lightly. Financial reward is only one of many interests, and in appealing to a man in terms of safety, it will be found he, in turn, will accept or reject the safety message in terms of how he relates it to his own objectives and goals (either expressed or subconscious).[1] If man *thinks* something affects him, even indirectly, he will be interested; if he *believes* he can "profit" by the message he will read or listen; but, if he is *convinced* that the story is of vital personal concern to his economic welfare, his health, his happiness, his family, or to his ability to achieve his short-range objectives, he will sit at your feet and absorb every word. Note the words *thinks*, *believes*, and *convinced* in the previous sentence. These three words represent crude measures of the degree of safety acceptance. If we are to achieve accident control, it must be by inspiring or diffusing into every man on the payroll—from the chief executive officer to the humble but vitally important night watchman, the undisputed fact that safety is vital to *his* personal interests, and that it will return him more in benefits than he invests in time, money, and thought. Safety is a blue-chip investment for an *individual* as well as for a *company*.

4. Safety must become a philosophy of life for each person, and must ultimately precondition each action, even in the subconscious state. As a popular slogan goes, "Knowing is not enough." Safety is not an esoteric subject, brewed up by do-gooders in unrealistic batches and spread like an unwelcomed plague to unconvinced man. Rather, it is the distilled essence of the lessons learned from thousands of deaths, from millions of injuries, and from billions of manhours of exposure.[2] If, as Abraham Lincoln once said, it is disgraceful to fall over the same log twice, it is even more disgraceful to permit accidents to recur simply because we have not instilled the potion into the eyes at the right instant to permit man to see properly. Puck said, "What fools these mortals be," but mortal man can act wisely as well as foolishly, if he is given both the knowledge and motivation he needs. Man, the only product of creation who can think creatively and modulate to conform to his moral and social orientation, must now be

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encouraged to actually follow safety rules because he believes in them, and respect standard operating procedures because he knows they were written for his best interests. He must become his brother's keeper in matters of safety, and sincerely believe, "I'm for safety because it is good for *me*." The *me* is used in the personal sense, but also implies the wide meaning of *me*, inasmuch as a man's contribution to his employer, and hence to society, is also a vital part of his self-interest.

Perhaps by another generation, we will have achieved that infusion into the minds and hearts of our employees—from top to bottom in the organization, and eventually achieve the goal of "Profitable Production Without Accidents." Then, safety, while not first, will have achieved its proper recognition as a dynamic force for progress, both for the individual, his employer, and society.

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3

Organized Labor's Interest in Safety

Elwood D. Swisher

"The conditions were unquestionably bad. In 1906, the year of the 'Pittsburgh Survey,' there were 526 industrial fatalities in Allegheny County, Pennsylvania. A trainman had one chance in 127 of death by accident in any given year. There was also plenty of outraged public opinion." I quote briefly from Chrystal Eastman, Secretary of the New York Commission, on employers liability and causes of industrial accidents.

We can set up a good argument for the other side of this picture. It is still true that at the time of the enactment of the first compensation law in 1911 in New Jersey, one-fifth of the litigation at the state court was concerned with liability for damages as a result of industrial injuries.

Today countless hours are spent before State Industrial Commissions or Workmen's Compensation Hearings on behalf of injured workers or the widows of those who died as a result of accidents occurring on the job. These hearings are further complicated by the increasing number of occupational diseases arising out of the increased number of toxic materials being used by industry today, and the worker is hampered because many states have failed to keep pace and update their lists of occupational diseases.

The first principle of any union is the general welfare of its mem-

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bers. A paragraph from the Preamble of the Oil, Chemical and Atomic Workers International Union Constitution states:

> It shall be the object of this Union to establish and maintain collective bargaining for the benefit of the workers within its jurisdiction and to conduct a neverceasing effort to secure just compensation for the Workers, reasonable hours of toil, and working conditions conducive to safety, good health and full enjoyment of life.

In this fast moving age, concern over safe working conditions is just as acute, if not more so, than at the turn of the century. At this point, tribute should be given to the many, many companies, who with a sense of deep consciousness, carry on well-rounded safety programs, both on the job and off the job. It is to their credit that we have fewer injuries and deaths than we would have otherwise. On the other hand, we still have too many companies who are callous in their concern for the safety of their workers.

Generally these latter interests are in the forefront at the state legislature fighting any improvement in their state safety laws or codes, and opposing improvements in workmen's compensation. They are the ones who help take the public's mind off good safe practices by stressing the fact of payments to injured workers under workmen's compensation. They are even opposed to acceptance of the American Standards Association safety recommendations, which are recognized as a minimum only, to be included in a state safety law or code. It is for these reasons that unions are finding it ever necessary to continue to strive for improved health and safety programs.

A survey in 1956 by the State of California titled "Think of the Dependents" starts by saying:

> You cannot measure the results of work injuries and deaths in dollars and cents only.
>
> You cannot measure the results in loss of production only, either.
>
> All the statistics in the world are of little consolation to a child who has lost his father, or a wife, who has lost her husband.
>
> California workers who died from on the job injuries in 1956, left 1781 dependents as follows: 966 Children, 651 Widows, and 164 other dependents.
>
> Of California workers who died from on the job injuries in 1956, nine out of ten had dependents, eight out of ten had wives, five out of ten had children under eighteen years old. Of the 651 widows, 382 had children, 259 had two or more children, 131 had three or more children and 59 had four or more children.

You might ask, "What steps are the unions taking to promote safety?"

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The AFL-CIO Standing Committee on Occupational Safety and Health has conducted a series of 120-hour courses at their headquarters in Washington, D. C. for international union leadership. They have also conducted courses at an area level to get a broader participation of local union leadership to improve safety education.

International unions and state and local central bodies are continuously holding summer schools devoted entirely to on-the-job and off-the-job safety. The AFL-CIO Standing Committee continues to put out pamphlets urging international unions and local unions to step up their activities in safety programs.

This is augmented by international as well as local union participation in the Labor Conference of the National Safety Council.[1] The efforts of the Labor Conference of the National Safety Council can best be summed up in the safety policy and program recommended for adoption by international and local union organizations. Only the Resolve itself is quoted:

THEREFORE BE IT RESOLVED,

THAT, each International Union establish a Safety Department with full time personnel. It is further recommended that the Safety Department be an independent department within the structure of each International Union subordinate to no other department, but rather a direct responsibility of a designated International Officer of each International Union.

THAT, each International who has not already done so, establish a policy of requiring a Safety Committee as a mandatory committee for each and every Local Union under their affiliation with provision for same in their respective constitutions.

THAT, all International Unions be urged to negotiate Safety and Occupational Health clauses in their contracts and seek to implement such clauses through joint labor-management committees.

THAT, each International Union urge their affiliated Local Unions to take out membership in the Labor Division of the National Safety Council.

THAT, each International Union establish a library of Safety films, pamphlets and posters as part of their Occupational Health and Safety Department and provide for the education of its members through the media of Region conferences, Summer Schools and any other means at their disposal.

RECOMMENDATIONS FOR LOCAL UNION SAFETY AND OCCUPATIONAL HEALTH COMMITTEES.

1. THAT, each Local Union select a committee to suit their own needs; depending on plant size.
2. In the case of joint labor-management committees, equal representation from both labor and management, with the union members to be selected by their local unions.

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3. THAT, safety Committee members be allowed to participate in plant safety inspections along with management.
4. THAT, they shall have the right to investigate plant accidents and make recommendations on any and all existing hazards.
5. THAT, the International Unions' Safety and Occupational Health personnel shall have the right of entry into plants for the purpose of investigation of existing hazards.
6. THAT, the committee be able to study all accidents and health records and recommendations of state factory inspectors.
7. THAT, Local Union Safety and Occupational Health Committees conduct an intensive educational program amongst their membership utilizing the media of press and the facilities of their respective International Union Safety Departments.
8. Because of the inadequacy of State and Federal Safety and Occupational Health Laws, that all future contracts contain safety clauses that require that American Standards Association Safety Codes be used as minimum requirements for Safety and Occupational Health.

One of the biggest problems in a good safety program is obtaining the worker's sense of responsibility to obtain the habit of good safety rather than the habit of poor safety. This, often times, becomes a most arduous task because of the difference in principle practiced by various companies in their safety programs.

All too often we hear workers say, "Our company's motto is safety first, so long as it doesn't interfere with production." This expression becomes understandable when you find a group of workers representing various companies gathered together in a safety school during open discussion.

Expressions, such as the above, become meaningful and understandable as the reasons come to light. Simply, it boils down to this: Company *A* and others who fall into this category, have acceptable and well balanced safety programs and a qualified staff of safety engineers. However, the safety engineer has only an advisory capacity. If a worker or workers complain that a job is unsafe and the safety engineer shares the workers' opinion he can only recommend that the job be discontinued until corrected, but the production supervisor makes the final decision and says, "production must go on, the job will be corrected on another shift." This then starts the doubt in the worker's mind. On the other hand, Company *B* and other companies who fall in this category, have an entirely different approach. There may be no difference in the safety program or the quality of the safety engineering staff; however, when a worker complains of an unsafe working condition and the safety engineer is in agreement, he has the authority under this system to shut down the job immediately and

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effectuate remedial action. This gives the worker a lift and a greater degree of confidence.

We can see from the above the frustration of instructors conducting safety schools in industrial unions such as the Oil, Chemical and Atomic Workers International Union. There are other irksome incidents that contribute to poor safety habits. There is the overzealous foreman (who probably never developed safety habits) who jumps in with a flurry to demonstrate to a worker how he possibly could speed up his job. This is impressive, especially to a new worker who does not stop to think that the foreman is not going to perform this job 8 hr a day, and the worker later comes up with an injury or at worst, his widow's grief.

Then we have the same type of foreman, who without safety goggles, mask, or other protective clothing, where called for, jumps into a dusty, toxic or otherwise dangerous area, and for a few brief moments sets the world on fire in a demonstration to the worker or workers on how the job should be handled. The foreman knows he is not going to be working in and around this dust for the full eight hours, day in and day out.

In the atomic energy field we have the same type of foreman, who wipes up his fingers full of alpha contaminated dust and eats it off his fingers in order to prove to the workers that the area in which they are working is not dangerously radioactive and, therefore, they shouldn't be concerned if the monitoring of the area has become haphazard. We wonder what this individual would do if he were made to do this 8 hr a day, 40 hr a week, and 50 weeks out of the year. But we would agree that his attitude would change.

It is difficult to understand such individuals as foremen, and therefore supposedly leaders of men. We can only assume that they are bucking for higher jobs or have developed such illusions of grandeur that they think they are paying for the operation of the plant out of their own pockets. We could go on and on and on with experiences such as above, and yet these are just examples of what is being practiced day in and day out throughout the jurisdiction of this international union.

One growing habit that is beginning to give nightmares to safety conscious people as it becomes more widespread is the use of poisonous solvents and other toxic liquids in plants. It is true they come into the plant in bulk form, properly labeled as to ingredients that are dangerously poisonous. But then they are dipped out or tapped out in unmarked containers and carried to that part of the operation where

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they are to be used. What happens when left unattended and workers not familiar with that particular job assignment come upon the scene with dirty and greasy hands looking for a solution to wash in?

The frequency and severity rate of injuries in the chemical and allied industries can and must be improved. That which, at present, is a fair to good rate, can with cooperation of all parties concerned become an excellent rate. This can become a reality by the industry and the union both accepting their full responsibility and recognizing that it is a mutual problem and not one sided.

In spite of the sagacious eighteenth-century thinking that still prevails in some sections of the chemical and allied industry in this country, one fact remains—unions are here to stay—and the welfare and safety of their members are paramount in their thinking and their actions.

To prove how effective a joint labor-management safety program can be, let's look at some of the experiences of the Pacific Coast Association of Pulp and Paper Manufacturers, the United Papermaker and Paperworkers International Union, and the International Brotherhood of Pulp, Sulphite and Paper Mill Workers working jointly in an industry classified as hazardous by definition of state compensation laws.

For the full year of 1963, their frequency rate was 4.77, as compared to the survey of the Bureau of Labor Standards for the first 9 months of 1963 showing a frequency rate of 10.0. This joint labor-management program became effective in 1945 at which time the frequency rate was 38.99—a drop of 88% over the last 18 years! It is also interesting to note that there were no fatalities for the years of 1962 and 1963 and no total permanent disability cases for the year 1963.

The Pacific Coast Association of Pulp and Paper Manufacturers through their joint safety program figure that 22,763 disabling injuries were prevented during the year of 1963. They arrive at this theoretical figure on the basis of 1000 disabling injuries for 32 million manhours worked in 1945 as compared to 240 disabling injuries for close to 60 million manhours worked in 1963.

What has become a reality in one industry through joint labor-management efforts can also become a reality in the chemical and allied industry if we accept modern day thinking where safety is concerned.

There is no valid reason why labor and management cannot unite in discharging their common responsibilities for safety and health

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despite allegations concerning the high cost of safety and the prerogatives of management.

REFERENCE

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4

Chemical Hazards and Worker Safety:

Relationship to the Interests of Governmental Labor Officials

Stanley F. Spence

All industry has changed during the past few decades, but the chemical industry has changed more than most.

In New Jersey we have a close-up view of the galloping advance in the chemical industry. Latest official data show that the chemical industry ranks first in that state in value added by manufacture; and by the same index New Jersey is the leading state in the country. Annual sales of chemicals in the state are estimated at $3.5 billion a year—about one-tenth of *all* United States chemical sales in 1963. Today accumulative value added by chemical manufacture in New Jersey exceeds $1.7 billion, nearly 60% higher than any other industry in the state.

Some industries start with a number of raw and semi-finished materials to make a single product, like the automobile. Others take a single raw material like petroleum and make a number of end products from it. But the basic raw material of the chemical industry is the molecule. The tremendous scope thus provided enables the industry to build the many thousands of distinct chemical entities of which more than 10 thousand are commercially available.

This industry has one of the highest capital investments per employee, and it must place great dependence upon the ability and the

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character of the employee. This chapter will cover the principal elements of the safety and loss-prevention problem and the control procedures which apply thereto in the chemical manufacturing industry itself, and then proceed on a logical route through the safety problems attending the conveyance of the chemical products to the user, and, lastly, the subject of the safe handling of chemical products by the customers of the chemical manufacturing industry.

Each of these areas of consideration has its own unique problems in chemical safety, even though the producer's sulfuric acid, as an example, is the same sulfuric acid in the tank truck of the motor carrier as it is in the customer's storage tank. The principal problem in chemical safety in the hands of the carrier or the ultimate user is one of insuring that the managements of these entities, and through them their employees, fully understand and follow those procedures which accident-free handling and storage demand. The title page of every *Chemical Safety Data* published by the Manufacturing Chemists' Association bears this statement:

> Chemicals in any form can be safety stored, handled or used if the physical, chemical and hazardous properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed.

Thus, it can be seen that the basic method of attacking the chemical safety problem in each of these three areas to be discussed—manufacturing, transportation, and use—contains the same principal elements: education and communication.

Perhaps the most important reason the chemical industry has progressed so far in safety is that it had to. It naturally has more complex safety problems than do most other industries. Hazards are not as naturally recognizable to the worker as are the hazards of a machine shop, for example. The new worker must be carefully educated in the characteristics of the materials with which he is working, and he must be given diligent training and follow-up by his supervisor. Since the materials he controls are usually in closed systems he must fully understand the changes going on in the process, and he must be able to interpret the messages provided by his instruments. He must always be influenced by the realization that any infraction of safe operating procedure on his part may produce an accident having injurious consequence not only to him, but also to his fellow workers.

It is this constant awareness on the part of the employer and the employee alike that has produced for the chemical industry an enviable safety performance. The record of the chemical industry in work

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injuries is illuminating, and a few of the salient facts are worth citing at this point. The National Safety Council reports that in 1963 the chemical industry experienced a frequency of 3.32 disabling injuries per million manhours work, as against 6.12 for all industries. The chemical industry *frequency* was 45.7% *lower*. The authority cites the chemical industry severity as 341 days lost or charged per million manhours worked, against 682 for all industries. The chemical industry *severity* was 50% *lower* than the all-industry rate. Now, what has produced this kind of safety performance? It was mentioned before that it resulted from an awareness on the part of employer and employee. But this awareness has its basis in a philosophy of conduct. This philosophy, in a nut shell, is this: The employer should provide a safe working environment, instructions on the hazards involved, and the safe way of doing the job. He should make available to employees those special protective devices or items of apparel required by injury exposures unique to their jobs, and should encourage their use by the employees. He should provide adequate supervision. It is the employee's responsibility to fully understand the instructions applying to the safe conduct of his work and to carry them out without deviation.

Because the safety efforts in the chemical industry are diligently oriented to the avoidance of what might be called "chemical type" accidents, a relatively small percentage of this category are experienced. The American Cyanamid Company's accident history might be of interest in this respect. Analysis of the January 1, 1959 to January 1, 1963 disabling injuries divulged the fact that only 8.9% were of the chemical type. In common with all other industries the greatest proportion occurred in the classifications: *falls, caught-between,* and *struck against* or *struck by*. The lost-time charges against the accidents in the four-year period were also significant: only 20.8% of the total lost days resulted from injuries of the chemical type.

The foregoing facts were cited to demonstrate that special effort has been expended in the direction of eliminating accidents arising out of chemical manufacturing operations since such accidents obviously can tend to be of a particularly serious and extensive nature. They can involve fires, explosions, and exposure to toxic and corrosive chemicals. They can be of the multiple-injury type, for the unsafe act of any individual can cause an accident hurting others and causing extensive damage, as mentioned before. All this does not mean, however, that we can permit giving the light touch to accident sources outside of chemicals. Our problem in controlling the usual run of industrial accidents is about the same as that of anyone else.

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The procedure followed at Cyanamid in producing a safe operating or research unit is not unlike that used by other responsible chemical manufacturing concerns, and perhaps a sketch will be of interest. The design for built-in safety starts in the laboratory or "glassware" stage and continues through to the manning and operation of the production facility. Briefly it is as follows:

1. The primary responsibility for obtaining necessary process information, including all safety aspects, lies with laboratory and pilot plant group leaders and their technical people. This responsibility is an integral part of their jobs and cannot be delegated elsewhere. The responsibility begins as soon as work is started on the process, whether it be on laboratory, prepilot, or pilot plant scale.
2. When transferring a product from pilot plant to a production unit is contemplated, review of process data is started with production, engineering, and safety people as early as possible before transfer. A detailed check list is used to insure that no areas are overlooked. This check list includes as primary items:

   Product description
   Chemistry of process
   Characteristics of raw materials
   Process flow sheets
   Equipment and instrumentation
   Chemical, equipment, and health hazards
   Operating procedures, including emergency procedures for malfunctions
   Analysis and process controls
   Final product characteristics: Stability, toxicity, flammability, and other essential data

   It can be seen from the above list and generally from a consideration of this overall procedure, that it is quite impossible to separate the "safety" from the "operation."
3. The plant design must incorporate the company's safety standards for methods and equipments, and all governmental laws and ordinances applying. As the design develops, frequent consultation is held between representatives of engineering, operations, and safety, to insure that the projected unit will be safely operable and safely maintainable.
4. The unit is continually checked during construction to make sure that the safety, fire protection, and operating features agreed upon are properly installed.

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5. The cadre composed of operating, technical, maintenance, and safety personnel who are to man the plant are thoroughly schooled in the process through direct instruction, review of the flow sheets, inspection of the physical plant as it develops, and operation of similar equipment on other operating locations of the company.
6. Before acceptance of the plant from the contractor, a final survey is made for safe operability and maintainability, and the necessary corrections are made.
7. The unit is staffed, personnel conducted through necessary training programs, and all procedures established for safety and loss-prevention as an operating unit.

Probably it has been observed during the course of this chapter that I have emphasized and re-emphasized the dependence that must be placed upon the individual. He should be selected for his chemical industry job with a view to his basic capability to handle that job. He should be properly trained. He should be instructed in such a way that he will understand not only *what* he should do, and *why* he should do it in the prescribed way, but also what will happen if he does not follow the given procedure. We are, at this point, directly at the heart of safety in operation—the human being. His own safety and often the safety of others depends upon this individual. Undoubtedly you have heard many times that the philosophy of safety is changing, that in the older days of the profession all of the emphasis was on the engineering or physical part of the problem, that now the engineering aspect no longer exists as a principal angle of attack, and that the "human element" is *now* being recognized as the primary objective. A veteran of 30 years in this profession can tell you that such observations are completely wrong, because the human being *always* has been the *primary* consideration in accident control. It will always be so.

Anything that is done in the way of physical revision is done as a *secondary* defense. Machine guards, handrails, floor opening protection, mechanical nonrepeat devices on presses, and so on, are installed with the foreknowledge that our human being, trained though he might be, is still subject to all of the frailties which befall humans. He occasionally is forgetful, is ill, is worried, and is preoccupied. When he is in such a vulnerable condition, whether it be for just a moment or for a longer period, we must do our best to keep him from accident by "pulling the teeth" of the physical hazard. And so it should be emphasized that as long as there has been an industrial safety effort, men competent enough to call themselves Safety Engineers have eval-

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uated each problem in the light of its own requirements and have planned their corrective actions on the basis of an appropriate balance between the engineering and the humanities.

One of the most important elements in the conduct of industrial safety is the investigation by supervision of significant accidents, and the instigation of prompt corrective action. Usually such accidents in the chemical industry, with their resultant injuries or damage, are found to have been caused by a combination of physical and human faults, and the preventive measures which are taken of course contemplate this same combination. To illustrate the point, there is quoted below from *Case Histories of Accidents in the Chemical Industry* (a publication of Manufacturing Chemists Association) Case History No. 477:

Description: Employees were attempting to install a new gasket in the line leading from the top of a titanium reducer. Apparently they neglected to vent inert gas pressure from equipment before removing bolts from flange. When flange was loosened, the twelve pound pressure in the equipment blew lower chlorides of titanium out to the air where they fired spontaneously and burned two employees on arms, chests, legs. Their safety glasses prevented eye injuries.

Cause: Failure to vent reactor pressure; inadequate protective clothing.

Preventive measures: In addition to proper venting of pressure, flange will be loosened on side away from body before all bolts are removed. Employees opening a reactor where lower chlorides might be present will wear asbestos hood, long coat and gloves.

Occasionally reference has been made to the Manufacturing Chemists' Association and a brief explanation of what it is, and how it functions in the area of chemical safety and fire protection might be helpful. It is a nonprofit membership corporation (New York), was founded in 1872, and is the oldest chemical trade association in the Western Hemisphere. The Association includes about 200 member companies in the United States and Canada, representing more than 90% of the productive capacity of the industry.

One of the active committees of MCA is the Safety and Fire Protection Committee. It is composed of the heads of Safety and Fire Protection of member companies, and of diversified chemical manufacturing interests. The committee acts as a clearing house for the exchange of information on safety and fire protection within the industry, and for the carriers and users of chemicals. It also extends its efforts in the direction of safety education for schools and colleges, through its publications. The Safety and Fire Protection Committee

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also has conducted safety workshops in various parts of the United States and Canada.

Out of the many billions of manhours of chemical operating experience of the member companies of MCA and the pooling of their knowledge in accident prevention, a number of informative works have been produced and published.

1. *Chemical Safety Data Sheets:* These are devoted to a full description of the known characteristics and properties of each subject chemical. Chemical subjects for Safety Data Sheet publication are selected on the basis of hazard and broadness of use in industry. In addition to an account of the properties of the given chemical, they contain all of the principal information on safety which the transporter or the user might need. Among the areas dealt with are: properties, hazards, engineering control of hazards, employee's safety, fire fighting, handling and storage, tank and equipment cleaning and repairs, waste disposal, medical management, and first aid.
2. *Safety Guides:* These cover safety procedures intended to be helpful to the manufacturer and user of chemicals. They are designed in such a way as to promote management stimulation and action, and at the same time to provide practical guidance to the individual who is directly concerned with the execution of the subject. Examples are: *Health Factors in Safe Handling of Chemicals, Entering Tanks and Other Enclosed Spaces,* and *Disposal of Hazardous Waste.*
3. *Accident Case Histories:* Newly available is a publication entitled: *Case Histories of Accidents in the Chemical Industry.* This is a cross-indexed volume of significant chemical industry accidents, including fires and explosions, reported by member firms of MCA during the past several years. Each case write-up is concisely presented, and is segmented according to description, cause, and preventive measures.
4. *Guide for Safety in the Chemical Laboratory:* This manual, prepared through the cooperative effort of member companies, is oriented toward the observance of safe techniques, procedures, and design of the large or small chemical laboratory. It has found its way to the reference book shelves of industrial laboratories, high schools, and libraries around the world.
5. *Color-Sound Film: Safety in the Chemical Laboratory:* This film is directed primarily to the level of the university chemistry undergraduate, but loses none of its educational value in use by industrial laboratories or among university post-graduate workers.

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There are many other activities and publications of the Manufacturing Chemists' Association which directly or indirectly serve the interest of safety to the public, to industry, and to transportation, and which undoubtedly come within the purview of your concern. To name a few, there are the subjects of air and water pollution abatement, chemical packaging, traffic and tank vehicles, education activities, medical, labels, and precautionary information.

The last may be of particular interest since it is directed toward the important effort of conveying essential information on identification, hazard, and precautions, to all who may in any way come into contact with chemical containers, be it in processing, transportation, storage, or use. The scope and limitations of the precautionary labeling effort are well defined in the "Introduction" to the Manufacturing Chemists' Association Manual L-1: *Guide to Precautionary Labeling of Hazardous Chemicals.* It is quoted in part:

> Many products present no hazard in normal handling and storage. For these products, no precautionary statements are necessary on the label. The development of new chemical products, and the introduction of chemical processes into ever-widening fields, has accentuated the need for furnishing appropriate information in those cases where there are hazards requiring special precautions. Precautionary information should, so far as is practicable, *reach every person using, handling, or storing hazardous substances.*
>
> The most practical means of disseminating this information appears to be by precautionary labels, affixed to containers of hazardous substances, bearing appropriate precautionary statements expressed as simply and briefly as possible. Such label information, however, cannot take the place of the education of personnel regarding product hazards and the use of safety clothing and equipment. This education is, and must remain, the direct responsibility of their employers.

We are now bridging over into the area of the transporter and the user of chemicals. In the transportation phase, particularly, there is encountered the problem of chemical exposures to persons who know nothing about chemicals, their characteristics, hazards, or safety measures which should be taken under given circumstances. These persons are largely composed of the carrier's employees, truck operators, railroad operating personnel, in-transit warehouse employees, and the general public who may be exposed at the time of chemical vehicle accident or in some other manner. The chemical industry recognizes a moral responsibility to do its best to insure that this segment of the population will not be harmed by those of its products which are hazardous.

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What are the controls that the chemical shipper has in this regard? Here are some:

Just as our chemical industry workers are instructed in the hazards and the safe handling of our products, so should the transportation employees be instructed. This does not mean, of course, that all railroad operating personnel should be given a course in chemical safety, but it does mean this: railroad employees and supervisors who may encounter an accident exposing them to flammable or harmful chemicals, should receive basic instructions, and drivers of motor tank transports should be similarly instructed. The shipper can help them much in this regard. The industry does its best to furnish to its carriers full information on the unique properties of, and safe procedures relative to, the products whose characteristics require special knowledge. This may not always be on an individual product basis, for generally it might best be communicated on the basis of principal classifications, somewhat as follows:

Flammability—low vapor pressure (example, acetone)
Flammability—high vapor pressure (example, LPG)
Chemical Reactivity
Radioactivity
Corrosivity

It is the carriers' responsibility to see that their personnel know and observe the precautions and safety procedures communicated to them.

In the shipping of corrosive cargoes such as acid and caustic, in tank trucks, we find that we must give special attention to the operators of contract and common carrier trucks. While these drivers are not our employees, we do have a moral responsibility to see that they are familiar with the hazardous properties of the products, that they fully understand their equipment and how to make safe deliveries, and that they have and use the necessary personal protective equipment. This requires constant surveillance. On more than one occasion the management of a Cyanamid plant has sent a cargo tank driver back home with his truck because he failed to observe necessary safety precautions or use prescribed personal protective equipment. This can hurt, if the plant desperately needs the delivery, but if it must be done as a last resort, then it must be done. It is the only way to protect the uncooperative outside driver. In shipping hazardous ladings by truck, owned or hired, we normally affix a special tag to the outlet connection. This tag does not conflict in any way with ICC regulations. It provides the name of the product and gives precautionary instructions.

We are all vitally concerned with the subject of the transportation of extra-hazardous materials, because of the catastrophic accidents which can, and have been, produced. Planning against injuries and losses arising out of such occurrences is a broader and a more detailed problem than is the safety education of a truck driver or a railroad man in the limited interests of his own personal safety. The large-scale transportation accidents such as the Roseburg, Oregon explosion of August 7, 1959 (involving an improperly parked truck

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containing 2 tons of dynamite and 4½ tons of a blasting agent), and the Norwich, Connecticut explosion in the spring of 1962 (involving a truck carrying over 38 thousand pounds of peroxides plus 10 drums of red label flammable liquids) impress upon us that further preventive measures must be taken in the interest of public safety. In the planning of such measures, thought should be given to the following considerations:

1. Extra-hazardous materials in transportation should be routed to avoid densely populated areas.
2. Explicit and conspicuous markings should be on the exterior of the truck to define the hazard.
3. Safety regulations covering highway vehicle transportation of hazardous chemicals should apply to intra-state transportation to the full extent it applies to inter-state transportation.

Another important aspect of safety in the transportation of hazardous materials is the emergency action which should be taken in the event of accident. Procedures should be established to cover emergency situations arising out of transportation accidents, where the ladings involved are of a high degree of hazard in themselves, such as class A poisons; where release of the ladings to the surrounding area may be of such high concentration as to have a serious effect upon the health of persons; or where explosives or unusually reactive chemicals are concerned. Some of these procedures may be informal, but still very effective; some may require considerable detail. Under any circumstances, they should be devised to produce these results:

1. To protect the public.
2. To reduce the damage to property.
3. To limit the effect of the immediate incident by guarding against its extension or the occurrence of secondary accidents.
4. To provide competent coordination at the site.
5. To provide to the press, radio, and television, factual data on the occurrence, avoiding speculation and imagination.
6. To provide immediate notification to the shipper and to the authorities having jurisdiction.

It is the responsibility of the shipper to formulate the emergency procedures, and to acquaint all who are concerned with them regarding their responsibilities.

It is the responsibility of the carrier to immediately notify the shipper and the authority having jurisdiction, in order that the emergency procedures can be set in motion. An example of very effective

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and informal emergency procedures is presented by the chlorine industry. The excellent and swift assistance by participants in this mutual aid program—manufacturers of chlorine and users alike—has served the public and industry well. An example of a detailed, though uncomplicated, transportation emergency procedure is provided by the bulk hydrocyanic acid industry, which brings into play the coordinated action of competent emergency crews, plant management, and local authorities.

In this chapter the highlights of safety in the manufacture of chemicals and in their transportation have been discussed. We come now to the user. Every purchaser of chemical products should observe the same precaution before he purchases them as do most responsible chemical manufacturers when *they* buy chemicals from the outside. Yes—most chemical manufacturers are, themselves, purchasers of chemical raw materials and intermediates from other concerns. The procedure may be simple, as in a small unit, or it may be detailed (though we hope not complicated) in the case of a large user of many different chemicals. Under any circumstances, the procedure would require that, before a chemical is purchased in quantity:

1. There would be obtained from the supplier full knowledge of the properties and characteristics of the product, and the manufacturer's recommendations on safety in storage, handling, and use.
2. Where necessary, additional data would be obtained from other authoritative sources, such as the MCA Chemical Safety Data Sheets.
3. Those responsible for insuring the safety of operations—generally production, technical, and safety—would satisfy themselves that the product can be stored and used safely under their circumstances, and only then would they give approval to its purchase.
4. Any special handling and storage facilities and equipment required by the nature of the product would be installed.
5. All personnel concerned would be fully educated in the procedures and equipment required for the safe storage, handling, and use of the product.

It is distressing to chemical safety men that so many users of chemicals do not take the trouble to learn the simple essentials covering the properties of the materials as far as stability, flammability, and other hazard characteristics are concerned. The proper use of chemicals requires more than a knowledge of what they will do in the course of producing a new end product, or how they will behave in performing a given end function. It requires an acquisition and

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application of all knowledge of the chemical's behavior in the circumstances under which it is to be stored, repackaged, and mixed in a given formulation, or used as a reactant in a consequent chemical process.

Recently an urban manufacturer of electronic parts exemplified this lack of knowledge. He used nitric acid and muriatic acid in a part of the process. The tanks were in a subterranean cell under the building, the fill lines extending from fittings in the outside sidewalk down underneath the building, and finally connecting into the tanks. A tank truck of nitric acid was delivered to the plant and the driver, as was proper, checked at the reception office to obtain instructions for making his connections. The customer's authorized representative went below, checked the outage on the nitric acid tank, then came up to the street and told the truck driver exactly where to make his connection. He made the connection to the designated fitting, and started the delivery of nitric acid to the underground storage facility.

In the meantime, as was customary, a sample of the nitric acid was taken for the customer's assay. As the acid was being "blown" to the underground tank the customer's representative chatted with the cargo tank driver. After a short time he went below to "see how things were going." But he came up to the street much faster than he went down, for he was pursued by billowing clouds of various-colored fumes. He had instructed the driver to make the connection to the wrong fitting, and the nitric acid, instead of going into the nitric acid tank, had been flowing into the muriatic acid tanks! The street and immediate neighborhood became filled with acidic fumes and mists. When assistance was offered to the manager of the plant by a chemical safety engineer employed by a local firm, neither the plant manager nor his chief chemist could explain what kind of tank facilities or connections were in the underground storage cell! Tremendous damage can be done through ignorance of proper storage and handling of ordinary chemicals.

This chapter has covered the accident situation in chemical manufacturing, transportation, and usage. Now, what can governmental labor officials do about all this? I submit a few observations and suggestions:

1. *Field consultation:* It would be well to train consultants representing the state Departments of Labor to study and evaluate management's ability to conduct its operations safely. This ability is reflected by attitude; by the systems and procedures management has

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established (and follows) in the interest of safety; by the completeness of operating instructions and the adherence to them by operating personnel; by the safety inspection and preventive maintenance program followed; by the method used in training personnel; by plant cleanliness and layout; and by the safety record itself. The consultant might then guide management in strengthening the weak spots divulged as a result of the appraisal.

2. Labor officials might find it advantageous to make a careful survey of chemical industry personnel to find out who the top specialists are in given subjects. These are the individuals who might be called upon for unofficial expert counsel in given situations. This is a "digging" job, but the industry safety supervisors should be able to help find out who these people are.

3. Review existing governmental codes to make sure they are realistic, practical, and adequate, and revise them as necessary. Industry's assistance can be counted upon.

4. Fashion government codes as performance codes, rather than cut-and-dried standards and specifications. This is the way such codes or standards must be fashioned even in our own privately owned multiplant companies, since we have many different situations in as many different plants. Consider, then, how much greater the problem becomes in a state, or in the nation! As a simple example, Cyanamid's basic safety requirement for tank car access platforms is that "provision shall be made for giving the employee safe access to the dome of the car, protecting him while he is performing his operations there, and returning him safely to his starting point." Our stairway standard supports this in part by providing guide lines for stairway pitch, tread, and riser limits, and other details. In other words, the *performance* is what counts; how it is produced should not be of important concern to the regulatory body.

5. The history of industrial injury incidence has shown that the smaller firms have the highest injury frequencies. This undoubtedly results from the fact that being small, such firms do not have the staff assistance which large companies often have. Thus, they lack safety, medical, and other important counsel. The chemical industry and the governmental labor officials should make a special effort to reach these smaller firms and to aid them in safety guidance, through their trade associations.

6. It is suggested that governmental labor officials enlist the full participation of industry specialists in the development of safety codes.

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In closing it should be emphasized that any accidents which occur through the use or handling of chemicals in any area—manufacturing, transportation, or usage—are of concern to the chemical industry. Governmental labor officials are invited to work with the chemical industry in each of these areas and the industry in turn will give of its knowledge and experience to them in their endeavors, for the benefit of all concerned.

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5

Safety Aspects of Site Selection, Plant Layout, and Unit Plot Planning

D. M. Liston

5.1. INTRODUCTION

In this chapter, we are concerned with the problems of relative physical locations of facilities. There is the problem of locating the plant relative to its surroundings and the problem of locating components of the plant relative to each other. If we consider these problems, starting with the most general aspects and working toward specific details, we will pass through four recognized phases: location, site selection, plant layout, and unit plot planning.

First, let us consider location. Given one proposed chemical plant and one world, the problem is where to locate said plant on said world. This is what we refer to as the location study. Obviously, the major considerations in this phase are economic ones. Thoughts about safety have little to contribute here. Before the threat of atomic war, we might say there were no safety considerations in this phase. Today we might deliberate at some length on steering clear of possible atomic blast or fallout. However, such deliberations will not be subject matter for this chapter. Of course, we cannot simply forget such factors as high wind velocities, earthquakes, snow loads, and frequency of electrical storms. But, as far as location of the plant is concerned, these factors, too, become submerged in the economics. This is because safety factors against these hazards can be designed into the plant at a given cost.

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For these reasons, this chapter will commence with the second phase, site selection. The location study may have told us to locate our plant on the east coast of the United States in the vicinity of Atlantic City, or in the northern Midwest where efficient transportation by water as well as rail is available. Now it is time for site selection—the selection of a specific plot of ground on which to build. The concern is still one of location of a whole plant relative to its surroundings.

The third step toward detail is plant layout. We are beyond studying surroundings and can concentrate on the plant itself. The blocks to shuffle around here are functional operating units of the plant. We will be setting up the relative locations of things like process units, boiler plants, water treating facilities, maintenance shops, administrative facilities, etc.

Finally, there is unit plot planning. Our playthings now become individual pieces of equipment like pumps, exchangers, drums, columns, pipes, etc. The problem is the proper location of these things within a given operating unit. In these latter three phases, what can we do to enhance safety? This is the content of this chapter.

5.2. THE HAZARDS AND THE LINES OF DEFENSE

In site selection, plant layout, and unit plot planning, it is possible to make allowances for only certain types of hazards. To facilitate discussion of these hazards, let us break them down into first degree hazards and second degree hazards.

First degree hazards are those which provide the *potential* for trouble. Under normal conditions, these hazards do not cause damage to either persons or property, but they set the stage for accidents that can cause injury, fires, or explosions. Typical of first degree hazards are:

1. The presence of flammable or combustible materials
2. The presence of heat
3. The existence of ignition sources
4. The presence of oxygen
5. The presence of compressed materials
6. The presence of toxic materials
7. The possibility of human error
8. The possibility of mechanical failure
9. The movement (normal or emergency) of people and equipment through the plant
10. Reduced visibility from vapor clouds, etc.

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When first degree hazards get out of hand, the result can be second degree hazards which are capable of directly inflicting damage to life, limb, and property. These second degree hazards are:

1. Fire
2. Explosion
3. Release of free toxic materials
4. Stumbling
5. Falling
6. Collision

In combating all of these hazards, we draw three lines of defense. The first line of defense consists of trying to deal with first degree hazards in such a fashion as to prevent the occurrence of second degree hazards. Success here depends mostly on careful engineering of the equipment we use. However, there are things to watch for during plant layout and unit plot planning to assist this first line of defense. For example:

1. Locating ignition sources upwind (based on prevailing wind direction) from points of possible release of flammable materials.
2. Providing adequate accessways for the movement of equipment and people.

Despite all such efforts, there are occasions when second degree hazards, such as fires, do occur. Now the second line of defense comes into play. In the event of a second degree hazard, how can we minimize the extent of damage to life, limb, and property? Here, again, there are steps we can take in selecting the site and arranging the plant to help limit such damage. Examples of these are:

1. Separating the most hazardous areas from the areas most often occupied by people.
2. Strategically locating fire fighting equipment.

But some damage will result from these hazards. People do get hurt in modern industrial plants no matter how carefully we plan against accidents. The third line of defense is to provide efficient first aid and hospital facilities to care for those who do get hurt. The essence of this last line of defense is the rapid repair of damages we have not been able to prevent.

The specific safety problems in Sections 5.1, 5.5, and 5.6, are all applications of these three lines of defense against first and second degree hazards.

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5.3. THE TOOLS AND TECHNIQUES OF DEFENSE

Now let us consider the tools and techniques that are available to us to help implement these lines of defense. Nature provides some of these tools and others must be supplied by man. Let us take the natural ones first.

Topography is one factor which we can use in planning for safety. Just as liquids flow downhill, so will many of the flammable or toxic gasses which may be released in an operating plant. Proper utilization of this feature can make it work for us as a safety tool in disposing of these hazardous gases.

Sources of large volumes of water are exceedingly valuable when it becomes necessary to fight fires. Adequate water supply can spell the difference between success and failure.

Another important natural element is the direction of the prevailing wind. The local weather bureau in almost any area can supply a wind rose which will tell the percent of the time the wind blows from the direction of each point on the compass. Prevailing wind will help in preventing flammables from drifting toward ignition sources. It will also help prevent vapor clouds or toxic gases from drifting through highly populated areas or across roads. Lest it should appear, later on, that we are overrating the value of this tool, let us emphasize that utilizing prevailing wind is a matter of playing the odds. Obviously the wind does not always blow in the prevailing direction, and everything in the plant cannot be either upwind or downwind as we seem to suggest. However, it is always best to be on the right side of the odds as often as physically possible.

Going beyond nature, the intelligence of man supplies some of the elements to enhance safety. Separation by distance is one such element. We can use distance to separate one hazard from another (such as a furnace from a relief valve which may discharge to the atmosphere). We can also use distance to separate hazards from people (such as high pressure vessels from a control house). A similar tool is separation by physical barrier. A typical example here is the confinement of liquid spills by walls, such as the dikes around storage tanks.

Two tools which work hand-in-hand are the *concentration* of hazards and the *identification* of hazards. Consider the location of pressure storage vessels (spheres and spheroids). It is best to isolate this type of vessel into one particular area of the plant. And the fact that hazards are thus concentrated, facilitates the demarkation

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of the area as being a particularly hazardous area. This helps in two ways. First, it becomes much more practical to keep people out of these hazardous areas except those who have specific duties there. Second, those people who must work in or pass through these areas can be made fully aware of the hazardous conditions which prevail. Hazards that are dispersed throughout the plant become all the more dangerous by their inconspicuousness. We must recognize that along with these advantages comes the possibility that a fire or explosion on one vessel may result in a larger total loss through the involvement of adjacent vessels. But the consensus of judgment is that the reduced likelihood of trouble with concentrated hazards which are properly looked after does result in a safer installation.

The final tool is the ability to design and build physical facilities with which to combat hazards. Fire water systems, safety showers, and first aid stations are all examples of applying this tool.

These are the tools we have. We must apply them as we select sites, lay out plants, and plot plan individual operating units. In this problem of application, we have found two techniques to be most helpful.

Enlisting the services of a consulting Safety Committee is extremely valuable. The members of the Safety Committee provide a strong bias toward a high level of safety. This helps balance the bias of the project manager who will normally lean quite heavily toward minimum costs. Actually, most good designers have an understanding of safety problems, and the function of the Safety Committee becomes one of *reviewing* and *recommending* arrangements to enhance the level of safety. It will be wise to include a representative of the operations side of the organization as a member of the Safety Committee. He will represent the people who must safely operate the plant after the project people have finished with it and moved along to the next project.

As a typical requirement, the Safety Committee should conduct a thorough review of the proceedings at these times:

1. Before the final selection of a building site.
2. When a rough, block-type layout of the plant is available—one that shows relative locations of operating units and administrative and service facilities. This layout should also indicate the major features of the surrounding community.
3. Before finalizing the plant layout when major pipe alleys, roadways, tank dikes, and similar physical features may be inspected.
4. Early in the plot planning of units before any considerable amount of detailed engineering is under way.

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5. In the final stages of design when it is possible to settle the exact locations of safety showers, hose cart stations, fire hydrants, etc.

Strongly supporting the efforts of the Safety Committee is the technique of scale modeling. Particularly during the plot planning of units, the scale model has much to contribute. The ability to see three dimensions at once adds much to the speed and effectiveness of searching out and solving safety problems.

In the early plot planning, we can make use of a model made up from simple rectangular and cylindrical blocks to represent the location and general size and shape of equipment. Placing these blocks on a cross-sectioned baseboard allows us to quickly observe the distances involved. For this purpose, a scale of one-tenth inch to the foot or smaller will suffice. Figure 5.1 shows an example of this type of scale model.

Reviews of the final design stages will require models of much more detail. Usually built to a scale of ¼ or ⅜ of an inch to the foot, these models show piping, valves, instruments, platforms, ladders, and all such details of the actual plant. Figure 5.2 shows a detailed model of the same plant that appears in Fig. 5.1. The progression from preliminary model to detailed model is quite well portrayed in these two photographs.

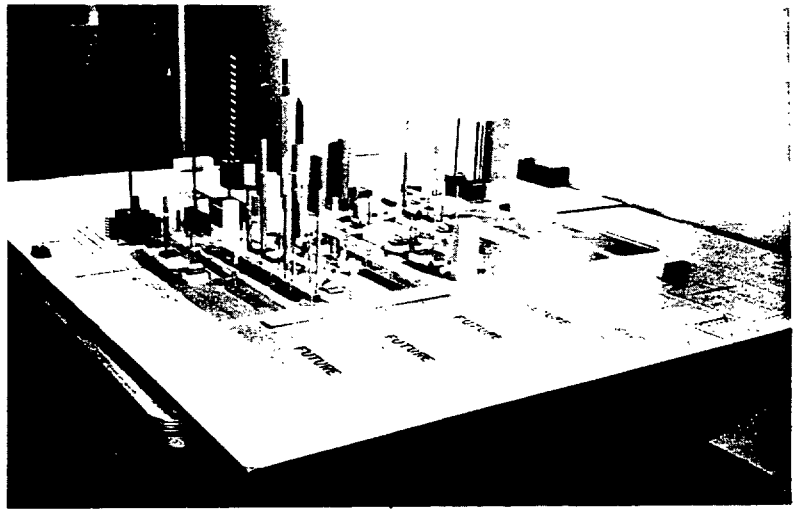

FIG. 5.1. A preliminary plot-planning model.

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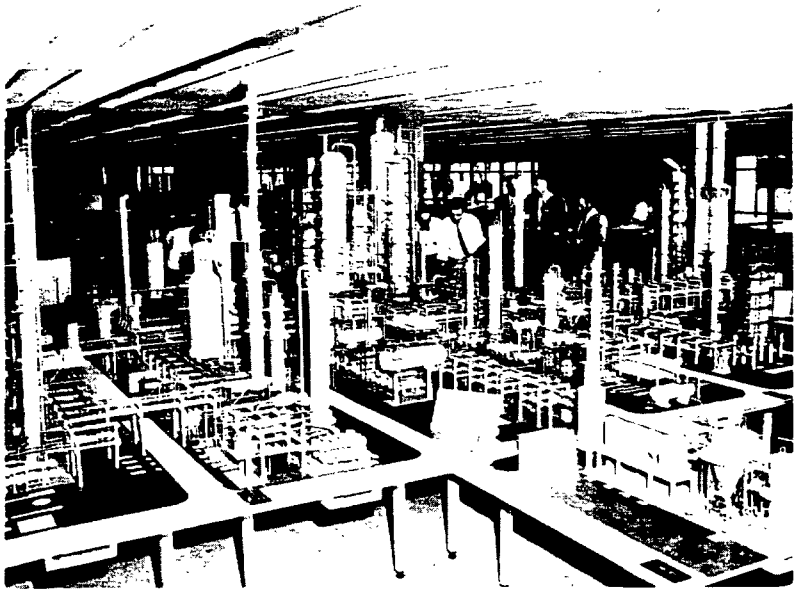

FIG. 5.2. A detailed engineering model.

Timing! Here is the big problem with models: models must be available soon enough for reviews, and the resulting changes to occur before much engineering is done that may be wasted. The greater the waste, the harder it is to justify the changes, be they for purposes of safety or whatever. Many companies, and contractors too, are adopting new design methods to accommodate scale models. Moving directly from detailed flow charts to models, completes the model before any appreciable engineering occurs on the drafting board. This method, of course, completely solves the timing problem. It does, however, require the services of people with combined designer-model building capabilities.

5.4. SAFETY PROBLEMS IN SITE SELECTION

We have been speaking in generalities up to this point. The discussion has covered the general principles, tools, and techniques to apply in achieving a good level of safety. Now, let us take the three areas of this chapter, one at a time, and discuss the specific problems involved.

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The first problem is site selection. Remember that the plant to be built may actually be hazardous to the community in which it will be placed. Toxic gases may drift out of the plant into residential areas or into other areas containing a concentration of people. Flammable gases may drift out of the plant to ignition sources such as incinerators or other industrial plants. Fog from cooling towers may drift across high-speed highways or roads with high-traffic density.

There are ways to combat these problems. Separation by distance is one. This can be accomplished by selecting an isolated site. If other considerations make this solution impractical, we may have to rely on the prevailing wind. Unfortunately, the wind does not always blow in the prevailing direction. Placing the plant downwind from the community simply improves odds against trouble occurring from the above hazards.

The possibility of collapse of high structures is another potential hazard to the community. In many cities, building codes require that tall structures or vessels be located a certain distance within property lines. This is to prevent such structures from falling on pedestrians, motorists, or neighboring facilities. The effective area of the site may thus be significantly reduced. Do not forget to check on similar local restrictions which may apply to the site under consideration.

The plant will have waste streams of which to dispose. We should be sure that the intended means of disposal will not foul the drinking water for the community. Toxic effect on marine life can be a serious problem especially where people depend on fishing for a livelihood. Here again, be aware of local, state, or federal regulations. Try to avoid routing sewers, which may contain explosive mixtures, across public or private property.

Be careful about the main point of entry to and egress from the plant. The sudden surge of traffic at starting or quitting time, in and out of the plant, may cause a serious highway hazard if not properly located or dispersed. High-speed highways adjacent to the plant present the danger of vehicles leaving the road and crashing into the plant.

Now turn about for a few moments. It is also entirely possible that the community may present some definite hazards to the plant and to the people who run it. Or if not presenting actual hazards the community may lack some of the facilities that would enhance the safety of the plant. Neighboring plants may emit toxic gases or flammable gases which could drift *into* the plant to sicken employees or ignite

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due to sparks or hot surfaces. In such cases, it would be better for the plant to be located upwind or again, separated by distance if such is feasible.

What can the community offer in the way of fire fighting assistance? There may come a time when such assistance could mean the difference between just a fire or a real disaster. In a similar vein, we may ask what can the community offer in the way of first aid and hospital facilities? The balance of life or death for injured persons may hinge on the existence of good medical facilities.

These latter two instances are examples where separation of the plant from a community by distance can be a disadvantage in safety terms. This serves well to illustrate that no pat formula insures maximum safety in site selection. The problem is simply to try to obtain the most favorable balance of forces for any specific situation.

An adequate source of water will enhance the ability to fight major fires. An adequate source can best be assured by having a stream or lake adjacent to the plant so that fire water does not have to be pumped from the ground. Have a look at the local city water system as a possible source or supplemental source of fire water.

Topography is also a factor to consider. Surely everyone involved in designing the plant will agree that a nice flat and level site is the thing to have. For safety, we would like to avoid low areas within the site which can form pools of toxic or flammable vapors or liquids. Relative to the surrounding area, it would be better for the site to be on high ground rather than in a basin.

Remember to check each proposed site for existing rights-of-way for pipelines, roads, railroads, and power lines. We must assess the existing or potential hazards to the plant which may develop as a result of such rights-of-way.

5.5. SAFETY PROBLEMS OF PLANT LAYOUT

Now, we move along to the layout of the plant itself. The center of attention here always seems to be the processing units—the real backbone of the plant—so we will discuss them first.

The processing units are probably the most hazardous areas in the plant. Here we purposely bring together in close proximity many of the first degree hazards. We find toxic or flammable materials, high temperatures, high pressures, and ignition sources. These areas are full of mechanical equipment, all of which is subject to failure. Things can happen fast in the process unit, enhancing the possibility for human

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failure. Perhaps the only redeeming factor is that normally there are few people in the process unit.

Processing units should be removed from the boundaries of the plant and should be consolidated rather than scattered. This latter point will improve their identification as hazardous areas and help reduce the amount of transient traffic passing through. Watch for the major ignition sources in the plant and the major concentrations of people. The processing units should be downwind from both of these since the release of flammable or toxic materials is a possibility. It is well to maintain a considerable separation of the process areas from the major tankage areas. These two are mutually hazardous to each other.

While we have said that process areas should be consolidated, we must be careful the area is not too consolidated. Some separation between units is necessary because here again they are mutually hazardous to each other. This is particularly true where the units are not integrated process-wise. In such a case, one unit may be in full operation while its neighbor is shut down for major maintenance, presenting an increased potential for trouble. Ignition sources, heavy activity, movement of machinery, and a concentration of people in a hazardous area are all signposts of which to beware.

To date, in the chemical industry, the spacing of process units, one from the other, remains a matter of good judgment for the most part. The major factors which come to bear on these judgments are:

1. Operating temperatures
2. Operating pressures
3. Types of materials present in the units
4. Quantities of materials present in the units
5. Types of structures in the units
6. Relative values (investment) of the units
7. Space required for fire fighting or other emergency operations

A good written source of material to assist in these judgments appears in a book on safety in petroleum and related industries by George Armistead, Jr.[1] Armistead's recommended minimum desirable distances, while applying specifically to petroleum refineries, will be found analogous to many similar situations in chemical plants. Another applicable reference in the handling of explosives is the American Table of Distances in the *Ordnance Safety Manual*.[2]

The integration of processes is a subject still wanting adequate treatment with regard to requirements for separating facilities by distance.

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We critically need some careful consideration of the effect on physical separation of facilities by these aspects of integration:

1. Process integration (elimination of intermediate tankage, etc.)
2. Mechanical integration (combined or multipurpose items of equipment)
3. Integrated or interacting control systems

Every plant, of course, will need some administrative facilities. Safety considerations dictate that the main offices should be located on the periphery of the plant and as isolated as possible from the hazardous components of the plant. There are several reasons for this.

First, salesmen, suppliers, and others who must conduct business with the plant personnel may do so, for the most part, without having to enter the plant proper. It is well to keep such visitors out of the plant whenever possible. They are not acquainted with the nature and locations of the hazards in the plant. Their normal habits may make them prone to inadvertent smoking in hazardous areas without thinking.

Second, isolated office buildings will permit smoking in the offices without endangering the plant. This also permits a very clear demarkation between the areas where smoking is permitted and those where it is not. Third, the offices will house probably the largest concentration of people in the whole plant. Separation of these people from the hazards improves the odds in favor of safety.

Fortunately, these motives for peripheral location of the offices are compatible with most of the other considerations in plant layout. There is one factor, however, that may be an opposing force on this point. Certain people including operating foremen and maintenance supervision must split their time between their offices and duties in the plant. They, of course, would like their offices adjacent to their in-plant duties. An ideal solution to this problem is not easy. Careful consideration of their needs, and provisions for efficient transportation may coax them into the main offices. If they insist on in-plant offices, do not forget the safety considerations we discussed during the plant layout.

Laboratories will normally be situated adjacent to the other administrative facilities from a functional standpoint. Fortunately, the laboratory is compatible with these facilities safety-wise with two glaring exceptions. Smoking is one. There are small quantities of flammables in laboratories which may be inadvertently released into the building. Toxics, too, may be present. For these reasons, a

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direct connection between the laboratory building and the other administrative buildings may be inadvisable.

Boiler plants are major ignition sources normally requiring an upwind location. Maintenance shops, too, represent a major ignition source as well as a concentration of personnel. Thus, the shops, too, should be upwind and separated by distance as much as practical. Warehouses will normally be adjacent to the shops and both will want to be accessible by railroad spurs. Good plant layout will avoid routing railroad spurs through the plant, thus avoiding the concomitant hazards. Thus, peripheral location of these items is desirable.[3]

Similar considerations prevail for tank car and tank truck loading and unloading facilities. Traffic to these areas must not pass through the plant. Spills of toxics or flammables may occur at loading racks suggesting a downwind location as desirable. Peripheral location, also, seems best, but care should be taken not to locate tank car loading racks too close to the main line of the railroad. Locomotives may be ignition sources, and during possible derailments, could cause extensive damage to loading facilities. Regardless of these considerations, some railroad spurs will probably have to be routed into the interior of the plant. Ignition and derailment hazards must be accounted for with regard to these spurs.

Waste water treating facilities may turn out to be the ultimate point of collection of toxics or flammables spilled anywhere in the plant and thus a downwind, as well as remote location, is indicated.

Cooling towers have the similar characteristic of collecting toxics or flammables which may leak into the water side of coolers in the operating units. This, in itself, would indicate a downwind location, a decision reinforced by the problem with fog. Cooling tower fog can block visibility on roadways, units, and in elevated structures frequently traveled by operating personnel. Thus, cooling towers should be downwind from roadways, units, and elevated structures.

Elevated flares or burning pots at grade present a contrary problem. As sources of ignition, we would tend to locate them upwind. But there is another consideration. Severe operating upsets can cause flares or burning pots to belch out considerable quantities of flammables which may fall, burning or not, on people or facilities. This, of course, would call for a downwind location. The only solution here is a location at the side (relative to the prevailing winds) of the facilities in question. We will call this a sidewind location. A sidewind location is a useful compromise in cases where combinations of location problems in plant layout prevent the ideal upwind or down-

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wind location of any single facility. Separation by distance is also very advisable in the case of flares or burning pots.

Storage vessels, such as tanks, spheres, and spheroids, are items to be handled with caution. Each such vessel is a tremendous storehouse of energy or of toxic materials, as the case may be. Obviously, it is wise to keep people, operating units, and tankage as far apart as possible. These vessels are capable of releasing tremendous spills of toxics or flammables and, therefore, by all means should occupy a downwind location. We have already mentioned that tankage should be relegated to its own private area in the plant to enhance the identification as a hazardous area and minimize all extraneous traffic through the area.

Three problems are inherent in the location and allocation of space for tankage:

1. Separation of tanks from each other
2. Separation of tanks from other facilities
3. Area required to provide adequate dikes

Two major hazards with tanks have great effect on the above three problems. First is the possible rupture of a tank shell releasing the entire contents in a very short time. Second is the boil-over tendency of some viscous stocks when tanks containing a water layer are heated above the boiling point of the water. As in the case of processing units, little has been compiled for the chemical industry in the way of actual dimensional recommendations for the three problems above. But here again, Armistead's book[1] contains recommendations which will be helpful guides.

Plant layout includes the problem of adequate roadways which are very important to safety. Each process unit should be completely surrounded by roadways. Every tank should be accessible on at least one side, preferably two opposite sides, from a roadway. Try for a layout which will make every point in the plant accessible by road from two directions. Along this same line of thought, it is good to have an alternate main entrance to the plant to be used when the normal entrance is blocked by traffic or road maintenance. This may be very important in emergencies. The roads which are heavily traveled should be arranged to minimize the chances of damage to hazardous equipment from vehicles leaving the road. The layout should also attempt to minimize the road crossings by ground-level pipe alleys.

The major transfer pipe alleys also come under surveillance at this point. One very influential factor in pipe alley layout is the need for looped piping arrangements in certain services. A looped system is

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one so arranged and valved that a failure at any point in the system can be isolated by closing valves, thus maintaining service to the rest of the system. To accomplish this, the layout must supply these services to the critical points in the plant from at least two directions. To enhance safety, especially during emergencies, the piping for these services should be looped:

1. Fire water
2. Steam for power or heat

Consider also the locations of the sources of these services. The boiler plants and pumping stations should occupy positions as well protected as possible from damage by fires or explosions occurring on other facilities in the plant. Try to minimize the number of road crossings. Pay particular attention where alleys cross above roadways. Overhead clearance must allow easy passage of heavy equipment such as cranes with minimum danger of collision. And, finally, pipe alleys must not pass through diked areas. A fire in a diked area can rupture pipes, adding to the fuel for the fire or interrupting the supply of important services like steam. Also, pipes passing through dikes present potential leaks in the dikes. Avoid a layout which requires using trenches for pipe alleys. Trenches transport flammables or toxics (liquid or vapor) from one area to another.

Electrical power, though carried in wires rather than pipes, is another service to treat in a fashion similar to the water and steam systems discussed above. It is most desirable to keep electrical power lines below ground inside the plant. If economics will not permit this, take care to prevent electrical power lines from falling on critical facilities. And, turning about, locate guy wires and elevated structures so they cannot fall across the power lines.

The plant may also involve docks for the loading or unloading of water-going vessels. The basic hazards here are similar to those of the other loading facilities, except that the quantities of materials involved compare more to a storage tank than to a tank truck or tank car. For docks, an isolated, downwind location is certainly desirable.

It is time now to look carefully at the locations for safety facilities. Particularly, the site for the first aid station is a problem for plant layout. The first aid station must be remote enough from the hazardous areas to remain unscathed in times of emergency. And yet, it is from these hazardous areas that most people will come who urgently need first aid. So it cannot be too remote. The time required to reach the first aid station may someday mean life or death to an injured

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person. Obviously, a compromise is the answer in this case. A similar compromise will be needed in the case of the fire station.

We should take a preliminary look at the general pattern of locations for safety showers, hose carts, and fire hydrants. However, the exact locations for these will carry over into the plot planning phase.

One final note on topography before we leave the subject, plant layout. It is, of course, not always possible to acquire the smooth, flat site that is so desirable. We may, in the final analysis, be stuck with a hilly or sloping site on which to lay out the plant. Several precautions will be in order. Sources of flammables, liquid or vapor, should not be uphill from points of ignition. Sources of toxics or flammable liquid should not be uphill from concentrations of people. The site may be subject to flooding. In this case, it is wise to locate boiler houses, electrical sub-stations, and pumping stations on high ground. Continued operation of these services becomes most imperative during emergency situations, such as will surely exist during periods of flooding. Tanks, too, are vulnerable to flooding. An empty tank will float on surprisingly little water. This can rupture lines connected to the tanks, perhaps resulting in very large spills, to further aggravate the emergency. We may even want to consider including a system of barriers to prevent the flow of liquids or the spread of fires from one area of the plant to another.

5.6. SAFETY PROBLEMS IN UNIT PLOT PLANNING

Proceeding into the final area of this chapter, we face the safety problems which arise in the plot planning of the process units. This involves the physical locations of individual pieces of equipment relative to each other within the battery limits of each processing unit. It is not easy to develop a plot plan which will minimize the construction and operating costs, and at the same time provide an adequate level of safety. In general, the more compact the unit, the lower will be the cost of piping, pumping, and real estate. On the other hand, safety considerations would dictate that the unit be well spread out for the separation of hazards and the provision of adequate space for fire fighting or other emergency operations.

A compromise is necessary. Fortunately, safety has a couple of allies which help to justify a more open plot plan with plenty of elbow room. Overcrowding will be very detrimental to the efficiency of the construction as well as the maintenance of the unit, adding to the initial and continuing costs.

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Experience, over the years, in trying to balance these various factors has led to a method of plot planning pretty well accepted by many people in the processing industries. The key element in this method is a long, straight, "in-line" arrangement of most of the towers, drums, exchangers, pumps, and the main pipe alley of the unit. Figure 5.3 will assist in discussing the "in-line" arrangement. This is a cross-section showing the main features involved.

Starting from the left side of Fig. 5.3, notice the main features are:

1. A roadway
2. A gantry-way, which is an area adjacent to the roadway along which travels a gantry crane on rails for handling the channels and tube bundles of the heat exchangers
3. Cooling water headers beneath the gantry-way
4. A line of fractionating towers, heat exchangers, accumulators, reflux drums, etc. It is usual for the grade below this line of equipment to be depressed about eight inches
5. The main pipe alley of the unit. If the unit includes fan-type air coolers, these can be mounted very nicely atop the pipe alley
6. A row of pumps
7. A roadway

In addition to serving well the operating and maintenance requirements of the unit, the "in-line" arrangement makes notable contributions to safety:

1. The two roadways flanking the "in-line" arrangement provide excellent access to both sides of a considerable portion of the processing equipment in the unit; ideal for fire fighting or other emergencies. The same two roadways plus the gantry-way serve as fire breaks, separating the "in-line" equipment from the other blocks of equipment in the unit.
2. The gantry crane is specifically designed for its job. Thus, it provides safe handling of the heavy exchanger components.
3. The area required for the gantry-way provides space for the tube bundles from exchangers to be worked on at the unit or stored until picked up and taken to the shops. All of this is possible while maintaining full traffic right-of-way on the roadway next to the gantry-way. In some of the smaller units, the gantry crane itself may be difficult to justify. Even so, the provision of some open area between the roadway and the line of equipment will help serve these purposes.

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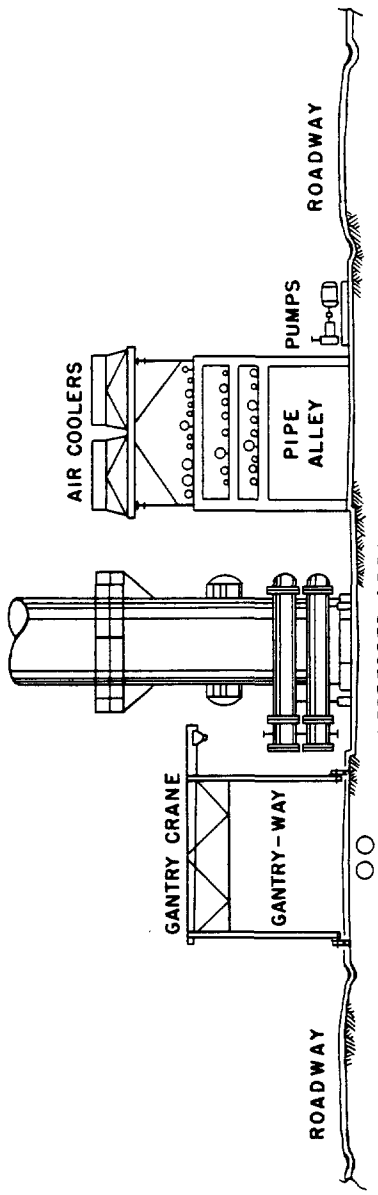

FIG. 5.3. A cross section of the "in-line" arrangement of processing equipment.

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4. The indicated location of the cooling water headers makes practically the entire cooling water system accessible for repairs without digging around and under the equipment.
5. The gantry-way provides an open area beside every fractionating tower. Tray segments and other tower internals may be lowered into this area or, in many cases, directly onto a truck bed for transportation to a working area. This minimizes chances of dropping these parts on the other equipment or on the men who may be working on the equipment.
6. The depressed area below the tower, drum, and exchanger line-up will retain spills of flammables or toxics from spreading into other areas until the sewers carry the material away. Firewalls 8 in. high crossing the depressed area from side to side break it up into segments. This prevents the spreading of spills along the length of the depressed area. Rather than the depressed area, some people prefer the use of low firewalls all the way around this line-up of equipment. The theory here is that the walls will prevent the spread of spills *into* as well as out of the area beneath the equipment. On the other hand, these walls may present somewhat more of a tripping hazard than the depressed area. Maintenance people seem to prefer the depressed area to the walls.
7. The strategic location of the pipe alley permits a clean and efficient piping layout. It virtually eliminates any runs of pipe with low overhead clearance or just above grade. Operating and maintenance personnel will find very few head-bumpers or tripping hazards in this type of arrangement. With this arrangement, there is no need for pipe trenches which are good carriers of hazardous liquids or vapors.
8. Notice that the row of pumps is immediately adjacent to a roadway and is completely free of overhead obstructions. This will permit the removal of pumps or drivers for maintenance, even while the unit is operating, with minimum chance for damage to any other equipment. Furthermore, the pumps may be safely handled by almost anything from a fork-lift truck to a large crane, whichever may be handy at the moment.
9. Fan-type air coolers are perplexing items in plot planning. Located at grade, air coolers require considerable space, and are hazardous to personnel. This is especially true in configurations which place the fans below the tube banks. Placing the air coolers above the pipe alleys relieves both of these situations without adding noticeably to the cost of structural support.
10. The arrangement provides clear areas for walking traffic along the

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length of the rows of equipment. The openness enables people to retreat rapidly from fires, explosions, or spills of toxic materials which may occur. It also allows rapid access to safety showers, fire hydrants, or monitors.

With the "in-line" equipment serving as the backbone of the unit plot plan, the other components of the unit (control house, compressors, reactors, knockout drums, surge drums, flash drums, furnaces, etc.) may be located along either side of the in-line grouping. This approach will usually result in a plot plan with battery limit dimensions approximating a square.

The "in-line" principle is also applicable in the case of integrated process units (integrated both process-wise and physically). In one specific instance, such a plot plan developed into a series of parallel, side-by-side, "in-line" groupings. The other components of the units occupied an area adjacent to these groupings extending along the ends of the lines of equipment. Separating these two basic areas was the "master" pipe alley for the entire process area. And, of course, branching from the master pipe alley were the individual pipe alleys for each "in-line" grouping. Figure 5.4 illustrates this concept graphically.

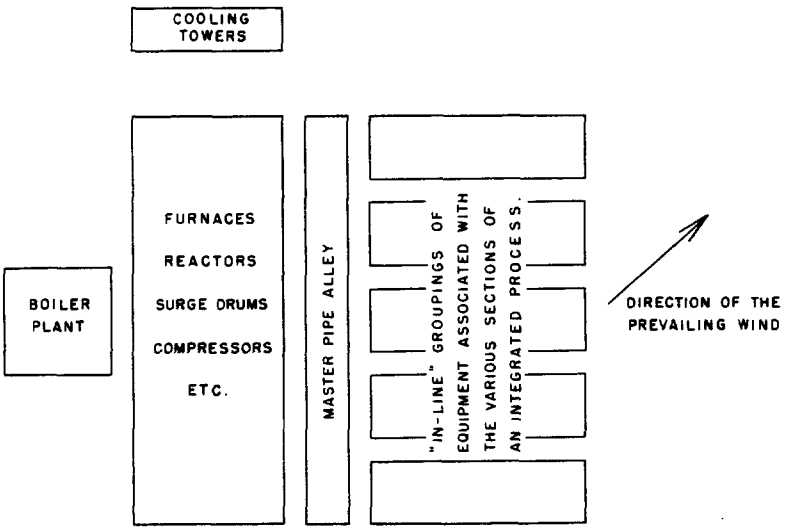

FIG. 5.4. An example of applying the "in-line" arrangement to integrated processing units.

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We shall turn now to discussing those components of the unit which are not part of the "in-line" group. The control house, the nerve center of the unit, will be our first topic. Operating considerations, by themselves, would probably put the control house in the center of the unit area. This would certainly make for the shortest routine tours of the operating check points. However, the glaring hazards thus created usually persuade us to locate the control house on the perimeter of the unit area. This will facilitate escape in the event of disaster. The control house should have doors to permit this escape in a direction away from the unit. The strategic placement of the control house for the best view of the total unit will also help. In units handling toxics, the control house should occupy an upwind location. Finally, keep the control house well separated from high-temperature or high-pressure vessels, or from vessels normally containing considerable amounts of flammable or toxic liquids.

Furnaces present two basic problems. As obvious ignition sources, they should be upwind from the rest of the unit. This, however, may cause a problem with flue gas drifting through elevated platforms on towers or other structures. In some cases, the best solution may be to compromise on a sidewind location. Make every effort to maintain at least a fifty-foot separation between the furnaces and other blocks of hazardous equipment.

Compressors may act violently, and, as such, should be respected with a reasonable separation from other hazardous equipment. They are also prone to leak gas, and, therefore, call for a downwind location. (Modern practice seldom puts compressors or pumps into houses because of this tendency toward leakage. In the few cases where weather protection is a must, it is best to stick to a pavilion-type building, having a roof but no sides.)

For reactors, the main consideration is to provide ample space and gear for safe handling of internals and the catalysts which may be involved. Sometimes we find reactors running hot enough to be dealt with as ignition sources. Occasionally, piping configurations outside the unit, causing pockets in the blowdown lines, will make it necessary to locate a blowdown drum at the unit. In such cases, the location of the blowdown drum must permit the piping from the relief valves to the drum to be as short and as straight as possible without any pockets ahead of the drum. Minimum pressure drop is essential.

Electrical power must enter the processing unit below ground. Try to arrange the point of entry so that there need not be any electrical manholes within the battery limits of the unit.

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If the unit will have an emergency dump valve or a snuffing steam manifold, these should be close to the control house and well removed from the most likely locations for fires or other hazards.

Fire hydrants or monitors must be close enough to the hazardous spots to be effective and yet not so close as to be inaccessible in emergencies. Watch for obstructions which might prevent the stream of water from reaching the critical points. See that there is a pathway for a quick retreat if necessary. Similar strategic locations are needed for hose carts, safety showers, etc.

Where it is absolutely necessary to bring railroad spurs into a unit area, try to provide adequate clearances for possible derailments. Also avoid locating equipment opposite the end of the spur in case railroad cars may overshoot, tearing out the bumper and colliding with the equipment.

Before finalizing the plot plan, give a good hard look at the possibilities of adding equipment in the future. A unit, beautifully arranged when built, can be completely fouled up by squeezing in additional equipment where inadequate space exists. Using the "in-line" arrangement, we usually find enough room in the pump row for some additional pumps and perhaps one or two additional drums. But consider carefully where to install future exchangers, towers, furnaces, reactors, etc.

There may be cases where it will be necessary to house a part or the whole of a processing unit indoors. Requirements for very precise temperature control or for constant operator attention are examples which might bring about such a necessity. In dealing with indoor facilities, two of the tools discussed in Section 5.3 become ineffective. There will, of course, be no prevailing wind to consider indoors. Separation by distance will most likely cause too great a financial burden because of the size of the buildings required. Even if this were not true, the effectiveness of distance is reduced indoors because released toxic or flammable vapors will be contained in the building and not dispersed as they would be outdoors.

However, we can still make good use of some of the other tools. For indoor installations, we will lean most heavily, perhaps, on separation by physical barrier. If ignition sources and sources of flammables both must be indoors, it will be well to allocate them to separate compartments of the building. The walls separating the two must have the absolute minimum of doors or other openings which would permit vapors or liquids reaching the sources of ignition. Facilities especially prone to fires, explosions, or the release of toxics (such

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as high-temperature, high-pressure, or large-volume containers) should be isolated from areas most often occupied by people, like the control center. Walls for this purpose must also have a minimum number of openings. But in addition, these walls should be designed for strength and fire resistance. Compartments subject to explosion may have one or more intentionally weak walls to help direct explosive forces in a direction away from people or other facilities.

A building of multiple floors or of varying floor levels will have a "topography" all its own. Sources of flammable or toxic liquids should not be "uphill" from ignition sources or from people. Where vapors are involved, the location of people and ignition sources will depend on whether the vapors are heavier or lighter than air.

As before, the concentration of hazards will be helpful in the demarkation of particularly hazardous areas. And, in addition, concentration of hazards will improve the practicability of providing special facilities for safety. Examples of such facilities are:

1. High-capacity ventilating systems to help keep air-vapor or air-dust mixtures below the explosive limits
2. High-capacity drainage systems for very quick removal of spilled liquids
3. Remotely operated handling devices
4. Automatic fire fighting devices such as water sprays, steam blanketing, and foam or inert gas systems

Despite these possibilities, when indoors, we must definitely limit the ultimate size of the possible combined effect of several hazardous pieces of equipment concentrated in one area or compartment because of the inherent proximity to people or other facilities.

As compared to outdoor facilities, the paths of retreat from housed facilities will be severely limited at best. It is difficult to overstress the need for a carefully planned system of platforms, ladders, stairs, walkways, doors, and escape chutes.

Permanent platforms should provide for access to all operating points in the unit which are not accessible from grade. From all operating platforms (with the possible exception of tower platforms) there should be two means of descent to help prevent trapping operating personnel during emergencies. Insofar as possible, all ladders, stairways, or slidepoles leading down from elevated platforms should land at grade at points which are least likely to be subject to fires or toxic spills. Also, these landing points should be close to pathways affording good retreat from the unit.

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The platforms at manholes on towers should provide enough working space for the safe handling of tower internals. The direction in which the manholes swing open should be away from the ladder leading down from the platform. Poorly placed valve stems can be head-bumpers, shin-splitters, and tripping hazards especially to personnel in a hurry.

Steam-trap discharges which are aimed across walkways, as well as uninsulated hot pipes may cause serious burns to the skin. Hot piping, where it passes within reach of operating people in their routine duties, must be insulated or otherwise protected.

Summary

This discussion has been oriented around the planning of new plants. The same problems, of course, apply to existing plants. While existing plants cannot be made over immediately to solve the safety problems built into them, the changes and revamps which occur over the years should follow a master plan which progresses toward a satisfactory level of safety. The ideas we have discussed here will help in developing such a master plan.

Sections 5.4, 5.5, and 5.6 have dealt most specifically with plants designed for the continuous processing of fluids. Nevertheless, many of the ideas in these three sections, plus the material in Sections 5.2 and 5.3 will find application in plants or units involving batch-type operations or the handling of solid materials.

5.7. SUMMARIZING CHECK LIST

The discussions in Sections 5.4, 5.5, and 5.6 are summarized in a check list to make them more useable. This check list appears in Table 5.1.

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TABLE 5.1. Check List of Safety Aspects, Site Selection, Plant Layout, and Plot Planning

Block or Unit of Facilities under Consideration	*Safety Aspects*
Site Selection	
Entire Chemical Plant	1. Downwind from populated areas
	2. Downwind from outside ignition sources
	3. Downwind from major highways
	4. Avoid stream and air pollution problems—check the legal restrictions
	5. Traffic problems at main entrance
	6. Isolated site—separation by distance from populated areas, ignition sources, or highways
	7. Topography of the site—flatter the better
	8. Sources of toxics or flammables not uphill from populated areas or outside ignition sources
	9. Rights-of-way across the site
Community surrounding the chemical plant	1. Sources of flammables or toxics downwind from the plant
	2. Ignition sources upwind from the plant
	3. Sources of flammable or toxics not uphill from the plant
	4. Proximity of fire stations to the plant
	5. Proximity of hospitals or first-aid stations to the plant
	6. Proximity of water sources to the plant
Plant Layout	
Processing Units	1. Separation from the boundaries of the plant
	2. Consolidated—not scattered
	3. Downwind from ignition sources
	4. Downwind from concentrations of people
	5. Separation from tankage[1]
	6. Separation from each other[1, 2]—effect of integration
	7. Not uphill from ignition sources or concentrations of people

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TABLE 5.1 (Continued). Check List of Safety Aspects, Site Selection, Plant Layout, and Plot Planning

Block or Unit of Facilities under Consideration	*Safety Aspects*
Administrative bldgs.	1. Peripheral location 2. Separation from hazardous areas 3. Upwind from sources of flammables or toxics
Boiler plants	1. Upwind from sources of flammables 2. Separation from hazardous areas 3. High ground if site is subject to flooding
Maintenance shops	1. Upwind from sources of flammables 2. Peripheral location because of railroad spurs and truck traffic
Loading and unloading facilities for tank cars and trucks	1. Peripheral location because of railroad spurs and truck traffic 2. Downwind from ignition sources 3. Separation from main line of railroad 4. Not uphill from ignition sources
Waste-water treating facilities	1. Downwind from ignition sources 2. Peripheral location 3. Downwind from concentrations of people
Water-cooling towers	1. Downwind from ignition sources 2. Downwind from concentrations of people 3. Downwind from roadways, operating units, and elevated structures
Flares or burning pots	1. Sidewind from ignition sources, operating units, or tankage 2. Downwind from concentrations of people 3. Separation from people and hazardous areas
Storage tanks	1. Separation of tanks from each other[1] 2. Separation of tanks from other facilities[1] 3. Size and arrangement of dikes[1]

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TABLE 5.1 (Continued). Check List of Safety Aspects, Site Selection, Plant Layout, and Plot Planning

Block or Unit of Facilities under Consideration	*Safety Aspects*
	4. Downwind location 5. Not uphill from ignition sources, process units, or concentrations of people
Roadways	1. All 4 sides of process units 2. One or 2 sides of each tank 3. Two-way access to every point in the plant, and two entrances 4. Minimum crossings of pipe alleys
Pipe alleys	1. Looped arrangement for fire water cooling water, boiler feed water, and steam 2. Minimum crossings of roadways 3. Clearances over roadways 4. Avoid passing through diked areas
Electrical power lines	1. Below ground if possible 2. Avoid passing over critical facilities 3. Separation from elevated structures which may fall across power lines 4. Looped arrangement to critical users
Electrical switch gear	1. Upwind from sources of flammables 2. High ground if site is subject to flooding 3. Not downhill from sources of flammables
Docks	1. Separation from other hazardous areas 2. Downwind from ignition sources
Unit plot planning	
Fractionating towers	1. See "in-line" arrangement Section 5.6
Drums	1. See "in-line" arrangement Section 5.6
Heat exchangers	1. See "in-line" arrangement Section 5.6

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TABLE 5.1 (Continued). Check List of Safety Aspects, Site Selection, Plant Layout, and Plot Planning

Block or Unit of Facilities under Consideration	*Safety Aspects*
Pumps	1. See "in-line" arrangement Section 5.6
Pipe alleys	1. See "in-line" arrangement Section 5.6
Roadways	1. See "in-line" arrangement Section 5.6
Control houses	1. Locate on perimeter of the unit 2. Doors facing away from unit as well as toward the unit 3. Locate for good view of unit 4. Upwind from sources of toxics 5. Separation from high temperature or high-pressure vessels 6. Separation from vessels containing flammable or toxic liquids
Furnaces	1. Upwind or sidewind from the rest of the unit 2. Separation by 50 ft from other hazardous equipment
Compressors	1. Downwind from rest of unit 2. Separation from other hazardous equipment 3. Not in closed building
Reactors	1. Space and gear for safe mechanical handling 2. Hot reactors may be ignition sources
Blowdown drums	1. Locate for best piping arrangement with minimum pressure drop
Electrical power lines	1. Below grade 2. No electrical manholes inside the unit
Emergency dump valves and snuffing steam manifolds	1. Close to control house 2. Remote from hazardous areas
Fire hydrants or monitors, safety showers, hose carts, etc.	1. Close but not too close to the hazardous areas 2. No obstructions for monitors 3. Good path for retreat

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TABLE 5.1 (Continued). Check List of Safety Aspects, Site Selection, Plant Layout, and Plot Planning

Block or Unit of Facilities under Consideration	*Safety Aspects*
Railroad spurs	1. Clearance for derailments 2. No equipment opposite the end of the spur
Indoor facilities	1. See Section 5.6
Elevated platforms	1. Permanent platforms for all operating points 2. Two routes for descent 3. Landings at grade in safe locations
Piping	1. Watch for head bumpers, shin splitters, and tripping hazards 2. Personnel protection from hot lines 3. Safe steam trap discharges

It is important to keep these items in proper perspective. Remember that these are factors related to safety only. They will not be compatible in every instance with the other factors which come to bear on site selection, plant layout, and plot planning. Compromises may be necessary. And, finally, do not accept this as the final, all inclusive, check list complete for all time. By applying the general principles discussed in Sections 5.2 and 5.3 of this chapter, we may make additions.

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3. D. V. Gagliardi and N. R. Pratt, "Guidelines to Follow When Designing for Plant Safety," *Plant Engineering,* **17,** pp. 108–111 (June, 1963).

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6

Services and Facilities

David T. Smith

The title "Services and Facilities" might be construed as all those functions which support chemical, manufacturing, and laboratory work, such as purchasing, engineering design, and training. For our purpose we will consider only those physical facilities and services directly used by personnel such as electricity, water, air, service gases, steam, heating, refrigeration, sanitary and process sewage, waste disposal, locker and shower facilities, eating facilities, traffic, parking and control of platforms, stairs, ladders, elevators, and over-pressure relief.

These items may be not only of tremendous importance in their direct contribution to safety of the employee, but failure to install, maintain, and use them properly may cause injury. It is not our province to tell how to design and operate these functions that support the manufacturing and laboratory work, but comments may be of value on key safety points that experience has shown need close attention.

6.1. ELECTRIC LIGHTING AND POWER

Each plant or laboratory should adopt definite rules and procedures for electrical installations and work. All installations should be in complete accordance with the National Electrical Code.[1]

It is good economy usually, as well as safety, to install all lighting, power wiring, and equipment in chemical operations according to requirements for Class I, Group D, Division II, Hazardous Locations. This protects against the temporary presence of explosive mixtures

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from leaks or spills of flammable liquids or gases. Regardless of the flammability of operations when installed, changes in process to use flammable materials always seem to occur, sometimes without anyone realizing the electrical installation is unsuitable. The Class I, Group D, Division II requirements include vapor-proof lighting fixtures, totally enclosed motors, oil immersed or properly enclosed switches, and complete absence of open sparking devices (see National Electrical Code for details).

It is generally more economical to prevent explosive atmospheres in rooms than it is to try to provide the special explosion-proof electrical equipment necessary for such conditions. Personnel should never be allowed to work in an explosive atmosphere. Where the creation of such atmospheres cannot be avoided through control of flammable liquids, gases, and dusts, the space involved should be limited and segregated by hoods or special ventilation. All electrical equipment exposed should conform to the requirements for Class I, Group D, Division I, Hazardous Locations, or whatever class and group the specific situation falls in.

Electrical equipment on open, outdoor structures more than 20 feet above ground usually are considered to be free from exposure to more than temporary, local explosive mixtures near leaks.

Even single phase, 110-volt fractional horsepower portable tools now come supplied with 3-wire circuits to provide a positive ground to the case. We recommend installing all light and appliance wiring and equipment the same way. This will be required some day; why not go ahead and be safe now?

All building steel and outdoor structures, all tanks, drums, pipelines, open-end hose, tank cars, trucks, and chemical equipment handling or using flammable liquids or gases, or in areas where handled, should be grounded to dissipate static electricity according to the National Electrical Code. Flexible grounds should be installed to large water pipes or driven grounds, and never to electrical conduit, branch sprinkler lines, gas, steam, or process piping. These grounds should be properly maintained and the electrical resistance to ground measured periodically. Grounding conductors to give lightning protection are of much larger capacity.

The voltage, name and number of equipment controlled should be clearly marked on all switch boxes, compensators, and starters. Pins and chains should be required on all butterfly switches.

Extension cords should all be 3-wire, and limited to 25 ft in length.

Only flashlights approved by Underwriters Laboratories for Class I, Group D, locations should be permitted in the plant. Unapproved

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flashlights have a tendency to find their way into hazardous locations from nonhazardous locations.

The present type hearing aids are capable of producing a spark of sufficient energy to ignite flammable vapors. The switch of a hearing aid should not be operated where there is a spill or leak which might result in an explosive mixture. Ordinary telephones make a high energy spark whenever dialed or rung. Explosion proof telephones are available. Radio paging system receivers may also present a problem.

Owing to the rapid development of new equipment and the lack of demand by purchasers, there is little Underwriters Laboratory approved electrical instrumentation available. Much of it can furnish an ignition source if faults develop. However, with care in selection and installation, it is not difficult usually to avoid ignition sources from normal operation of the electrical instruments. Sometimes, instruments can be enclosed and continuously purged by a very low flow of clean air through a small air line. Often the instrument can be located outside the danger zone.

Electrical work should be done only by qualified electricians or other specially authorized personnel.

Before starting work on electrical circuits or equipment, voltage tests should be made to make certain that the circuits are not energized. All voltage tests on systems at 2300 v or higher should be made by means of a potential transformer and voltmeter. An approved voltage tester may be used on circuits at 550 or lower voltages.

Following major maintenance or construction work on electrical circuits they should be tested for grounds by an approved method before the circuits are energized.

Work on energized electrical circuits and equipment, at any voltage, is not only unnecessary in most cases, it is a result of poor planning and false pride in being able to "get away with it." No "hot work" should be permitted if it is reasonably possible to arrange for a shut down, and where it is permitted, only by written exception in each case, signed by top members of management.

All portable electrical equipment should be inspected and tested periodically for electrical faults. Equipment exposed to severe conditions such as extension cords and portable drills in operating buildings and shops should be inspected monthly. Laboratory equipment under moderate exposure should be inspected semiannually, and other equipment which receives light usage such as office machines should be given annual inspections. Each piece of equipment should be identified

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by an affixed number and records kept or shown on the equipment to prevent overlooking inspection dates.

The fuse capacity of every circuit should be determined and marked at the fuse holder. Only authorized personnel should be permitted to replace or change fuses, and periodic checks should be made to see that proper size fuses are actually in place.

Avoid using metal rules, metal tapes, metal hard hats, or other metal objects near energized electrical equipment where there is the possibility of an exposed electrical conductor.

Seeing depends not only on lighting intensity as measured in footcandles, but on difference in color, in light value contrast, and in reflectivity of surfaces. Accenting hazard points, controls, and other

TABLE 6.1. General Recommended Values of Illumination (Illuminating Engineering Society)

	Footcandles
Most Difficult Seeing Tasks	200 to 1000*
Finest precision work involving finest detail, poor contrasts, over long periods of time.	
Examples: extra fine assembly, precision grading, extra fine finishing	
Very Difficult Seeing Tasks	100
Precision work involving fine detail, fair contrasts, long periods of time.	
Examples: fine assembly, high-speed work, fine finishing.	
Difficult and Critical Seeing Tasks	50
Prolonged work involving fine detail, moderate contrasts, long periods of time.	
Examples: ordinary bench work and assembly, machine shop work, finishing of medium-to-fine parts, office work.	
Ordinary Seeing Tasks	30
Involving moderately fine detail, normal contrasts, intermittent periods of time.	
Examples: automatic machine operation, rough grinding, switchboards, continuous processes, conference and file rooms, packing and shipping.	
Casual Seeing Tasks	10
Examples: stairways, reception rooms, wash rooms and other service areas, active storage.	

* Obtained with a combination of general lighting plus specialized supplementary lighting. Care should be taken to keep within the recommended general brightness ratios (Table 6.2) and to avoid glare conditions when light-colored materials are involved.

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TABLE 6.2. Recommended Permissible Brightness Ratios of Areas of Appreciable Size within Range of Vision

Areas Involved	*Permissible Brightness Ratios**	
	Plant Areas	*Office Areas*
Between tasks and immediate surroundings	5 to 1	3 to 1
Between tasks and more remote surfaces	20 to 1	10 to 1
Between luminative surfaces and surface areas adjacent to them	40 to 1	20 to 1
Anywhere within worker's environment	80 to 1	40 to 1

* The ratio of brightness of task to brightness of surrounding varies as to whether the task is darker or lighter surface.

key points with contrasting color is an important aid to better seeing. Reducing or removing glare is necessary, as is eliminating too great a contrast in the light intensity of the field of sight. If the general illumination is high, we cannot see into an exceptionally dark area. Similarly, in an area of low illumination, a very bright spot such as an unshielded light tends to blind us. However, contrast within the limits shown in the table helps us to see quickly.

6.2. WATER

Hot water is used by many plants for washing down floors and equipment. Do not connect steam and water lines directly to make hot water for this purpose except through an adequately designed and maintained water-steam mixer that will shut off completely when the cold water supply is interrupted. The maximum possible hot water temperature should be known and posted, as well as all lines identified by name at the mixer and at all outlets. Water hotter than 135°F coming in contact with the skin usually results in at least first degree burns.

Never make hot water for bathing or washing by direct mixing of steam and water—always use a water heater involving heat exchange, which will give accurately controlled water of predetermined temperature. Water at shower heads or wash basins must not be hotter than 135°F, regardless of the operation of shower mixing valves under the control of the user.

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Hot water heaters should not only have a pressure relief valve for over pressure but also a fusible plug for over temperature relief.

In many plants water which is not of drinking water purity is used for cooling or other process use. It is important that all water outlets in such cases be identified as to *type* of water, and precautionary rules should be posted to warn employees to drink, wash, and bathe only from potable water.

Safety showers should be installed where handling corrosive or toxic materials. Even where employees wear flame-retardant treated clothing, safety showers may be of great value in extinguishing fire on employee's clothing when handling flammable liquids. It is important that a large volume, low velocity discharge from directly overhead be used, so that the employee will be drenched completely and continuously. A satisfactory minimum flow is 50 gpm. The high velocity spray from the ordinary domestic type shower head is unsuitable.

Water to outside showers may be heated by chasing the water line with a low temperature electric "ground heating" cable having a maximum temperature of 80°F.

The valves of all safety showers should be at the same height and same relative position to the shower head. They should operate in the same direction and exactly alike. An employee needing a safety shower may be groping for it, unable to see.

The shower station should be identified by bright, contrasting color paint and a special colored light.

Frequent, scheduled testing of the shower is essential. Training and retraining in the location and use of the safety shower is important.

Safety of water supply is important both from the standpoint of securing a supply that is adequate in purity for the use required, and from the standpoint of prevention of contamination of the source of supply.

There appears to be no problem in direct connection with municipal or other public sources for sanitary and drinking use. Extreme care must be taken with certain types of flush toilets to prevent sewage contamination to water supplies in case of loss of water supply pressure. Anti-siphon devices are required.

Any connections made to water supplies or systems for process supply water or process cooling water must be made in such a manner that there *can be no back flow* of possibly contaminated water to the municipal or public source, or to the plant system that is used for drinking, bathing, or washing purposes. We should not rely on check valves. There must be a positive mechanism to prevent siphoning back of water in case of loss of pressure in the supply line. An effective arrangement

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is to have the municipal supply empty by free fall into a tank from which we take water to a pump inlet for process purposes. The tank is supplied with an overflow outlet beneath the inlet from the municipal supply.[2]

It is important to check that all installations are in conformance with local and state plumbing and building codes. Permits issued only after official inspections are required in many cases both for original installations, alterations, and periodically thereafter.

6.3. AIR

Air is generally compressed and piped to various locations for process use, instrumentation, and for breathing by humans using air masks. Separate systems should be provided for each of these three uses.

Air for human consumption must be free of contaminants such as carbon monoxide, oil vapors, flakes of rust, or other foreign materials. The ordinary oil lubricated air compressor cannot be relied on to deliver air of this quality during continued operation. Special air compressors designed for producing breathing-quality air are required.

After producing air of breathing quality, it must be kept pure. The only way to insure this is to have no interconnections for process or instrument usage. Check valves have been known to fail.

Cylinder air for human consumption may be purchased in many areas, but should be clearly marked and guaranteed as being "Breathing Air."

When using piped air systems for air masks, filters and traps should be installed near the outlets to intercept and remove foreign particles and liquids, such as condensed moisture. Piping down stream from the filters should be nonferrous, preferably copper, brass, or "Delrin." It is not necessary to add or remove moisture from breathing air as the body can tolerate extremely wide variations in humidity without discomfort or harm.

All breathing air outlets should be plainly identified and personnel trained never to use an unidentified outlet.

Emergency breathing apparatus should always be of the self-contained type, either the air cylinder or "Chemox" type. Canister-type masks which filter out harmful gases cannot be depended on in emergencies because of the possibility of their being used where the percentage of harmful gas is of greater concentration than they can handle, or the possibility of an oxygen deficiency. The canister mask if used should be limited to scheduled outdoor use where there is a known maximum concentration to be encountered, where plant supplied

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breathing air is not available, and where the exposing gas is readily noticeable in low concentrations such as sulfur dioxide and ammonia. Cylinders of oxygen should not be used for emergency breathing because of the additional fire hazard they present. See Chapter 23, Respiratory Hazards and Protection.

Ventilation

Satisfactory indoor general ventilation requires air to be of comfortable temperature and humidity and free from harmful or disagreeable contaminants. Humidity alone is not a major factor, humans can exist in comfort in air of widely varying percentages of humidity if the temperature is adjusted accordingly.

Natural ventilation through windows and roof ventilators may suffice if adequate to prevent overheating in the summer. However careful checks should be made to assure that concentration of air contaminants does not build up above maximum allowable limits in the winter when the building is closed up.

Forced ventilation systems require individual design. Exhausted air must be replaced by fresh, clean air. Exhaust collection at the points of liberation of contaminants is generally more satisfactory than frequent changing of the entire room air. Balancing of exhaust flows is often tricky, and field tests are necessary after installation. It does no good to exhaust contaminated air and discharge it where it will be drawn in again with the fresh air intake. Locate exhaust outlets where effluent cannot enter the fresh air intakes.

6.4. SERVICE GASES

Nitrogen, carbon dioxide, and other inerting gases are sometimes referred to as "service gases" rather than process gases. Usually installed with schedule 40 piping for use at 150 psi or less, the principal safety problem has been one of identification. Fatalities have occurred when inerting gases have been mistakenly used for air during work inside tanks or confined spaces. While color coding is helpful, all outlets and valves of service gases (as well as all other materials) should be identified by having the name of the material affixed. Pressure-sensitive tapes, metal and plastic tags, or painted signs are all suitable.

6.5. STEAM

Only low pressure steam, 15 psi or less, is suitable for most room-heating equipment. Identification of steam lines by pressure is im-

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portant if there are steam services of more than one pressure. Discharge of steam traps, blow downs, and such should always be carried to points where unpredicted discharges will not expose personnel. An outside stone-filled dry well can be used for a small steam trap condensate discharge. If steam condensate discharges into a sewer line, provision must be made to prevent buildup of pressure in case of trap malfunction and escaping steam. Severe burns can result from persons contacting unprotected lines or radiators. All lines, fittings, and radiators less than seven feet above the floor should be insulated or guarded if located where personnel may contact them.

6.6. WASTE DISPOSAL

Air pollution, a subject of growing concern to the public, demands that we do not liberate gases in harmful concentrations to the air, and that we limit to an absolute minimum the emission of visible smokes and vapors. Each case is an individual engineering problem, involving consideration of absorbers, adsorbers, and scrubbers for gases, cyclones, electrostatic precipitators, or other equipment for solids. Revisions in process to eliminate the cause of the emission can sometimes be accomplished.

Open burning grounds for solid and liquid wastes are permissible now in only a minority of locations, and they will undoubtedly be restricted further in the future. Liquid and solids incinerators are now available which will handle nearly all wastes. Heavy oils and tars can be diluted in many cases with light oils to permit incineration under conditions that create a minimum of smoke. Large volume solid wastes containing a high percentage of paper, rags, and wood can be successfully burned with a minimum of smoke by the use of the "teepee" type incinerator.

Some wastes may have to be buried instead of burned because of toxicity. Radioactive wastes and contaminated equipment can be disposed of through firms contracting for that service.

The disposal of liquids containing chemical wastes to public sewers or streams requires that we have sufficient neutralization and treatment to insure that they are harmless in the concentration present in the carrier stream when they leave our property. Skimmers and traps must be used to remove any oils or other nonwater soluble materials. Settling basins can be effective in removing entrained solids.

Transportation of wastes by underground piping systems may present the problem of explosive mixtures in the air space in the pipe if flammable volatile materials are handled. We must prevent all volatile

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flammable waste materials from entering closed underground sewer lines. There should also be enough openings for clean-out and maintenance in the sewer pipe. Sometimes it is necessary to install open ditches for waste liquid sewers with adequate fire stops. The open ditch, lined with or constructed of material resistant to the chemical exposure, has the added advantage of accessibility for clean-out and ease of inspection. Properly treated, laminated, wood-box ditches have proved very successful. Dilution with sufficient quantities of water before entering the waste stream disposal system helps with most waste disposal problems.

Waste material discarded on the premises as trash presents a challenge not only to appearance but to safety and quality of production. The overall effectiveness of management of a chemical plant or laboratory can usually be accurately judged by the housekeeping observed.

We are a nation of litterers, because we are inherently lazy. To prevent employees from discarding waste paper, gloves, gaskets, and a hundred other miscellaneous objects on our ground, walks, and even in out of the way corners of buildings, we must make it easy for them to dispose of waste materials quickly and with a minimum of physical effort. This means we must provide commodious, attractive trash collection containers at strategically placed locations, frequently spaced. We must have an efficient system for keeping them collected and emptied. Separate containers for metals and for glass are usually justified. Each should be so labeled and their use enforced.

Each employee should be required to keep his own work location clean. If an employee knows he has to clean up he is much more careful not to create a housekeeping problem.

The example set by supervision usually determines the overall effectiveness. If the supervisor or foreman ignores an item of discarded trash, or contributes one, then his area will be trashy. The housekeeping efficiency of an employee is usually a little less than that of his boss, seldom any higher.

Efficient methods of collection and return of unused maintenance and repair materials can not only prevent poor housekeeping but result in major savings. "Tote" boxes for collection and return of unused materials are useful.

6.7. PLATFORMS, STAIRS, AND LADDERS

Falls constitute a surprisingly large percentage of serious injuries in the chemical industry considering that the human race has been walking and climbing as long as it has. The condition of access routes such

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as platforms, stairs, and ladders accounts for many injuries; their misuse accounts for more.

Walking Tips

Look where you are stepping.
Walk only on recognized pathways unless required to walk elsewhere.
Do not step on railroad rails or other possibly slippery surfaces unnecessarily. Do not step into puddles, on wet spots, or on oily spots.
Climb and descend stairs one step at a time, with one hand on or near rail. Never use stairs with both hands occupied in carrying objects.
Run only in case of extreme emergency.

Platforms

Platforms forty-eight inches or higher from the ground should have guard rails at waist height. Where material is being moved from such a platform the rail may be removed temporarily if the edge is clearly marked with a broad yellow stripe and all persons warned of the falling hazard. Toe boards should be installed on platforms where height and traffic present a hazard of objects falling off the platform on persons.

On platforms under forty-eight inches in height, the guard rail may be omitted, but if there is any likelihood of the edge not being clearly observed, stripe painting of the edge is desirable.

Stairs cut into the edges of a platform should always be guarded by rails, and hand rails are always desirable even when the steps are exterior to the platform.

The importance of adequate illumination on platforms cannot be overemphasized. It is difficult to predict when some person will cross or use a platform.

Ramps

Ramps should have non-slip surface, and not have a gradient of more than one inch rise per ten inches of horizontal run. They are preferable to stairs for movement of groups of people at one time. They should be provided with hand rails as if stairs. When used for vehicles they must also have curbs.

Stairs

a. All stairs should meet the requirement of the Building Exits Code (N.F.P.A. No. 101, A.S.A. Code A-9.1).

b. Maintenance of stairs requires periodic scheduled inspections, covering at least these points:

Are they kept free from tripping hazards?
Are hand rails provided and free of rough or sharp points?
Are the nosings excessively rounded, worn, slippery?
Are there cracks, loose treads, or other repair work indicated?
How nonskid is the tread surface? It is kept dry, clear of snow and ice?
Is the landing adequate in size, and arranged so that there is no change in level as one passes through a door?

Ladders

Ladders are a second choice to stairs. Permanently installed ladders should be of steel, not wood. Cage guards should be installed on all fixed ladders which extend more than 20 ft above the ground, and should when installed, start at the 7-ft level. Straight ladder runs over 30 ft should be broken with platforms every 20 ft or less.

Fixed ladders providing access to roofs and other places where installed at a wall should have the rungs a minimum of 8 in. from the wall. Where the ladder reaches the access level, the side rails should be carried 42 in. above. This permits the climber to hold firmly while changing from the ladder to the level or vice versa. Such point of entry should always be protected by a chain or gravity swinging bar gate to protect a person from falling from the elevated surface.

Avoid the installation of ship's ladders in buildings. They present a fascinating temptation to employees to be used as a stair, descending facing away from the ladder, and to some the allure of a sliding chute. Use either standard stairs or ladders; nothing in between.

All portable ladders, either straight or step, should be purchased in accordance with A.S.A. Standard A 14.1. "Heavy-duty" ladders give an extra margin of safety. Stepladders should have a metal tie rod beneath each step.

All portable straight ladders should be equipped with nonskid feet, and with permanently affixed tie ropes 9 ft in length, spliced to the second rung from the top. Extension ladders should be equipped with box-type enclosed dogs to prevent fingers from being crushed.

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When using ladders, all portable straight ladders either single or extension should be held until tied or clamped at the top. Use of extra long ladders by personnel who are not specially trained in their use should be avoided. A good rule of thumb limit is 16 ft for a straight single ladder, 30 ft for a straight extension ladder and 12 ft for a stepladder.

The proper positioning of a portable straight ladder is to have the base one-fourth of the height from the wall or support plane.

Never overreach from the ladder, straight or step-type. Never stand on the top step of a stepladder, always work with the knees against the top for support. The safety platform type is preferable from this viewpoint. Only one man should work from a single ladder at a time. Face the ladder, keep both hands free, and take only one step at a time when ascending or descending a ladder. Use belt fastening or lifting line for movement of tools and materials.

Do not cover the surface of a wood ladder with paint or plastic. This prevents inspection of the surface of the wood for cracks or flaws. Wood ladders should be treated with linseed oil, or shellac and spar varnish.

The user of a portable ladder should inspect it each time before use, but in addition there should be a regular periodic inspection of all ladders. Each ladder should be marked with an identifying number and the date of inspection.

6.8. ELEVATORS

A.S.A. Code A17.1 covers the requirements for installation of elevators, hoists, dumb waiters, and escalators and should also be used as a guide for inspection and maintenance.

All elevators should have mechanically and electrically interlocked car gates and hoistway gates. Safety dogs to check free fall are required. Biparting type doors should be equipped with safety astragals to prevent crushing of a hand caught during closing.

Monthly testing and inspection of interlocks by qualified personnel should be carried out, and records should be kept.

6.9. EXITS AND AISLES

It is important that exits of buildings be adequate to accommodate all the employees in case of fire or other emergency. The Building Exits Code (N.F.P.A. No. 101) covers requirements of construction.

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In general every building must have at least two means of escape from each floor. Where quick egress from hazardous operation is vital, quick opening emergency doors and chutes should be provided. Each employee should see that exits are not obstructed.

Each employee should be able to reach his work area and carry out his duties without being exposed to bumping, tripping, or slippery hazards. This requires clean, adequately maintained floor surfaces, freedom from protruding objects, and 7 ft of head room. Where obstructions are necessary, they should be padded if possible, and marked with yellow paint. Minimum aisle widths for one-way foot traffic should be 3 ft, for two-way foot traffic, 5 ft. Greater width is preferable.

Plastic tape 3 in. wide or paint stripes should be used at blind corners to designate center lines of halls and aisles, and personnel instructed to "keep to the right."

6.10. TESTING AND INSPECTION PROCEDURES FOR UNFIRED PRESSURE VESSELS AND RELIEF DEVICES

A program should be established for inspecting and testing unfired pressure vessels on a periodic schedule. The same applies to safety valves and rupture discs on all pressure vessels. The A.S.M.E. Code for unfired vessels furnishes an overall guide. See Chapter 11, Pressure Vessels.

6.11. BATHING, WASHING AND CLOTHES CHANGING

All employees must be encouraged to adhere to high standards of personal bodily cleanliness for health reasons in both chemical manufacturing, laboratory, and sales work. In many operations, this justifies mandatory daily showering and changing to clean work clothes, and mandatory washing of the face and hands before smoking, drinking, or eating. If exposed to chemicals, the hands should also be washed thoroughly before touching the more sensitive parts of the body such as the pubic region. Providing separate lockers for street and work clothing is often advisable. The opinion of a qualified industrial physician should be sought in establishing adequate health control measures. See Chapter 16, Effects of Toxic Agents.

To reduce slipping hazards in shower rooms, perforated rubber mats may be used if cleaned and dried regularly. A nonabsorbent floor surface with roughened surface is generally much more desirable.

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Grab rails installed at waist height on the walls at the showers have been found helpful to prevent slips and falls.

The round group wash basin of nonabsorbent cement is excellent from the standpoint of service and ease of maintenance.

Liquid or powdered soap recommended by the industrial physician is preferable to bar soap. Soap scraps frequently remain on the floor as slipping hazards.

As mentioned in the section on water service, all water to showers and wash basins must be delivered to the outlet at a temperature not in excess of 135°F. Water hotter than this will burn. Showers should be fitted with a dial-type mixing valve which requires the user to go through the cold water phase before reaching the hot water. Direct mixing of steam and water to make hot water for use on the body is forbidden. Hot water must be manufactured by use of a water heater involving heat transfer.

Adequate ventilation, control of humidity, and efficient janitor service are a must for expecting cooperation from employees in maintaining the needed cleanliness in shower, lockers, and toilet facilities.

In spite of advertising to the contrary, foot baths of various liquid antiseptic solutions present little assistance in controlling or preventing athlete's foot, a fungus disease. Complete drying of the feet after bathing, keeping them dry, and use of antiseptic powders recommended by a capable industrial physician are far more effective measures.

Lockers with sloping tops discourage employees from leaving articles on top. Periodic inspections in the presence of the occupant insures good housekeeping and cleanliness in lockers.

6.12. EATING FACILITIES

Humans love to eat, not only at meal times but between meals. This has been attributed to hunger, boredom, frustration, sociability, desire for recognition, and many other reasons. Regardless of cause, we must recognize that employees will eat frequently whether we like it or not, so we must make provision for that fact.

Provide refrigeration for safe storage of perishable foods that the employees bring to work. The household refrigerator, if of sufficient size and frequently cleaned, is satisfactory. Both the refrigerator and lunch-box storage facilities should be convenient and free from the likelihood of chemical contamination. This means they should be away from places where chemicals are handled.

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Provide a clean, well-lighted location for eating, drinking, and smoking away from chemical operating or laboratory work. In most cases it is necessary to prohibit the carrying of food or chewing materials in work areas.

We must require (and provide convenient facilities for) washing the face and hands before handling or consuming foods, gum, cigarettes, chewing tobacco, or other materials that will enter the mouth.

6.13. TRAFFIC AND PARKING

We are a nation on wheels. Outside the plant or laboratory, we ride. Inside we may walk, but not far. This means parking lots for employees' cars close to their place of work, and adequate walking facilities from the parking location to the job. Snow and ice removal from the parking lot and walks is usually a management responsibility. For buses, loading and unloading facilities should be located for off-the-street access.

Parking lots with guide lines will require about 9 by 26 ft parking space per car plus drive width of from 16 to 30 ft, depending on the parking angle. Without guide lines or personal control, more space will be required.

Employees tend to stagger their arrival time over a much longer period than their exit, so employees simultaneously backing out of parking spaces into the drives often have minor collisions. To avoid this some employers have found that having employees back into the parking space so that they can drive out facing the drive is very effective. In some arrangements, a drive-through system can be used.

Concrete or wood parking guides to insure uniform and minimum space per car appear effective, though other plants get adequate control with painted lines alone plus training. Fixed parking guides are an obstruction during snow removal.

Separate pathways to provide employee protection while traversing the parking lot appear to be diminishing in use. Since these are not provided in the usual commerical lot, people seem to be able to get along safely without them.

Whether separate walkways should be provided inside the plant or the employees requested to use plant roadways for walking depends of course on the adequacy of the road surface and lighting, its width, the traffic level, and speed. If roads are used for walking, it is generally better to paint walkway boundaries on them and give the pedestrian the right of way inside the walk lines than to depend on

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employees facing traffic. On sparsely used roads employees may walk on the edge safely if facing traffic.

A 5 ft width of walk appears to be adequate for the usual walk involving movement of several people at the same time.

Lighting of plant roads and walkways for pedestrian illumination is a must if there is night travel on them. Illumination levels for paths, and roads used for walking should be 10 footcandles. Lights should be elevated and shielded so they do not tend to blind pedestrians or drivers approaching them. Great contrast in illumination levels on the same path should be avoided.

Blind intersections between paths and vehicle routes, either automotive or railroad, should be avoided. Guard rails and gates are useful solutions.

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7

Hazards of Commercial Chemical Reactions

George T. Austin

Commercial chemical production of useful products results from the conversion of one substance into another. Some conversion reactions are simple and subject to very little hazard, but some are most complex and hard to control or understand. When the exact chemical nature of the reactants and products is known, it would appear that it should be possible, by applying known laws of chemistry, to assess the hazards of commercial production of the substance. In practice, this has not proved to be true. The exact paths taken by substances in changing from one substance to another are often devious. The alternate and sometimes dangerous paths which the substances may take under only slight variations in temperature, pressure, or composition, and the kinetics of the various steps are rarely known and frequently most difficult to foresee.

The effects of temperature on chemical reactions are the most frequent cause of surprises, so it is well to consider the known facts concerning their relation to reaction rate. One of the oldest known rules-of-thumb of chemical work is the observed fact that reaction rate approximately doubles with every 10°C rise in temperature. This is a surprisingly good approximation for a wide variety of types of reactions and can be used in estimating when no other data are available. One implicit assumption in this statement is that the temperature of the reaction mix is uniform. This is rarely true in commercial

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reactors, so reaction rates may vary considerably within a unit, particularly if a considerable radial temperature gradient exists.

The Arrhenius equation is more exact than the rule of thumb and expresses the effect of temperature on the reaction rate in the form:

$$k = \mathbf{A}e^{-\frac{E}{RT}} \tag{1}$$

where k = rate constant for the reaction
$\mathbf{A}$ = a constant
E = energy of activation for the reaction
R = gas constant
T = absolute temperature
e = natural base for logarithms

A reaction whose rate changes with temperature in accordance with equation (1) is generally thought of as a normal reaction. Figure 7.1 (*a*) shows this type of behavior graphically. Also Fig. 7.1 shows several other types of rate change with temperature curves frequently observed in practice. It is interesting to note that if k doubles for a 10°C rise, this corresponds to an energy of activation of approximately 13,000 cal/mole.

It is evident from Fig. 7.1, that many other types of reaction speed changes occur besides the simple Arrhenius (logarithmic) one. Walas[2] has tabulated the reasons for the existence of the types shown in Fig. 7.1 as follows:

a. Normal behavior; rapid increase in rate with increased temperature.
b. The behavior of certain heterogeneous reactions dominated by resistance to diffusion between phases, a slow increase in rate with increased temperature.
c. Typical of explosions, where the rapid rise takes place at the ignition point.
d. Catalytic reactions controlled by the rate of adsorption (in which the amount of adsorption decreases at elevated temperatures) and enzyme reactions where high temperatures destroy the enzyme.
e. Some reactions, combustion of carbon for example, complicated by side reactions which become significant as the temperature is increased.
f. Diminishing rate with increased temperature, for example, the reaction between oxygen and nitric oxide, where the equilibrium conversion is favored by lower temperatures and the rate appears to depend on the displacement from equilibrium. Only Fig. 7.1

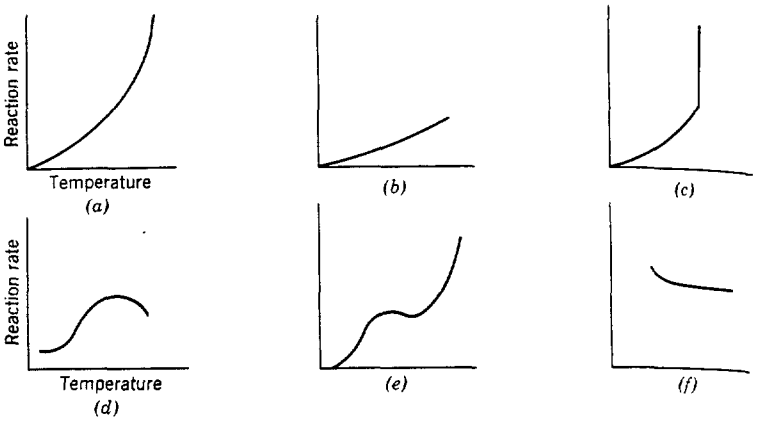

FIG. 7.1. Effect of temperature on reaction rate.[1]

(*a*) is a simple reaction; all the others result from complex reactions or are controlled by exterior physical rate processes.

Before a chemical reaction can occur, there must be a collision (or collisions) between the reacting molecules. It is a rare case indeed that follows precisely the path indicated by the usual chemical stoichiometric equations, which merely show the weight and energy relationships between the reactants and the products. When a collision occurs, a reaction will occur only if the participants possess sufficient energy to penetrate each others electron fields to such a degree that rearrangement occurs. The amount of energy required to cause a chemical change to occur as the result of a collision is called the activation energy. The rate of a chemical reaction depends upon the number of collisions occurring per unit of time and the fraction which possesses sufficient energy to make the collisions effective. The larger the energy of activation, the slower the reaction at a given temperature, for only a few pairs of colliding molecules will have sufficient energy to react. Conversely, fast reactions will have low activation energies.

Consider the case of two molecules A and B which react to form two other molecules C and D. When A collides with B, there is a period in which they are essentially a unit, commonly called an activated complex. If the energy content of the AB pair is low, they then simply fly apart again. If energy is large, there may be exchanges of energy and matter between A and B, resulting, on their separation, in the emergence of C and D, rather than the original sub-

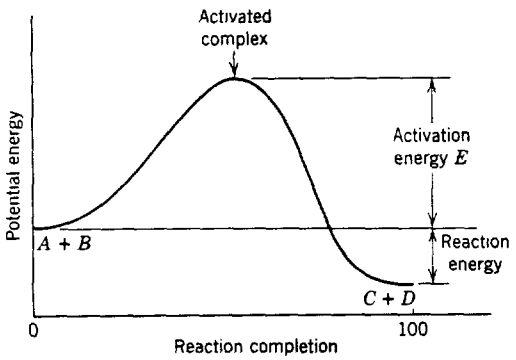

FIG. 7.2. Potential energy change for a reaction.

stances. A potential energy diagram for this system is shown in Fig. 7.2. The horizontal axis shows the percent of the total reaction which has occurred (0 = none, 100 = all finished). The distance E shows the amount of energy which must be acquired by A and B before they can react to form C and D. Since C and D have a lower potential energy than A and B, the reaction is exothermic, $A + B \rightarrow C + D +$ Heat. The effect of a catalyst on a reaction is to make the activation energy much less. End products are the same, but reaction is faster at a given temperature because the number of successful collisions is increased since the energy required for success is lower.

Reaction rate theory is complicated in the extreme because, in general, several choices of the ultimate product may be open to the activated complex. The reader interested in pursuing this in greater detail is referred to standard works on kinetics.[1, 2, 3]

Commercial reactions must be examined carefully for possible side reactions, and the kinetics of these side reactions should also be observed, if possible. The existence of reactions of the types shown in *c* and *e* of Fig. 7.1 are the usual cause of difficulty.

Hazards associated with flammability, toxicity, or instability of the primary product are usually discovered in the laboratory. Those which arrive in the form of unexpected explosions are not. The fact that laboratory scale tests have been completed without incident is no guarantee of freedom from hazard in the pilot plant or the production plant. Difficulties arise in the plant because impure chemicals replace pure ones, radial temperature gradients lead to maximum temperatures well above the averages indicated by thermometers, processing times are often much longer, by-products accumulate and

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may have catalytic effects, pressures are often higher, and the use of metals instead of glass apparatus may exert profound effects on the course of the reaction. Safe practices require that tests be run on the reactants at conditions substantially worse than the averages expected. Laboratory screening tests have been suggested[4, 5] and add greatly to the safety of pilot plant work.

A particularly difficult kind of reaction to control occurs in the manufacture of certain types of explosives. Partial decomposition of the compound being formed occurs at hot spots in the reactor and the products of the decomposition are catalysts for the decomposition. This, of course, leads to a hotter hot spot, a faster reaction, and a runaway reaction which, if explosion does not occur, is commonly called a "fume off." Properly speaking, a better term for this type of runaway is an autocatalytic reaction. Control requires elimination of "hot spots," removal of the source of catalysis or destruction of the catalytic agent as rapidly as it is formed.

Runaway reactions which are sufficiently slow have been controlled by dumping the charge into large quantities of water, rapid dilution, limiting of the quantity of reactable material in process, and by providing large doors and good hiding places for operators with urgent business elsewhere. With the advent of more rapidly responsive sensors for mechanical agents, it has become possible[6] to suppress explosions which have already begun by the use of explosion suppressors. These devices act with great rapidity on quick rise of temperature or pressure and suppress the explosion by any of several techniques such as venting, isolation, automatic shutdown, and sudden quenching.

The fundamental physical and chemical qualities governing chemical reaction velocities are currently not well understood. Each reaction must be studied in the laboratory to obtain kinetic data; this data must then be used to estimate the constants for plant size reactors. Concentration of reactants, pressure, temperature, and the presence of reaction promoting or inhibiting substances are the fundamental variables involved in determining reaction rates.

It is rarely possible to carry out enough experiments to determine the effect of all the variables under all conditions which may be encountered, for such experiments are expensive. Rate constants for all the reactions, side reactions, and by-reactions may all be determined without ever determining the actual mechanism by which the reaction occurs.[7] The mechanism of a reaction is the exact series of steps by which the reaction takes place. Such exact mechanisms are known for only a few reactions and the experimental determinations of them

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are most difficult. Most design engineers feel that a satisfactory rate equation is one that may be used with confidence to design commercial scale equipment for carrying out the reaction.[8] It should always be remembered that in speaking thus of a "reaction," the principal reaction is usually meant and this may be insufficient knowledge from a safety standpoint, since another reaction may become predominant at slightly changed conditions. Design kinetic equations are universally empirical.

Where rate is controlled principally by concentrations, we have the so-called homogeneous reactions and these are classified by the "order" of the reaction. The reaction rate, r, of a constant volume homogeneous reaction can be expressed by:

$$r = k_c C_A^a C_B^b \tag{2}$$

where r = reaction rate, moles/hr-volume
k_c = reaction rate constant, concentration units
C_A, C_B = concentration of A and B moles/volume
a, b = constants

The order of the equation is $a + b$, the number of molecules which combine in the actual rate-determining step—not the molecular proportions shown in the usual equation as frequently erroneously used. All reaction orders are empirical, and the methods for obtaining them are summarized by Corrigan.[9] An approach is being made to predicting reaction rates from absolute physical properties of systems, but this approach is many years away from commercial usefulness. Computer use is sharply reducing the number of laboratory experiments which must be performed before reliable kinetic data are possible.

Rate equations, once determined with a fair degree of accuracy by laboratory observation can be applied, along with proper other equations, to the design of optimum reactors, but there are complicating factors which may obscure kinetic effects as limiting factors in reactor design. Stevens[10] lists the following limiting factors which must be carefully considered, in addition to the validity of all the mathematical assumptions made: longitudinal diffusion, radial gradient, wall effects, impurity accumulation, and catalyst life. There are others.

Reactions used industrially have been classified by Shreve[11] into 26 categories, or unit processes, which offer a systematic approach to the study of chemical reactions. These have been expanded and studied in detail in several major works concerned with industrial chemical reactions.[12, 13, 14] Using a somewhat less comprehensive list

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than Shreve's, we shall briefly consider each of these types of unit processes, looking for some typical hazards characteristic of the reaction.

1. *Combustion.* Solid, liquid, and gaseous fuels oxidized for the creation of heat represent such common reactions that they are rarely considered to be chemical. Normal combustion reactions are fast, but controllable. The ranges over which controls are possible are known for many substances in both air and oxygen. Tables of explosive and flammability limits are available in the literature[12] and should be observed with great care when setting up furnaces. Rates are usually held under control by regulating temperature, availability of oxidizing substances, or availability of fuel. Under most conditions, ignition of mixtures is necessary, but reactive substances, for example oxygen + tung oil, may ignite spontaneously.

2. *Oxidation.* Oxidation differs from combustion only in the fact that the decomposition reaction is stopped enroute to CO_2 and H_2O. A combustion hazard always exists if sufficient oxidant and fuel are present. Oxidation reactions are all highly exothermic. Equilibrium is nearly always in favor of the complete reaction and steps must be taken to limit the extent of the oxidation to prevent loss of product. Marek, in Groggins (*op. cit.*), lists 10 types of oxidative reactions which represent the principal types encountered industrially. Vigorous oxidizing agents are frequently used, and the following should be used with extreme caution: salts of permanganic acid, hypochlorous acid and salts, sodium chlorite and chlorine dioxide, all chlorates, all peroxides, nitric acid and nitrogen tetroxide, and ozone. Safety is usually represented by low concentrations of oxidizing agents, low concentrations of fuel, low temperatures, or better yet—all three.

3. *Neutralization.* Aside from thermal effects resulting from the too rapid addition of reactants, these reactions are relatively free from hazard.

4. *Electrolysis.* Reaction hazards are almost nonexistent. The usual hazards present where large amperages are used, poisoning hazards from the use of cyanides,[15] possible explosion hazards due to the presence of combustible gases and products in high oxidation states (persalts, etc.) are present, but not reaction problems.

5. *Double decomposition.* These reactions are usually of the equilibrium type with small driving forces and relatively low heats of reaction. Hazards are low.

6. *Calcination.* As endothermic reactions, there are readily controllable and rarely troublesome.

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7. *Nitration.* All nitration reactions are potentially hazardous, not only because of the frequently explosive nature of the end products, but also because most nitrating agents are also strong oxidizing agents. This dual nature of nitrating agents makes many by- and co-products possible and some of these reactions are rapid and uncontrollable. Both the nitration reaction itself and the oxidation reactions are highly exothermic.[16] Temperature control must be exceptionally good if runaway reactions or explosions are to be avoided. Maximum temperatures permissible during nitrations can be estimated from temperature sensitivities of the final products, which may be found in Kirk and Othmer, Groggins, Davis,[17] and others. It must be remembered that sensitivity to temperature is increased by the presence of impurities, particularly oxides of nitrogen in liquid phase nitrations, for these act as catalysts for the further oxidation. Rapid, autocatalytic decompositions sometimes occur without explosion. These are known as "fume offs" and may be quite violent. Heat evolved is rapid and end products include N_2, nitrogen oxides, and free carbon.

The heat of nitration of benzene is 761 Btu/lb, but the heat of reaction in commercial apparatus is greater (895 Btu/lb), for the water formed in the reaction causes a large heat of dilution and the heat capacity of the mixed acid used in nitrating is not large. Temperature control of liquid phase nitrations is, therefore, both vital and difficult.

Continuous processes for nitration are most attractive because they limit the amount of material in process and hence greatly reduce the explosion potential.

Vapor phase nitrations also offer the competition between oxidation and nitration and are usually controlled by carefully regulating the concentration of a critical reactant and careful design of the heat exchange apparatus.

8. *Esterification.* Both organic and inorganic esterification reactions are generally slow. Catalysts are usually necessary to force reaction completion. Hazards are usually small except when the esterifying material is a powerfully reacting material (esters of nitric or perchloric acid, for example) or one of the reacting materials or products is unstable.

9. *Reduction.* Hazards of the reaction are negligible and difficulties are associated almost solely with handling reactive reducing agents.

10. *Amination by Ammonolysis.* The aminating agent is usually ammonia. Reactions, which are frequently second order, usually appear to be first order because of the necessity of using a large excess of ammonia. Gas phase reactions are usually run under pressure. Most common reactions are exothermic, but not strongly so.

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11. *Halogenation.* Chlorine, fluorine, bromine, and iodine represent the industrially important halogens, and in that order of importance. Chlorine derivatives are most important because of their much lower cost. All heats of reaction are highly exothermic, with fluorine being extremely high. Chain reactions occur in both liquid and gaseous addition and substitution reactions, making detonations possible over considerable concentration ranges. Corrosion effects are extraordinarily difficult to solve in halogen systems.

Chlorination: Addition and substitution reactions are common with a wide variety of chlorinating agents and systems: chlorine gas, hydrochloric acid, sodium hypochlorite, phosgene, thionyl chloride ($SOCl_2$), sulfuryl chloride (SO_2Cl_2), phosphorus chlorides. Liquid and gas phase chlorinations are common and the extremely diverse paths which these reactions run make prediction without experimentation impossible. All reactions are potentially hazardous.

Fluorination: Fluorine is the most reactive element and its reactions are, therefore, the most difficult to control. Direct reaction with hydrocarbons are violent and frequently explosive. Unwanted C—C bond cleavage is frequent. The new bonds formed between fluorine and other substances are so strong and the heats of reaction liberated are so great that extreme precautions are necessary to keep the reaction under control. Gas phase reactions are usually controlled by dilution with an inert gas. Extreme care is essential.

Bromination and Iodination: Essentially the same remarks under chlorination apply, but all reaction conditions are far less critical.

12. *Sulfonation.* Most commercial sulfonations use sulfuric acid as the sulfonating agent. The reactions require strong concentrations to give good driving forces and usually high temperatures. Reactions are mildly exothermic, but usually relatively easy to control.

13. *Hydrolysis.* Hydrolysis means decomposition with water, but only a few reactions (usually inorganic) use water alone and unaided to effect hydrolysis. The inorganic reactions—lime slaking and sulfuric and phosphoric acid formation—have problems not common to the usual organic reactions. While the inorganic hydrolyses have control problems, they are all concerned with heat removal and contacting and none is sufficiently unique to warrant discussion.

Organic hydrolyses are run in both liquid and vapor phases and utilize the following reagents: (1) water alone, (2) acidic solutions, (3) alkaline solutions, (4) alkali fusion (usually anhydrous), and (5) enzymes. Most such reactions are comparatively slow and only slightly exothermic. The most important problem is how to speed

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up the reaction. High temperatures and/or pressures sometimes help.

14. *Hydrogenation and Hydrogenolysis.* The use of high pressure hydrogen in a plant is always hazardous, but, aside from this problem, hydrogenation is not excessively troublesome. Hydrogenation is usually exothermic and the reactions frequently require the use of a catalyst in order to proceed at a reasonable rate. Since the heat released by the reaction is on the surface of the catalyst, local catalyst temperatures may be extremely high—perhaps enough to cause sintering. When such high temperatures are allowed to occur, cracking and various side reactions may occur which cause waste of reactants. Many hydrogenation reactions are operated at high pressure, but conditions of uncontrollability are rare.

15. *Alkylation.* Carbon alkylations are generally mildly exothermic reactions which proceed slowly, even under high pressures and temperatures and in the presence of a catalyst. Competing reactions such as polymerization, isomerization, hydrogen transfer, and destructive alkylation occur when catalytically alkylating isoparaffins and aromatics with olefins. Thermal alkylations require high temperatures and pressures, but are less generally used than catalytic alkylations. Hazards exist from the use of powerful corrosives (HF, dimethyl sulfate, and so on) as alkylating or catalytic agents, but the reactions themselves are very trouble free.

16. *Condensation.* The energy of activation for polymerized substances lies between 15,000 and 30,000 cal/mole, which is close to the requirement for the corresponding monomers. Condensations are equilibrium reactions and the split-off condensation product (usually water) must be removed in order for the reaction to proceed to high molecular weight. As molecular weights become high and the reaction mass becomes quite viscous, agitation and heat removal become extremely difficult and burning can occur, since these reactions are exothermic. All condensations are step-wise and are generally easy to manage.

17. *Polymerization.* Polymerization differs from condensation since as the materials combine, nothing is split off. The intermediates are usually short-lived active radicals or ions and the step-wise process is rarely observable. The polymer chain is generally formed in a single reaction and in a fraction of a second. Chain reactions proceed quickly following slow initiation by some readily decomposible substance such as tertiarybutylhydroperoxide or benzoyl peroxide. The reaction proceeds by (1) activation, (2) chain propagation, (3) termination, and (4) chain transfer. Heat effects can be sudden, uncontrol-

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lable, and catastrophic, and control suffers as the viscosity of the reacting mixture becomes high.

18. *Diazotization and Coupling.* These reactions proceed favorably only at ice temperatures and are universally handled safely by operating at 0°C or below in the presence of an excess of melting ice.

19. *Fermentation.* Aside from relief of the gases formed and the possibility of explosions, there are few difficulties with such reactions.

20. *Pyrolysis (or Cracking).* Coal, petroleum, wood, and miscellaneous natural waxes and oils are converted by processing under high temperatures and pressures. The object is generally the formation of smaller molecules, but heavier molecules are inevitably formed in small yield.[18] The reactions are endothermic and generally reasonably easy to regulate providing that attention is paid to careful control of temperature and the elimination of hot spots on the catalyst. The "fluid catalyst" system, which makes use of a very large weight of catalyst per unit weight of material being processed has made temperature control of this reaction less difficult than most reactions.

21. *Aromatization and Isomerization.* The end results of these two processes are dramatically different, but the hazard problems are similar. Pressures, temperatures, and the presence of hydrogen offer conventional problems. The reactivity of the catalysts used must be regulated by careful temperature control, and this problem is similar to those discussed under several other unit processes since the heat generation is logarithmic in temperature and its dissipation is linear in the temperature differences between reactants and cooling water. This effect is discussed in detail in Chapter 8.

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8

Hazards of Commercial Chemical Operation

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The physical operations utilized in the manufacture of chemicals into the so-called unit operations may be divided up in a variety of ways. The number of unit operations involved in commercial chemical work will vary somewhere between 6 and 100 depending upon the person making the subdivisions. We shall not attempt to examine all of the current unit operations of significant importance in the field of chemical manufacture, but shall instead limit ourselves to the ones which occur repeatedly in common use. These will be discussed under the following subdivisions: (1) heat transfer and reactors, (2) size reduction, (3) mixing, (4) materials handling, (5) mass transfer, (6) simultaneous heat and materials transfer—humidification, (7) simultaneous heat and materials transfer—drying, (8) simultaneous heat and materials transfer—evaporation and crystallization, (9) momentum transfer—pumps, compressors, and agitators, and (10) momentum transfer—phase separations based on fluid mechanics.

It is customary to think of hazards which exist within chemical manufacturing operations as being functions of the physical properties of the materials being handled or the condition of the immediate environment. Thus, toxicity, corrosivity, fire and explosion hazards, falls, and other miscellaneous health and safety features are considered to be the operative risks of a chemical process. While this is true to a degree, it is also true that there are certain hazards funda-

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mentally connected with the unit operations which make them a good jumping-off place for planning for safety. This is particularly true during the process design stage. It is far simpler and cheaper to consider safety features during the design stage than to attempt to incorporate them as an afterthought after the plant or unit has been completed. Success in producing a safe design depends upon an inquisitive and alert attitude toward safety.[1] The existence of hazards has been adequately pointed out in prior chapters and should be used along with the wealth of experience gained over past years in considering the role of unit operations in the safety picture. It is not enough to consider the conditions of normal operation, but it is vitally important to examine abnormal operation, startup, shutdown, and other possible conditions that may offer difficulty, such as storms, extreme cold, and interaction with surrounding units.

A substantial number of federal, state, and local ordinances must be complied with in selecting equipment of all types. Although old, the section on safety in the *Chemical Engineers' Handbook*[2] is excellent since it shows the extremely wide range of available reference materials on individual hazards and gives a very good list of sources from which helpful material may be obtained. This is also true of several of the preceding chapters in this book.

Designers have too frequently assumed that reactions would always work in the desired way and have made little or no provision for deviations from the normal course when such provision could have been incorporated into the original design at very low cost. An astonishing number of chemical reaction accidents can be blamed on elementary design inaccuracies—at least, they seem elementary in the illumination of hindsight.[3] Much trouble could be saved if, during design, the concept commonly used in the atomic energy field of the *Severest Credible Incident* were adopted. Under this concept, the engineer considers the results of the malfunction of each item in a particular operating system and then the possible results of combined malfunction. This is an excellent method of arriving at a sensible estimate of the worst that can conceivably happen. It is usually possible to plan for something less than the severest possible combination of factors, but it is well to understand most clearly the scope that this might possess. Instrument failure must be planned for and arrangements made to always fail safe or to be backed up with limit controls. An operation may be said to "fail safe" if, upon any type of failure of its control system, the unit is automatically shut down, its temperature reduced, the flow of reagent stopped, or some other acts performed which make it impossible for the unit to attain an unsafe status.

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Fire, and the emergencies which it may occasion, and the difficult problems associated with either elementary start-up, or emergency or regular shut-down require careful prior planning.

Storage areas require particular attention when designed for new materials because provision must be made to prevent, contain, or control fires and explosions conceivable with the material. A frequent error encountered here is an attempt to save money by omitting dikes, sprinklers, emergency pumpouts, and similar devices. Their use is infrequent but their importance in limiting the intensity of a disaster is very large indeed. Dikes offer an inexpensive method of preventing the spread of fire and a second chance to pump away combustibles during a major fire. Foam may also be applied within dike areas to aid in reducing the exposure of nearby tanks. Pumping away material from a burning tank can greatly reduce the severity of a fire impossible to extinguish, and it can salvage much valuable material. Emergency pump-out devices, portable and fixed in place, are excellent investments. Weather can cause such difficulties as venting explosive vapors from tanks and overflow of materials by rapid increase in temperature, so drains and vents must be studied with some care.[4] Two articles by Jennett[5, 6] are particularly valuable.

8.1. HEAT TRANSFER

Heat transfer is the most widely used single operation in the conversion of chemicals. Equipment has been standardized to a large extent over a long period of time. Commercial heat-transfer apparatus operates from temperatures of approximately 455°F below zero to very high temperatures which rarely exceed 4000°F because of the difficulty of containment. There is no particular hazard associated with the heat-transfer act itself, although it is, of course, essential to keep streams which might react catastrophically with each other from coming in contact under conditions of whole or partial failure. These require very special considerations in such cases as heat transfer involving liquid metals and cooling waters for nitrators to be used with explosives.

The accumulation of materials which reduce the rate of heat transfer across a boundary is very common in heat-transfer work, and this accumulation usually means a slow reduction in the effectiveness of heat transfer equipment with age. In the case of very rapid heat transfer, such as occurs in furnaces, this reduction may lead to the rapid increase of temperature at a spot or spots and the ultimate softening and destruction of these hot spots by pressure within the heat

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transfer apparatus. In the case of jackets or exterior or interior pipes and coils for chemical reators it may mean inability to run at the desired batch size, but it may also mean inability to control reaction. Some method of constantly checking to assure that effective heat exchange surface has not been reduced below a safe figure must be made. Fortunately, the provision of inlet and outlet thermometers and pressure gages is usually sufficient to enable determination of the condition of the heat transfer surface. Within furnaces, it has become customary to install instruments to detect the existence of dangerous conditions, and these may also actuate visible or audible alarms. Other types of instruments automatically shut off fuel supplies, close fire doors, alert the fire prevention system, or start auxiliary ventilating systems.[7]

Generally speaking, the idea of heat exchange is to control or balance a reactive process, and in the case of a reactor it is always necessary for stable operation that the heat removal exactly balance the heat of reaction. Since, in general, the rate of heat production of exothermic reactions is exponential with temperature rise (see previous chapter), while the ability to remove heat varies linearly with the difference in temperature between the materials being reacted and the cooling water in the jacket, a sharply critical condition exists in reactors which is not generally appreciated. Much trouble arises when an attempt is made to move from small to larger scale equipment. Since volume (and hence the amount of material involved in reacting) goes up as the cube of the dimension of an apparatus while the area through which heat can be conveyed away goes up as the square of the dimension of an apparatus, it becomes increasingly necessary to provide some type of extended surface (such as cooling coils) as reactors become larger and larger.

Secondary difficulties come into play because of the fact that unless agitation is very good, the material being handled is not very viscous, and the temperature drop across the cooling surface is not large, there may exist a substantial radial temperature gradient within a reactor itself. If this radial temperature gradient should be as much as 10°C, the reaction rate at the center of the reactor would be approximately twice as great as that at the walls. Since it is customary to install thermometers at fixed spots within the reactor where they indicate approximately the temperature of the materials about them, the radial temperature gradient may well not be observed, and the temperature indicated may be far away from the average temperature existing. This may create a situation fraught with great danger.

When a reaction is sufficiently exothermic to make possible an ad-

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iabatic temperature rise of around 200°C if all the reagent present should react without loss of heat to the surroundings, special considerations must be given to design of the reactor. Reactors designed to control such reactions show extraordinary sensitivity to very small changes in water jacket or reaction temperatures, and they are not controllable unless the temperature at which they run is only a few degrees above surrounding temperature.[8] The design of such sensitive reactors, which because of their sensitivity to a particular parameter are referred to as parametrically sensitive reactors, is discussed in detail by Amundson and his students.[9, 10] The following example is taken from Boynton, Nichols, and Spurlin.[8] Consider a simple exothermic reaction of the Arrhenius type (see previous chapter) whose rate doubles for a 10°C rise in temperature. Operation is to be at about 120°C which corresponds to an activation energy E of about 23,000 cal/mole. The rate of heat production then will be

$$\frac{dQ}{d\theta} = \mathbf{A}e^{-\frac{E}{RT}} \tag{1}$$

If this reaction is operated in a jacketed cooled kettle, the rate of heat transfer out is given by

$$\frac{dQ'}{d\theta} = B(T - T_0) \tag{2}$$

where Q = heat of reaction, cal/mole
Q' = heat transferred, cal/mole
θ = time, sec
$\mathbf{A}$ = a constant
E = activation energy, cal/mole
R = gas constant cal/mole K°
T = temperature of reacting mixture K°
$B = hA$ = constant including heat transfer coefficient h and Area for heat transfer, cal/sec—K°—mole
T_0 = wall temperature—K°

Figure 8.1 shows plots of equations 1 and 2 for the system in question. If the jacket temperature is 116°C and the heat-transfer coefficient is such that line A represents the rate loss from the kettle to the jacket, the line will intersect the reaction heat curve at 123° and 143°C. The intersection at 123°C is stable because the temperature will tend to return to this point if displaced slightly above or below it. The 143°C intersection, however, is unstable. A slight drop in temperature would cause the contents to drop to 123°C, and the slightest

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rise would cause the temperature to go up until the reagents were exhausted or explosion or volatilization brought the reaction to a halt. Thus operation at a 7°C temperature differential represents stable operation.

As the jacket temperature is increased, the heat-loss line moves in a direction parallel with the original heat-loss line unless the jacket temperature change is sufficiently large to result in a change in the heat-transfer coefficient, which is rarely true. The line becomes tangent to the heat production curve at a 130°C, a Δt of 14°C. This is the maximum stable temperature of operation possible for the reaction mixture and vessel described. The maximum safe Δt is, therefore, 14°C with no factor of safety.

By increasing the heat-transfer surface, operation at higher temperatures can be brought about as shown by the third line (*C*) of Fig. 8.1. Here jacket temperature is 134°C and the point of tangency is 148°C; again, the maximum Δt for stable operation is 14°C.

This result is a general one for a reaction which doubles in rate for a 10°C rise in temperature. For the general case, equations 1 and 2 may be differentiated and equated to demonstrate that the maximum stable temperature differential $(T - T_0)_{\text{critical}}$ is:

$$(T - T_0)_{\text{critical}} = RT^2/E \tag{3}$$

Since reaction rates rather than activation energies are often available, another similarly derived relationship is also useful:

$$(T - T_0)_{\text{crit}} = \frac{2T^2}{E} = 2(\ln 2)T_d = 1.4T_d \tag{4}$$

T_d is the temperature increase required to double the reaction rate.

Since reactions requiring as much as 20°C to double are rare and operation near the critical point leaves no factor of safety, an unknown exothermic reaction should never be operated even experimentally at rates demanding a Δt of more than about 10°C for heat removal unless rapid and effective means for added cooling or quenching the reaction are available. Among the methods that may be used for controlling the exothermic reactions are the following: (1) Use dilute solutions or suspensions. (2) Feed one component slowly enough so that the rate of heat increase can never approach a dangerous value. (3) The addition of around 10% of volatile solvent will usually control temperature if means for refluxing are available. (4) Operation with a large Δt may be possible if the time available for reaction is long enough. Controls responsive to catch incipient runaway reaction

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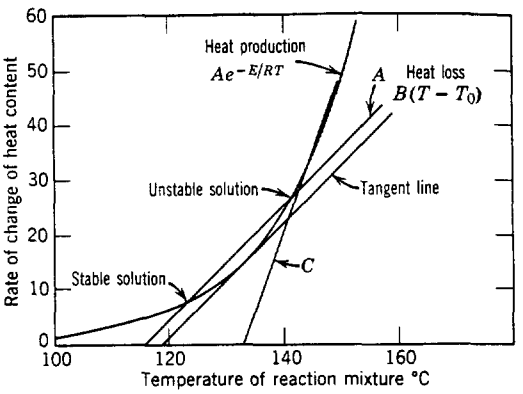

FIG. 8.1. Rates of heat production (curve) and heat loss (straight lines).

should be a part of any unit operating in this fashion. (5) Design coil reactors to remove the heat of reaction using small Δt.

Another source of difficulty occurs when an attempt is made to store hot materials in bulk. Powders placed in containers at very reasonable temperatures may absorb oxygen from the air, and they may rise in temperature because of the inability of the generated heat to be carried away. The author recalls a particular case in which storage of finely powdered zinc stearate in boxes 18 in. x 18 in. x 2 ft resulted in melting of the inner contents over a period of two days.

8.2. SIZE REDUCTION

Most of the difficulties occurring in size reduction occur from the dangerous combination of combustible materials, an oxidizing agent, and a spark. Wherever possible, attempts should be made to eliminate one or more of these vectors in order to minimize the possibility of explosion. It is desirable to provide some means of removing stray iron immediately ahead of the grinding machinery, magnetic separation and/or screening usually being most effective. It is also essential to ground the system with great care in order to prevent the accumulation of static electricity, and these ground connections should be of extremely low resistance. Whenever a combustible is being ground in the presence of air it is wise to avoid rigid confinement and to provide safety reliefs to eliminate the possibility of danger from explosive pressure build-up.

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Where hazardous substances must be ground, it is possible to reduce the hazard by reducing the concentration of oxidizing agents in the grinding atmosphere. Stern[11] reports that a sulfur grinding unit has operated for years without fires using cooled flue-gas atmospheres containing half or less of the normal oxygen content of air. Explosive mixtures of air and dust are similar to air-vapor mixtures that are explosive in that there are minimum and maximum concentrations which form the explosive limits. It should be remembered that within a grinding and classifying system, it is quite possible to be on both sides of the explosive limit within a single unit. Safety codes for the prevention of dust explosion have been issued by the United States Department of Labor and the National Fire Protection Association. Explosion-proof lights and nonsparking fan and mill surfaces are among useful materials which reduce the hazards of grinding. The common hazards associated with rotating machinery are found around grinders.

8.3. MIXING

Commercial mixing operations include mixing of all possible combinations of gas, liquid, and solid.

Mixing gas with gas. Normally there is little difficulty in bringing about the intimate mixing of two gases, even with very simple mixing devices. The only hazards that need be considered in mixtures of this sort are the usual ones concerning explosive mixtures.

Gas-solid mixtures. Commercial applications of this type are largely limited to solid fuel burners, and in this case there are not unusual or peculiar hazards. Where gases and solids mix intimately to accomplish chemical reaction, as for example in fluid bed processing, the extremely high heat capacity of the solid compared with the gas which suspends it usually makes temperature control relatively simple. In conveying solids with gases, great care must be taken to see that all units are adequately grounded in order to prevent accumulation of static electrical potential.

Gas-liquid mixing. Where liquid is agitated with a gas solely for the purpose of mixing, it has been observed[12] that the explosion temperature of the air-vapor mixture produced in such agitators is within 1°F of the Pensky-Martens flash point and that in large agitators it is not affected by the rate of blowing. When the materials involved in an air-gas mixture are capable of forming an explosive mixture, due care must be exerted to eliminate possible sources of ignition. Grounding is particularly vital, and it should be remembered that it is nec-

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essary to have not only a high-voltage static charge but also a certain minimum current density and the presence of an explosive mixture in order to bring about an explosion. Particular attention should be paid to the possibility of forming combustible foams where gases are being blown through liquids. In addition to being hazardous the presence of foams can prove to be major irritants, for foams have gotten out of hand and completely buried plants. There are a variety of foam-controlling agents available which have greatly reduced the nuisance of ordinary foams.

Liquid-liquid mixing. Where liquids are of low viscosity, some type of high-speed mixer is generally used. Aside from the hazards of possible combustion and the common hazards concerned with rotating machinery, there are no special hazards. It is usually unsound to operate side-entering propellers in large tanks with the propeller only partially submerged because of the possibilities of bent shafts and destroyed motors, but this difficulty will usually show itself as an extreme nuisance long before it becomes a hazard. Where liquids of extremely heavy viscosity are to be mixed in heavy-duty kneaders or rolls, it is extremely important that extraneous solids be excluded in order to avoid possible damage to man and machine. Where explosive materials are being handled it is desirable to provide weak walls, barricades, and some type of snuffing device.

Liquid-solid mixing. Low-viscosity mixes are generally done with high-speed propellers or turbines. Light slurries are frequently mixed using air-lift agitators, and here again the remarks made under gas-liquid contactors apply. No special hazards exist peculiar to these machines, and the problems of processing are concerned primarily with material properties.

Solid-solid mixing. Devices used for this type of work are generally quite simple but all must be regarded as potentially hazardous when a combustible material is present with air, because there is a very strong tendency to build up static charges unless extreme care is taken in grounding. In some types of ribbon mixers involving close clearance, it is necessary to take the usual precautions for the elimination of possible tramp iron or similar spark-causing substances.

8.4. MATERIALS HANDLING

This section will be restricted to techniques involved in moving solids, since techniques involving pumps and blowers are covered elsewhere. An almost endless variety of devices are utilized for the in-

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termittent and continuous movement of solids within a plant. The most important from the standpoint of tonnage handled are the various types of conveyors, cranes, and bucket elevators. Most of the hazards connected with the use of these devices arise from the possibility of injury from contacting moving machinery, and these hazards are not special or characteristic of the chemical industry. Particular attention should be paid to the loading and unloading section of all types of conveyors since it is usually at these points that trouble develops. Bucket elevators, in particular, have difficulty with jamming of materials between the buckets and the side of the boot. Chutes can be most troublesome, due to the accumulation of materials on the sides, and it may frequently prove to be very difficult indeed to accomplish regular discharge of material from them. If the chute is too steep, it gives the same effect as dumping material and may result in dusting or damage to fragile material or to a hazard from the movement of toxic materials in dust form. If the incline is too flat, material cannot be made to slide over it.

8.5. MASS TRANSFER

Most mass-transfer problems such as gas absorbtion and solvent extraction show no unique problems that characterize this group, although fire hazards are quite common. Columns operating at high temperatures, particularly those which use some steam in processing should be designed with great care to prevent the possible accidental injection of liquid water into the tower. One of the most spectacular accidents which the author ever witnessed came about from the injection of a few gallons of water into the bottom of a fractionating tower distilling hot tar. The ensuing rain of bubble caps, which covered almost ten acres, testified to the vigor of the flash evaporation that took place within the tower. Towers should, in general, be equipped not only with pressure, but also with vacuum-relieving devices. Connections made to tanks which are designed for wash-out during periods of nonoperation can prove to be disastrous if opened at inopportune times. A lead-lined still 6 ft in diameter by 10 ft high which had not been properly equipped with a vacuum valve was reduced to a mass of crumpled wreckage when a spray of cold water was injected into it by opening the wrong valve. The still was full of steam, which condensed at once, forming a high vacuum inside. This permitted atmospheric pressure to crush the still.

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8.6. SIMULTANEOUS HEAT AND MASS TRANSFER I—HUMIDIFICATION

Humidification in itself is generally a most innocuous operation. The blower and exhaust systems, however, may constitute a fire hazard in themselves, and the ducts may introduce hazards contributing to the spread of fires. Ducts should not pierce fire walls, floors, or make connections between hazardous areas. Where it is essential that this be done, provision must be made for automatic shut-off in case of fire or explosion.

Fume scrubbers designed to reduce the amount of combustible or objectionably odored material released into the atmosphere may accumulate large quantities of dangerous combustibles at points within their systems unless they are specifically designed to hold up a minimum of combustible liquid or solid.

8.7. SIMULTANEOUS HEAT AND MASS TRANSFER II—DRYING

Drying equipment comes in a wide variety of types which differ sharply in the hazards of their operations. Those which possess moving parts are subject to the usual difficulties found around moving machinery. Where the material being dried may become dusty, release a combustible substance, or is simply combustible, it is advisable to provide some type of emergency overrange protection to insure that overheating of the dryer does not result in a fire or explosion. Sprinkler systems are ideal, but they are rarely used. The design of continuous dryers should be carefully examined to eliminate the possibility of the deposition of combustibles on electric heaters or the undue accumulation of dusts at points within the apparatus itself. Spray dryers are subject to the same possibilities of dust explosions that one might find handling any other combustible material in an atmosphere containing oxygen. Flash dryers should be treated in the same fashion as grinding equipment, and their ducts should be provided with explosion vents if there is a possibility of an explosive mixture being formed. Hazards can frequently be greatly reduced by using flue gases rather than straight air as the drying medium. Drum dryers should have their feed scavanged for large-size particles which might be thrown out from between the rolls with violence, damaging operator and rolls.

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8.8. SIMULTANEOUS HEAT AND MASS TRANSFER III—EVAPORATION AND CRYSTALLIZATION

Because most evaporation is conducted within a closed system, there is rarely a major difficulty with this type of equipment. It is desirable that the bodies be equipped with pressure and vacuum relief valves and with provision to protect the equipment in case of fire or accident within the unit area. Like heat exchangers, evaporators can become fouled, thus greatly reducing the heat transfer ability. Scale accumulations are particularly troublesome when the scale is soft, and hence they are a very poor conductor of heat. Scales should be removed at regular intervals by means of standard commercial devices.

Crystallizers are generally simple agitated tanks or vessels designed to form crystals of carefully controlled size from saturated or slightly supersaturated solutions. These units possess almost no hazard other than those associated with the materials being handled. It is sometimes desirable to provide protective equipment such as shear-pins to prevent strain on motors or gears in case of an interruption or freeze-up.

8.9. MOMENTUM TRANSFER-PUMPS, COMPRESSORS, AND AGITATORS

Pumps and compressors are among the most thoroughly standardized, widely used, and trouble-free devices found within the plant. Most difficulties with new pumps and blowers arise from corrosion, cavitation, water hammer, or misuse. It is commonly said by plant installers that if a pump can get through the first hour of operation that it may expect a reasonable life. This simply confirms the fact that almost all difficulties with pumps occur during their start-up. J. R. Caddell,[13] has an excellent discussion concerning the operation and maintenance of fluid-flow equipment which is particularly valuable in its description of the hazards of starting centrifugal pumps. J. E. Troyan,[14, 15, 16] has provided an excellent comprehensive report on what we should actually do to prepare for a plant start-up including training operators, preparing manuals, and debugging.

Pumps and connecting valves, installed where normal working pressures are reasonable, fail because of ram effects caused by sudden shutting of valves. This is commonly known as "water hammer." If water is flowing in a pipe and it is suddenly stopped, its kinetic energy

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is suddenly released. The head h (in ft of water) thus suddenly developed is:

$$h = \frac{cV}{g} \tag{5}$$

where c = velocity of pressure wave disturbance up the pipe ft/sec
V = reduction in velocity ft/sec
g = gravitational constant ft/sec^2

c, the velocity of wave propagation, may be estimated by Jonkowsky's formula:

$$c = 4660/\sqrt{1 + KB} \tag{6}$$

where K = ratio of elastic modulus of water to pipe shell material (0.01 for steel)
B = ratio of pipe diameter to pipe thickness

These equations are both rather approximate, since they assume instantaneous closing, but the results are conservative.

Water-hammer effects can be large and destructive, particularly to concrete or similar fragile pipe and to large cast-iron pumps. Prevention includes providing air cushions within the system or by making it impossible to close valves fast.

If a pump operates in such a fashion that areas within the stream of fluid around the impeller fall to pressures below the vapor pressure of the fluid being pumped, cavities form in the flowing fluid. When these cavities move into an area of higher pressure, they collapse very suddenly. When the bubbles collapse, fluids meet at high velocity and pressures at the point of collapse become quite high. If the point of collapse occurs on the surface of the metal, it may be stressed beyond its elastic limit and the impeller and the casing may be quickly eroded and destroyed. Cavitation is best avoided by providing ample net-positive suction head to the pump in question.

Much of the difficulty that occurs in the installation of pumps arises from the lack of understanding of the basic differences between positive displacement and centrifugal pumps. Centrifugal pumps utilize the least electrical current when their outlet valves are completely closed, and they utilize the most electrical current when the outlet valve is open and there is no pipe attached to them. Positive displacement pumps, on the other hand, utilize their maximum electrical energy when they have their outlet valves shut off, and they utilize the least current when their outlet valves are wide open. Centrifugal pumps frequently have their motors destroyed by attempts to test them on a job without

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connecting the outlet pipe, or by running water through a pump designed for a less dense material. When starting a centrifugal pump, the fluid to be pumped should be free from dirt, abrasive material, and any foreign objects. While it is not always necessary that the fluid being pumped be entirely free of solid, it is always desirable that large objects be excluded unless the pump has been especially designed for this purpose. A strainer of adequate capacity and efficiency in the suction line is desirable. Damage to the pump will result if it is not filled at the time of starting or if the net positive suction head is less than a minimum.

It is usually wise to check for strains placed on the pump by installed piping. If mis-alignment is appreciable it will often be detectable by the fact that the pump shaft cannot be moved by hand power. Piping stresses lead to rapid wear of the seals on the pump and, if sufficiently large, may cause rubbing of the impeller or case cracking. Care must be taken to see that piping is so installed that thermal expansion (or contraction) does not set up intolerable stresses. Pump and prime-mover bearings should be checked thoroughly for proper lubrication. Suction and discharge pressure gages should be installed with each pump, as this will permit an immediate check on the operating conditions of the pump.

When starting a centrifugal pump, it is desirable to close the discharge valve to reduce the load on the driver, and this valve should not be opened until the motor has come up to speed. If this valve is then left closed for any substantial length of time, the work done on the small volume of liquid contained within the casing may result in its boiling, and trouble may arise from this volatilization (such as loss of prime or destruction of the packing). Packing glands on pumps must be kept so adjusted that there is a continuous drippage from them. This drippage serves as a lubricant and coolant between the packing and shaft. After a shutdown, the centrifugal pump should not be started again until the discharge valve is shut off and the shaft rotation stopped, otherwise the pump motor may burn up while coming up to speed. Care in selecting packing is necessary and is usually done by trial.

Much of the personal hazard in use of pumps arises from the requirement that there be a certain amount of leakage around the shaft packing or shaft seal. It is generally possible, by selection of one of the various sealing methods, to have a leakage to the outside which is tolerable, but this may not be so in the case of some toxic, corrosive, or reactive substances. The use of mechanical seals can frequently reduce or entirely stop the losses around packing glands, but mechan-

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ical seals must be installed and maintained with more than the usual care.

Starting up reciprocating or other types of positive displacement pumps requires as much care in seeing that the valves are open as is required in seeing that the valves are closed in the case of centrifugals. Most difficulties with reciprocating pumps arise from lack of attention to their automatic lubricators. Do not exceed the speeds recommended by the manufacturers and watch carefully for vibration in pipe supports which may lead to failures in the pipelines.

It is now possible to move significant quantities of solids in pipelines, and this operation has become increasingly popular. The maximum allowable particle diameter of the solid to be handled should not exceed one half of the smallest canal dimension of the pump, and the maximum permissible size of the particle to prevent blockage of the lines must be such that the particle diameter is not greater than 1/3 that of the pipe. Stability of operation of this type of unit is most important, and start-up and shutdown can be most troublesome. Data on designing and operating this type of unit have been presented in the literature.[17, 18, 19]

8.10. MOMENTUM TRANSFER—PHASE SEPARATIONS BASED ON FLUID MECHANICS

Filtration, centrifugation, screening, elutriation, jigging, classification, and sedimentation all show only the difficulties which we would expect due the handling of difficult materials. Care must be taken to avoid fires, or excessive exposure of personnel to toxic materials. Centrifuges require heavy supports of highest quality. Care should be taken in the installation of pressure filters to assure that personnel are not liable to be sprayed with injurious or offensive materials, but the precautions are no more elaborate than those taken in the installation of virtually all types of pressure equipment.

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9

Process Design

W. G. *Hudson*

9.1. INTRODUCTION

In a direct sense, the process designer is the architect of the process plant. Like the architect, he must produce a set of drawings and specifications that will serve as the basis for the detailed engineering design of the final entity. His ultimate goal is to develop a processing scheme that will most economically produce the desired products in a safe fashion. The fulfillment of the following requirements serves as his standard of safety:

1. The process must operate safely at design conditions.
2. Suitable provisions must be made to cope with unsafe deviations from design conditions.
3. Safe start-up and shut-down procedures must be established.

Although these requirements may seem rather elementary in concept, compliance with them is mandatory. Failure to provide sufficient cooling surface at critical points or to make inadequate allowance for inert-gas purging would be examples of disastrous designs in which these requirements were *not* satisfied.

In assuring that the requirements of safety are fulfilled, the designer must evaluate the hazards involved. Commonly confronting the process designer are four groups:

1. Fire hazards, either inherent in the process or from external sources
2. Sources of excessive overpressure, explosion hazards

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3. Hazards resulting from abnormally high or low temperatures
4. Hazards created by toxic or highly corrosive materials

The following sections will trace out the technique of safe process design, the methods of controlling the process variables to ensure the safety of the design, and the evolution of safety in new-process development.

9.2. THE TECHNIQUE OF SAFE PROCESS DESIGN

The Flow Sheet

The key to safe process design is the preparation of a complete, detailed flow sheet. This development starts with the basic process calculations and then determines that each step of the process meets the safety requirements. Potential hazards must be evaluated and removed, or else suitable provisions must be made to restrict them.

The problem is complicated, somewhat, by the fact that most processes are so highly integrated that each step in the process affects the operation of other steps. It is desirable, therefore, to divide the process into sections, and to analyze each section not only for its internal safe operation but for its effect on the safety of other sections. Convenient subdivisions can be made by dividing the process into reaction, separation, materials handling, and storage sections.

REACTION SECTIONS

Reaction sections must be considered first because they determine the dynamics of the whole process. Such sections may be quite simple, involving only a stirred batch tank, or they may be as sophisticated as a cat-cracker; yet, they can all be systematically analyzed for safe operation by breaking them up into feed, reactor, and outlet subsections, or *systems*.

THE FEED SYSTEM

Examine the effect on the reaction of an abrupt change of flow of each of the reactants. Combustion reactions, for example, may pass through either upper or lower explosive limits because of such a rate change. The necessity of providing appropriate warning devices, spare pumps or compressors, and automatic start-up of such pumps or compressors may be evaluated on the basis of safety.

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In a similar fashion, ascertain the consequences of failure of temperature control in the feed system. Such a failure may lead to disastrously high, or low, temperatures in the reactor causing either dangerous overheating, or loss of reaction and accumulation of materials in an unsafe composition range.

For batch systems, make certain that reactants will be added in the correct order. The familiar procedure of adding sulfuric acid to water is an example of where order of addition is important.

Start-up and shut-down procedures must be worked out quite carefully. The order in which feeds are cut in or out, and the attendant control of their temperature and pressure under transient conditions, must be established. Facilities may be required for purging the system of air prior to start-up, and of flammable or noxious materials at shut-down.

All equipment and instrumentation should fail safely. In extreme cases, emergency power or instrument-air supplies may be required. Safe materials of construction must be specified in detail.

THE REACTOR SYSTEM

Ascertain that the reaction is chemically safe. The reaction must be in a stable area of composition, pressure, and temperature. Evaluate the effect of changes in these on the stability.

In particular, consider the possibility of undesirable side reactions occurring. These may produce noxious or explosive materials or lead to dangerous fouling or plugging. Certain reactions, such as combustion or halogenation, may proceed at explosive rates. Explosive limits for combustibles in air are published by the National Fire Protection Association.[1] Other systems may require literature search or explosive limits tests. Where corrosive conditions prevail, safe materials of construction must be specified.[2]

The chemical ground-rules having been established, the mechanical safety features of the reactor can be defined. Here are some salient features to be considered.

What are the effects of poor distribution of reactants on the safety of the reactor? In simple flow reactions, poor distribution may lead to hot spots, resulting in equipment failure or to undesirable side reactions. In stirred reactors, poor agitation may lead to similar ends, and accidental stoppage of agitation may be disastrous.

As a special case of poor distribution, consider the possibilities of plugging due to sedimentation. Safety valve outlets and connections for control devices must be so located and designed as to prevent

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plugging. Continuous purging of such outlets may be required. Pockets where materials can accumulate are, in general, to be avoided.

Specifications for pressure relief devices must provide for the worst predictable possibilities. In the most hazardous cases, special shielding and isolation of the reactor may be required.

Provisions must be made for maintaining the temperature of the reactor within safe limits. Heat transfer surface is often required, and its arrangements and the provisions for supplying it with cooling or heating media are of grave concern in most reactor design problems.

Poor distribution of heat-transfer surface in the reactor can lead to inordinate local temperatures, causing hazardous side reactions or direct equipment failures. The possibilities of fouling the surface, both on the reaction and medium side, must be considered in the same vein.

The adequacy of supply and control of medium to the heat-transfer surface must be critically reviewed insofar as it affects safety. Adequate provisions, similar to those discussed under the feed system, must be made, to guard against failure of the supply and, in event of failure, to insure an orderly shut down of the reactor.

The proper selection of the heat-transfer medium is of importance. Direct firing may lead to "hot-spots." High temperature heat-transfer fluids may be overheated, causing fouling or plugging, or they may freeze up in colder portions of the circuit. Hazardous conditions resulting from leakage between reactor and medium side of the exchange surface should be evaluated as a basis for the mechanical specifications for the surface.

The whole manipulation of the heat-transfer system during start-up and shut-down must be developed. Special provisions for heating or cooling the circulating medium may be required, in particular, for emergency shutdowns.

The freeboard requirement in liquid-phase reactors must be specified. Expansion of liquids with temperature, the extent of foaming, height of swirl caused by agitation, and the effect of liquid carry-over on the safety of downstream equipment, must all be considered.

THE OUTLET SYSTEM

In concluding the safety analysis of the reaction section, consider the products withdrawal system. All the undesirable events so far noted culminate here, and they are in position to effect the rest of the process downstream. Consequently, it is here that monitoring devices to warn of impending danger are quite commonly located. From the previous evaluation of the feed and reactor systems, the degree to which

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composition, pressure, and temperature may be effected at the reactor effluent can be determined and used as a basis for the selection and specification of such devices. Equipment to transfer materials to the next section, an adequately sized intermediate storage, and provisions for emergency blow-down tanks and flare systems must, likewise, be carefully designed.

Separation Sections

Safety Significance. Operations involving the physical separation of constituents are of special safety significance insofar as their effect on other plant sections is concerned. The production of off-specification material could result in, for example, unsafe conditions in other portions of the plant or unsafe finished materials. Separation processes to be considered here will include crushing and grinding, size separation, distillation, absorption, extraction, filtration, and drying.

Crushing and Grinding, and Size Separation. These operations can produce copious quantities of dust so that the possibility of dust explosion must be considered.[3] Facilities to prevent the discharge of dust into the atmosphere may be required. In some instances the safe performance of other operations may hinge on the reliability of the size separation equipment. Excessive fines may cause reactions to proceed at unsafe rates, and oversize material may result in plugging of equipment.

Distillation. Control of product composition may be of special significance. If a recycle stream is being produced, hazardous material may be built up in the recycle either through poor design or operation. Unwanted materials may be inadvertently left in outgoing products by malfunctioning of the unit. In either case suitable detection and warning devices must be specified.

Possibilities of coking or polymerization in reboilers may constitute a special hazard. Vacuum distillations of flammable materials may be hazardous in that air insemination may lead to the formation of explosive mixtures.

Absorption. Where noxious materials are being absorbed prior to the discharge of a gas into the atmosphere, special care is required in monitoring the composition of the gaseous effluent.

Extraction. Extraction systems may contain large volumes of flammable liquids. The codes of the National Fire Protection Association[1] are recommended as a basis for safe design. Where liquid-filled sys-

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tems are contemplated, allowance must be made for the thermal expansion of the liquid.

Filtration. Filtering operations can present special safety problems where they involve the removal of harmful constituents from a food product or a product to be used in conjunction with food. Monitoring devices and testing procedures must be provided that will satisfy the particular requirements of the Federal Food and Drug Administration.

Drying. Drying operations may cause similar dust hazards to those mentioned under Size Separation. Safe drying conditions for heat-sensitive materials must be evolved. Control of humidity may be important in the prevention of undue caking. Explosion and fire hazards are attendant to the removal of flammable solvents.[4]

Materials Handling

The same principles apply, of course, both to the intersectional materials handling and to internal materials handling within the plant sections. As previously noted, the capacity of materials-handling equipment may be determined by safety demands for temporary overloads. The selection and detailed specification of the equipment must also be made with safety considerations in mind.

PIPING

Drainage. Drainage valves should be provided at the low points of the system and all piping should slope downward, toward them.

Valving. The specification of safe-valving arrangements is required. Double block valves should be used for the dependable shut-off of hazardous materials. By-passes must be provided around control valves where possibilities of emergency operation are evident. Check-valves are to be provided to prevent inadvertent backing-up of flows into feed systems, of corrosive materials into corrodable equipment, or of flammable or noxious materials into unsafe areas. Valving required for isolation of equipment during shutdown, or for start-up conditions, must be specified.

Corrosion and Erosion. Ordinary corrosion data are useless where erosion is coincident. Tests under simulated conditions may be required in order to define material specifications.

Relief Valves. For liquids that have a high coefficient of expansion, such as light hydrocarbons, pressure relief valves must be provided

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between block valves. Relief valves must also be provided on the discharge of all positive acting pumps and compressors.

SOLIDS HANDLING

Mechanical Conveyors. Various types such as belt, flight, and screw-conveyor are examples of mechanical conveyors. Common hazards to be controlled are dust explosions and the escape and dissemination of noxious or flammable dusts.

Pneumatic Conveyors. The following two items must also be considered in designing pneumatic systems: (1) If the material handled is readily flammable, inert gas must be used as the pneumatic fluid. Pressure systems are preferred over vacuum systems because they obviate the possibility of air infiltration. (2) Where poisonous or noxious materials are being transported, special attention must be given to recovery of fines from the exit air. A complete recycle of the carrier gas may be desirable.

Storage Sections

SIZING

The previously noted effects of process upsets must be considered in sizing the storage capacity. These effects are particularly important in the sizing of intermediate or recycle storage. In cases where unsafe finished products may be produced, adequate "off-spec" storage must be provided. The total quantity of storage having been determined, the next problem is to arrange for its convenient and safe disposition.

SOLIDS STORAGE

Types of Storage. Solid materials may enter or leave the plant in bags, drums, or by bulk carrier. They may be stored in their own containers, in hoppers or silos, or in bulk piles, either indoors or outdoors. Recycle or intermediate storage is usually provided by hoppers, silos, or bulk piles.

Safety Considerations. Flammability of the material must be established to determine the safe size and spacing of storage units and the design bases for the electric and fire-protection systems. The possibility of spontaneous combustion,[3] either in bulk piles or piles of bags may limit the safe depth of storage. Temperature measurements of

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such piles may be required. Susceptibility to dust explosions will determine grounding equipment required.

Wind-borne dusts from outside storage piles may be eye or lung irritants. Absorption of atmospheric moisture may cause swelling of the materials or lead to the formation of corrosive liquids or gases. The swelling of grain in silos and the reaction of water with $AlCl_3$ to yield HCl are familiar examples. Oxides of nitrogen (silo-filler's disease) may result from silaging fresh fodder.

Purge systems using CO_2, N_2, or other inert gas may be required for flammables storage bins.[3] Bins and silos should be equipped with level indicating devices to warn of over-filling or near-emptiness.

LIQUID STORAGE

General Requirements. Liquids are generally received or shipped in drums, carboys, tank cars or trucks, or by pipeline. They may be stored in their shipping containers or in tanks. Intermediate storage is usually in tanks.

Hazards. In evaluating the hazards involved, the following points may be considered.

1. The National Fire Protection Association publishes lists of the flash points of common liquids and classifies their fire hazard according to the flash point.[1] The safe sizing of storage units, the spacing of such units, and the grounding, electrical, and fire protection systems required are determined on the basis of this classification. Highly flammable liquids may require inert purging of vapor spaces.
2. The vapor pressure of the liquid at storage temperature will set the design basis for pressure vessels, pumps, and piping. Where vapor pressures are subatmospheric, adequate vents must be provided, or the containers must be designed for vacuum service.
3. Special caution must be taken in the storage of very corrosive or poisonous liquids. The possibility of accidental spillage and the accidental discharge of toxic vapors are two principal hazards.
4. As in solid storage, the indication of levels in all storage tanks is a "must."

GAS STORAGE

General Methods of Storage. Gases may be received or shipped, in liquid or gas phase, in shipping cylinders, tank cars or trucks, or by pipeline. Storage may be in the shipping containers, in pressure storage

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vessels, or in gas holders. Intermediate or recycle streams are usually stored in pressure vessels or gas holders.

Liquefied Gases. The standards of the NFPA should be followed when designing handling and storage facilities for liquefied petroleum gases.

Gaseous Storage. Gases present the usual hazards of flammability and explosivity associated with combustible liquids. Unlike liquids, however, gas storage tanks cannot be effectively diked. Consequently, leakage can disseminate to a distant source of ignition and the resulting fire flash back to the storage vessel.

Gas-holders must be protected from sub-atmospheric pressures that could lead to their collapse. Liquid-sealed holders should be provided with high-level warning devices. Sealing liquids must be chosen that will not freeze in winter, or provisions must be made for heating the liquid. Detailed information for the safe storage and handling of gas cylinders is given in the *Matheson Gas Data Book*[5] and in publications of the Compressed Gas Association. Where noxious gases are being stored under pressure, the discharge from relief valves must be conducted to a safe place.

Flow Sheet Review

The foregoing analysis has been designed to aid the process engineer in development of a safe flow sheet. This flow sheet should now be carefully rechecked by making an imaginary start-up of the plant, by running it "on paper" at design conditions, by checking it out for operation under emergencies, and by shutting it down safely. Document all pertinent safety data such as flash-points, explosive limits, and toxicities[6] to assure proper design of the electrical and fire protection systems and provisions for personnel safety. The safe design of the plant rests on the accuracy and completeness of the data furnished by the process designer.

Batch or Continuous Processing

In the selection of processing schemes, the designer is quite often in a quandary as to whether to proceed via the batch or continuous route. Considerations of size of plant and relative complexity are of importance in making this selection. Economics can be brought into play, and finally, the relative safety of the two modes of operation can be

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compared. The following analysis is intended to guide the designer in making this latter comparison.

CONTINUOUS PROCESSING

1. At a given production rate, smaller quantities of materials are held-up in the processing system. Where flammables are involved the fire hazard is proportionately reduced.
2. Hazardous intermediate products may be consumed as fast as they are produced, thus minimizing their hazard.[4]
3. Since there is no variation of process conditions with time, automatic control is more readily applicable. Chances of operator-error are thereby minimized.
4. Process equipment is not as subject to cyclical fluctuations in pressure and temperature.

BATCH PROCESSES

1. Where hazardous operations are involved, units may be isolated from one another. Spread of fire or explosion can be easily minimized by dividing the process into small, isolated parallel units.
2. Where product purity is of safety significance, batch processing may be advantageous. This presumes, of course, that careful analytical control of the product quality is made on each batch.

Reaction Conditions

In discussing the reaction section, no special consideration was given to the type of reaction being performed. In the following discussion, reactions will be classified according to their thermal behavior, such as endothermic or exothermic. Either of these types may be operated in one of three ways:

1. Isothermally, that is, by either adding or removing that amount of heat required to maintain the reaction at constant temperature.
2. Adiabatically, where no heat is transferred through the reactor walls, and the adiabatic temperature change determines the final reaction temperature.
3. Nonisothermally, nonadiabatically, where some heat transfer is provided in the reactor but the temperature does not remain constant throughout the reaction.

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ENDOTHERMIC REACTIONS

Isothermal Case. Batch reactors may be run isothermally by continuously varying the heat supply. Fluid-bed systems offer the best means of maintaining uniform temperature conditions in continuous, gas phase reactors. Liquid-phase reactions may be run either at the boiling point of the constituents or of a common solvent. The principal dangers associated with isothermal operation are that a failure of heat supply can result in unreacted materials being carried in unsafe amounts into the next process section, and that poor temperature control can result in undesirable side reactions.

Adiabatic Case. Here, the heat of reaction must be supplied by the heat content of the incoming reactants. Poor temperature control of the reactants will lead to the same undesirable conditions as noted for the isothermal case.

Nonisothermal, Nonadiabatic Case. Fired tube reactors are examples of this case. The usual hazards resulting from coking and undesirable side reactions are prevalent. Good control of firing, over the length of the tube, is important not only in these respects, but to avoid the attainment of dangerously high metal temperatures. Provisions must be made to keep temperatures at a safe level if the feed system should fail.

EXOTHERMIC REACTIONS

Importance of Temperature Control. Boynton, Nichols, and Spurlin[7] present an analysis of the requirements for the temperature control of highly exothermic reactions for which a 200°C adiabatic temperature rise is possible. Their general conclusion is that, in order to prevent reaction run-away, a maximum of 10°C should be maintained between the reactor and the cooling surface. Safe designs may be provided by insuring that sufficient cooling surface is available to prevent additional temperature rise, and by the use of auxiliary cooling in the form of refluxing liquid or additional cooling surface controlled by reliable instrumentation. A rise of 10°C above the set-point requires twice the original cooling effect to bring the reaction back under control.

Isothermal Case. The methods of operation listed under Endothermic Reactions are applicable here, excepting that heat is now being removed. Loss of cooling effect may result in a run-away reaction.

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Adiabatic Case. Since the heat of reaction is removed by the products, the peak temperature achieved is dependent on the temperature of the incoming feed materials. Diluents may be added to the reactants to increase the heat capacity of the incoming feed stream. The close control of diluent addition and feed temperature is essential in maintaining the maximum temperature within safe limits. Provisions for additional diluent or auxiliary cooling of reactants may be required to prevent run-aways.

Nonisothermal, Nonadiabatic Case. Where diluents cannot be used, a cooling surface must be provided to what would otherwise be an adiabatic reactor. Here, both cooling surface and/or reactant temperature control must be designed to prevent excessive temperatures or run-away conditions.

9.3. SAFE CONTROL OF THE PROCESS VARIABLES

Definition and Scope

Control will be defined, for present purposes, as the total concept by which the process variables are contained within design limits. The concept includes instrumentation, equipment design, and safety devices. Rather than attempt to describe all of these in any detail, attention will be focused on the application of instrumentation to process systems and to the constructional details required for the safe containment of the process.

Control of Temperature in Thermal Systems

A thermal system is defined as consisting of the instrumentation, heat-transfer surface and medium, and the pumps and piping required for the addition or removal of heat. Figures 9.1 through 9.4 are illustrative of typical systems to be described below. Table 9.1 defines the nomenclature used in the figures.

Direct-Fired Kettle. Figure 9.1 illustrates the control system for a direct-fired batch kettle. Owing to the large heat capacity of the kettle, temperature control is achieved by controlling the flue-gas temperature with a two-position controller. A stirrer is provided to equalize temperatures in the kettle to improve heat transfer and to minimize local overheating. Provisions are made for automatic shut-off of the fuel supply in event of flame failure. The pilot-light by-pass

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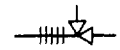
TABLE 9.1. Drawing Symbols

FD	Flame detector
ThRC	*Temperature recorder controller* Thermobulb actuated
TRC	Temperature recorder controller Thermocouple actuated
TR	Temperature recorder
TR W	Temperature recorder – with overtemperature warning device
TIC e	Temperature recorder controller – electric transmission – 2 position
PRC	Pressure recorder controller
LLC	Liquid level controller
	Steam trap or air-vent trap
	Line strainer
	Pneumatic control valve – air to close
	Pneumatic control valve – air to open
	Electric control valve – 2 position
	Electric control valve with manual reset
	Orifice fitting
	Relief valve
	Block valve
	Check valve
	Pressure gage
	Thermocouple or thermobulb

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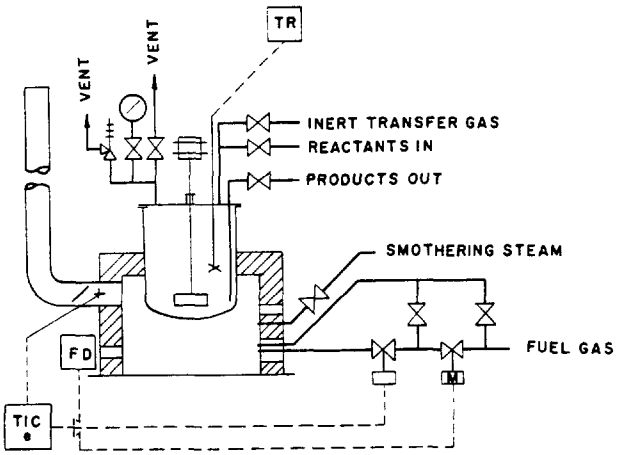

FIG. 9.1. Direct-fired batch kettle.

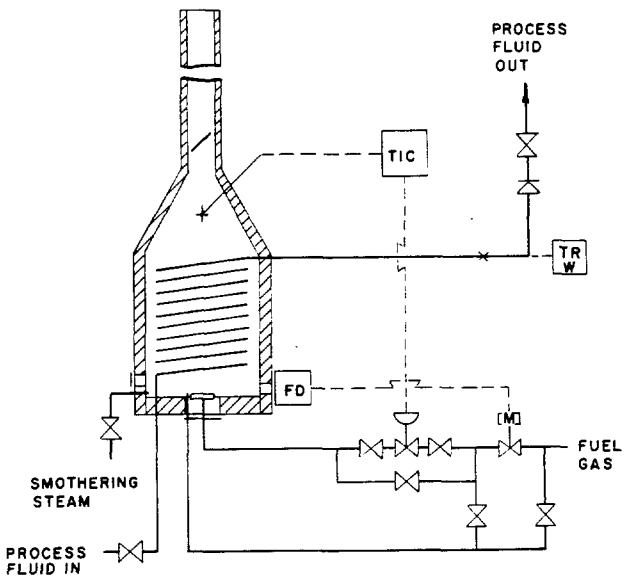

FIG. 9.2. Direct-fired process heater.

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valve can be interlocked so that it is closed during normal operation. Steam smothering is provided where the process fluids are flammable.

Direct-Fired Process Heater. Similar safety features are incorporated in the continuous process heater shown in Fig. 9.2. Here, temperature control is achieved by maintaining a constant flue-gas temperature with a proportional-plus-reset controller. The outlet process temperature is continuously recorded and, should it rise to a dangerous level, a warning device is actuated. The fuel gas valve closes on instrument air failure.

Steam-Heated Tubular Reactor. In Fig. 9.3 a fluid-filled bulb sensor is used to obtain an average process outlet temperature. The

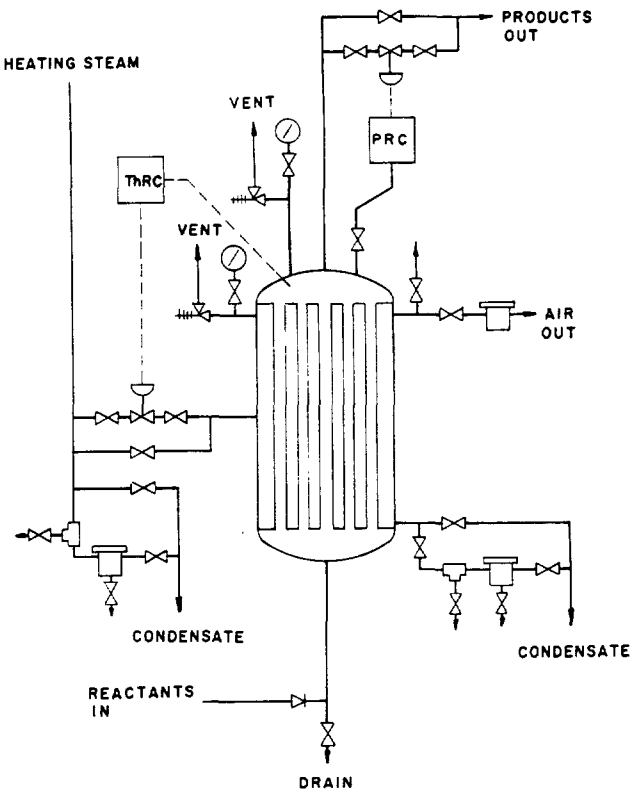

FIG. 9.3. Steam-heated vertical tube reactor.

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controller is of the proportional plus reset type, so that load changes can be accommodated. Note that a steam trap is provided ahead of the control valve to remove line condensate. An air-vent trap is provided to purge noncondensables from the steam chest. Strainers are used ahead of all traps.

Boiling Liquid-Cooled Tubular Reactor. Figure 9.4 illustrates a method for controlling the temperature of exothermic catalytic reactions. The boiling water provides for rapid heat removal and, by using small diameter tubes, high local catalyst temperatures can be avoided. In designing such a system attention must be given to the following points:

1. The heat-transfer surface provided must be sufficient to allow operation with a maximum of 10°C temperature difference between water and reaction for cases as noted in the section on the Reactor System. In other cases this differential must be small enough to preclude the possibility of film boiling on the water side.
2. The catalyst level should be somewhat lower than the water level to allow for surges.
3. Water feed-pump capacity must be sufficient to take care of possible surges in the heat output of the reaction.
4. An upper limit switch may be required on the temperature controller which will cause interruption of the flow of reactants to the reactor.
5. Likewise, a low-water switch, which will cause shut-down of reactant flows, may be required as a part of the water-level controller.

EFFECT OF TEMPERATURE ON EQUIPMENT DESIGN

Low Temperature Construction. Materials of construction for low temperature work must have good impact strength at working temperature. Most common materials are suitable for use at temperatures down to −20°F. For colder temperatures aluminum, copper and nickel, or austenitic stainless steels are required. Fluorocarbon plastics such as Teflon and Kel-F are recommended for use down to −400°F by the manufacturers.

Insulation for low temperatures must be sealed against the influx of atmospheric moisture. The elimination of water from the processing system is, of course, essential.

High Temperature Construction. Metallic materials for high temperature are chosen on the basis of creep-strength. Stresses normally used are those at which creep is limited to 1% in either 10,000 or

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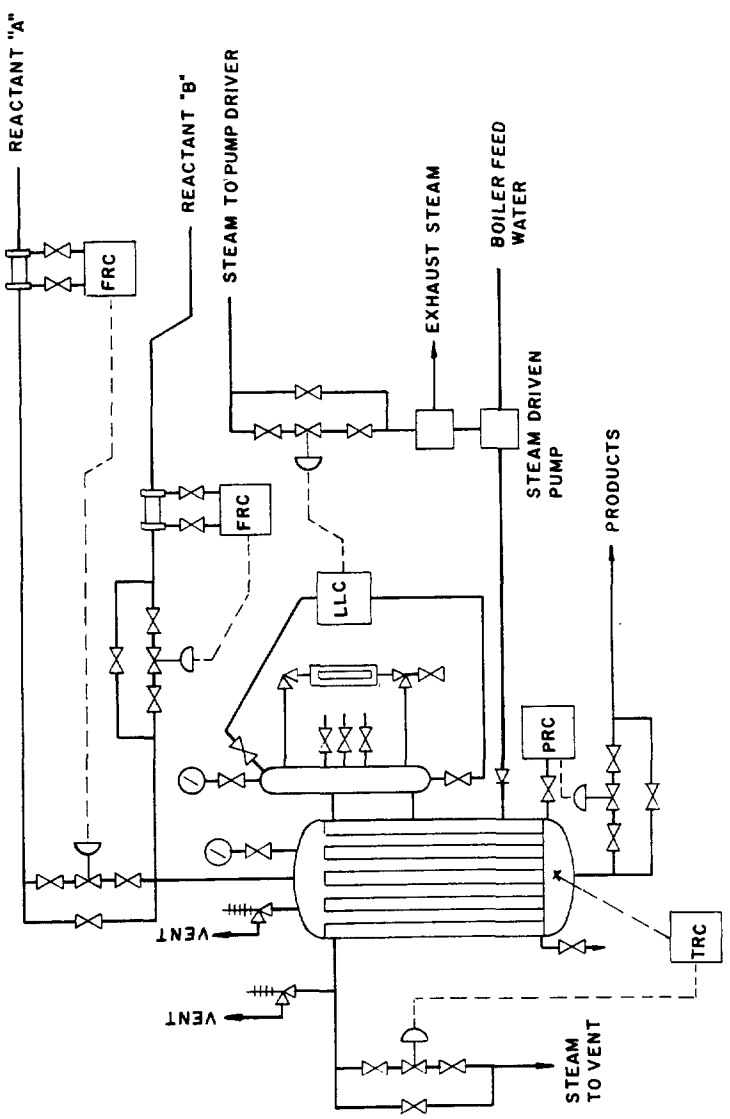

FIG. 9.4. Boiling liquid cooled tubular reactor.

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100,000 hr. Corrosion rates are markedly accelerated at high temperatures. However, much more severe corrosion may occur in parts of the system where condensation of corrosive agents can occur. Resistance to atmospheric oxidation[8] and hydrogen attack[9] should be investigated where applicable.

High temperature vessels may be internally insulated to reduce the temperature on the metal shell. Certain precautions must be taken in designing such vessels.

1. A common practice is to line the vessel with low conductivity insulation and to protect this with a further inner-lining of brickwork. Owing to the porous nature of such insulation the pressure drop through the vessel must be held to a minimum to prevent passage of hot gas up through the insulation. Where pressure drop is unavoidable, baffles may be inserted in the insulation or a prestressed brick lining[10, 11] may be used.
2. Where condensation of corrosive process fluids can occur at the temperature of the metal shell, or where shell corrosion is otherwise imminent, the shell must be built of a suitable alloy or protected by a corrosion-resistant nonmetallic liner.
3. Provisions may be made for cooling the external shell, either continuously or upon demand.
4. The temperature of the shell should be under constant surveillance. Where cooling is used, the rise in temperature of the cooling medium can be monitored.
5. Rapid pressure or temperature changes should be avoided.

SAFETY DEVICES

Except for instrumentation specifically designed to detect and alleviate over-temperature conditions, the use of fusible plugs constitutes the only positive means of reducing the stress in pressure parts when they are subjected to higher than design temperatures. Rossheim et al.[12] point out the relatively small control that the designer has over the temperature that his equipment may experience in operation. This is particularly true in the case of internally-insulated vessels.

Pressure Containment

Pressure Vessels and Piping. The Code for Pressure Piping[13] covers the safe mechanical design of piping. The American Society of Mechanical Engineers Boiler and Pressure Vessel Code[14] gives rules and

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design stresses for the safe design of vessels for use up to 3000 psig. Perry[15] covers the general design procedure for high-pressure equipment. Under any circumstances, the rules applicable within a particular state must be complied with.

All the above codes and rules set a safe standard insofar as structural safety is concerned but they do not, necessarily, guarantee the pressure tightness of the design. Where hazardous materials are contained under pressure, special attention must be directed to the assurance of pressure tightness and to the monitoring of leaks. Vacuum systems containing flammables must be so designed that the possible influx of air does not allow the attainment of concentrations within the explosive limits.

X-ray and magnaflux inspection of welded joints provide reasonable assurance that pressure integrity will be obtained. The main source of leakage, however, occurs at mechanical joints.

Stationary Mechanical Joints. These include threaded and flanged connections. The selection of thread sealant and gasketing must be made on the basis of reliability in containing the pressure, resistance to corrosive media, and thermal stability. Thermal stability should include not only stability at processing temperature but also at temperatures likely to occur in event of fire.

Moving Seals. Moving seals may be required to contain pressure at points of entry of either rotary or reciprocating parts. Rotary joints occur at valve stems, centrifugal-pump shafts, and agitator shafts. Reciprocating joints occur at control-valve stems and at the shafts of reciprocating pumps and compressors.

Valve-stem seals are usually of packed construction, packing being selected on a basis similar to gaskets. Where absolute tightness is required metal or plastic diaphragms or bellows may be used ("packless" construction). Rotary seals on pumps or agitator shafts may consist of packed stuffing boxes or mechanical seals.[16] Where loss of material from the system would constitute a serious safety hazard, two mechanical seals may be arranged back-to-back and the intervening space pressured to somewhat above system pressure with an inert sealing fluid. A "canned" motor may also be used under these conditions.

Lubricated stuffing boxes are applicable to control-valve stems and reciprocating pump and compressor rods. Nonlubricated packings are available for use with oxygen. Diaphragms or bellows can be used for the absolute sealing of control-valve stems.

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Inert-gas purged "distance-pieces" can be provided on the atmospheric side of compressor stuffing boxes to prevent the possibility of air sucking into the cylinder during the suction stroke. A similar distance piece vented to a safe place can be used to trap off the leakage of noxious gases.

SAFETY DEVICES

Signalling and warning devices can be actuated by the pressure sensors. Over-pressure relief is ordinarily provided by spring-loaded relief valves or rupture discs. Both these devices are available in a wide variety of materials of construction. Relief valves are available for use at 750 psig at 900°F to 45,000 psig at 100°F. The range for rupture discs depends on the applicability of the disc material, but the ranges generally available are from up to 1000 psig at 1000°F to 55,000 psig at 100°F.

Rules for the sizing and location of pressure relieving devices are given by the ASME Pressure Vessel Code, the National Fire Protection Association,[1] and governmental agencies. In general, the set pressure must coincide with the design pressure of the vessel.

Relief valves are selected for use on clean fluids and where automatic closure of the relief port is desired subsequent to discharge. Where rupture discs are used under fluctuating pressure or very corrosive conditions one of the arrangements shown in Fig. 9.5 is recommended. If used under vacuum conditions a vacuum support should be used under the disc.

Needless to say, passageways to relieving devices must not become obstructed. Discharge piping must be sized to carry the effluent to a safe place and with minimum pressure drop. Blow-down tanks may be provided for liquid discharges, and gases can be exhausted to stacks or flares. Discharge piping must be anchored to resist shock effects.

Analytical Procedures for Control of Composition

The desirability of accurately monitoring the composition of process streams is of obvious safety significance. Controllability of the process can, thereby, be enhanced, and the approach of unsafe ranges of composition detected sufficiently early for corrective measures to be applied. The analytical procedures to be used must be specified by optimizing the requirements for accuracy, frequency, and time required

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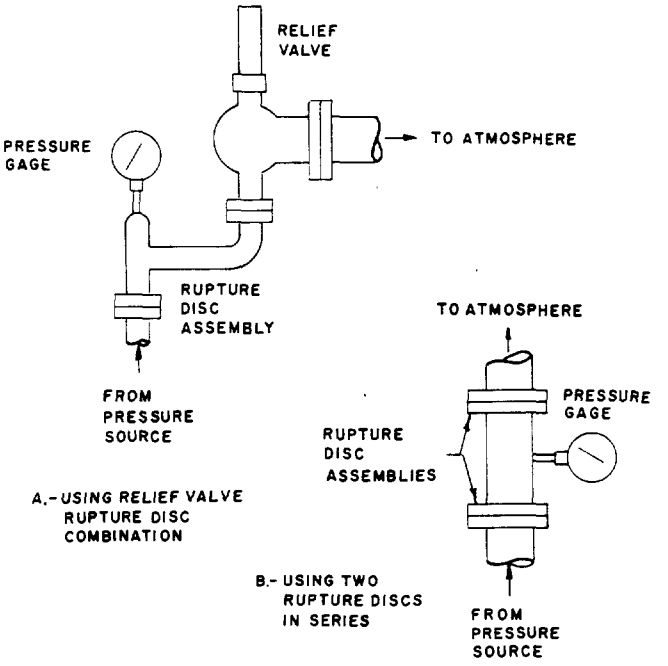

FIG. 9.5. Use of rupture discs under corrosive or fluctuating pressure conditions.

for analysis. Instrumentation, where applicable, is to be recommended over laboratory-type procedures.

SAMPLING

Where process instrumentation is being used, it is necessary that its sensing element either be located in the process stream or that a sample stream be withdrawn from the system and run through the instrument. In the first case it is necessary that the element not be located in stagnant areas. If solids are present, means must be provided to prevent their accumulation on the sensor or to allow for their frequent removal. Corrosion of the element may cause loss of calibration. Where sampling is employed it is important that the sample be representative of the process contents. Provisions must be made to prevent the accumulation of materials on the wall of the sample piping. Since only small sample flows are ordinarily required, it is well to minimize the length of sample lines and, thereby, reduce time lag.

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SAFETY APPLICATIONS

Although some analytical instruments offer no continuous control feature, they can all be arranged to operate warning or emergency shut-down devices. In addition to monitoring process streams, such instruments can be used to warn of the presence of toxic or objectionable materials in the plant atmosphere and in the discharge from stacks or sewers. Mercury-vapor detectors and explosive-limits meters are common examples of the former, and SO_2 detectors and pH meters are common examples of the latter.

9.4. SAFETY AS A PART OF PROCESS DEVELOPMENT

Evaluation of Hazards

The evaluation of potential hazards must begin in the earliest stages of process development. The ensuing program must include provisions for the complete solution of all problems that may affect the safe operation of the projected process. Where not available in the literature, data relative to flash-points, explosive-limits, toxicity, and corrosion must, of course, be obtained experimentally. An alertness in detecting unexpected safety problems, and a high degree of ingenuity in solving or averting them, is a prime requirement for the successful completion of many development programs.

Pilot Plants

The piloting of a new process often begins with a small bench-scale unit in which the feasibility of a doubtful procedure can be demonstrated. Here we obtain the first indications of any unusual safety problems. Corrosion rates, under process conditions, are experienced for the first time; the safe limits of operation can be roughly determined; and indications of plugging and fouling are discernable. The data are generally crude at this point and offer only indications of trends, but all further development along safe lines depends on the skill with which the unit is operated and the data are interpreted.

Larger pilot plants are built to obtain more precise engineering data and to secure reliable information on the product. Integrated pilot plants, which include all of the proposed process steps, may be built to demonstrate the whole process on a suitably large scale. The accumulation of data, suitable to the development of a safe flow sheet as under

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Section 9.2, may serve as one of the prime motivations for this latter program. Methods of controlling hazardous reactions, the safe handling and storage of materials, prevention of the accumulation of hazardous materials, and the production of a safe product must all be developed to a satisfactory degree.

Scale-Up

Piloting is not generally required for unit-operations equipment. Where experimental data are required, such as for filtration or size-reduction equipment, manufacturers tests, with scale-up on the basis of physical laws, will usually suffice.[17]

Chemical reactors are scaled up by applying the principles of chemical kinetics to empirical data.[18, 19] The process designer must assure himself of the accuracy with which the process variables have been controlled and the degree to which adiabatic (or other) conditions have been maintained. In a similar vein Stevens[20] points out the limitations in the application of kinetics resulting from longitudinal diffusion and radial gradients in the pilot-plant reactor, and the effects of wall surface and impurity accumulations.

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10

Instrumentation for Safe Operation

Donald Richmond

Automatic control of chemical processing equipment has made it possible for a chemical operator to assume the responsibility of additional units of operation. This is because controllers are performing tasks which were formerly handled by men. This simple concept of greater productivity applies to batch as well as to continuous operation. This chapter presents some of the safety considerations which are engineered into process design, where safety engineering begins. While this chapter covers only a few of the most common safety devices generally associated with instrumentation, it illustrates the type of thinking which is required of designers in order to maintain a high degree of safety in present day plants.

For the purposes of this discussion the term *instrumentation* means the use and application of industrial instruments of measurements and control. This definition includes indicators, recorders, controllers, and transmitters for measurements such as temperature, pressure, flow, liquid level, and analysis. Instrumentation also embraces the fields of data reduction, alarms, and interlocks.

At the present time 5% of the capital investment in large chemical plants may be in instrumentation. The rate of growth of instrumentation cost in one plant over the past 5 yr has been approximately four times as fast as the plant average. The total invested capital per employee in this company has increased approximately fourfold in the

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past 10 yr. In a large oil refinery the investment per employee may be as high as $200,000. These statistics provide clues as to the long range effect of the increasing demands of greater productivity upon instrumentation.

Process design engineers are just becoming generally aware of the safety concepts of instrumentation, including some of its inherent dangers. Actually, safety and instrumentation go hand in hand because good engineering includes safety in its design. The types of manufacturing equipment which we will find in the plants of tomorrow will dictate special safety requirements in engineering. The hazards that we find associated with special products and special materials which have to be handled, will generally dictate a certain amount of safety instrumentation. Efficient control implies safety. Everyone is interested in safety from the standpoint of protection of personnel and equipment. The operating department, however, has an extra interest in safety because of the desire to prevent production losses such as spills. The maintenance department likewise has a special interest in safety because of the desire to easily maintain the operating facilities. For example, instead of installing a control valve near a hazardous area where a man might easily injure himself, it might be better to locate the valve at a safe location where the maintenance crew can easily repair it. A few of the common safety devices which are commonly used in chemical plants will be discussed.

Self-acting Pressure Regulators

Two basic types of pressure regulators are shown in Fig. 10.1. One is the type with the integral downstream pressure tap, and the other has the external downstream pressure tap. The first valve is a single-seated valve which normally is used either with small flows and small valve sizes or on those applications involving small pressure drops. The other valve is double seated generally because of large flows or large pressure drops. Usually double seating begins at the 1½ in. size. In both cases, however, the action of the spring is opposed to the pressure that is placed upon the diaphragm. The purpose of the regulator is to reduce a fluid pressure to a smaller value. Rupture of the diaphragm is the commonest cause of failure in these self-acting regulators. Should the diaphragm fail for any reason, the action of the spring in both valves will be to return the valve to the wide open position. Because of its design, therefore, pressure regulators fail in the unsafe position, such as open. Upon such a failure full upstream-line pressure will exist on the downstream side of the valve.

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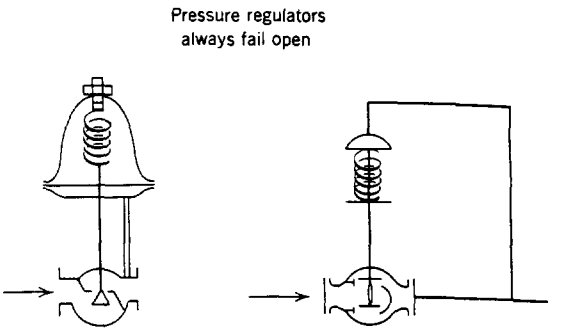

FIG. 10.1.

This brings up the first rule about pressure regulators—they always fail in the unsafe position. Because of this inherent weakness, it is customary to find pressure relieving devices or safety discs installed downstream of self-acting pressure regulators to safeguard equipment from over pressure.

Self-acting Temperature Regulators

In Fig. 10.2 the diaphragm motor is replaced by a bellows motor in which the vapor of a fluid in a temperature sensitive bulb exerts its pressure. The bulb contains a liquid such as ether or alcohol. The temperature sensitive bulb is located in a tank or vessel which is to be temperature controlled. The heating medium for the vessel passes through the automatic valve as the fluid pressure inside of the bulb increases because of an increased temperature. The pressure in the bellows motor will gradually close off the valve. This action reduces the rate of heat input to the system and in that way the temperature is regulated. As in the case of the pressure regulator a failure of the thermal system will cause the valve to fail in the wide open position because of the action of the spring. These regulators with valve plugs on top of the valve seats are used on heating service. This points up the similar rule—all self-acting temperature regulators on heating service fail in the open position which is the unsafe position.

For cooling service the same instrument is used by reversing the

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action of the valve. The plug is on the underneath side of the seat instead of the top side. A failure of the thermal system will cause the spring to close the valve, in which case the coolant is shut off. Therefore, self-acting temperature regulators for cooling service fail in the unsafe position. Because of the inherent weakness of self-acting temperature regulators some external temperature switch is required in order to protect vessels from overheating. There are self-acting temperature regulators on the market which feature "fail-safe" design. This is because the fluid chosen for the bulb operates in the vacuum range. This is unsatisfactory because of the limited available power for the movement of the valve stem. One other disadvantage of the self-acting temperature regulator is that the temperature is not controlled very closely.

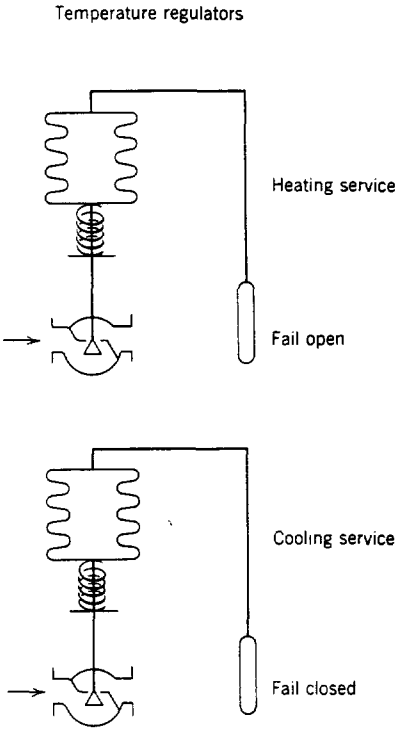

FIG. 10.2.

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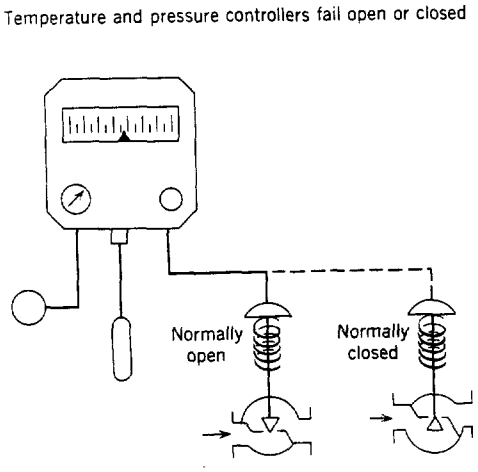

FIG. 10.3.

The Pneumatic Controller

The need for closer control of temperature usually justifies the installation of an instrument such as in Fig. 10.3. This is a temperature controller wherein the internal bourdon tube is connected to a temperature-sensitive bulb, and becomes a pressure controller when the internal bourdon tube is connected directly to a pressure vessel or pipeline. In this particular instrument the sensitivity, proportional band or throttling range (these terms are synonymous), can be easily adjusted to suit the process. Furthermore, the action of the controller can be easily changed so as to use normally open or normally closed diaphragm motor valves as shown in the sketch. Many believe this arrangement constitutes a fail-safe system because the control valve can be chosen to fail open or closed, but it is not. The control valve fails safe only in the event of an air supply failure. However, a failure of the thermal element will result in the pointer falling to the lower end of the temperature scale. This makes the instrument think the temperature is too low, so the action of the controller will then be to cause the valve to open wide regardless of the action of the valve. Therefore, the normal closed-tube temperature systems likewise never fail safe. However, it is now possible to buy completely fail-safe

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temperature controllers at an additional cost. A piece of invar inside of the thermal bulb causes the fluid pressure to drop on a rise in temperature, which is the reverse action of the conventional system just described. Under this condition, when the tube system fails the pointer moves up-scale. In this way the instrument thinks the system being controlled is too hot and the control valve will be automatically closed. This particular controller is advantageous on small process vessels which are easily overheated; that is, small in relation to the rate of heat input.

The Potentiometer Controller

A temperature controller of the electric potentiometer or wheatstone bridge type in Fig. 10.4 is more commonly used in process control. They are generally considered the safest because on a failure of the primary element the pen moves up scale. Upon an electrical failure the pen stops moving. If the pen happens to be above the control point at the time of electrical failure, the controller fails safe. If the pen is below the control point at the time of electrical failure, the controller fails in the unsafe position. This is especially true on those controllers with automatic reset. Again, the engineer has the choice of using a normally open or normally closed valve depending upon which is the

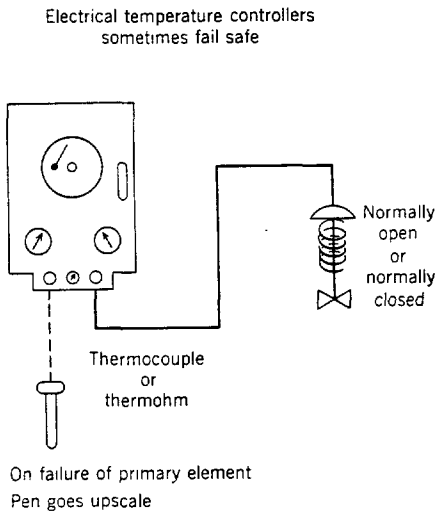

FIG. 10.4.

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safest way for the valve to fail in the event of a failure of the air supply.

Float Switches

Two types of float switches are shown in Fig. 10.5. The first one is the simple float operated switch which is generally installed at the top of a tank. As the float rises because of a rise in level a magnet which is connected to the float rises into the magnetic field of the external magnet. This action attracts and tilts the mercury bottle, and in that way switch action is obtained. In the lower picture of Fig. 10.5, the side entrance float switch is shown. In this case the same size of ball float is used to operate a micro switch through a packless flexure tube.

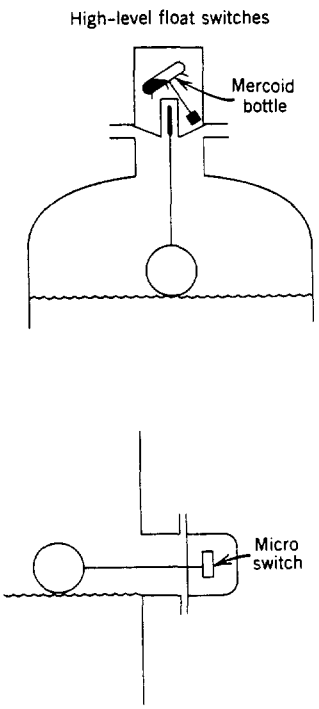

FIG. 10.5.

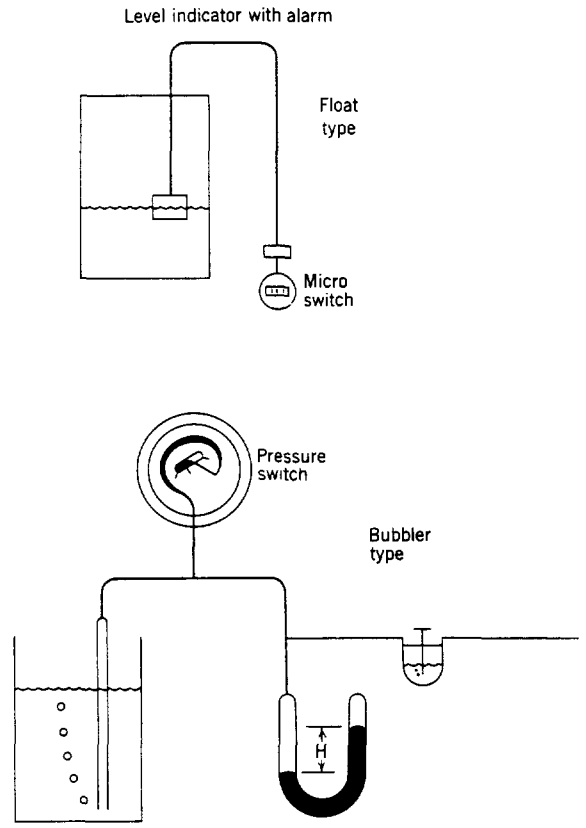

FIG. 10.6.

Figure 10.6 illustrates another version of a float operated level gage. This type of level gage is accurate and quite dependable. For this reason, it is generally advisable to attach the level switch alarm to it.

Bubbler-Type Level Gages

The lower part of Fig. 10.6 shows the bubbler-type level gage. The back pressure in the dip pipe which motivates the U tube manometer for liquid level measurement can also be used for actuating an ordinary pressure switch. A contactor manometer shown in the lower half of Fig. 10.6 is used to indicate liquid level and to provide switch action.

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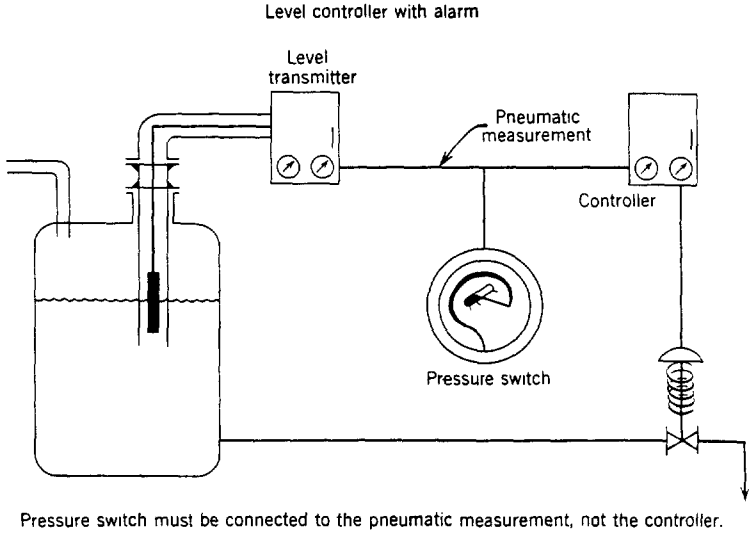

FIG. 10.7.

Tungsten probes are adjusted down into the mercury. The motion of the mercury will either close or open the electrical circuit which will actuate other devices as required. The mercury U tube contactor manometer, while inexpensive, cannot be made explosion proof.

Displacer Type Level Controllers

Another type of level alarm is usually associated with level controllers. This type of level controller, shown in Fig. 10.7, is the displacer type. A metal weight is suspended in a liquid in which the level is to be controlled. The instrument measures the change in weight of the displacer as the liquid level changes. The output pressure of such a level controller is 3 to 15 psi, which is the standard pneumatic signal range. Regardless of how the level is measured, it is important to recognize that the pressure switch should be connected to the transmitter signal as shown in Fig. 10.7. Sometimes engineers have been known to connect the pressure switch to the output of the controller on a simple level control with adjustable proportional band only. The disadvantage of this method is that switch action will occur when the process requires very high or very low flows through the control valve. This results in false alarms. The advantage of the system as shown

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in Fig. 10.7 is that the pressure switch is actuated only as a result of a liquid level change and not because the control valve became closed or wide open. If the pressure switch for high and/or low level alarm is connected to the transmitter signal to the controller there will never be false alarms. Therefore, the rule associated with level controllers is always locate the pressure switch on the transmitted measurement signal and not on the control valve pressure.

Alarms on Recording Controllers

Figure 10.8 is a picture of any controller scale. The shaded portion represents the normal control band and the heavy black marks indicate the low and high alarm. If the controller can be depended upon to hold the measurement within the limits of the shaded portion, then alarm contacts would serve a useful purpose if their settings were made just outside the normal control band. This method is generally accepted in practice among the industry today, because it usually provides adequate advance warning of system failure.

Alarms on Multipoint Recorders

Figure 10.9 illustrates a conventional multiple point recorder. These are most widely used for temperature measurements where the thermocouple or resistance bulb becomes the primary element. It is possible to have selected temperature alarms even on a multiple point recorder. The circuit consists of a terminal board, selector switch, print switch,

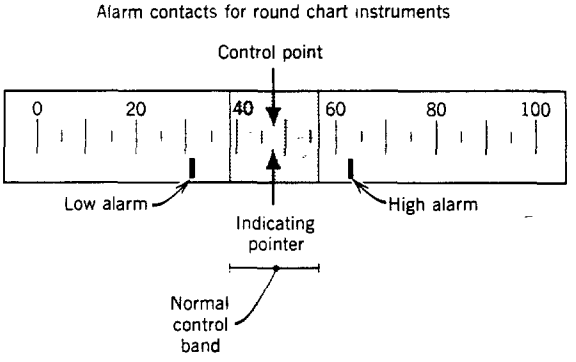
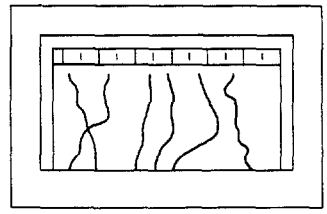
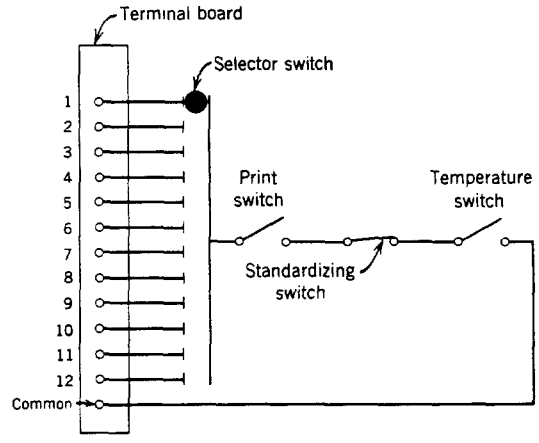


FIG. 10.8.

Alarm contacts for multipoint recorders





One temperature only

FIG. 10.9.

standardizing switch, and a temperature switch which is shown arranged for one temperature only.

The standardizing switch is normally closed and opens only when the instrument goes into standardization, either automatic or manual. When the print wheel comes down to print, the print switch makes a momentary contact. Should the temperature of the selected point be in excess of what it was set for, the temperature switch will close and the entire circuit which is normally open will be momentarily closed when the print switch closes. It is this momentary signal which can be used for alarm and other shutdown purposes.

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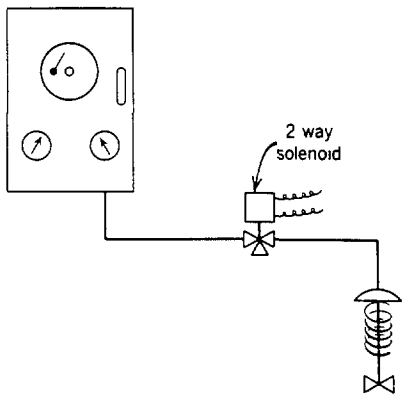
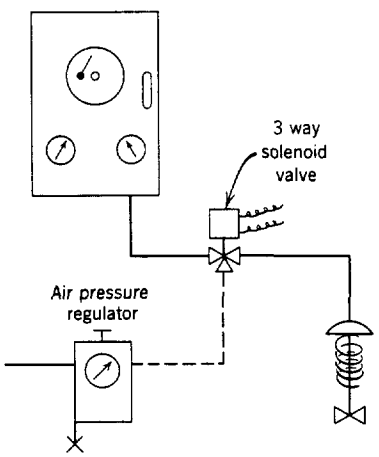
Applications of solenoid valves



On failure, valve is stuck in last position before failure.

FIG. 10.10.

3 way solenoid valves



On failure, valve is vented, moved to a preset position or controlled by another source.

FIG. 10.11.

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Solenoid Valves

Some applications of solenoid valves are shown in Fig. 10.10. It is assumed that on air failure the control valve is to be held in the last position before the air failure. A two-way solenoid valve connected to a pressure switch in the air line will accomplish this purpose.

Figure 10.11 illustrates the use of three-way solenoid valves. Of course, three-way solenoid valves can easily be made into a two-way solenoid valve merely by plugging off the third port. In this particular application the control valve can either be vented upon failure, or by using a pressure regulator the control valve can be moved to any preset position between wide open and fully closed merely by setting the pressure regulator at the desired pressure. Solenoid valves can be actuated by other process controls, master shutdown devices, and other devices, upon loss of agitation, pump failures, or even fire alarms.

10.1. ANNUNCIATORS

When an instrument engineer considers alarms for shutdown devices he usually thinks of three basic design premises:

1. All the *critical* points of operation should be protected by alarms and/or shutdown devices.
2. The device should fail safe.
3. Field testing should be simple.

An annunciator is a device which calls the operator's attention to the fact that something has gone wrong. This is usually accomplished by an audible and visual alarm.

Horn and Light Annunciator

The simplest and most elementary annunciator system is the one that is shown in Fig. 10.12. An alarm contact such as a pressure switch, temperature switch, or contact inside an instrument (any contact that signifies an unsafe condition or act) will close, and upon closing a light will go on and the horn will sound. The disadvantages of such a system as this are quite obvious. A contact which is normally open will eventually become corroded or dirty and probably cannot be depended upon to function when it should. It is impossible to turn off the horn in the event the alarm is sounded. The horn will not stop blowing

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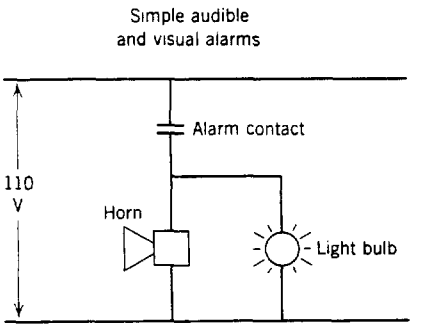


FIG. 10.12.

until the alarm condition has been corrected. This generally results in tampering with the alarm to render it inoperative. There will also be confusion if there are several units of this kind because there will be an excessive number of horns and lights. The use of the horn is practically limited to only one alarm.

Horn and Light Annunciator with Manual Switch to Silence Horn

The alarm shown in Fig. 10.13 is a little improvement in that the operator may turn off the horn manually once the signal has been acknowledged. The obvious disadvantage of this alarm is that the operator can leave the alarm in the off position all the time.

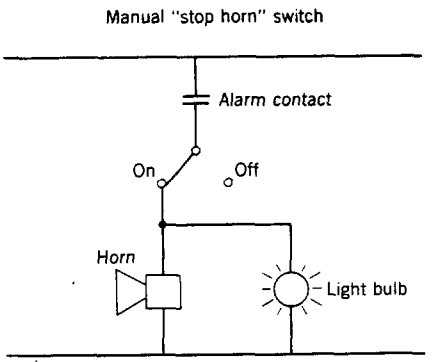


FIG. 10.13.

Annunciator with Manual "Stop Horn" Button and Automatic Reset

Figure 10.14 illustrates how to overcome this disadvantage by using a relay and a push button. Again the alarm contact which closes up will actuate the horn and light in the same manner; however, after the operator acknowledges the alarm, all he must do is manually push the normally open momentary contact push button and the relay does the rest. The advantage of this system is that when the unsafe condition has been corrected the alarm system automatically returns to the original condition so that the horn will sound on the next occasion. The operator does not have to remember to turn the alarm back on.

Annunciator with a Flasher for the Light

Figure 10.15 shows a further improvement, in that we now have a flasher to signify which is the new alarm to come in, instead of the light just burning steady bright when there is an alarm condition existing. When the operator desires to silence the horn when a new alarm comes in, he merely pushes the push button as in the former case. The relay not only de-energizes the horn, but it also causes the light bulb to burn in the steady bright condition. This is called the pending or the acknowledged position. This is a distinct advantage when there are several lights on a board in a concentrated area. The disadvantages are still the same however, namely, that this alarm is good only for

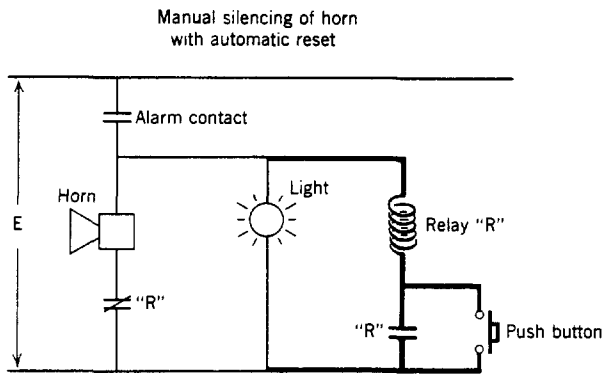


FIG. 10.14.

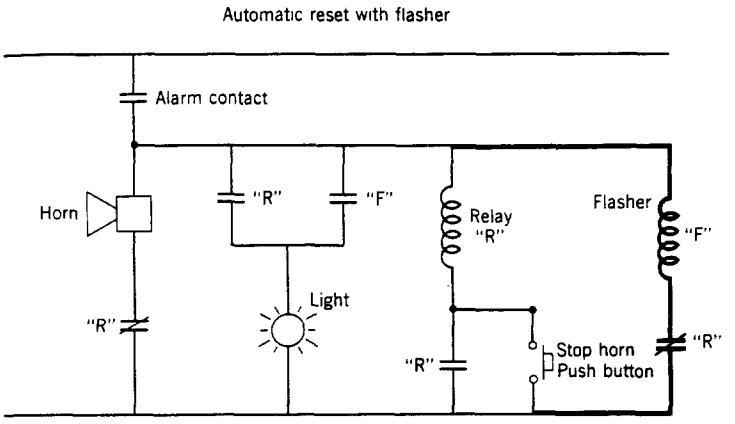
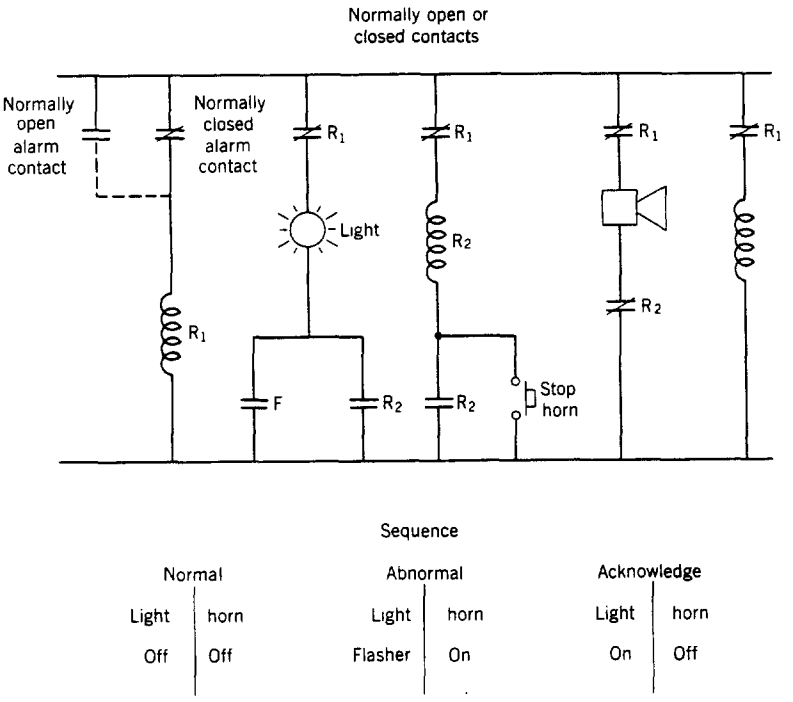


FIG. 10.15.



Sequence

Normal		Abnormal		Acknowledge	
Light	horn	Light	horn	Light	horn
Off	Off	Flasher	On	On	Off

FIG. 10.16.

normally open contacts, and the use of the horn is still limited to one alarm.

Annunciators which can be Actuated by either Normally Open or Normally Closed Field Contacts

Figure 10.16 shows the use of the normally open or normally closed actuating contacts. Another relay is required to do this job. The advantage of using normally closed actuating contacts lies in continuous monitoring of the contacts, connecting wires, and alarm relays. A failure of any part of this circuit will result in an alarm, and at least a false alarm is better than no alarm at all. The action of the remainder of the alarm system is identical to Fig. 10.15. In the acknowledged position the light burns steady bright, and the horn is off. When the unsafe condition has been corrected the relays all return to their normal position ready for the next alarm. The chief disadvantage of this system is the high initial cost (between $300 and $400) and high maintenance cost. For several units space requirements for the electrical gear present a major problem in plant design. Maintenance of faulty contacts is also costly.

The Unitized Annunciator

The annunciator which is shown in Fig. 10.17 overcomes all the disadvantages presented thus far. It is called a unitized annunciator and is manufactured by several reputable manufacturers. The "A" and "B" relays are contained in one hermetically sealed can in an atmosphere of nitrogen. The relay cans are plugged into a conventional radio socket. Under normal operating conditions both relays are energized. Since the normally closed actuating contacts are recommended, the contact, connecting wire, and the relays are completely monitored. This is a completely fail-safe annunciator. It features a stop horn and acknowledge push button, same as before, and also a test push button so that the operator may test the alarm. The circuits preferred generally are circuits in which both light bulbs are connected in parallel. This means that there is an installed spare bulb. The plug-in relay can with the two lights mounted on it is located behind a translucent white plastic nameplate with black letters engraved upon it. Several such units are arranged in rows in cabinets. When the alarm comes in, the lights will be flashing while the horn sounds. The operator can read the engraving at a considerable distance. This permits location of the annunciator on top of the panel board rather

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The unitized annunciator

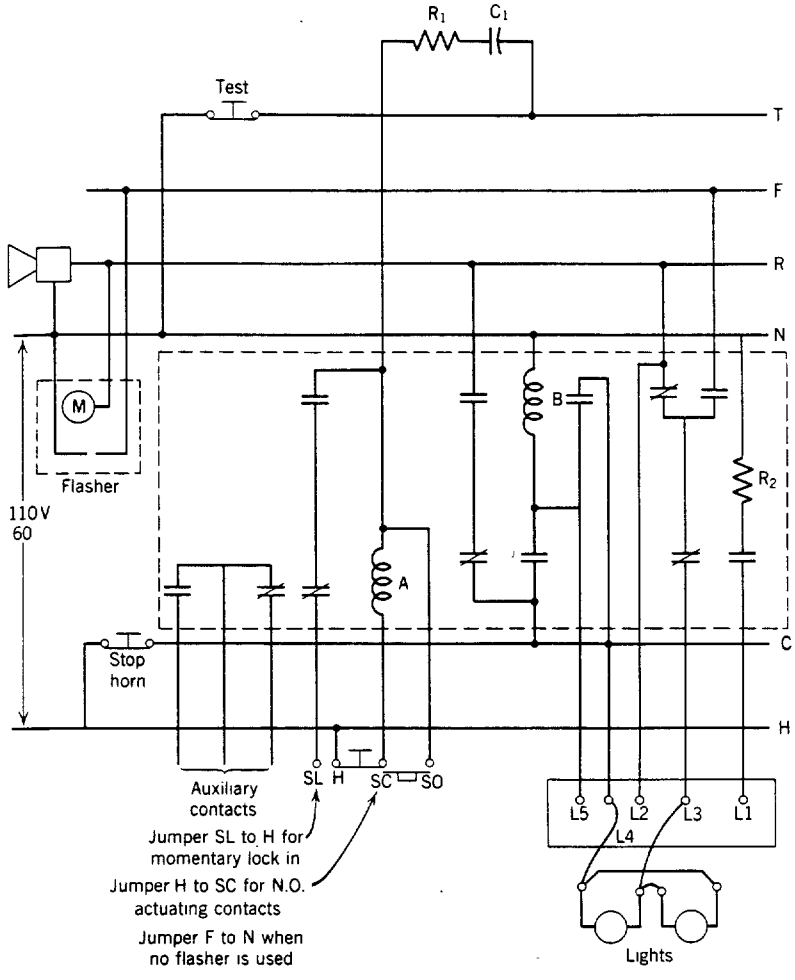

FIG. 10.17.

than in the panel board which consumes valuable board space. The cost of each plug-in relay and flasher is around $38 to $40 each. One horn now serves a whole cabinet. Additional relays are connected to the six bus bars shown by merely plugging them into spare sockets of the prewired cabinet. One may easily purchase 100 or 200 such units

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all in one cabinet and still use only one horn and only one flasher. The installed cost per point is reduced from $300 or $400 down to about $50 per point.

The use of hermetically sealed relays and flashers is the answer to the corrosion problems that are found in the chemical plants. The advantages of the unitized annunciator are: low initial cost and low maintenance cost. Over a period of two years, one plant has experienced only around six relay failures in several hundred units. The relays are hermetically sealed in nitrogen which eliminates oxidation, corrosion, and accumulation of dirt on the contacts. Identity of trouble is quick and accurate. It consumes no more than 70 milliamps of current. The use of the horn is unlimited. It is versatile. Over 100 circuits are available in this universal circuit shown in Fig. 10.17. Another circuit arrangement that is available is a momentary "lock-in" feature which is used with momentary type alarms. Auxiliary contacts are available. The name plates are back lighted but turret lenses or bulls-eye lights are available with the basic universal plug in relay. The flasher and test button are optional features. To change circuit arrangements it becomes necessary only to change jumper wires. It is possible to add counters to this system so as to count or totalize the number of times each alarm relay is actuated. For an additional cost another device may be installed which tells the first alarm to go off in a given series. The choice of dim lights or low lights for the normal position also is optional.

10.2. INTERLOCKS

High-Level Interlocks

Interlocks are really controls for safe operation. In the event of a serious process upset the interlock does something about it in addition to warning the operator of danger. Figure 10.18 shows an interlock for high level. A float switch on top of a tank can be easily interlocked with a pump which pumps the material into the tank in order to prevent spills or overflows of that tank. The way in which it is accomplished is shown in the lower section of Fig. 10.15. Notice that the control voltage is limited to 110 v. Since most motor voltages are 440 v, three phase, it is merely necessary to install a small 4 to 1 step-down transformer inside the magnetic starter box in order to obtain the 110 v required for the system. The normally closed contact of the level controller or level switch is connected in series with the stop circuit of the magnetic starter.

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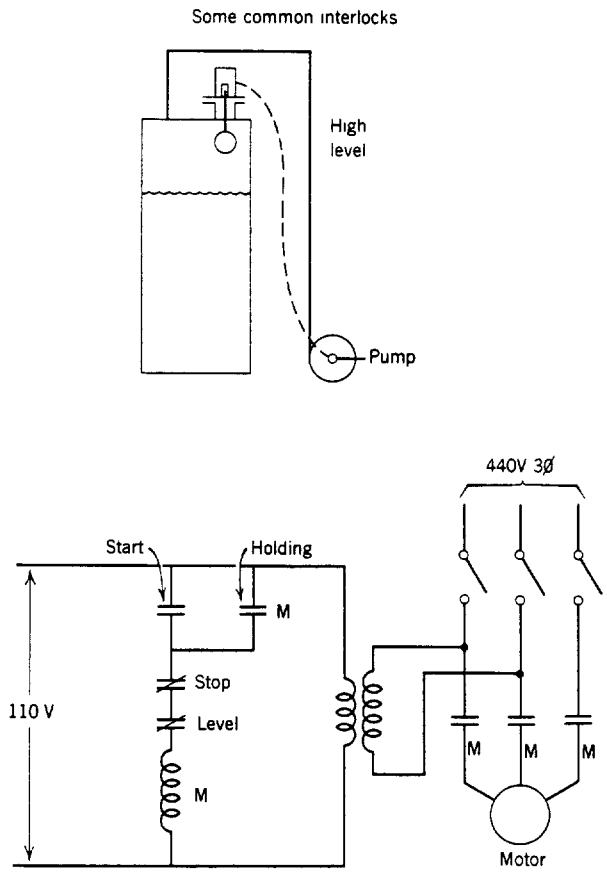

FIG. 10.18.

Prevention of Operating Errors

Figure 10.19 shows one versatile method of preventing operating errors. Let us assume that this process calls for the sulfonation of an organic material in three batch sulfonators. Oleum is measured out in a weigh tank for each batch. In operation the valves are lined up to the proper sulfonator. Full cooling is applied to the sulfonator. The temperature is controlled either manually or automatically by the rate of oleum addition until the oleum weigh tank is empty. It is not unusual to make an operating error by leaving a valve open on another

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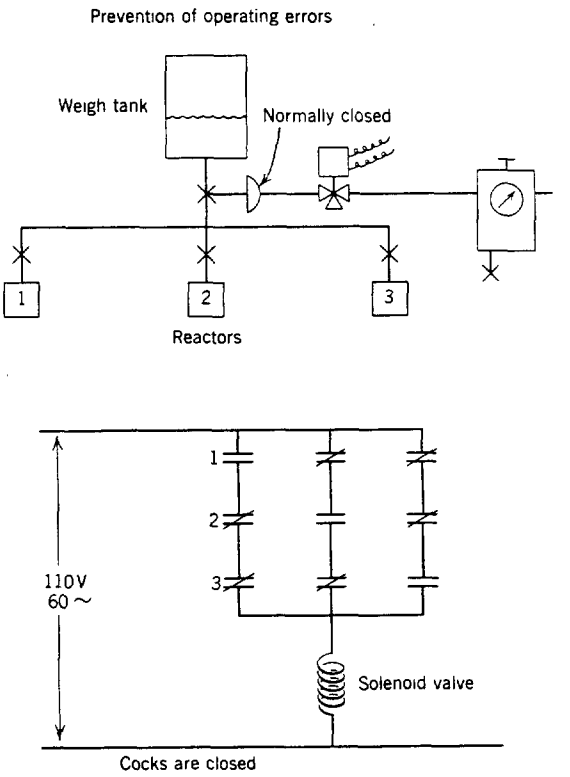

FIG. 10.19.

sulfonator. In many cases such an error is hazardous as well as costly in wasting valuable chemicals. To prevent this kind of error, it is necessary first to mount a lever switch on each of the three cocks. On each switch will be mounted three mercury bottles. In practice there will be the same number of bottles mounted on the shaft on each lever switch as there are cocks which are included in the interlock system. These 4-amp bottles are arranged as shown in the electrical drawing, and the bottles are all shown when the cocks are in the closed position. Assuming it is desired to sulfonate #1 sulfonator the cock to it is opened and when it is open, current will automatically flow through the first circuit through the solenoid valve. However, if any one of the other cocks are opened, the flow of current to the solenoid valve will be interrupted. This causes the oleum flow to be shut off by vent-

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ing the diaphragm motor of the normally closed control valve. This technique is being used at the present time with very good results with negligible maintenance.

Agitation Failure

Another common interlock is known as agitation failure protection. It is designed to prevent accidents which can occur in many chemical reactions when agitation ceases. Since the agitator shaft or the gears can break off, a measure of the current flow to the motor can be used to detect loss of agitation. A current sensitive relay or current switch is connected in series with one wire which is connected to the motor. On large motors a current step down transformer is inserted here and the relay is connected to the secondary of the transformer. The switch is set when the liquid level is about ⅓ of normal. At higher levels, more than enough current will keep the relay energized. A drop in current below the set point will de-energize the relay. A typical wiring diagram is shown in Fig. 10.20 using a three-way solenoid valve in the control air line to the diaphragm motor valve. Upon loss of agitation the current switch de-energizes the solenoid valve which in turn vents the diaphragm of a normally closed control valve. This shuts off the flow of chemicals to the reactor to prevent an explosion. The switch action can also be used to actuate an annunciator system and perform other jobs as required by safety considerations.

Miscellaneous Interlocks

Other interlocks include temperature and temperature differential, pressure and pressure differential, liquid level, flow, pH, conductivity, density, and analyzers. All of these interlocks or contacts can be made to shut down pumps, blowers, vacuum jets, or other parts of processes. Interlocks can be used to shut off steam, natural gas, cooling water, or fluid flow or to vent vessels.

In summarizing, remember to use normally closed actuating contacts whenever practicable. Of course this cannot be done in the case of multipoint temperature recorders because of the cyclical nature of a multipoint instrument. Select valves which fail safe, employ normally energized circuits, provide for easy start up; use timers if necessary, protect all the critical points of operation. Do not over instrument processes. Avoid high-control voltages in alarm systems and do not mix up voltages as this practice may cause electrical difficulties. Avoid temporary wiring and exposed terminal boards. Limit the use

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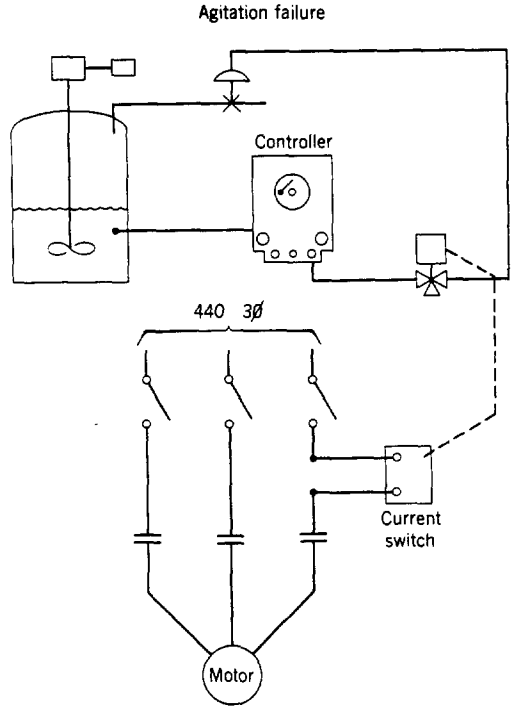

FIG. 10.20.

of plant air on alarms; never use sprinkler air. Avoid bypasses whenever possible or practicable. Do not locate control valves in dangerous areas, and do not forget to put drains in the low sections of piping in order that the entire line may be properly drained when parts of the piping or control valves must be taken down.

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11

Design and Inspection of Pressure Vessels

Elliott MacDermod

11.1. DEVELOPMENT OF THE BOILER AND PRESSURE VESSEL CODES[1, 2]

The need for a boiler and pressure-vessel code was demonstrated during the latter part of the nineteenth century and the first decade of the twentieth century when some 10,000 boiler explosions killed an equal number of people and seriously injured 15,000 others.

Massachusetts issued the first rules for the construction and installation of boilers in 1907 following disastrous explosions in 1905 and 1906. Other states and cities followed the example of Massachusetts and enacted laws or ordinances for the construction, installation, and inspection of steam boilers with resulting chaos. The lack of uniformity in requirements of the different states did not allow a manufacturer to build stock boilers that would be acceptable in other states, second-hand boilers could not be shipped across state lines, and a qualified boiler inspector in one state was not recognized in others.

The American Society of Mechanical Engineers was requested to formulate standard specifications for the construction of steam boilers and pressure vessels, and in 1911 a committee, later known as the Boiler Code Committee, was formed.

The first ASME Boiler Code was issued in 1914. Since that time

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and through 1962 the Boiler Code has been revised 16 times. The first edition of the Unfired Pressure Vessel Code was issued in 1925 and has also been revised 16 times through 1962.

The petroleum refining industry has long been a user of large high-pressure, high-temperature pressure vessels, and was particularly interested in welded construction for containing flammable liquids and gases. In 1934 a joint ASME-API (American Petroleum Institute) committee issued the first edition of the API-ASME Code for Unfired Pressure Vessels for Petroleum Liquids and Gases. This code was regarded as less conservative than the ASME code as it used a factor of safety of 4 rather than that of 5. There were 5 editions of the code by 1951. The API-ASME Code was discontinued in 1956 in favor of the ASME Unfired Pressure Vessel Code which was being adopted as a legal requirement by an increasing number of states, cities, and provinces.

The code gives no definition of a pressure vessel. A pressure vessel is usually considered to be a closed container of a fluid under pressure used to perform some process function such as a storage tank, heat exchanger, evaporator, or reactor. Code jurisdiction over piping external to the vessel terminates at the first circumferential seam or joint for welding end connections; the face of the first flange for bolted connections; and at the first threaded joint in that type of connection.

Paragraph U-1 of the Unfired Pressure Vessel Code lists the exceptions from code jurisdiction, however the "Synopsis of the Boiler and Pressure Vessel Rules and Regulations" and the local authority having jurisdiction should be consulted for further details as to requirements and exemptions which may vary widely from place to place.

A non-code pressure vessel may be defined as a vessel not meeting the minimum construction requirements of the code for design, fabrication, inspection, and certification. It could not be stamped with the code symbol and could not be installed in a jurisdiction that had adopted the ASME Code unless some special ruling was in effect.

11.2. THE ASME BOILER AND PRESSURE VESSEL CODE AND THE NATIONAL BOARD OF BOILER AND PRESSURE VESSEL INSPECTORS

Those in the chemical industry associated with the procurement and operation of pressure vessels should have a thorough understanding

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of the functions and relationship of the ASME Boiler Code Committee and the National Board of Boiler and Pressure Vessel Inspectors. For that reason, excerpts from the ASME Code Foreword and the NBBPVI Code of Practice are reproduced here, as being the least known or most frequently overlooked or misunderstood functions of the two organizations.

Excerpts from the ASME Code Foreword[3]

The Boiler and Pressure Vessel Committee's function is to establish rules of safety governing the design, the fabrication, and the inspection during construction of boilers and unfired pressure vessels, and to interpret these rules when questions arise regarding their intent. In formulating the rules, the committee considers the needs of users, manufacturers, and inspectors of pressure vessels. The objective of the rules is to afford reasonably certain protection of life and property and to provide a margin for deterioration in service so as to give a reasonably long, safe period of usefulness. Advancements in design and material and the evidence of experience have been recognized.

The Boiler and Pressure Vessel Committee meets regularly to consider requests for interpretations and revisions of the rules. Inquiries must be in writing and must give full particulars in order to receive consideration.

Interpretations of general interest are published in *Mechanical Engineering* as "Code Cases," and inquirers are advised of the action taken. Code revisions approved by the committee are published in *Mechanical Engineering* as proposed addenda to the code to invite comments from all interested persons. After final approval by the committee and adoption by the ASME Council, they are printed in the addenda supplements to the code.

Code cases (interpretations) may be used in the construction of vessels to be stamped with the ASME Code symbol beginning with the date of their approval by the ASME Council.

Manufacturers and users of pressure vessels are cautioned against making use of revisions and cases that are less restrictive than former requirements without having assurance that they have been accepted by the proper authorities in the jurisdiction where the vessel is to be installed.

After code revisions are approved by council they may be used beginning with the date of issuance shown on the pink-sheet addenda. Revisions become mandatory as minimum requirements 6 months

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after such date of issuance, except for boilers or pressure vessels contracted for prior to the end of the 6-month period.

The National Board of Boiler and Pressure Vessel Inspectors is composed of chief inspectors of states and municipalities in the United States and of provinces in the Dominion of Canada that have adopted the Boiler and Pressure Vessel Code. This board, since its organization in 1919, has functioned to uniformly administer and enforce the rules of the Boiler and Pressure Vessel Code. The cooperation of that organization with the Boiler and Pressure Vessel Committee has been extremely helpful. Its function is clearly recognized and, as a result, inquiries received which bear on the administration or application of the rules are referred directly to the National Board. Such handling of this type of inquiry not only simplifies the work of the Boiler and Pressure Vessel Committee, but action on the problem for the inquirer is thereby expedited. Where an inquiry is not clearly an interpretation of the rules, or a problem of application or administration, it may be considered both by the Boiler and Pressure Vessel Committee and the National Board.

It should be pointed out that the state or municipality where the Boiler and Pressure Vessel Code has been made effective has definite jurisdiction over any particular installation. Inquiries dealing with problems of local character should be directed to the proper authority of such state or municipality. Such authority may, if there is any question or doubt as to the proper interpretation, refer the question to the Boiler and Pressure Vessel Committee.

The specifications for materials given in Section II of the code are identical with or similar to those of the American Society for Testing Materials as indicated, except in those cases where that organization has no corresponding specification.

Excerpts from NBBPVI Code of Practice[4]

Protection of life and property is the first duty of any government. Many governmental subdivisions in the United States and Canada, recognizing this duty, have adopted mandatory laws requiring that the design, fabrication, and inspection of boilers and unfired pressure vessels comply with the rules of The American Society of Mechanical Engineers' (ASME) Boiler and Pressure Vessel Code as administered by The National Board of Boiler and Pressure Vessel Inspectors (National Board).

The development of rules and codes and the construction of safe

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boilers and unfired pressure vessels, confirmed by competent inspection, is a 3-pronged endeavor:

1. Voluntary co-operation of the ASME Boiler and Pressure Vessel Committee which writes the rules;
2. Boiler and pressure-vessel manufacturers who comply with the rules; and
3. The National Board which issues commissions to inspectors who diligently enforce the rules.

Boilers and unfired pressure vessels which meet these requirements in every respect proudly bear the symbols of approval in the form of the ASME and National Board stamps.

For a manufacturer to become a fabricator of code vessels he must first apply for the official symbol of the ASME and authorization for its use for a specified period. Form letters for this purpose are included in the Codes as is an illustration of the Certificate of Authorization. After obtaining the authorization, the manufacturer must make arrangements for shop inspections, either with an insurance company or with the local authority.

The ASME Boiler and Pressure Vessel Committee—a voluntary group of engineers organized in 1911—is composed of designers, manufacturers, users, and insurance and inspection authorities, all of whom are interested in developing and maintaining a safety code for boilers and unfired pressure vessels.

The National Board of Boiler and Pressure Vessel Inspectors is a voluntary organization of officials who are charged with the enforcement of boiler and pressure-vessel inspection regulations of any political subdivision of the United States and Canada that has adopted one or more sections of the ASME Boiler and Pressure Vessel Code. The National Board was organized in 1919 for the purpose of promoting greater safety to life and property by securing concerted action among the states, cities, and provinces; and uniform inspection practices and consistency in the construction, installation, and inspection of safe boilers and pressure vessels. National Board inspectors' commissions have been issued to over 2000 men who have met and maintained the board's high standards of qualification.

In order to retain the confidence necessary to maintain the integrity of the codes and the inspection authorities, complete co-operation must be exercised by all concerned. Any deviation from the codes would tend to discredit them as a safety measure.

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TABLE 11.1. Status of ASME Sections I and VIII in the United States

State	*Section I*	*Section VIII*	*State*	*Section I*	*Section VIII*
Alabama			Nebraska	L	L
Alaska	L	L	Nevada	L	L
Arizona			New Hampshire	L	NJ
Arkansas	L	L	New Jersey	L	L
California	L	A	New Mexico		
Colorado			New York	L	NJ
Connecticut	L	NJ	North Carolina	L	L
Delaware			North Dakota	L	NJ
District of Columbia	L	L	Ohio (SI)	O	O
Florida			Oklahoma	L	NJ
Georgia			Oregon	L	L
Hawaii	L	A	Panama Canal Zone	LX	LX
Idaho			Pennsylvania (SI)	L	L
Illinois	L	NJ	Puerto Rico	L	L
Indiana	L	L	Rhode Island	L	A
Iowa	L	A	South Carolina		
Kansas	L	NJ	South Dakota		
Kentucky			Tennessee	L	A
Louisiana	L	NJ	Texas	L	A
Maine	L	A	Utah	L	L
Maryland	L	NJ	Vermont	L	L
Massachusetts	L	L*	Virginia	L	L
Michigan	L	A	Washington	L	L
Minnesota	L	L	West Virginia	L	A
Mississippi	NJ	L**	Wisconsin	A	NJ
Missouri			Wyoming		
Montana					

L — Legal requirement
A — Acceptable
NJ — No jurisdiction
* — Compressed air tanks only

X — Under Coast Guard jurisdiction if on floating equipment
** — LPG containers and equipment
O — Ohio Rules
SI — Shop Inspectors must have state commission in addition to National Board

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11.3. SECTIONS OF THE ASME BOILER AND PRESSURE VESSEL CODE

Section I	Power Boilers
Section II	Material Specifications
Section III	Boilers of Locomotives (discontinued) Now Nuclear Vessels
Section IV	Low Pressure Heating Boilers
Section V	Miniature Boilers (discontinued)
Section VI	Rules of Inspection (discontinued)
Section VII	Suggested Rules for Care of Power Boilers
Section VIII	Unfired Pressure Vessels
Section IX	Welding Qualifications

11.4. STATUS OF THE ASME CODE IN THE UNITED STATES AND CANADA[5]

While much effort has been expended to obtain uniformity in Boiler and Pressure Vessel Laws and Regulations, there still exist wide differences in practice. A chemical industry contemplating construction of a plant in another state may obtain information concerning that state's rules and regulations in the *Synopsis of Boiler and Pressure Vessel Laws, Rules, and Regulations,* published by the National Bu-

TABLE 11.2. Status of ASME Code Sections I and VIII in Canada

	Section	
	I	*VIII*
Alberta	L	L
British Columbia	L	L
Labrador		
Manitoba	L	L
New Brunswick	A	L
Newfoundland	L	L
Northwest Territories	L	L
Nova Scotia	L	L
Ontario	L	L
Prince Edward Island		
Quebec	L	L
Saskatchewan	L	L
Yukon Territories	L	L

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TABLE 11.3. Status of ASME Code Sections I and VIII in Cities and Counties of the United States

	Section I	*Section VIII*		*Section I*	*Section VIII*
Albuquerque, N. Mex.	L		Niagara Falls, N. Y.	L	NJ
Barton, Fla.	I and I	I and I	Niles, Mich.	L	NJ
Buffalo, N. Y.	L	L	North Miami Beach, Fla.	L	NJ
Chicago, Ill.	L	L	Oklahoma City, Okla.	L	NJ
Dade County, Fla.	L	L	Omaha, Neb.	L	L
Dearborn, Mich.	L	L	Oswego, N. Y.	L	NJ
Denver, Col.	L	NJ	Peoria, Ill.		
Des Moines, Iowa	L		Phoenix, Ariz.	L	L
Detroit, Mich.	L	L	Pueblo, Col.		
East St. Louis, Ill.	L	L	Richmond, Va.	L	L
Evanston, Ill.			St. Joseph, Mo.	L	L
Greensboro, N. C.	L	L	St. Louis, Mo.	L	L
Jefferson Parrish, La.	L	L	St. Louis County, Mo.	L	L
Kansas City, Mo.	L	L	San Francisco, Cal.	L	L
Los Angeles, Cal.	L	L	Seattle, Wash.	L	L
Memphis, Tenn.	L	L	Spokane, Wash.	L	L
Miami, Fla.	L	L	Tacoma, Wash.	L	L*
Miami Beach, Fla.	I and I	I and I	Tampa, Fla.	L	L
Milwaukee, Wis.	L	L	Tulsa, Okla.	L	L
Mt. Vernon, N. Y.	L	L	University City, Fla.	L	NJ
New Orleans, La.	L	L	Yonkers, N. Y.	L	NJ
New York, N. Y.	L	NJ			

I and I — Covers field Inspection and insurance
L — Legal requirement

* — Air tanks
NJ — No jurisdiction

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reau of Casualty Underwriters. Tables 11.1, 11.2, and 11.3 are based on the synopsis which gives additional information concerning:

Department having jurisdiction and address
Date of law
Rules of construction and stamping
Objects subject to rules
Objects subject to field inspection
Inspection required
Insurance company requirements
Certificate of inspection
State inspection fees

11.5. BOILER AND PRESSURE VESSEL REQUIREMENTS IN FOREIGN COUNTRIES[6]

Many chemical industries have or may contemplate foreign manufacturing facilities. Table 11.4 lists the legal standing and administration of pressure-vessel codes in various countries.

11.6. THE PRESSURE-VESSEL DESIGNER

The ASME Unfired Pressure Vessel Code is not a design manual and does not contain rules to cover all details of design and construction. The code covers only the minimum requirements for design, fabrication, and inspection of unfired pressure vessels. Whether these minimum requirements are suitable for a vessel's service conditions or whether more exacting criteria is indicated is the responsibility of the pressure-vessel designer. The importance of design and the views of some pressure vessel designers are contained in references 7 and 8.

The design of the many shapes, sizes, and types of pressure vessels used in chemical plants requires the skills of an experienced engineer specializing in this field. Vessel design requires a thorough knowledge of the code requirements, the properties of the fluid being contained, the properties of suitable materials of construction, and the problems involved in the fabrication of these materials. Design factors may be so varied that the engineer can only rely on his engineering judgment and his experience with similar problems to produce a safe economical design that will last the intended life of the equipment.

Due to space limitations, no attempt will be made here to discuss or interpret the requirements of the pressure-vessel code in detail.

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TABLE 11.4. Legal Standing and Administration of Pressure-Vessel Codes in Various Countries

Country	*Laws Relating to Construction of Boilers and Pressure Vessels*	*National Code*		*Legal Standing of Code*	*Code Writing Body*	*Administration*		*Acceptability of Imported Vessels*
		Title	*Scope*			*Organization Responsible for Code Administration*	*Submission of Drawings*	
Australia	The Factory and Machinery Acts of the various states (e.g. the Factories & Shops Act 1912-1957 of New South Wales) under which boiler and pressure-vessel regulations are issued	Standards Association of Australia Boiler Code Pts. I to V	Boilers and unfired pressure vessels	Code has the force of a state regulation in most states and is acceptable, with modifications, in the remainder	Standards Association of Australia	State inspecting authority	Drawings must be approved by state inspecting authority before starting construction	Vessels fabricated outside Australia may be accepted at the discretion of the State Chief Inspector
Austria	Art. 48 Verwaltungsentlastungsgesetz (VEG) Bundesgesetzblatt No. 277/1925 as amended by BGBl No. 55/1948	Dampfkesselverordnung (DKV) BGBl No. 83/1948 and Werkstoff und Bauvorschriften (WBV) BGBl No. 264/1949	Boilers and unfired pressure vessels	Codes have the force of a state regulation	Dundesministerium fur Handel und Wideraufbau	Government or government-licensed inspectors	Drawing approvals recommended but not mandatory	Vessels must meet the requirements of the Austrian Code

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Belgium	La Reglement General pour la Protection du Travail. La Reglementation des Appareils a vapeur	None. A code is currently being written by N.B.N. Most major national codes are acceptable in Belgium at the present time				Ministere du Travail, Inspection technique		Vessels built to major national codes are acceptable
Canada	The Boiler and Pressure Vessel Acts of the various Provinces	C.S.A. Standard B51-1957. This standard specifies the use of the ASME Code, with some amendments	Boilers and unfired pressure vessels	C.S.A. Standard B51-1957 (and hence the ASME Code) has been adopted by all Provinces. It has the force of a Provincial regulation	Canadian Standards Association and American Society of Mechanical Engineers	Provincial inspecting authority	Drawings must be approved by the Chief Inspector of the Province before starting construction	Vessels must be inspected by an inspector holding the Canadian National Board Commission
Finland	Finlands Forfattnings-samling No. 573-575, which constitutes the pressure-vessel code	Dimensioning, Materials and Welding of steel pressure-vessels	Boilers and pressure vessels	Code is a state regulation				

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TABLE 11.4 (Continued). Legal Standing and Administration of Pressure-Vessel Codes in Various Countries

Country	*Laws Relating to Construction of Boilers and Pressure Vessels*	*National Code*		*Legal Standing of Code*	*Code Writing Body*	*Administration*		*Acceptability of Imported Vessels*
		Title	*Scope*			*Organization Responsible for Code Administration*	*Submission of Drawings*	
France	The laws, decrees, and circulars collected and published as Reglementation des Appareils a Vapeur and Reglementation des Appareils a Pression de Gaz	S.N.C.T. No. 1 (published by Syndicat National de Chaudronnerie et Tolerie)	Unfired pressure vessels (There is no national code for boilers)	Only legal requirements are those collected in the two documents given in column 2. These do not constitute a code as normally understood. The S.N.C.T. Code has no direct legal recognition	S.N.C.T.	Service des Mines is responsible for verifying that boilers and pressure vessels are in accordance with legal requirements	Not normally required	Vessels must conform with French law and in particular Article 4 of the decree of April 2, 1926, which specifies the tests and certificates which are required
Germany	Various decrees of the Ministry of Labour	Dampfkessel-Bestimmungen (currently replacing Werkstoff und Bauvorschriften fur Dampfkessel)(W.U.B.)	Boilers	Dampfkessel-Bestimmungen, those parts of W.U.B. still applicable, and the AD-Merkblatter have the force of law	Technische Überwachungs Vereine (T.U.V.)	Technische Überwachungs Vereine (T.U.V.)	Drawings must be submitted to T.U.V. before construction is started	Vessels, including those manufactured outside Germany, must be inspected by T.U.V., A.S.M.E. Code generally accepted for operating temperature below 650°F.
		AD-Merkblätter	Unfired pressure vessels					

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Holland	Stoombesluit dated 22.12. 1953 (boilers) and Outwerp Drukhouder-besluit dated 15.3.1960 (unfired pressure vessels)	Grondslagen waarop de beoordeling van de constructie en het materiaal van stoomtoesteelen, damptoestellen en drukhoudersberust	Boilers and unfired pressure vessels	The Code "Grondslagen. . . ." has the force of a state regulation	Dienst voor het Stoomwezen	Dienst voor het Stoomwezen	Drawings must be submitted to Stoomwezen before starting construction	Imported vessels must meet requirements of Stoomwezen
India	Indian Boilers Act 1923	Indian Boiler Regulations, 1950	Boilers	Code is a regulation under the Indian Boilers Act, 1923	Central Boilers Board	Chief Inspector of Boilers, India	Submission of drawings may be required by approved inspecting authority before starting construction. Drawings of completed boiler must be submitted to Chief Inspector of Boilers, India and approved before boiler is registered and used	Design must be approved by Chief Inspector of Boilers. Inspection during manufacture is delegated to an approved inspecting authority, e.g. Lloyds, which must submit inspection certificate to Chief Inspector of Boilers, India, before vessel can be approved, registered, and used

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TABLE 11.4 (Continued). Legal Standing and Administration of Pressure-Vessel Codes in Various Countries

Country	*Laws Relating to Construction of Boilers and Pressure Vessels*	*National Code*		*Legal Standing of Code*	*Code Writing Body*	*Administration*		*Acceptability of Imported Vessels*
		Title	*Scope*			*Organization Responsible for Code Administration*	*Submission of Drawings*	
Israel	Factories Ordinance Sections 31, 32, and 33. This law is almost identical with the relevant sections of the British Factories Act	None. A.S.M.E., British, Austrian and German Codes are commonly used and all are accepted				No national inspection authority responsible for the acceptance of new construction. Periodic inspection of boilers, however, is carried out by inspectors authorized by the Chief Inspector of Labour	Not required	Vessels constructed to American, British, Austrian, and German Codes are acceptable
Italy	Various royal and governmental decrees dating from September 9, 1926 which, together with a number of A.N.C.C. circulars, form the A.N.C.C. Code	A.N.C.C.	Boilers and unfired pressure vessels	The A.N.C.C. Code constitutes the law relating to boilers and pressure vessels. The new proposed Code published as "Proposta di Nuova Regolamentazione	A.N.C.C.	A.N.C.C.	Not required	Imported vessels must meet the A.N.C.C. requirements

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				di Stabilita degli Apparecchi a Pressione" has not yet received legal sanction and is applicable only to certain classes of vessel not covered by the original code, e.g. refinery vessels				
New Zealand	Boilers, Lifts and Cranes Act, 1960	New Zealand Boiler Code. New Zealand Fusion Welded Pressure Vessels Code	Boilers and unfired pressure vessels	The code has the force of a governmental regulation	Marine Department, New Zealand	Marine Department, New Zealand	Drawings must be submitted and approved prior to use, preferably prior to construction	Design must be approved by Marine Department. Inspection during manufacture not required. Final inspection prior to certification and use by Engineer Surveyor of Marine Department. Certificate of Workmanship must be submitted by inspecting authority (e.g. Lloyd's) for vessels manufactured outside New Zealand

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TABLE 11.4 (Continued). Legal Standing and Administration of Pressure-Vessel Codes in Various Countries

Country	*Laws Relating to Construction of Boilers and Pressure Vessels*	*National Code*		*Legal Standing of Code*	*Code Writing Body*	*Administration*		*Acceptability of Imported Vessels*
		Title	*Scope*			*Organization Responsible for Code Administration*	*Submission of Drawings*	
Norway	Kongelig resolusjon av 29 September 1925, Kjelsforskrifter (Boiler Laws)	Norwegian Code under revision. Norway uses Swedish Tryck-karlsnormer, German and A.S.M.E. Codes	Boilers and unfired pressure vessels	When current the Norwegian Code has the force of law	Arbeidstilsynets Kjelkontroll, in cooperation with technical committee appointed by Ministry of Labour	Arbeidstilsynets Kjelkontroll.	Drawings must be submitted and approved before starting construction	Imported vessels must be acceptable to Kjelkontroll.
Pakistan	Pakistan Boilers Act, 1923	Pakistan Boiler Regulations, 1951, are currently under revision				Chief Inspectors of Boilers of East Pakistan, West Pakistan, and federal capital		Until revision of regulations is complete, boilers constructed to other codes will be acceptable subject to modification of construction and working pressure at the discretion of the Chief Inspector of Boilers

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South Africa	Mines and Works Act, No. 27 of 1956 and the Factories, Machinery and Building Works Act, 1941	None. South Africa uses B.S.1500, the A.S.M.E. Code and the German Codes				Department of Mines is broadly responsible for boiler and pressure-vessel construction. Detailed supervision carried out by inspection authorities such as Lloyd's		Governmental authorization or inspection of imported vessels is not normally required
Sweden	Arbetarskydds-lagen: Svensk Forfattnings-samling No. 1/1949 (Law for the Protection of Workers) and Arbetarskydds-kungorelsen: Svensk Forfat-tningssamling No. 476/1956 (Notice for the Protection of Workers)	Tryckkarls-normer Angpanne-former Pannsvets-normer	Boilers and unfired pressure vessels Boilers only Boiler Welding Code (applicable also to pressure vessels)	Code has no legal status but has been accepted by Workers Protection Board and is in practice mandatory	Pressure Vessel Commission of the Swedish Academy of Engineering Sciences	National Board of Workers Protection (W.P.B.)	Drawings of welded vessels must be approved by welding supervisor authorized by W.P.B.	Vessels must meet the requirements of the Swedish Code

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TABLE 11.4 (Continued). Legal Standing and Administration of Pressure-Vessel Codes in Various Countries

Country	Laws Relating to Construction of Boilers and Pressure Vessels	National Code		Legal Standing of Code	Code Writing Body	Administration		Acceptability of Imported Vessels
		Title	Scope			Organization Responsible for Code Administration	Submission of Drawings	
Switzerland	Federal Regulations dated April 9, 1925 and March 19, 1938	Regulations of Swiss Association of Boiler Proprietors	Boilers and unfired pressure vessels	Code has the force of a federal regulation	Swiss Association of Boiler Proprietors	Swiss Association of Boiler Proprietors	Drawings must be submitted before construction is started	Vessels manufactured outside Switzerland must conform to Swiss regulations
Turkey		Draft Code based on German rules has been prepared but is not yet in force	Unfired pressure vessels		Turkish Institution of Mechanical Engineers			

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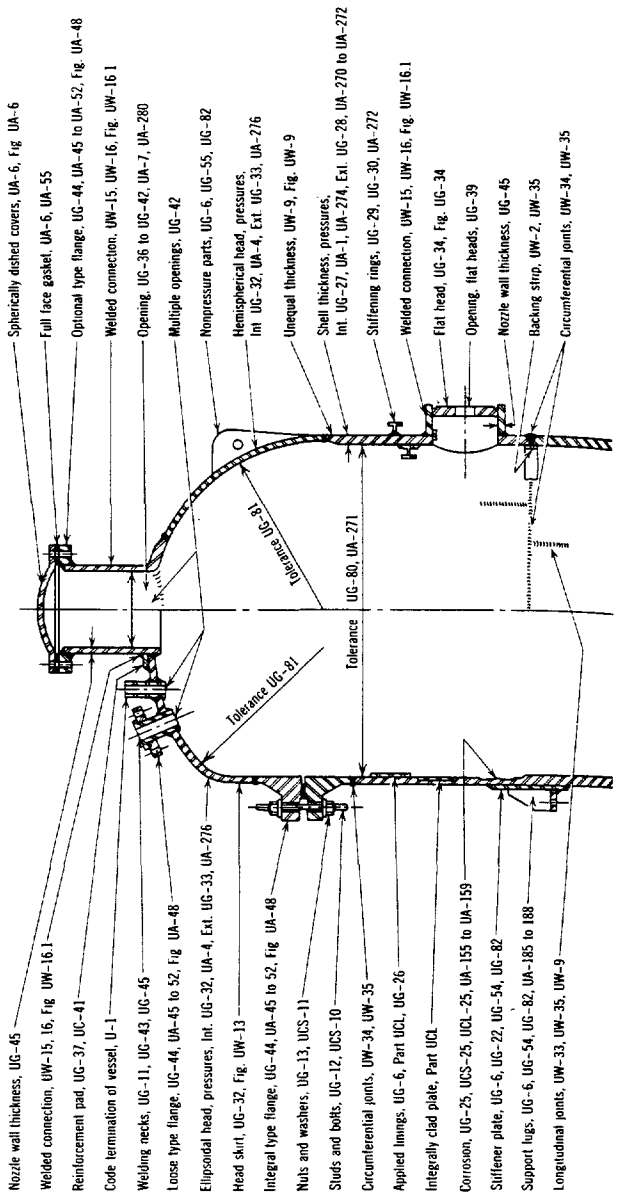
United Kingdom of Great Britain	Sections 29, 30, and 31 of Factories Act, 1937	Lloyd's Rules	Boilers and unfired pressure vessels	None. Safety is the responsibility of the user who must ensure	Lloyd's Register of Shipping	Lloyd's Register of Shipping	Drawings must be submitted and approved before construction is started	Regulations as to the acceptability of imported vessels are lacking
		Rules of the Associated Offices Technical Committee (A.O.T.C. Rules)	Boilers and unfired pressure vessels	that steam boilers are of "good construction, sound material, adequate strength, and free from	A.O.T.C.	A.O.T.C.		
		B.S.1113 B.S.1500	Boilers Welded pressure vessels	patent defect" (Section 29 of the Factories Act)	British Standards Institution	None	Drawings approved by purchaser	
United States of America	Various states and municipal regulations	A.S.M.E. Code	Boilers and unfired pressure vessels	In those states and municipalities where it has been adopted, the code has the force of law	American Society of Mechanical Engineers	Inspection authorities of states and municipalities adopting code	Not required by state or municipality. Authorized Code Inspector examines drawings	Imported vessels subject to approval by individual local authorities and are normally acceptable if they meet A.S.M.E. Code

ETC 03202


Spherically dished covers, UA-6, Fig UA-6
Full face gasket, UA-6, UA-55
Optional type flange, UG-44, UA-45 to UA-52, Fig. UA-48
Welded connection, UW-15, UW-16, Fig. UW-16.1
Opening, UG-36 to UG-42, UA-7, UA-280
Multiple openings, UG-42
Nonpressure parts, UG-6, UG-55, UG-82
Hemispherical head, pressures, Int UG-32, UA-4, Ext UG-33, UA-276
Unequal thickness, UW-9, Fig. UW-9
Shell thickness, pressures, Int. UG-27, UA-1, UA-274, Ext. UG-28, UA-270 to UA-272
Stiffening rings, UG-29, UG-30, UA-272
Welded connection, UW-15, UW-16, Fig. UW-16.1
Flat head, UG-34, Fig. UG-34
Opening, flat heads, UG-39
Nozzle wall thickness, UG-45
Backing strip, UW-2, UW-35
Circumferential joints, UW-34, UW-35
Tolerance UG-80
UG-80, UA-271
Tolerance
Tolerance UG-81
Nozzle wall thickness, UG-45
Welded connection, UW-15, 16, Fig UW-16.1
Reinforcement pad, UG-37, UG-41
Code termination of vessel, U-1
Welding necks, UG-11, UG-43, UG-45
Loose type flange, UG-44, UA-45 to 52, Fig UA-48
Ellipsoidal head, pressures, Int. UG-32, UA-4, Ext. UG-33, UA-276
Head skirt, UG-32, Fig. UW-13
Integral type flange, UG-44, UA-45 to 52, Fig UA-48
Nuts and washers, UG-13, UCS-11
Studs and bolts, UG-12, UCS-10
Circumferential joints, UW-34, UW-35
Applied linings, UG-6, Part UCL, UG-26
Integrally clad plate, Part UCL
Corrosion, UG-25, UCS-25, UCL-25, UA-155 to UA-159
Stiffener plate, UG-6, UG-22, UG-54, UG-82
Support lugs, UG-6, UG-54, UG-82, UA-185 to 188
Longitudinal joints, UW-33, UW-35, UW-9

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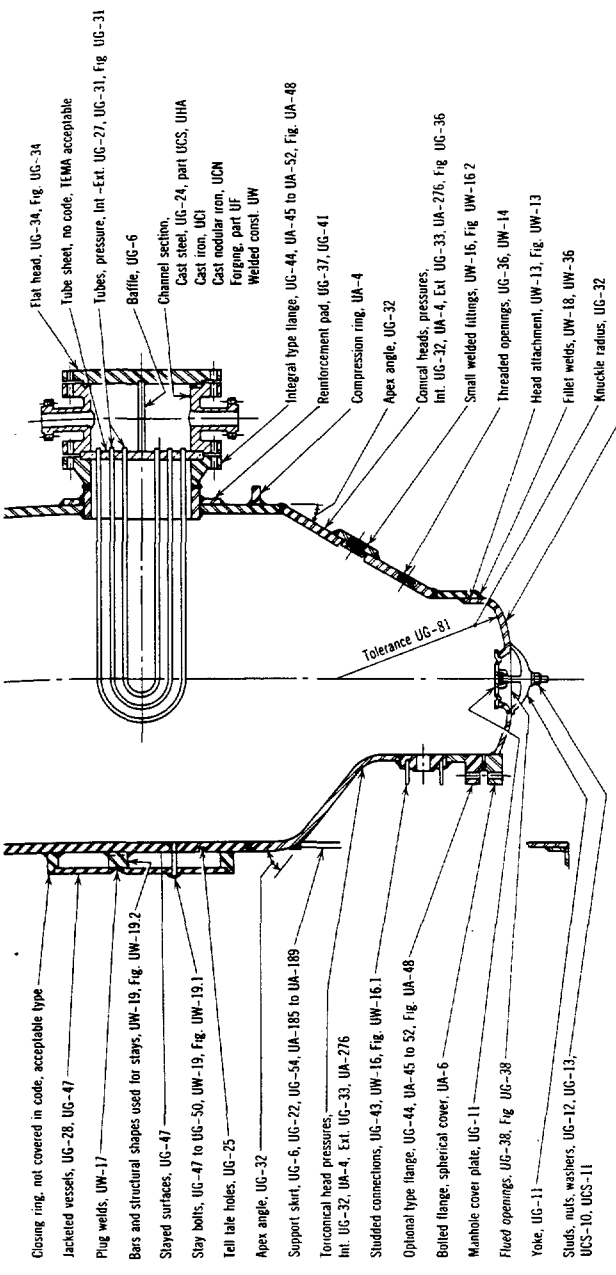

FIG. 11.1. Reference guide to ASME unfired pressure vessel code.

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Figure 11.1 illustrates the various features of pressure-vessel construction referenced to the applicable code paragraphs. The table of references is arranged by subject for those whose interest may require more detailed information.

11.7. BASIS FOR DESIGN

Pressure and Temperature

The design pressure is customarily set at 15 psi or 10%, whichever is the greater, over the operating pressure for vessels without cyclic swings. For the latter the design pressure is usually 5 to 10% above the highest pressure anticipated. The design temperature is usually 50°F above the maximum temperature that will not result in a decrease of the code-allowable stress which would cause an increase in thickness.

For example, a carbon steel vessel operating at 350°F should have a design temperature of 650°F, not 400°F, as the allowable stress is the same for either temperature. If the vessel is code stamped at the lower temperature, and at some future date it is desirable to raise the operating temperature, complications arise in having the code stamp changed to the desired increased temperature. For the same reason the vessel should be stamped with the maximum allowable working pressure based on the nominal thicknesses of the parts rather than the design pressure used to calculate the minimum thicknesses.

Minimum Plate Thickness

The plate thickness of large-diameter low-pressure vessels is often based on arbitrary plate thicknesses rather than on calculated thickness based on design pressure. This results in a calculated maximum allowable working pressure that may be much greater than the design pressure. The reason for using the heavier plate is that large-diameter thin-plate shells are difficult to handle in the shop without spiders or rings to hold the shell sections cylindrical. The purchaser benefits by paying for and obtaining a heavy tank rather than paying for jigs, fixtures, or structural rings. The thicker plate also allows for better fit up.

The API-ASME Code specifies that the plate thickness should not be less than (D-100)/1000, where D is the nominal diameter in inches. The minimum plate thickness specified for welded construction by

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many organizations is $\frac{3}{16}$ or $\frac{1}{4}$ in. The code minimum for riveted construction is $\frac{3}{16}$ and $\frac{3}{32}$ in. for brazing or welding of carbon steel.

External Pressure or Vacuum

Many process vessels operate under external pressure or vacuum or may be accidentally subjected to these conditions. The code specifies that a code vessel occasionally subject to an external pressure of 15 psi or less need not meet the code requirements for construction for external pressure. Consideration should be given to many consequences before taking advantage of this waiver, such as personnel hazard in event the tank collapsed, cost of replacing vessel, property damage, and hazards, due to release of contents, and value of lost contents. If at all possible, the use of a vacuum breaker or a seal leg is much cheaper than designing for vacuum.

Designing for external pressure is a trial and error affair that has resulted in many unnecessarily expensive vessels. Many times the plate thickness required for internal pressure has been used and stiffener rings added as necessary, when it would have been more economical to increase the shell thickness and eliminate some or all of the stiffeners. Unless the designer has reliable fabrication costs it would be worthwhile to submit several alternates to a fabrication shop for pricing.

Selection of Material

The selection of construction materials is in most instances a matter of experience. The material that has proved satisfactory in the past under similar conditions is likely to be used again, unless there is a very good reason for changing. When experience is lacking, a number of factors must be considered.

Stress Limitations. The material's allowable stress should not require excessive thicknesses for the design pressure and temperature:

Temperature Limitations. Some materials such as copper and aluminum, and their alloys, and cast iron have specific limitations on temperature (400–450F).

Materials Resistance to Corrosion by Process Fluid. The resistance to corrosion that may be expected of a construction material used in a process vessel may be approximated by field tests conducted under identical conditions as those of the vessel's operation. The actual operating corrosion rate and the simulated operating corrosion rate

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obtained by laboratory test are often at great variance because of the many unforeseen operational factors. An excellent reference for corrosion rates is *Corrosion Data Survey.*[9] It furnishes information at least as reliable as that obtained by laboratory testing. For new processes and with no previous experience under similar conditions, the services of an experienced corrosion consultant would be desirable.

Permissible Contamination of Process Fluid by Corrosion Products. While high purity requirements may limit the selection of material it does not necessarily mean that the most expensive material is the best. Where pressure and temperature conditions permit, cladding, glass, rubber, lead, gunnite, or plastic linings may be used rather than expensive alloys.

Relative Fabricated Cost of Vessel for Various Materials Considered. It is often desirable and profitable to request alternate proposals from fabricators such as stainless steel versus aluminum and clad material versus solid alloy. Clad material does not always effect the savings anticipated on thicknesses ½ in. and less. Although the cost of the clad material may be less than that of the solid alloy the cost of fabrication may be approximately the same for either, with the overall cost remaining about the same.

Design of Equipment for Periodic Replacement Rather than for Plant Life. For other than large, complicated vessels difficult to remove, it may be economically feasible to design equipment using less expensive metals and replace the vessel after a few years than design the vessel for a 10- or 15-year plant life using an expensive or super alloy. A cost comparison of a vessel fabricated of carbon steel will range to about 1½ for a low-alloy steel, to around 4 for stainless, and to 10 or more for the more expensive alloys presently in use.

In the past a corrosion allowance was customarily employed in the design of carbon steel vessels. This was usually an arbitrary value added to the calculated minimum thickness, and it was applied indiscriminately to all vessels in a unit process regardless of the vessel's importance. Present day techniques in determining corrosion rates by inserting corrosion racks in vessels and pipe lines should result in more realistic corrosion allowances for similar process conditions.[10] As the corrosion rates can be predicted more accurately, so may the vessel's operating life expectancy.

In specifying material for code-construction vessels either the ASME SA number[3] should be used or the complete ASTM A number[11] including the year and any suffix such as ASTM-A987-49T. The

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ASTM may reissue the specification with a new year and without the tentative (T) with the result that the shop inspector may reject the material as not conforming to ASME requirements.

ASME and ASTM Specifications include grades for plate, pipe, tubing, forgings, and castings with similar chemical and physical properties to allow for compatibility or matching of materials.

Loadings other than Pressure

The vessel and its supports must be designed to accommodate loadings resulting from:

weight of vessel and contents
weight of internals–trays, baffles, coils, etc.
weight of externals–equipment, agitators, exchangers, drums, etc.
weight of externals–structures, ladders, platforms, piping
weight of externals–dead and live loads
weight of insulation and fireproofing
wind and earthquake loads

In addition to the foregoing, investigations may be necessary as to the effect of reactions due to supporting lugs, ring stiffeners, piping, and thermal gradients that may cause excessive localized stresses.

Estimating weights can be tedious and time consuming unless the vessel designer has manufacturers catalogue and reference material, records or tabulated data from previous jobs, and assorted handbooks.

The weights of structural shapes may be obtained from *Steel Construction.* Lukens Steel Company catalogues *Spun Heads* or *Clad Steel Heads* furnish volumes and weights of different types of heads.

The weights of flanges, fittings, piping, or valves, can be obtained from any of the suppliers catalogues such as Ladish, Tube Turns, Midwest, Crane, or Taylor. The weights of trays, agitators, exchangers, drums, or other equipment should be obtained from the manufacturer unless the designer has sufficient experience to make an educated guess as to probable weights.

For estimating the weight of caged ladders and platforms, 25 lb lineal ft and 50 lb sq ft are fair averages for the weight of steel. Platforms should be designed for a live load of 100 lb/sq ft if a walkway only, 150 lb/sq ft if a working platform, or 150% of the weight of any equipment the platform may support during turnarounds.

The minimum wind load should not be less than that specified by the AISC or 20 lb/sq ft on the vertical projection of the finished structure.

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Lacking any local legal requirements the recommended wind pressure may be obtained from the American Standard Building Code ASA A58.1, or if the maximum sustained gust velocity is known it may be determined by an empirical formula developed by the United States Weather Bureau.[16]

The design of the vessel should be such as to be self-supporting under the combined conditions of wind with vessel full, operating, or during erection. The combination of erection weight and wind is usually the governing condition.

In addition to designing the vessel so that the stresses are within those permitted by the code, it is desirable that the deflection of the tower be checked as excessive deflection may upset operation of the top trays, and it is also disconcerting for workmen.

Many areas require that consideration be given to earthquake hazard in design. The seismic probability in various localities of the United States has been outlined by the United States Coast and Geodetic Survey (see Fig. 11.2) according to the amount of damage caused by earthquakes in that locality. The areas are designated Zone 0–no damage, to Zone 3–major damage. The seismic coefficients used in design range from 0.02 to 0.20 depending upon the zone and the vibration period of the structure.

Data and detailed design procedure for vertical vessels subject to applied forces, vibration, earthquake, and their supports and foundations may be found in references 12 through 19.

To prevent localized stresses due to lugs, brackets, and supports for platforms, equipment, and piping, circumferential rings are often used to distribute the load. These rings may cause excessive secondary stresses in the shell immediately adjacent to the ring unless the rings are properly proportioned. The design of these rings and resulting shell stresses are discussed in references 20 and 21.

Until recently the effect of piping reactions, moments at vessel nozzles, and the magnitude of the resulting secondary stresses at the shell openings had no satisfactory solution in general usage. The designer usually applied a heavy reinforcing pad around the nozzle with a number of gussets to distribute the loading around as large an area of the shell or head as he deemed practical. Satisfactory methods have been developed within the past few years for computing the stresses in cylindrical and spherical shells resulting from pipe loads.[22, 23, 24, 25] Reference 26 presents the data and formulas of 22 through 25 in readily useable form. This reference[26] also gives basic formula for thermal stress calculations at nozzles not readily available in standard texts.

ETC 03209

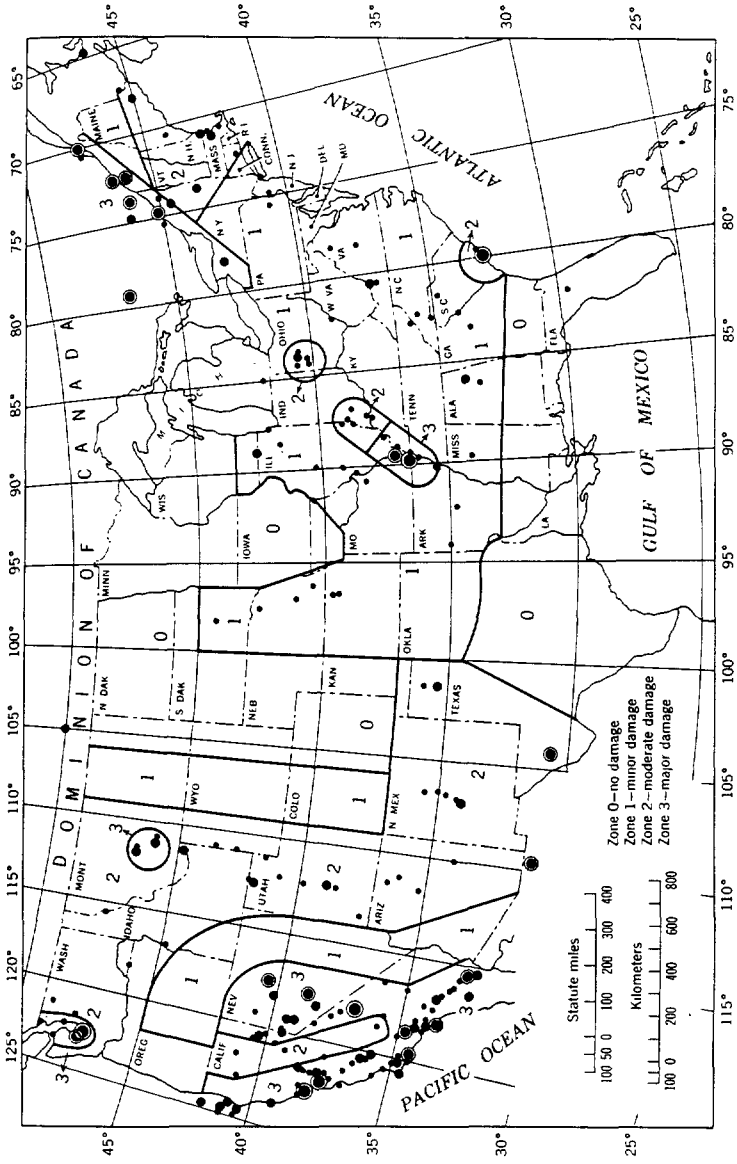

FIG. 11.2. Seismic map (U.S. Coast and Geodetic Survey).

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Vessels are insulated for any or all of three reasons, which are to conserve heat, to prevent temperature variation affecting the process, and personnel protection, 150°F max. The diameter over the insulation should be used in determining the area on which the wind acts, and the weight of the insulation should be used in weight calculations.

The supports, skirts, saddles, legs, and lugs, of vessels containing flammable fluids are customarily fireproofed with 2 to 4 in. of gunnite or 1 to 2 courses of brick. Vessels over about 4 ft in diameter will be fireproofed both inside and outside of the skirt. As the skirt and baseplate usually support the fireproofing and give the vessel greater stability under wind conditions, the weights are included in the calculations.

The effects of wind pressure and earthquake are seldom figured in design as acting simultaneously. Each is figured separately, and the worse condition governs the design.

Computation sheets such as those illustrated may be of use but too much dependence should not be placed on them, especially where widely different conditions exist in the design of vessels for a plant. The computation sheets illustrated were prepared for us in the design of vessels in one plant where pressures and temperatures were relatively low and not cyclic. Earthquake was not a factor and the minimum thickness specified by the client was ¼ in. Unless the form sheets are used judiciously the tendency is to plug in values in the formulas and grind out the answers without due consideration of all the factors that may be involved.

Supports

The design of supports for other than small tanks, either horizontal or vertical, may be quite complex due to secondary stresses, moments, and shears caused by support attachments.

Vertical vessels may be supported by legs, lugs, or brackets, either with or without a ring girder, or a skirt may be used. Large, heavy vessels supported by legs or lugs should have the support reactions at the shell carefully investigated. Methods for analyzing the reactions are given in reference 27. Skirt attachment has been accomplished in a number of ways, but the consensus seems to be to have the skirt and shell outside diameter the same, with the skirt butted to head knuckle and welded. This arrangement should not be used for other than ellipsoidal or spherical heads; for flanged and dished heads, the skirt should be fitted to the outside diameter of the bottom head flange and

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NAME OF COMPANY_____ J. O. No_____
Sheet No_____ of_____
VESSEL OR TANK_____ EQUIP. No._____ REQ'D_____ Date_____
Comp. By_____ C'k'd By_____

SKETCH OUTLINE OF EQUIPMENT SHOWING PRINCIPAL DIMENSIONS, NOZZLES & SIZES, ETC.

Shell

Mat'l_____
_____ C.A._____
Contents_____
_____ Sp. Gr_____
Operating
Pressure_____ psig @_____ °F
Vacuum or
Ext. Press_____ psig @_____ °F

Jacket

Mat'l_____
_____ C.A._____
Contents_____
_____ Sp. Gr_____
Operating
Pressure_____ psig @_____ °F
Vacuum_____ @_____ °F

Heater coils or lances

Mat'l_____
_____ C.A._____
Contents_____
_____ Sp. Gr_____
Type_____
_____
Dia_____ Spacing_____ Sq. ft_____
Operating
Pressure_____ psig @_____ °F

Trays

Material_____
_____ C.A._____
Type_____
_____
No.
Caps_____ Size_____ Spacing_____

Special conditions

_____
_____
_____
_____
_____
_____
_____
_____

FIG. 11.3. Process specifications—vessels and tanks.

ETC 03212

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No._____
Sheet No._____ of_____
SUBJECT_____ EQUIP. No._____ Date_____
Comp. By_____ C'k'd By_____

Diameter_____(OD)(ID) T.L.-T.L._____(Hor.)(Vert.) Support_____

Operating Press._____psig @_____°F Static Press. = .433 × _____ = _____psig

Design Press. (use larger value of)
- operating press. + 15 = _____ + 15 = _____psig
- operating press. × 1.15 = _____ × 1.15 = _____psig
- operating press. + static press. = _____ + _____ = _____psig

Min. Des. Temp. (larger value) = 1.10 × operating temp. = ___°F or operating temp. + 50 = ___°F

Base Mat'l ASME SA_____Gr._____Qual._____Inter. Case_____

Clad Mat'l ASME SA_____Gr._____Type_____Th'k _____

XR____SR___Shell E =____Hd. E =____ C.A. = c = ___min. t = .094" or_____"

Atm. Temp. Shell and Head S_a = _____psi S_aE = _____psi

Des. Temp. Shell and Head S_d = _____psi S_dE = _____psi

t = calc. thickness without corr. allow. $t + c$ = calc. thickness including corr. allow.

$t_n - c$ = nom. thickness without corr. allow. t_n = nom. thickness including corr. allow.

	I.D. (D) Shell	O.D. (D_o) Shell	2:1 Ellipt. Head	Code F&D Head
$t + c$	$\dfrac{P(D+2c)}{2S_dE - 1.2P} + c$	$\dfrac{PD_o}{2S_dE + .8P} + c$	$\dfrac{P(D+2c)}{2S_dE - .2P} + c$	$\dfrac{.885P(L+c)}{S_dE - .1P} + c$
MAWP	$\dfrac{2S_dE(t_n - c)}{(D-2c) + 1.2(t_n - c)}$	$\dfrac{2S_dE(tn - c)}{D_o - .8(t_n - c)}$	$\dfrac{2S_dE(t_n - c)}{(D+2c) + .2(t_n - c)}$	$\dfrac{S_dE(t_n - c)}{.885(L+c) + .1(t_n - c)}$
MAP	$\dfrac{2S_aEt_n}{D + 1.2t_n}$	$\dfrac{2S_aEt_n}{D_o - .8t_n}$	$\dfrac{2S_aEt_n}{D + .2t_n}$	$\dfrac{S_aEt_n}{.885L + .1t_n}$

S.R. req'd it at any welded seam $t_n > \dfrac{D+50}{120} = \dfrac{\quad}{120} =$

Press. – Temp. Rating of_____ASA Flanges = _____psig @_____°F

Max. Test Pressure on Flanges = _____psig

FIG. 11.4. Pressure vessels—shells and heads.

ETC 03213

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No._____
Sheet No._____of_____
SUBJECT_____ EQUIP. No._____ Date_____
Comp. By_____C'k'd By_____

Shell

Diameter_____(OD)(ID) T.L.-T.L._____Corr. Allow. = c = _____"
Mat'l ASME SA_____Gr._____Type or Qual._____Y.S. = _____
If jacketed, jacket design press. = _____psi @_____°F
Ext. press. due to full or partial vacuum = _____psi @_____°F
Design External Pressure (sum of above) = P = _____psi @_____°F
Min. Des. Temp. – greater of (max. operating temp. × 1.10) or (max. operating temp. + 50)
t = nom. req'd th'k without corr. allow. $(t + c)$ = nom. req'd th'k including corr. allow.
D_o = outside dia. P = ext. design press. P_a = allowable external press.
L = design length of vessel section (See UG-28 and 29)
Use chart (Fig. #_____) Appendix V
Check for P_a (or MAP_a) with given D_o = _____t or $(t + c)$ = _____L = _____

$\frac{D_o}{t}$ or $\frac{D_o}{(t+c)}$	$\frac{L}{D_o}$	B (from Chart)	P_a or $MAP_a = \frac{Bt}{D_o}$ or $\frac{B(t+c)}{D_o}$

Check for L with given P = _____ and D_o = _____ with variable t

t	$\frac{D_o}{t}$	$B = \frac{PD_o}{t}$	$L - D_o = X$ (from Chart)	$L = D_oX$	$t + c$

Stiffening Rings

E = mod. of elast. for max. temp. under ext. press. conditions = _____
I = mom. of inertia of ring $\geqq I_s$ = req'd mom. of inertia
A_s = cross-sect. area of ring. A and B = Chart factors—Appendix V

D_o = _____D_o^2 = _____$\frac{D_o^2}{14}$ = _____D_o^3 = _____

Trial $I_s = \left(\frac{.14D_o^3P}{E}\right)L = \left(\text{_____}\right)$___ = Use_____
W = _____A_s = _____I_____

t	L	$\frac{A_s}{L}$	$t + \frac{A_s}{L}$	PD_o	$B = \frac{PD_o}{t + \frac{A_s}{L}}$	A	$\left(\frac{D_o^2}{14}\right)L$	$I_s = \left[\left(\frac{D_o^2}{14}\right)L\right]\left[t + \frac{A_s}{L}\right]A$

FIG. 11.5. Pressure vessels—external pressure—shells.

ETC 03214

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No._____
Sheet No._____of_____
SUBJECT_____ EQUIP. No._____ Date_____
Comp. By_____C'k'd By_____

Diameter_____(OD)(ID) Type_____Corr. Allow. = c = _____

Mat'l ASME SA_____Gr._____Type or Qual._____Y.S._____

If jacketed, or intermediate head, design press. on convex side_____psi @_____°F

Ext. press. due to full or partial vacuum on concave side_____psi @_____°F

P = Design ext. press. = sum of above = _____psi @_____°F

Min. Des. Temp. = greater of (max. operating temp. × 1.10) or (max. operating temp. + 50)

Atm. Temp. S_a = _____psi Design Temp. S_d = _____psi E = 1.0

t_h = Nom. th'k without C.A. $(t_h + c)$ = Nom. th'k with C.A.

D_o = OD for F&D = _____ or ID + $2(t_h + c)$ for Ellipt. = _____

L_I = (Rad. of Dish + c) for F&D = _____ or $K_I D_o$ for Ellipt. = _____

B = Factor from Chart (Figure #_____) Appendix V

Max. Allow. Ext. Working Pressure

t_h	$\frac{L_I}{100t_h}$	$\frac{L_I}{t_h}$	B	$P_a = \frac{B}{L_I/t_h} \geqq P$

Use larger value of t_h above, or $t = \frac{1.67P(\text{ID} + 2c)}{2S_d - .334P}$ (Ellipt.) or $\frac{1.475PL_I}{S_d - .167P}$ (F&D)

Max. Allow. External Pressure

$(t_h + c)$	$\frac{L_I - c}{100(t_h + c)}$	$\frac{L_I - c}{(t_h + c)}$	B	$\text{MAP}_a = \frac{B}{(L_I - c)/(t_h + c)} \geqq$ jacket MAP

Use larger value of $(t_h + c)$ above, or $(t + c) = \frac{1.67(\text{MAP})(\text{ID})}{2S_a - .334(\text{MAP})}$ (Ellipt.) or $\frac{1.475(\text{MAP})(L_I - c)}{S_a - .167(\text{MAP})}$ (F&D)

FIG. 11.6. Pressure vessels—external pressure—heads.

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No_____
Sheet No_____ of_____
Date_____
SUBJECT_____ Comp. By_____ C'k'd By_____

Estimated Weights	*Estimated*	*Corrected*
Top head		
Shell		
Manholes		
Nozzles		
Tray support rings		
Weight *A*		
Bottom head		
Sump shell		
Sump head		
Weight *B*		
Skirt		
Base plate		
Weight *C*		
1. Insulation		
2. Fireproofing		
3. Ladders and Platforms		
4. Trays		
5. Liquid on trays		
6. Liquid holdup: shell = head =		
7. Total liquid: shell = heads =		
8. Others: piping, reboilers, etc.		

FIG. 11.7. Pressure vessels—estimated weights.

ETC 03216

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No_____
Sheet No_____of_____
Date_____
SUBJECT_____ Comp. By_____C'k'd By_____

Shipping Weight (D)	Operating & Test Weight @ Bot. T.L. (E)	Test Weight on Skirt (F)	Operating Weight @ Base (H)	Test Weight @ Base (K)
A =	A =	A =	A =	A =
B =	1 =	B =	B =	B =
C =	3 =	1 =	C =	C =
3 =	4 =	3 =	1 =	1 =
4 =	5 =	4 =	2 =	2 =
8 =	8 =	7 =	3 =	3 =
		8 =	4 =	4 =
			5 =	7 =
			6 =	8 =
			8 =	

FIG. 11.8. Weight summary.

ETC 03217

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No._____
Sheet No._____ of_____
SUBJECT_____ EQUIP. No._____ Date_____
Comp. By_____ C'k'd By_____

Point under consideration (Base) (Bot. Tang. Line) other_____
P_w = Wind pressure per sq. ft. of projected area_____
D_o = OD shell section plus 2 × insulation thickness_____
L = Length of shell section under consideration_____
H = Moment arm of shell section under consideration_____
W_s = Wt. of any eccentric load_____ e = moment arm of W_s = _____
M_w = Wind moment = D_oLP_wH = _____
M_e = Eccentric moment = W_se = _____
M = Summation of M_w and M_s about point under consideration_____
P = $MAWP$ = ____ or $P = P_a$ = ____ S_a = ____ S_d = ____ E = ____
d = Nom. shell dia. in._____ D = Nom. shell dia. ft._____
$Z = 9.42D^2$ = _____ $C = 37.7D$ = _____
L_t = Tension, lbs. per linear in. L_c = Comp. lbs. per linear in.

AT BOTTOM TANG. LINE OR OTHER POINT_____

$\pm\frac{M}{Z}$ = ____ = + −
$-\frac{W_A}{C}$ = ____ = xxxxxx −
$L_t(+)$ or $L_c(-)$ + −

Use larger value of t or t_h
$t = L_t/S_aE$ = _____
L_i = I.R. = ____ $L_i/100t_h$ = ____
B = ____ ≧ (L_c/t_h = ____) ≦ S_a

$\pm\frac{P_d}{4}$ = ____ = + −
$\pm\frac{M}{Z}$ = ____ = + −
$-\frac{W_E}{C}$ = ____ = − −
$L_t(+)$ or $L_c(-)$ ± −

Use larger value of t or t_h
$t = L_t/S_dE$ = _____
L_i = I.R. = ____ $L_i/100t_h$ = ____
B = ____ ≧ (L_c/t_h = ____) ≦ S_d

$\pm\frac{M}{Z}$ = ____ = + −
$-\frac{W_F}{C}$ = ____ = + xxxxxx −
$L_t(+)$ or $L_c(-)$ + −

Use larger value of t or t_h
$t = 2L_t/S_a$ = _____
L_i = I.R. = ____ $L_i/100t_h$ = ____
B = ____ ≧ (L_c/t_h = ____) ≦ S_a

AT BASE LINE OR OTHER POINT_____

$\pm\frac{M}{Z}$ = ____ = + −
$-\frac{W_d}{C}$ = ____ = xxxxxx −
$L_t(+)$ or $L_c(-)$ + −

Use larger value of t or t_h
$t = 1.54L_t/S_a$ = _____
L_i = I.R. = ____ $L_i/100t_h$ = ____
B = ____ ≧ (L_c/t_h = ____) ≦ S_a

$\pm\frac{M}{Z}$ = ____ = + −
$-\frac{W_k}{C}$ = ____ = xxxxxx −
$L_t(+)$ or $L_c(-)$ + −

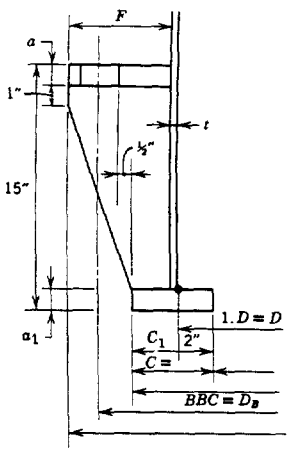
Use larger value of t or t_h
$t = 1.54L_t/S_a$ = _____
L_i = I.R. = ____ $L_i/100t_h$ = ____
B = ____ ≧ (L_c/t_h = ____) ≦ S_a

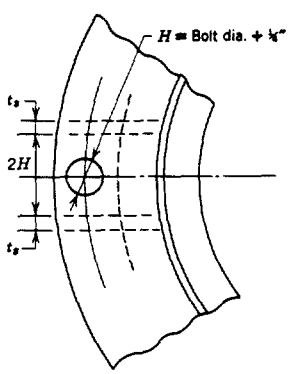
FIG. 11.9. Pressure vessels—combined loading.

ETC 03218

COMPUTATION SHEET

NAME OF COMPANY_____ J. O. No._____
Sheet No._____ of_____
Date_____
SUBJECT_____ Comp. By_____ C'k'd By_____





L_c @ Base Line = _____

$$C = \frac{L_c}{500} = \frac{\qquad}{500} = \qquad "$$

$a_1 = .335C_1 = .335x$ ____ = ____ "

Wt. "D" = _____ lbs.

M @ Base Line = _____ ft. lbs.

N = No. of anchor bolts = _____

Dia. Bolt Circle = D_B = _____

$$T_M = \frac{4M}{ND_B} = \qquad =$$

$$C_W = \frac{\text{Wt. } D}{N} = \qquad =$$

$$T_B = T_M - C_W \qquad =$$

$$A_B = \frac{T_B}{15000} = \qquad =$$

Bolt size (d_b) = _____ A_a = _____

$T = 15000A_a = 15000x$ ____ = ____

$4H = 4x$ ____ =

$1.5d_b = 1.5x$ ____ = ____

$S = \quad = 4H - 1.5d_b \quad =$

$$M_a = \frac{TS}{8} = \frac{x}{8} = \qquad$$

$$a = \sqrt{\frac{M}{3333(F - 1.5d_b)}}$$

$$= \sqrt{\frac{\qquad}{3333x \quad}} = \qquad$$

$$t_s = \frac{A_a}{2(C_1 - t_s)} \quad = \qquad =$$

$$t_s \geqq \frac{15 - (a + a_1)}{21} = \qquad =$$

FIG. 11.10. Pressure vessels—base ring.

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TABLE 11.5. Stresses Due to Saddle Supports

Longitudinal Bending Stress

$$S_1 = \pm \frac{3K_1QL}{\pi r^2 t} \leqq S_a - \frac{Pd}{4tE} \leqq \frac{S_y}{2} \leqq \left(\frac{E}{29}\right)\left(\frac{t}{r}\right)\left(2 - \frac{66.6t}{r}\right)$$

$$\left|\leftarrow \text{neglect if } \frac{t}{r} \geqq .005 \rightarrow\right|$$

Tangential Shear Stress

$$S_2 = \frac{K_2Q}{rt}\left(\frac{L - 2A - H}{L + H}\right) \leqq .8S_a \text{ (saddles away from head } A \leqq .25L)$$

$$S_2 = \frac{K_2Q}{rt} \leqq .8S_a \text{ (stress in shell—saddles at head)}$$

$$S_2 = \frac{K_2Q}{rt_n} \leqq .8S_a \text{ (stress in head—saddles at head)}$$

Circumferential Stress at Horn of Saddle

$$S_3 = -\frac{Q}{4t(b + 10t)} - \frac{3K_3Q}{2t^2} \leqq 1.25S_a \text{ when } S_c = S_t\,(L \geqq 8R)$$

$$S_3 = -\frac{Q}{4t(b + 10t)} - \frac{12K_3QR}{Lt^2} \leqq 1.25S_a \text{ when } S_c = S_t\,(L < 8R)$$

Additional Stress in Head used as Stiffener

$$S_4 = \frac{K_4Q}{rt_h} \leqq 1.25S_a - S_h \text{ (saddles at head)}$$

Ring Compression in Shell over Saddles—Wear Plates

$$S_5 = \frac{K_5Q}{t(b + 10t)} \leqq \frac{S_y}{2}\,(t = t_s + t_{wp})$$

Design of Ring Stiffeners

$$S_6 = -\frac{K_7Q}{na} \pm \frac{K_6Qr}{nZ} \leqq \frac{S_y}{2} \quad \text{or} \quad S_a$$

Design of Saddles

$$F = K_8Q \quad \text{acting} \leqq .33r \text{ below shell } S \leqq .66S_a$$

NOMENCLATURE

Q = load on one saddle (lb)
L = tangent length of vessel (ft)
A = distance from ℄ saddle to T.L. (ft)
H = depth of head (ft)
R = radius of shell (ft)
r = radius of shell (in.)
t = thickness of shell (in.)
t_h = thickness of head (in.)
b = width of saddle (in.)
F = force across bottom of saddle (lb)
$S_1S_2S_3$ = calc. stresses psi
$K_1K_2K_3$ = constants
S_a = allowable stress psi
S_y = yield stress psi
S_h = head stress due to int. press. psi
E = mod. of elasticity psi
Z = section modulus in.^{3}
n = no. of stiff. each saddle
a = cross. sect. area each stiff. sq in.
θ = contact angle of saddle with shell
t_{wp} = thickness of wear plate (in.)

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TABLE 11.6. Values of Coefficients in Formulas for Various Support Conditions

Saddle Angle, θ	*Maximum Long. Bending Stress, Min. K_1**	*Tangent Shear, K_2*	*Circumf. Stress Top of Saddle, K_3†*	*Additional Head Stress, K_4*	*Ring Compres. in Shell, K_5*	*Ring Stiffeners*		*Tension Across Saddle, K_8*
						Circumf. Bending, K_6	*Direct Stress, K_7*	
			Shell unstiffened					
120	0.63 (A/L = 0.09)	1.171	0.0528	—	0.760	—	—	0.204
150	0.55 (A/L = 0.11)	0.799	0.0316	—	0.673	—	—	0.260
			Shell stiffened by head, $A \leqq R/2$					
120	1.0 (A/L = 0)	0.880	0.0132	0.401	0.760	—	—	0.204
150	1.0 (A/L = 0)	0.485	0.0079	0.297	0.673	—	—	0.260
			Shell stiffened by ring in plane of saddle					
120	0.23 (A/L = 0.193)	0.319	—	—	—	0.0528	0.340	0.204
150	0.23 (A/L = 0.193)	0.319	—	—	—	0.0316	0.303	0.260
			Shell stiffened by rings adjacent to saddle					
120	0.23 (A/L = 0.193)	1.171	—	—	0.760	0.0577	0.263	0.204
150	0.23 (A/L = 0.193)	0.799	—	—	0.673	0.0353	0.228	0.260

* See Fig. 11.12, which plots K_1 against A/L, for values of K_1 corresponding to values of A/L not listed in table.
† See Fig. 11.13.

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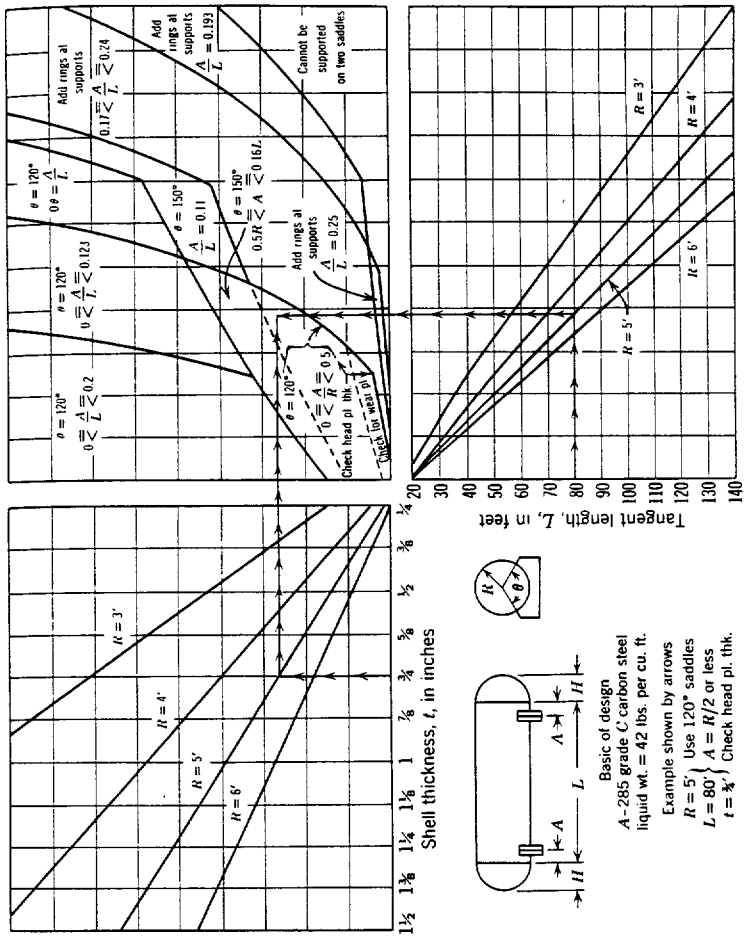

FIG. 11.11. Location and type of support for horizontal pressure vessels on two supports.

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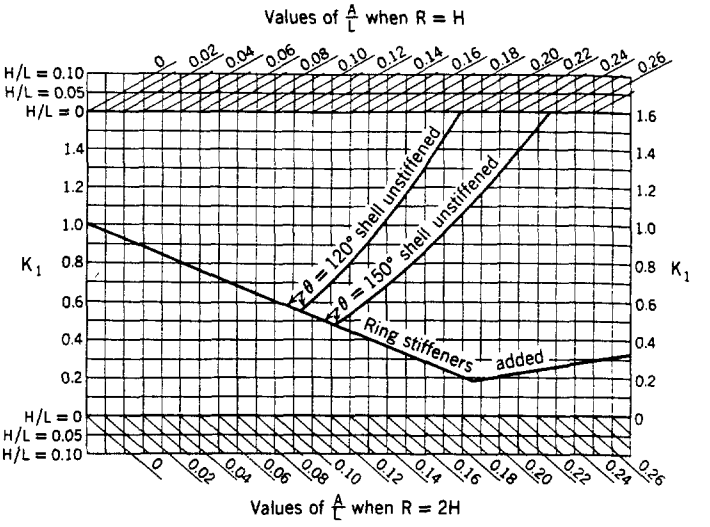

FIG. 11.12. Plot of longitudinal bending-moment constant K_1.

fillet welded. The effects of securing heads by various methods are discussed in references 28, 29, and 30.

Large, horizontal tanks frequently have been supported on three or more saddle supports. This is a hand-down from riveted construc-

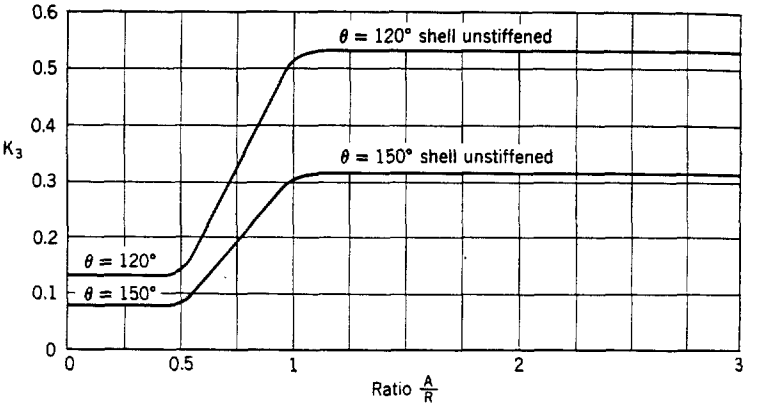

FIG. 11.13. Plot of circumferential bending-moment constant K_3.

ETC 03223

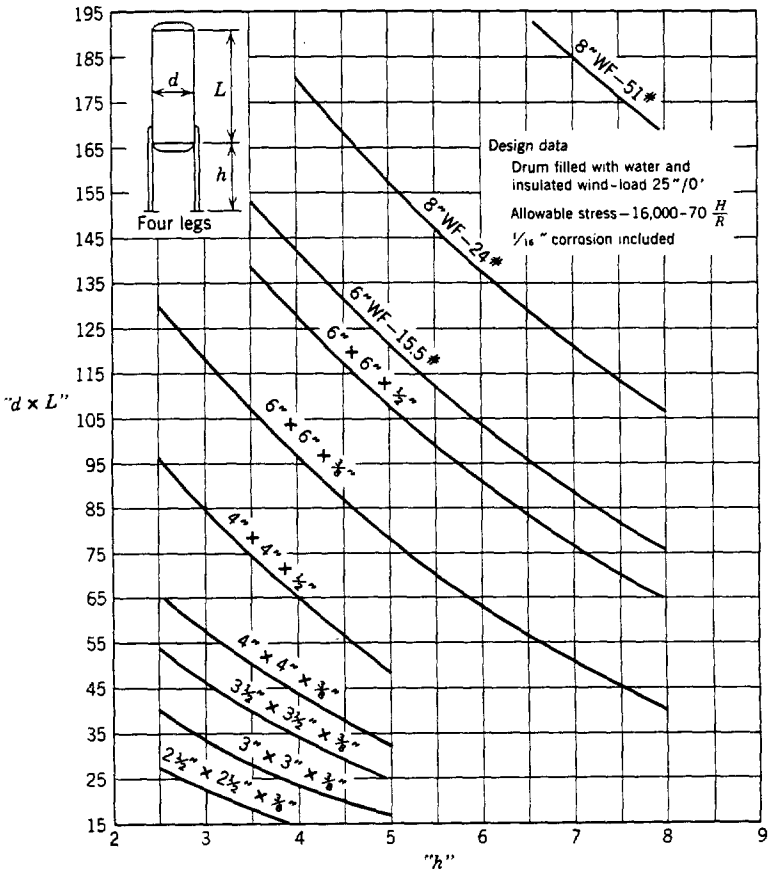

FIG. 11.14. Leg supports for vertical vessels.

tion when it was usual practice to provide a saddle adjacent to each riveted girth seam in an effort to prevent leakage at the riveted seam. Preferred practice today is not more than two supports. The saddles are designed and located so as to utilize the strength of the heads to maintain roundness of the shell, or stiffening rings may be employed. Tanks over 10 ft in diameter and 50 ft long are supported in this manner. See references 31, 32, 33, and 34, Tables 11.5 and 11.6, and Figs. 11.11, 11.12, and 11.13.

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Heads

Pressure-vessel heads may be any of the following which are listed in order of increasing thickness for a given pressure, diameter, and material. (The approximate shell thickness t = .06 in./ft diam/100 psi for an allowable stress of 10,000 psi.

1. Hemispherical	(t = ½ shell thickness–approx.)
2. Ellipsoidal	(t = shell thickness–approx.)
3. Conical	(t = shell thickness/cos of half apex angle)
4. Torispherical (F and D)	(t = 1.77 shell thickness–approx.)
5. Flat	no simple relationship

Hemispherical heads have the best stress distribution of any of the head types, with less material required to contain a given volume. Relatively few fabricators have the forming equipment necessary for producing these heads, and therefore they are not as commonly used as are ellipsoidal heads and flanged and dished heads.

Ellipsoidal heads having a major to minor axis ratio of 2 to 1 have a better stress distribution than torispherical, and for pressures over 150 to 175 psi and for diameters over about 5 ft they are usually more economical than the F and D head. Ellipsoidal heads are usually sized by their inside diameter rather than by their outside diameter as are F and D heads.

Conical heads are usually formed by pressing, not by rolling or spinning, and they are expensive to fabricate. They are used for digestors, rendering tanks, or where it is desirable to drain off solids or heavy viscous materials. A truncated conical head is commonly used as a transition piece connecting two different diameters of a vessel. Conical heads without a transition knuckle are permitted by the code under certain conditions, but they should be used only for low-pressure, low-temperature conditions.

The Lukens Steel Company catalogue, *Lukens Spun Heads* lists 3 types of flanged and dished heads:

1. Flanged and dished heads–Standard
2. Flanged and dished heads–ASME
3. Flanged and shallow dished heads

Standard flanged and dished heads have a dished crown radius equal to, or less than, the outside diameter of the head skirt or straight flange, but the transition knuckle between the crown and the skirt has a

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radius of only 3 times the metal thickness. About 30 years ago the code refused further acceptance of heads having these knuckle proportions following the discovery of many cracked heads, and after several disastrous explosions that were traced to cracks that had developed at the knuckle as a result of the stress intensification at the short radius. These heads are used for atmospheric tanks and should not be used for pressure vessels.

The ASME flanged and dished heads have a dished radius equal to or less than the outside diameter of the head skirt or straight flange, and a knuckle radius not less than 6% of the outside diameter of the head skirt but not less than 3 times the metal thickness. The latter provision increases the knuckle radius for thicker heads. When flanged and dished heads are used ASME F and D heads should be specified.

Flanged and shallow dished heads have a dished crown radius greater than twice the head diameter, and they more nearly approach a flat or flanged only head.

The use of welded flat heads, except for small, low-pressure closures, are seldom justified as, in addition to the extreme thicknesses required, severe discontinuity stresses are introduced in the cylindrical shell. A more satisfactory closure is obtained by a pipe cap or a code head. Bolted on blind flanges are used as manhole or access openings but above 24 in. in diameter, and for high pressures and temperatures it is often possible to save money and effect easier handling by using a formed head attached to a pipe flange. Illustrative of this is that a 6 ft diameter vessel carrying 350 psi required a flat head 12 in. thick weighing 13,800 lb, whereas a 2 to 1 ellipsoidal head $\frac{7}{8}$ in. thick weighing 1700 lb could have been used (the equivalent of the bolting portions of the closure not included for either type head).

Literature on the stresses occurring in pressure vessel heads is extensive. Some references are 30 and 35 to 37.

11.8. FABRICATION

Pressure vessels may be fabricated by bolting, riveting, forging, casting, brazing, welding, or a combination of any of these. Other than for flanges, bolting has never been used extensively for pressure-vessel construction, although for years the box header for one make of water-tube boiler had been bolted to the steam and water drum.

Riveted construction is almost a thing of the past, and it is doubtful if more than a handful of shops in the country today still have equipment for bull riveting a boiler or pressure vessel.

Forgings, other than forged fittings, may be used for high-pressure

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drums where the ratio of thickness to diameter is high, and it would be difficult to form a cylindrical shell by rolling or pressing. The code has no provision for forging by hammer welding, although this method was used for years in the fabrication of large paper-mill digestors.

Castings may be used for unusual shapes. Cast iron has definite pressure-temperature limitations established by the code. Cast steel has no such limitations. Brazing has been used extensively for production of small air tanks for service station use. The code limits the temperature to 406°F and the thickness to 1 in. maximum. Many nonferrous materials are brazed.

With the exception of a few special cases, practically all industrial pressure vessels are of welded construction. Welding processes are many and consist essentially of brazing, forge welding, gas welding, thermit welding, arc welding, induction welding, resistance welding, and flow welding. Pressure-vessel welding is usually either arc welding or gas welding and may be manual or automatic. Gas welding may be air-acetylene, oxygen-acetylene, or oxygen-hydrogen. Arc welding covers a wider range as follows:

Carbon Electrode	Metal Electrode
Shielded-carbon arc	Consumable electrode
Inert-gas carbon arc	Nonconsumable electrode (tungsten)
Unshielded-carbon arc	Shielded electrode (coated)
Unshielded twin-carbon arc	Submerged arc
	Inert-gas metal arc
	atomic hydrogen
	impregnated tape

The most common arc-welding processes used in pressure-vessel fabrication are shielded or coated electric, submerged arc, and inert-gas metallic arc. For details of these and other processes consult references 38, 39, and 40.

For fabricating pressure vessels by welding or brazing the code requires that the manufacturer qualify the welding or brazing procedure to be employed and the welding or brazing operator that will use that procedure in the fabrication of the vessel.

Section 9, "Welding Qualifications," of the ASME Boiler and Pressure Vessel Code details the requirements for qualification of procedure and operators. Although a procedure or procedures may have been qualified for certain welding positions, materials, and filler rod, it may be necessary to requalify if any changes are made. Unless there

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is a very good reason the designer should not specify any welding details, groove dimensions, or filler metal, that will require the fabricator to change from his qualified procedure and necessitate a new procedure and operator qualification. Qualifying a welding procedure and welding operators is expensive.

11.9. INSPECTION AND TEST

While the code has requirements for forming, fit-up, and tolerances it is well for the purchaser to have his own inspector in the shop to supplement the code inspector. The code inspector is only concerned that the code requirements are met, and not with location, orientation, and projection of nozzles, installation of internals and other attachments, cleanliness, or finish. What the code inspector sees he will no doubt report, but vessels have been shipped with certain idiosyncrasies such as a column shipped to the field with all 5 manhole davits, including the hinge, welded only to their respective coverplates. Tolerances that are generally available are shown in Fig. 11.15. Closer tolerances may be specified and obtained but usually at additional cost.

For critical service it is often desirable to have more stringent requirements for testing than those presently required by the code, such as ultrasonic testing (now covered by a Code Interpretation Case for plate only), magnetic particle testing, fluid penetrant examination, and helium leak testing. Much time and effort may be saved by extracting procedures and acceptability standards from MIL–STD–271 which covers these test methods in detail.[41] Similarly, MIL–C–19874 is a convenient reference for cleanliness requirements.[42]

11.10. CERTIFICATION

Upon completion of fabrication and testing of the vessel it is stamped as required by the code in the presence of the code inspector who will also sign the proper ASME form:

1. U-1 Mfg. Data Report covering shop and/or field assembly inspection,
2. U-1A for single chamber shop fabricated vessel,
3. U-2 partial data report for a part fabricated by one manufacturer for another manufacturer,
4. U-3 data report for vessels that owing to small size are not shop inspected and are certified by the manufacturer and stamped UM.

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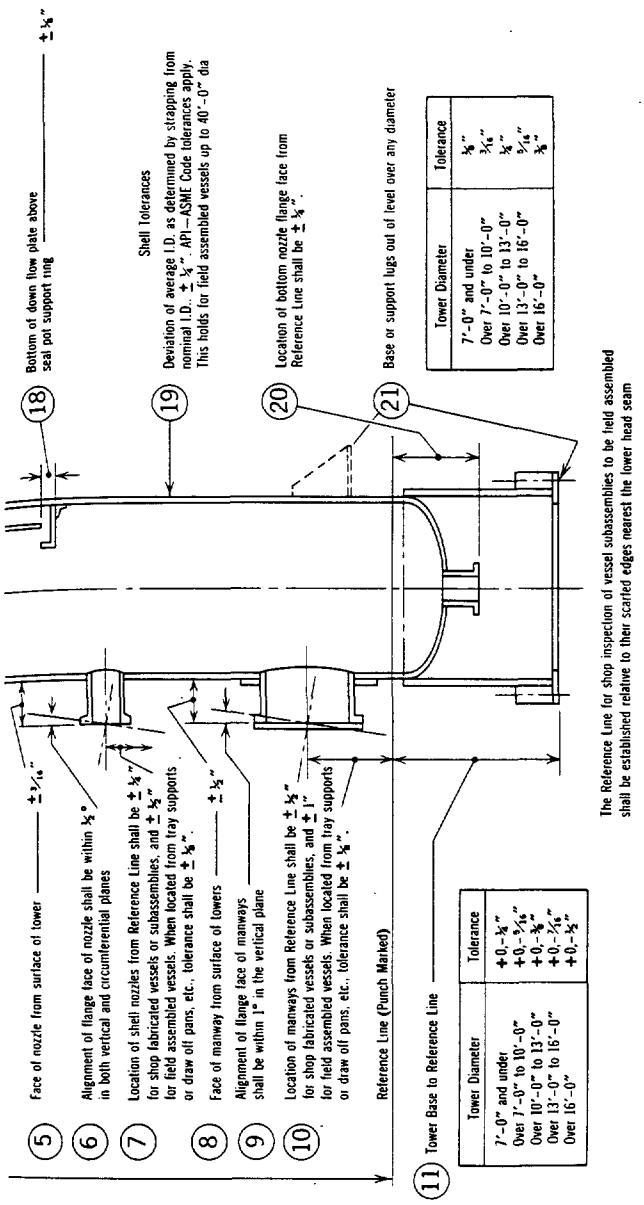
Tower Diameter	Tolerance
4'-0" and under	1/8"
Over 4'-0" to 7'-0"	3/16"
Over 7'-0" to 13'-0"	1/4"
Over 13'-0" to 16'-0"	5/16"
Over 16'-0"	3/8"

Tower Diameter	Tolerance
7'-0" and under	1/8"
Over 7'-0" to 13'-0"	3/16"
Over 13'-0" to 16'-0"	1/4"
Over 16'-0" to 24'-0"	5/16"
Over 24'-0"	3/8"

ETC 03229



Tower Diameter	Tolerance
7'-0" and under	+0, -¼"
Over 7'-0" to 10'-0"	+0, -9/16"
Over 10'-0" to 13'-0"	+0, -⅜"
Over 13'-0" to 16'-0"	+0, -7/16"
Over 16'-0"	+0, -½"

Tower Diameter	Tolerance
7'-0" and under	¼"
Over 7'-0" to 10'-0"	5/16"
Over 10'-0" to 13'-0"	⅜"
Over 13'-0" to 16'-0"	7/16"
Over 16'-0"	½"

FIG. 11.15. Vessel tolerances.

ETC 03230

The purchaser usually specifies the required number of copies to be finished of:

1. Data forms,
2. Rubbings or facsimiles (photographs are better) of the stamping on the vessel,
3. Stress relief or heat treatments, time-temperature recordings,
4. Pressure recordings,
5. Mill test certificates,
6. Other records pertinent to the vessels fabrication.

Similar documents are furnished to the state or other jurisdiction where the vessel will be installed. Future possible difficulties in relocating in another state may be avoided if National Board inspection has been specified and documents sent to their headquarters.

11.11. INSTALLATION

When a new vessel has been installed with its necessary piping and appurtenances, such as relief valve, vents, drains, gage glass, and controls, local requirements may require state or local inspection prior to putting equipment in service, or inspection may be made by an insurance inspector in lieu of the state inspection. If the installation is satisfactory a certificate of inspection is issued that is valid for 1 year or 2 years depending on the jurisdiction. Prior to the expiration of the certificate arrangements must be made for removing the vessel from service to permit internal inspection.

It is extremely important that the user of pressure vessels have a thorough knowledge of the local laws concerning the installation and operation of pressure-vessel equipment, otherwise he may experience considerable inconvenience and expense. If through ignorance (or contempt) of requirements, equipment is installed and operated without authorization, the user may be subject to penalties which include shutting down the equipment. This could mean a plant shut down depending on the nature of the installation.

After some costly experience a nice degree of cooperation usually exists between the user and the inspection agency whether it be an insurance company, a municipal agency, or a state agency.

The inspector is kept informed as to new equipment installation with inspection and certification a matter of routine. Subsequent inspections are made without disrupting the plant's operation by notifying the inspector when scheduled downtime occurs, and inspection may

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be made then rather than to wait for the inspection certificate to expire which would require a shut down when it may be least convenient.

11.12. SECOND-HAND EQUIPMENT

No statistics are available as to the money wasted on the purchase of second-hand boilers, pressure vessels, heat exchangers, and refrigeration vessels, that are rejected as being non-code or otherwise unacceptable for operation after reinstallation at a new location.

Any user contemplating the purchase of second-hand equipment should have the equipment inspected by an authorized code inspector and obtain a written report that the equipment meets the requirements of the jurisdiction where it is to be reinstalled. The report should also furnish sufficient information concerning the condition of the equipment for the user's decision in purchasing. The code inspector will report conditions and make recommendations for repairs, but will not make a recommendation that purchase be made, his function is inspecting, not appraisal. Arrangements for inspection of second-hand equipment can usually be made with the user's insurance company or through his insurance agent. The cost is a per diem charge for the inspector's services plus expenses.

11.13. REPAIRS

Nonmandatory Appendix X of the Unfired Pressure Vessel Code covers recommended practices for inspection, repair, and allowable pressure for vessels in service. Further information concerning inspection and repair is given in the National Board Inspection Code[4] which will guide a code inspector in code jurisdictions.

The recommended procedure is for a competent pressure vessel designer to prescribe the nature and extent of repairs to be undertaken together with correct welding procedures, heat treatment, and nondestructive testing, that may be required depending on the original construction of the vessel and its present or future intended service. The proposed repair should then be discussed in detail with a code authorized inspector, regardless of whether or not the vessel is under any code jurisdiction. If the vessel is not insured or not under any legal jurisdiction the services of a code inspector may be obtained as outlined in Section 11.12. After the inspector has approved the proposed repair, the work should be done by a reputable fabricator, preferably one listed as authorized under the National Board.[4] After witnessing the satisfactory completion of the repair and testing the inspector will

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sign the manufacturers Record of Welded Repair to be furnished the governmental unit having jurisdiction.

This may appear as an unduly rigorous approach to a seemingly simple problem, but consider, an unauthorized repair in a code jurisdiction may result in an immediate condemnation of the vessel when the inspector learns of it. At best the inspector will demand removing the vessel from service immediately in order that he may inspect the repair and judge its acceptability. This requires an equipment and possibly a plant shut down. Should the worst happen and a failure causing loss of life occur with resultant public hearings it would be exceedingly difficult to justify the repair.

11.14. HIGH PRESSURE VESSELS

Owing to the somewhat ambiguous wording of Paragraph 1b of the Unfired Pressure Vessel Code an erroneous conclusion has frequently been drawn that because no specific rules were laid down for vessels carrying over 3000 psi, that such vessels were exempt from any and all code requirements. A proposed revision appearing in *Mechanical Engineering*, April, 1962 reads as follows:

> UNFIRED PRESSURE VESSELS, 1959
>
> Paragraph U-1(b), revise to read:
>
> The rules of this section of the Code have been formulated on the basis of design principles and construction practices applicable to vessels designed for pressures not exceeding 3000 psi. For pressures above 3000 psi, deviations from and additions to these rules usually are necessary to meet the requirements of design principles and construction practices for these higher pressures. Only in the event that after having applied these additional design principles and construction practices the vessel still complies with all of the requirements of the Code may it be stamped with the Code symbol.

The design of a high-pressure vessel is, as it should be, usually done by an organization or individual with long experience in this highly specialized field. Pressure, temperature, nature of process, and whether hydrogen embrittlement must be considered will influence the material selection and may determine which of the various theories is to be used in computing thicknesses. The theories that may be considered in high-pressure vessel design are:

Maximum principal stresses theory (Lamé)
Maximum strain theory (Clavarino or ICC)
Maximum strain energy theory
Maximum shear theory

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The maximum principal stress theory (Lamé) is ordinarily used for pressures around 3000 to 5000 psi and the maximum strain energy theory for higher pressures.

The vessel may be made of two half shells hot formed and welded together, a turned and bored forging, or a number of concentric, thin shells making a composite heavy wall. The heads may be formed hemispherical, ellipsoidal, or flanged.

In order that material thicknesses may be reduced, it is desirable that the inner material of the shell be in compression, which is accomplished by prestressing. This is done in multilayer construction by each successive shell compressing its inner shell. Solid shells are prestressed by overstraining hydrostatically.

Extensive literature is available on the design of high-pressure vessels. See references 43 through 51.

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12

Safety Education and Training

M. A. Gimbel

12.1. TRAINING OF PERSONNEL
(Management, Supervision, Worker)

Education may be said to deal primarily with broadening knowledge and understanding, while training deals primarily with the development of skill in performance. Both are needed to develop safe work techniques and practices.

One of the problems in industry is establishing suitable communication. Information must pass from top management through the supervisor to the man on the job. In reverse, word from the worker must reach to top management. After management recognizes the need for accident prevention, and takes steps to get willing cooperation from all men under its direction, it is prepared for a training program.

Undoubtedly motivation is a factor in directing and controlling activities of people. Employees will work hard and will have regard for quality, for courtesy, and for safety if they have reason to think they will benefit from so doing.

Since production, which includes safety, quality, scheduling, efficiency, and employee relations, is implemented largely through efforts of foremen and other supervisors it is essential that they receive training to increase the all-around productivity of their departments. After foremen and supervisors are properly trained it is their responsibility to see that their subordinates are trained and motivated in the pride of achievement, safe practices, and good workmanship.

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Employee Training Procedures

Some form of systematic training of employees is necessary in order to have work done efficiently and safely. This is a definite requirement even though employees are carefully selected, have aptitude, and have experience for the jobs assigned.

Training may be given by the foreman or supervisor responsible for the job. Management in large plants is finding it desirable to have training specialists for the general training and to set up a procedure so that training can be done by the best qualified persons in the plant. The specialist prepares the training manuals and other details for conducting the program and supervises the activity in the individual departments.

In chemical plants as well as general manufacturing companies, two methods are followed.

VESTIBULE INSTRUCTION

This is a plan to teach specialized, general, or advanced techniques peculiar to the industry before the employee actually starts work. Thus it precedes "on-the-job training." Accident prevention is included in all instructions, particularly when new or unusual hazards are characteristic of the job.

On-The-Job Training

Job training acquaints the employee with a new job or teaches him additional skills. Usually the department supervisor or some one designated by him takes the time to train whenever it is required. This applies to new operations, new employees, and changes in methods and equipment. A changed job is considered a new one and some breaking-in is required.

A good instructor is friendly, sincere, patient, has a thorough working knowledge of the job to be taught, and knows the principles of teaching. He should have the ability to break down the job into its component steps, use an outline for each assignment, and follow a step-by-step analysis of the job.

Job Instructor Training

During World War II the government realized the need of improved training in industry and sponsored the Job Instruction Training

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courses known as J.I.T. The same basic principles are appropriate today.

HOW TO GET READY

To instruct a new worker or an experienced one on a new job:

Have a Plan

How much skill you expect him to have, and how soon.

Analyze the Job

List principal steps.
Pick out the key points.

Have Everything Ready

The right tools, equipment, and materials.

Have the Work Place Properly Arranged

Just as the worker will be expected to keep it.

HOW TO INSTRUCT

Step 1—Prepare:

Put him at ease.
Find out what he already knows about the job.
Get him interested and anxious to learn the job.

Step 2—Present:

Tell, show, illustrate, and question carefully and patiently.
Stress key points (knack, important, and special points).
Instruct clearly and completely, taking up one point at a time—but no more than he can master.
Check, question, and repeat.

Step 3—Perform:

Test him by having him perform the job.
Have him *Tell* and *Show* you; have him explain key points.
Ask questions beginning with *Why, How, Who, What, When,* or *Where.*
Observe performance and correct errors. Repeat instructions if necessary.

Step 4—Follow Up:

Put him on his own.
Check frequently to be sure he follows instructions. Encourage questions.
Get him to look for key points as he progresses.
Taper off extra coaching and close follow-up until he is qualified to work with normal supervision.

If the worker hasn't learned,
the instructor hasn't taught.

Breaking Down a Job into Its Component Parts

It is generally accepted that 80% of most jobs are very simple operations and can be done by the average person with a minimum of

training. The remainder, or 20%, represents the skills or tricks of the trade resulting from training and experience. These important steps must be emphasized and made clear in the training procedure.

A job break-down sheet is invaluable in analyzing a job as well as in instructional work. A simple job break-down sheet shown below for training new men can be made quickly for almost any job. The proper procedure of diluting acid will serve as an example.

Job Breakdown Sheet for Training Man on New Job

Part or Material	*Operation*
Sulfuric Acid	Diluting Acid with Water
Important Steps in Operation	*Key Points—Knacks—Hazards, Feel, Timing, Special Information*
Step 1	
Add 100 gal of water to tank.	Use dip stick to measure water depth before adding acid.
Step 2	
Start agitator.	Make certain agitator is operating.
Step 3	
Open the valve on the 1 in. 98% acid line and run it into the measuring tank until 10 gal are in the tank.	Wear safety protection such as acid goggles, rubber gloves, and apron. Use face shield when checking contents of tank.
Step 4	
Transfer acid from measuring tank to the water in the receiving tank.	Add acid to the water in the receiving tank slowly and keep the agitator operating. Always add the acid to water slowly. *Never* add water to acid because of reaction heat generated and danger of splashes.
Step 5	
Make specific gravity test.	Use Baumé scale.
Step 6	
Run mix into holding tank.	Make certain that there is room in holding tank and discharge valve is closed.

On-The-Job Training

On-the-job training is the best method of presenting a full, clear, and actual picture of the work to be performed. It is here that previous

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instruction is tested by demonstrating its application on the job itself. When the employee performs the work, using the training he has received, he combines the abstract and the concrete phases and completes the picture of the why, how, who, what, when, or where.

GROUP TRAINING

Small discussion groups are sometimes used to impart information. These give the participants a feeling of belonging. The discussion leader prepares the outline, presents it to the group, and directs the discussion toward the goal he has in mind.

If a problem is to be considered he should present it at the beginning of the discussion and have pertinent questions prepared. He should not dominate the discussion but direct it.

Meetings and Instructional Presentations

There are many useful methods to be included in a training program so that the work is done the right way, which means the safe way also. Important among these methods are meetings and discussions. Preparations for leading the discussion or following the program must be made in advance.

The meeting place should be adequate in space, with sufficient ventilation, comfortable seats, good illumination, and a blackboard or charts. Start the meeting promptly and keep it moving toward the goal. Do not try to cover too many subjects in one session. Keep discussion going and have all participate. Keep the meetings short.

Instructional Aids

Sensory aids may be grouped under these classifications:

Motion pictures	Models
Slides	Charts and diagrams
Photographs	Flannel boards
Posters	Audible examples with pictures
Opaque projectors	Display boards
Textbooks	Damaged equipment
Take-home material	The job itself

MOTION PICTURES

Motion pictures are a major tool for instructional purposes. The sound track added to the film presents the explanation well and en-

courages discussion after the film. The teaching information reaches the mind of the trainee by means of the auditory route as well as the visual.

SLIDES

Slides are a convenient method for packaging a collection of material to assist in clarifying the course of instruction. Photographs and posters may be used in the same manner.

CHARTS AND DIAGRAMS

Charts and diagrams assist in maintaining interest as well as clarifying pictorially certain facets of the information presented.

MODELS

Models may be working miniatures made to scale. They may be designed to provide motion as when machines are under discussion. Plant layout in model form to illustrate movement of product and production requirements are used to stimulate discussion as well as to explain the problem and presentation.

FLANNEL BOARD

Flannel boards allow for advance preparation and save more time than the blackboard presentation. A better job of presenting the facts in a clear and concise fashion is achieved by flannel boards.

DISPLAY BOARDS

Display boards showing the right and wrong way, damaged material, waste prevention, and ways to improve production have a place in the instructor's book.

AUDIBLE EXAMPLES

Audible examples taken from actual experience show the advantages of certain ways compared to the disadvantages of others.

TEXTBOOKS AND RULE BOOKS

Textbooks and rule books dealing with the subjects are invaluable. The trainee should be given an opportunity to review the subject at

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home if possible and then have a reference for future application. These are handy reference books for instructors and supervisors when they wish to spell out a safe and proper procedure to be followed.

12.2. TRAINING AND EDUCATION IS NEVER COMPLETED

After the initial training or break-in period is completed there is a definite need of follow-up—to keep alive the need of good practices.

In promoting safety meetings as part of the program for production —and safety cannot be disassociated from production—we can summarize the procedures and things to keep in mind. For example:

1. The purpose is to make the employee understand why he must work *SAFELY*. He benefits.
2. Exchange ideas and arrive at a logical conclusion.
3. Develop personal contact with men.
4. The foreman should deal with specific hazards in his department.
5. The foreman should lead the meeting.
6. He should be prepared, and his subject should be appropriate to the occasion.
7. If subjects are interesting, employees will want to talk and participate.
8. Present a problem or experience, and let the employees carry on, but arrive at a conclusion.
9. Guide the discussion and avoid a gripe session.
10. Focus attention on a specific accident, problem, or new and better method.
11. Do not try to cover too much at one session. Establish at least monthly meetings on definite days.
12. The foreman or leader must be sincere.
13. Praise employees when a good job is done.
14. Provide safety equipment and explain its use and the need for using it.
15. It may be well to give advance notice of subjects.
16. A panel with question and answer session helps to change routine.
17. At a contest to decide the best stunt to promote safety, 70% of all replies indicated the best stunt is to have supervisors meet with the men to discuss the problem.
18. Be careful about leaning on undependable slogans and labeled thinking, such as "Safety First."
19. Safety is not first. We must have training, education, explanation, engineering, and enforcement. We must put our hearts, minds, and souls in our work and *then* we will have safety.

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No attempt has been made in this chapter to deal with other useful motivating methods, such as contests, slogans, dramatics, suggestion systems, bulletin boards, and specialized training.

12.3. STANDARD OPERATING PROCEDURES

Chemical Operation Process and Flow Sheets

Provision of the right physical facilities is not all that is necessary for the safe operation of a plant. Just as important are the practices of persons operating it and the information and procedures which they must be given to follow.

In general, the research organization develops the formula for the product and studies the prospects for customer use and demand. The effectiveness of the product and the means of producing it are then reviewed. During the research period notes are made of the mixtures, quantities, availability, reactions, and hazards. After it has been decided to consider making the product, the details for production are given to the pilot plant. Here small batches are made under the direction of the men who will decide on what equipment to use, the place of manufacture, the methods of controlling temperatures, pressures, and gases, the general procedures to follow, and standard methods necessary to control quality, hazards, waste, and time.

During this period process sheets and flow charts are prepared. They specify the best, safest methods and are written as definite instructions which must be followed in the manufacturing department. During the pilot plant period many problems are resolved, the yield is determined, costs are prepared, hazards are listed, and precautions are indicated.

The engineer assigned to the job makes plans for the space and equipment required and accompanies the project to the manufacturing department, so that he can assist in the training program and assist the foreman and operators to achieve normal production. He also makes whatever changes and improvements are required, and he is the contact man with production, pilot plant, engineering, development, and research.

Process Sheets and Flow Charts

Process sheets are available to operators. They include safety precautions required and, when hazardous chemicals are involved, symptoms of exposure and immediate first aid treatment to be given. Suitable fire extinguishment equipment is also specified where flammable material is used.

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A sample safety sheet, which may accompany the process sheets when new chemicals are introduced in the manufacture, follows. This sheet tells the operator what to look for and what action to take if things go wrong.

12.4. PERCHLOROETHYLENE (PCE) (TETRACHLOROETHYLENE) SAFETY SHEET

Properties

Colorless, nonflammable liquid with an ether-like odor, and a density of 13.4 lb/gal at 25°C. It is completely soluble in alcohol and ether and miscible with all common solvents and oils, but the solubility in water is only 0.01%.

Boiling point = 121°C at 760 mm
Melting point = −23°C

Safety

This solvent can be handled safely if proper precautions are observed constantly. Prolonged, excessive, or repeated exposures to PCE in any form are hazardous.

Perchloroethylene is not corrosive or dangerously reactive, but it is toxic on inhalation, on prolonged or repeated contact with the skin or mucous membrane, or when ingested by mouth. The liquid can cause eye injuries also.

The maximum allowable concentration in air is 100 ppm for an 8 hr working day. Exposures to vapor concentrations greater than 200 ppm cause irritation, lachrymation, and burning of eyes, irritation of nose and throat, and may cause vomiting. Perchloroethylene is less volatile than water, but the vapors are almost 6 times heavier than air. Good ventilation in the working area is required, particularly at floor level. PCE should not be stored in pits, basements, or unventilated areas.

Perchloroethylene is nonflammable and nonexplosive, and it will not support combustion. However, if the vapor is exposed to high temperatures (open flames or electric heaters) it may be decomposed to toxic substances.

Spillage

Spills should be mopped up and the rags used placed in closed containers or dried outdoors in a safe place. If clothing is wet with PCE it should be removed immediately and not used again until free of solvent odor. A shower should be taken, washing all affected areas thoroughly with warm water and soap. Prompt medical attention should follow.

To protect the eyes, approved chemical goggles or face shield must be worn when handling PCE. If liquid PCE should contact the eyes, wash immediately with copious amounts of water for at least 15 min. Medical attention should be obtained after this.

Suitable respiratory equipment approved by the U.S. Bureau of Mines should be available for use in an emergency. If an excessive amount of

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vapors are inhaled there will be irritation of the eyes, nose, and throat, fullness in the head, and mental confusion. Prompt removal from the contaminated area is necessary. If breathing has stopped, artificial respiration should be started immediately, and a physician called at once. Oxygen should be administered by oxygen inhalation apparatus when available.

Numerous trade associations and other organizations provide safety service and information. The most useful of these in the scope of chemical safety are cited in Appendix I.

Depending on the product to be made, the instruction or process sheets may include references, specifications, flow diagrams, equipment required, yield expected, hazards, precautions, reactions expected, method of sampling, heats and cooling required, disposal of residue and waste, use of by-products, health hazards, protective equipment required, running time, costs and action to take in emergencies such as power failure, water failure, fire control, and extreme reactions.

It is important that standard operating procedures be kept up-to-date and that the operators follow them very carefully. No changes are permitted without first obtaining proper authorization.

Start-Up—Shut-Down Routine

The start-up operations and the shut-down (normal) and (emergency) are extremely important. In chemical manufacture we cannot just pull a switch and stop the work. We must consider the operation cycle at the time, the danger of explosion, set-up of material, how to clean out the equipment, what must be added in material, cooling or heating, and the dangers of various reactions.

Plans should be made in advance for a normal or an emergency shut-down and these should be made as part of the regular operating sheets. Closing down operations in a continuous chemical plant might take hours and starting up preparations often take days. Consideration is given to the possibility of releasing fumes and causing damage to areas outside of the plant.

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13

Personal Behavior—Rules and Regulations

M. A. *Gimbel*

13.1. RULE BOOKS—SAFETY MANUALS

Whenever we read a book of rules and regulations we know that accidents have occurred which prompted the writing of the rules. The use of safety manuals is general in industry. Plants usually write their own and include information which is applicable to their operations.

Workers, however, are not inclined to read material which ordinarily has no immediate appeal to them. A recent trend is to use cartoon style and comic book techniques for eye appeal. Some books are written for special crafts or operations while others are more general.

Passing out rule books to new employees is not sufficient. The books must be interesting, have informational value, and serve as an educational device and reference book. Supervisors must be familiar with the contents and use the books in training, in discussion periods, and in safety meetings. The problem is to keep the contents of the book always fresh in the minds of the employee.

The distribution of pocket-size safe-practice cards at regular intervals, to be followed up and discussed at a meeting serves as a quick but impressive reminder. Some companies prefer to use books showing pictures of a hazard and having a few words of explanation indicating what not to do as well as what to do.

Most of the large chemical companies have prepared their own

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safety books, and some of these are equivalent to a textbook for safe operation. They are available in most instances on request.

Subjects usually covered include:

The policy of the company regarding accident prevention
Reporting accidents
Emergency first aid
Information for laboratory workers
Handling chemicals
Unloading chemicals from drums, trucks, and cars
Housekeeping
Safety equipment available
Waste disposal
Use of tools
Fork truck operation
Eye protection
Fire prevention
Smoking regulations
Welding rules
Use of fire extinguishers and fire alarm
Sprinkler systems
Flammable liquids
Health hazards
Inspection of equipment
Shutting down processing equipment
Safety organization
Specific instructions
General safety information

13.2. SPECIAL SAFETY INSTRUCTIONS FOR SUPERVISORS

Usually safety instructions to employees are not sufficiently detailed to include special information which supervisors should have. To compensate for this a supervisor's book is prepared in loose leaf form and information and instructions are added as needed.

Subjects for this special book may include information on:

Mandatory eye protection
Standard goggles in use at the plant
Precautions with flammable liquids
Use of available fire extinguishers
Grounding portable electric tools

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Bonding and grounding vessels—static electricity
Welding and burning permits
Men working alone
Use of hose clamps and hose connections
Hazards of toxic solvents
Standard paint colors for pipes (if used)
Flame arrestors—maintenance
Use of freight elevators
List of maximum allowable concentrations and explosive limits of various chemicals
Rules for men working in tanks, tank cars, kettles, or other confined spaces
Rules for operation of fork trucks and other power equipment
Respirators and gas masks—purpose of use and kinds available
Safety contest rules
Table of hazardous substances
Pressure relief valves—uses, kinds, and maintenance
Lock out of electrical switches before working on equipment
Mandatory head protection with hard hats
Disaster and plant emergency plan

The Manufacturing Chemists' Association[2] Safety Guides and Chemical Safety Data Sheets are written primarily for issuance to supervisory personnel to fit the above pattern. The National Safety Council[3] and other organizations also furnish suitable material. (See Appendix B.)

13.3. SAFETY STANDARDS

It is necessary that safety standards be established to cover such subjects as guarding, machine controls, employee behavior, truck operations, lighting, ventilation, housekeeping, fire prevention, rules of operation, preparation of process instructions, and many others. It is management's responsibility to state clearly the safety standards so that there can be no misunderstanding or cause for confusion.

The safety standards must fit into the general operating pattern of the plant, must be short and to the point, and must make sense to the supervisors and employees.

Safety is a part of business and must be given the same attention as other problems in plant operation. There can be no procrastination in the plans and no neutral zone.

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To integrate safety into the operation, management should:

1. Establish definite written plant safety standards.
2. Clearly outline each employee's and supervisor's responsibility. Hold supervisor responsible for the safety of those working for him.
3. Plan safety into each job and process and provide suitable facilities.
4. Supervise according to safe methods with no deviation.
5. Make frequent inspections in all departments of conditions and practices.
6. Have a sincerity of purpose and insist on safe performance through the supervisors to the men on the job. Men expect positive leadership in safety problems.

Guelich[1] describes a number of chemical accident situations and discusses the problems of supervision.

Smoking Privileges

Smoking privileges are a serious problem in the plant. In recent years the rules have been modified in order to avoid loss of time and to accommodate the employees. In chemical plants it is essential that we establish the rules, allow time for smoking, but be firm about enforcement. It is best to write down or post notices in places where smoking is permitted, and inform employees that it is prohibited in all other locations. This obviates the need of many NO SMOKING signs throughout the plant. Visitors and contractors must be properly informed of the smoking rules and required to conform.

PERMITTED AREAS

Usually in chemical plants smoking is permitted only in the office areas, locker or change rooms, eating rooms, and special areas established for the purpose. This fact should be posted in conspicuous locations.

PROHIBITED AREAS

No smoking is permitted on the roads or outside of buildings. A notice to this effect is usually posted at the entrance. Under no circumstances would smoking be permitted in areas involving polishing, dusts, flammables, material storage, waste material, gases, paints, solvents, manholes, tunnels, gasoline, or any fire hazard areas.

In some plants carrying on unusual operations it is advisable to

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extend the No Smoking rule to include the surrender of matches and automatic lighters from the person at the entering area. Powder, chemical, and petroleum plants would fall within this category. More willing cooperation will be obtained if the reason for the rules is explained.

Where smoking is permitted suitable disposal units for butts should be provided. In areas where matches and lighters are not allowed, stationary electric lighters may be installed for the men.

Men Working Alone

In many instances we have an operation where one man only can be efficiently employed particularly after the regular work hours and at weekends. The work he is expected to do must be carefully studied and hazardous operations eliminated or minimized. Usually arrangements are made with the lone worker to telephone the guard office every hour at a specified time to report everything satisfactory. In addition to this the guard or watchman is instructed to check the man on his regular tour.

If the man working alone fails to report on schedule, the guard will attempt to reach him or, if necessary, go to the place where the man is working to investigate. Whenever possible it is desirable to use the buddy system where men look after each other. This system has paid off in many instances.

Prompt Reporting of Occupational Injuries or Illnesses

It is necessary that all industrial injuries be reported at once. In this way prompt treatment affords a quicker recovery and reduces danger of infection. A record of the case is made, steps are taken if a correction is necessary to avoid future injuries, and department heads are informed of what is happening in their departments. Reports for workmen's compensation can be initiated at once when disabling injuries occur.

Plant Dispensaries and Physicians

The plant physician is in an excellent position to diagnose and treat cases that are peculiar to the chemical industry, more especially so in occupational diseases due to exposure to chemicals.

Large chemical companies usually develop methods of treatment for possible exposure to new and other hazardous chemicals. They also

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keep a supply of medicines and equipment needed for special treatment. Their medical departments are closer to the work and better prepared for prompt attention.

Therefore, it is advantageous to the employee to go to the plant dispensary promptly for minor ailments and injuries. He may be directed to a specialist if the case warrants it. (See Chapters 12 and 13.)

Should We Penalize the Worker for Infractions?

Many persons who have had repeated accidents are below average in learning ability, intelligence, and hard work. There is some indication of a relation between accidents and low scores on intelligence tests.

On the other hand, we find also many accidents occur in work involving men of higher learning and experience. Normally these injuries are explained by statements: *I just didn't think—I know better—I was pressed for time—I took a short cut.*

Should we penalize the victim of an injury for his failure, or has he suffered enough? The reaction of other employees as well as the injured might be adverse in some instances if the case is improperly handled. The time for a penalty is not after the accident but when infractions of safe practices occur, particularly when willful. Sound judgment must be used in the administration and treatment, and decisions must be consistent.

Usually this subject is discussed by management with supervisors and union representatives, if any, who in turn carry the message down the line. The rules and penalty provisions should be in writing, well publicized, and apply to everyone without exception.

WARNING NOTICES

For the first violation the employee may receive a written warning, for the second violation a written warning which indicates the penalty for a third offense, and both should be signed by the person being warned and filed with his record. The third offense carries with it suspension, discharge, or other drastic action such as transfer or demotion.

This is the accepted practice for all infractions of good work practice, and safety is merely a part of normal performance such as suitable production, punctuality on job, safety, and good conduct while

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at work. The fact that an employee signs a notice of this kind impresses him with the sincerity of management, and he has no excuse that he was not informed about his actions.

Those cases where warnings apply include:

1. Failure to wear eye protection, masks, protective clothing, or hard hats when required.
2. Unauthorized removal of guards from equipment.
3. Hitching a ride on materials handling equipment.
4. Unauthorized use of machines or other equipment.
5. Failure to report promptly for first-aid treatment after any injury.
6. General failure to follow rules listed in the safety manual.

The exceptions to the above warning routine where immediate dismissal is warranted are for stealing, fighting, intoxication, smoking in certain areas, and other serious offenses.

Correction of Unsafe Acts

The causes of all accidents can be divided into two categories: *unsafe physical condition* and *unsafe personal acts.* Investigation of accidents invariably reveals several underlying conditions which finally resulted in the accident. We must keep in mind that a large proportion of accidents do not result in personal injury or damage of some kind. How often has a load been dropped from a crane hoist without damage or injury merely because nobody was near the load at the time or the material did not break. How many explosions occur when nobody happens to be in the vicinity?

Heinrich[4] stated that only 15% of accidents are due solely to unsafe conditions and thus unsafe acts figure in 85% of all cases. Human error lies behind many unsafe conditions such as inadequate guarding, improper design and construction, poor maintenance, or poor illumination or ventilation.

UNSAFE ACTS OF PERSONS

Some injuries or accidents occur because of the behavior of the individual. Included under this heading are:

The personal factor, the mental or bodily characteristic which permitted or occasioned the unsafe act

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The unsafe act which might be a violation of a commonly accepted safe practice or procedure: like improper lifting, incorrect mixing of materials, working under suspended loads, pouring chemicals too fast or adding them incorrectly or at the wrong time, or allowing equipment to operate while making repairs
Performing operations without previous training or permission
Removing safety devices or making them inoperative
Operating at unsafe speeds
Using unsafe tools
Horseplay or other acts which distract attention
Failure to use personal protective devices or equipment
Failure to follow standard practices and procedures established for plant operation
Flagrant disregard of danger
Inattention to the job at hand
Undue haste and impatience
Distraction
Indifference or resentment of authority
Smoking in unauthorized areas

Correction of unsafe acts or behavior and of the underlying causes lies squarely in the hands of first-line supervision. The supervisor may choose counseling, retraining, discipline, or a combination of these methods but he cannot allow unsafe acts to continue. The employee who persists in such behavior patterns is statistically certain to injure himself or someone else.

Deal Through Lines of Organization

In dealing with departmental problems it is necessary to work through the supervisor, because he is the one who is responsible for production and for his employees and equipment. It is always best to go through regular organizational channels in order to get willing cooperation. The extent to which management and supervision believe in the need of safe operations and the sincerity and consideration given the problems has a direct bearing on the success of the plan and determines the attitude of the entire organization.

Never has there been a safety device or a safety program that some human being could not disrupt or impair. The total working atmosphere must be considered for man controls his environment. Everything which makes it warm, friendly, pleasant, and secure contributes to safety and the cooperation to prevent accidents.

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4. H. W. Heinrich, "Industrial Accident Prevention," 3rd ed., McGraw-Hill, New York, 1963.

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14

Impact of Occupational Medicine on Safety

D. J. Kilian, M.D.

A common feeling is prevalent in the small chemical plant, that the scope of occupational medicine[1, 2] is limited only to the treatment of occupational injuries, diseases, and necessary emergency care of personal illnesses. As long as this limiting concept remains, occupational medicine will have little to offer the field of safety in the chemical industry. Many times management does not have a full understanding of the contribution of a good occupational health program. Their

TABLE 14. 1. A Dynamic Occupational Medicine Program

What most people think

1. Treatment of injuries and illnesses

Actual

2. Preventive Medicine
   - *A*. Periodic physical exams.
   - *B*. Environmental health
   - *C*. Education

3. Rehabilitation

4. Mental Health
   - *A*. Counseling
   - *B*. Rehabilitation
   - *C*. Education

5. Disaster Planning

6. Consultations with Management
   - *A*. Absenteeism
   - *B*. Alcoholism
   - *C*. Insurance
   - *D*. Other

7. Research
   - *A*. Toxicology
   - *B*. Occupational disease
   - *C*. Epidemiology
   - *D*. Insurance statistics

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fears of "empire building" and their inability to exercise proper controls in a field completely foreign to them may overshadow their realization of the potential of a good program (see Table 14.1). The full or part time industrial physician may fail to realize that prevention of industrial injuries is as much a part of preventive medicine as prevention of industrial diseases through proper environmental controls. In this chapter will be discussed ways that the industrial physician and other members of his department can contribute to the field of safety.

14.1. RELATIONSHIP BETWEEN THE SAFETY ENGINEER AND THE INDUSTRIAL PHYSICIAN

Far too often there exists a lack of understanding and communication between the safety engineer and the industrial physician. Each feels that the other does not have a true understanding of his problems. The occupational physician may feel that the safety engineer is far more interested in numbers as a record rather than the actual injury to the individual. On the other hand, the safety engineer may feel that the treating physician does not appreciate that the maintenance of a good safety record is one of the most dynamic forces in motivating employees to work safely and to prevent accidents and injuries. A resolution of these differences is essential before a plant can have a truly progressive safety program.

It should be apparent to the industrial physician that the safety engineer is a front-line ambassador of good will for his services in the plant. On the other hand the safety engineer should realize that medicine is an inexact science where experience, training, and attitude give rise to honest differences of opinion as to the choice of treatment and the injured employee's ability to work. To exploit these honest differences is one of the surest ways of destroying good working relationships between the medical and safety departments. Setting aside a portion of time each month for better communications would do wonders at improving this relationship and developing understanding of common problems.

14.2. TREATMENT OF OCCUPATIONAL ILLNESSES AND INJURIES

Treatment facilities and the people who staff them have an important bearing upon the safety record of any particular plant. It is usually within the walls of these facilities where the most accurate

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history and accountability for an accident are really obtained. It has been the experience of every occupational physician of obtaining an accurate history while treating the patient then later seeing this history distorted by various participants in the safety appraisal of trying to determine the responsibility of the accident. Again the communication between the occupational physician and the safety engineer is vitally important if the true causes and preventive aspects of industrial injuries are to be uncovered.

Convenient medical facilities and an enlightened attitude by management is necessary to keep minor injuries from becoming complicated and turning into major disabilities. Many times a small burn has become infected and resulted in a lost-time accident due to the employee's delay in seeking medical treatment because of fear of condemnation from his fellow employees or his supervisor. For this reason, using minor injuries as an index of safety performance within a department is an unwise procedure. It may lead to a reluctance on the part of the worker to report his injury. Departmental indexes of safety performance should be based on the severity of the injury and the potential serious injury rather than numbers of minor injuries reported to the industrial medical clinic.

Physicians have long been disturbed by the emphasis that is given to the lost-time injury of a man who loses a small fragment of bone from the tip of his finger in a relatively minor incident, and the lack of attention to an incident such as an explosion blowing a propelled piece of metal past an individual and only scratching him. In this instance a few millimeters position in space by chance was the difference between life and death, but because it was not recorded as a "lost timer" it was soon forgotten and seldom reviewed.

Medical personnel can be a valuable adjunct to the total safety effort by being alert and understanding the need for safety protection and safety vigilance. This must be done skillfully in a nonpreaching, noncondemning manner that will teach a lesson rather than alienate the feelings of the worker. For example, it is ridiculous for an industrial nurse to tell a man with a broken toe that he should have been wearing safety shoes. Nobody is more painfully aware of this fact than the man with the broken toe. Comments of this nature only serve to make the individual defensive and consequently unreceptive to good safety counseling. If that same nurse would devote this same energy at recognizing the lack of foot protection at a time when the man's foot was not injured, far more would be accomplished. Medical personnel represents a powerful voice of authority when it comes to advice regarding safety. The employee recognizes that medical staff

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members have had first-hand experience with injuries resulting from lack of safety protection.

Chemical Exposure

One of the "gray areas" which many times creates problems is in accurately determining whether loss of time from the job is due to a chemical exposure or to a superimposed personal illness. A good example is when a man has been working around benzene, does not give a history of any unusual exposure, but becomes nauseated and has to be off the job for a few days. Another example is an individual who inhales a minimal amount of an irritating gas such as chlorine or sulfur dioxide and develops an upper respiratory infection which necessitates loss of time. In both instances the occupational physician is hard pressed to make an accurate decision because of the lack of real objective evidence upon which he can base his judgment. Invariably, too much time elapses before the environment can be monitored to determine the concentration of the material to which he was exposed.

Within the past few years a number of useful tests have been developed which take many of these situations out of the area of speculation and give the physician real objective laboratory evidence to help in this situation. Figure 14.1 is such an example and is called the forced expirogram.* This is a timed vital-capacity measurement and shows the sequence of events from a chlorine exposure and demonstrates objective evidence of the physiological response of the human body to this particular irritating gas. Chlorine produces a temporary spasm for constriction of the air passages in the lungs and consequently restricts the rate at which the individual can exhale the air from his lungs. It can be seen in Fig. 14.1 that there is not only a reduction in total amount of air expired but also a slowing down of the rate that it can be expired.

This and other objective tests such as the use of serum transaminases after exposure to many organic chemicals provides the physician with valuable evidence to judge the true nature of a person's disability.

Pre-Employment Examinations

Uncovering physical defects that may play a role in the future safety performance of a prospective employee is one of the main ob-

* Collins Vitalometer expirogram record, Warren E. Collins, Inc., 555 Huntington Ave., Boston, Mass.

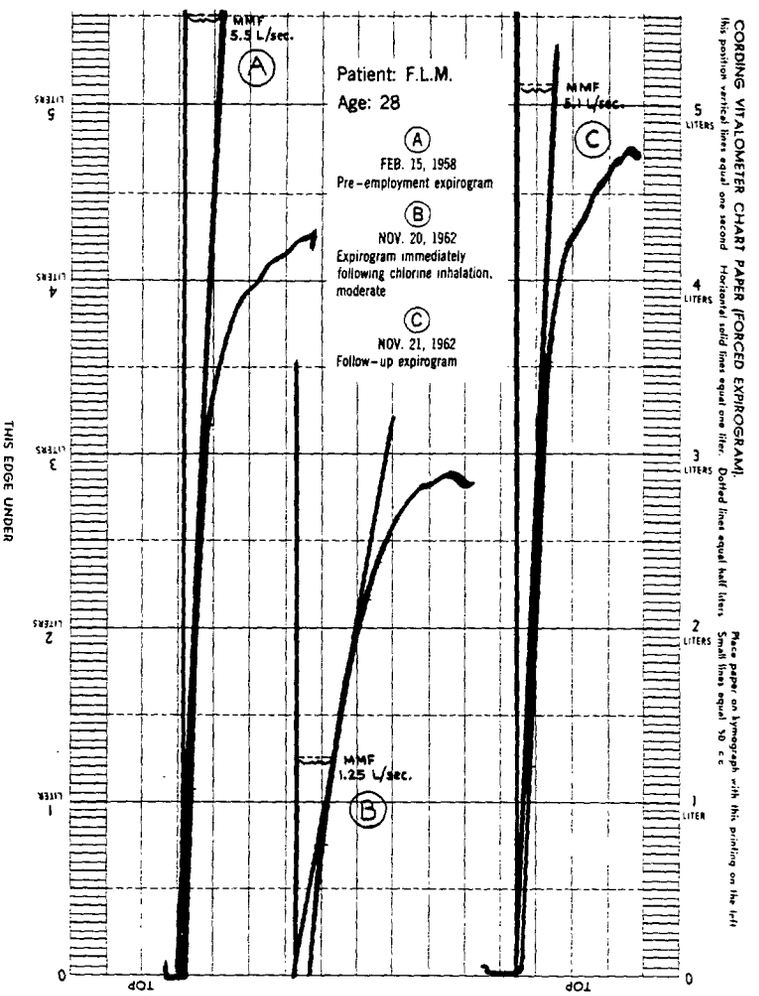

FIG. 14.1. Expirogram record.

jectives of the preemployment physical examination. However, only a small percentage of applicants who are examined in a good preemployment examination are found to be perfect specimens. Most people have one or more minor defects. They are overweight, have visual defects, some difficulty of hearing, allergy, or an unstable blood

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pressure. At the time of the examination these may not be judged serious, but because they are potential problems the new employee's supervisor should be informed.

Frequently there is a lack of communication between the medical department and the new employee's supervisor regarding these minor defects so numerous companies have found it advantageous to devise a profile system to let the supervisor know what some of these significant defects are. For example, a prospective employee might be almost blind without his glasses and pass the pre-employment testing with flying colors because his vision was examined while he was wearing his glasses. He might then report to the job without his glasses and be a serious safety hazard unless this communication between the medical department and supervision was operating. Within the Dow Chemical Company a profile system is used which was developed by Dr. Harold Gordon* and patterned after the armed forces PUHLES system. This system is called the PESREP profile system which is an abbreviation for the following categories: physique, extremities, skin, respiratory, eyes, and psyche. The physician grades each category from one to five depending upon the severity of the physical defect and a copy of this profile is then sent to the personnel office and to the prospective employees' supervisor. This establishes the communication link that is so important and yet does not break down any of the confidential medical information that should be maintained as only those defects that directly affect work performance are included.

There is a great trend in industry to slice up the prospective employee into various jigsaw pieces and test each piece independently. The various pieces may be a security check, check of his social status, personnel interview, physical examination, temperament testing, I. Q. testing, mechanical aptitude testing, lie detector test, plus many future tests which will beguile the imagination and probably divide the person into smaller jigsaw pieces. Each of these things are important but it is distressing to see how infrequently the man is evaluated as a whole unit instead of in various pieces. Dr. W. Donald Ross, an associate professor of psychiatry at the University of Cincinnati, brings out in his book *Practical Psychiatry For Industrial Physicians*[3] that lumbar X-ray results when evaluated with psychological testing are far more meaningful than when evaluated alone. Industry should spend more time putting the pieces back together and interrelating the results.

* Harold Gordon, M.D., Medical Director, Midland Division, Dow Chemical Co., Midland, Mich.

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Periodic Physical Examination Program

There is scarcely a segment of the chemical industry where the employees do not come in contact with toxic or injury-producing materials that are often insidious in their disease-producing ability. By the time these occupational diseases give rise to definite symptoms that are noticeable to the workman, it may too late to do an effective job of reversing the disease process. For this reason periodic physical examinations are a necessity in some areas.

The safety engineer can be of invaluable assistance to the occupational physician by making him aware of the job demands and chemical exposures encountered in various areas. Many times the results of these periodic examinations must be evaluated statistically to determine the exact reason for the employee's disability. For example, if a physician had examined a group of twenty paint sprayers and found evidence of chronic lung disease in one, he will be hard pressed to draw a conclusion definitely establishing the respiratory exposure to the disability since this condition might be due to something totally unrelated to plant exposure. On the other hand, if he found ten people with respiratory abnormalities, there could be no denial that the job in question would be incriminated unless proven otherwise. This is one of the soul-searching problems in interpreting the results of periodic physical examinations as this enters the field of statistical significance, opinion, and frequently, disagreement.

EDUCATIONAL

One real problem that faces any safety program is the lack of interesting material relative to safety that is available for presentations. This is an area where the occupational physician can be of great benefit since nobody has seen more of the sadness and heartbreak from poor safety practices then the physician himself. Because of these facts he is regarded as an authority and his words fall upon receptive ears. It would be ideal if the physician could devote a great deal of his time giving talks in the plant, but unfortunately other demands of his medical practice have priority over personal appearances. Some physicians have solved this problem by presenting material by slides and tape recordings[4] and Fig. 14.2 illustrates a sample slide along with the written commentary that may be used in such instances.

Another area where the medical department can make a valuable

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FIG. 14.2. Photograph of an eye (35 mm color transparency). A representative case of a chemical burn to the eye over 20 years ago with no impairment of vision but with permanent loss of many of the eyelashes on the lower lid.

contribution lies in the field of advanced first aid training since the chemical industry has unique problems relative to first aid that are not covered in the standard first aid courses. Ideally a physician should train a selected group as teachers to instruct all of the plant personnel. Again the liberal use of slides and tape recordings made by the physician can be of great benefit.

REHABILITATION

One of the most positive and humane benefits that occupational medicine can contribute to the total safety effort lies in the field of rehabilitation and proper placement of disabled employees. Whether their disability is from an occupational or a personal illness, the end result in most instances is the same—a lack of productivity to the company involved and economic loss to the worker. In rehabilitating an employee back to a job, the cardinal principle to remember is that "you benefit neither the employee nor the company unless you can place him on a job where he is productive and earning his pay." Creating a job just as an excuse to pay a man invariably leads to a disgruntled employee because of the subtle but powerful and emotional condemnation by those employees around him. We must remember that all workmen have certain basic emotional needs on the job. They need to feel accepted by co-workers and must maintain an inner feeling of security by earning their salt rather than being a charity case. Unless a man feels productive an improper job transfer is only a temporary solution at best.

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The safety engineer as well as the industrial physician should work with the personnel department in effecting proper job transfers. The fundamental role of the industrial physician in this sphere is to evaluate the mental and physical abilities and outline those work restrictions which are necessary in order to avoid future disability. Because of the time pressures of his medical practice he usually does not have an intimate knowledge of each job requirement. On the other hand the safety engineer is in an enviable position of knowing more about job requirements and potential job transfers than any other single person in the plant because of his field work and working relationships with supervisors. Unfortunately, most safety engineers do not consider this within the scope of their activities.

A workable program of rehabilitation and proper job assignment is often impossible because of existing labor contracts, seniority rights, economic losses to the individual by changing to a job of lesser skill or lower classification, and to plain old lack of human motivation and doing nothing until an accident happens. The latter reason is an old story to the safety man and should point out the necessity for continuing pressure to break down these obstacles.

The field of rehabilitation and proper job placement is frequently frustrating and unrewarding but like so many other problems with human beings, the difficult ones are the truly important ones. In Table 14.2 we see a suggested systematized approach to rehabilitation and proper job placement.

TABLE 14.2. Rehabilitation

Steps Involved	*Personnel Involved*
1. Recognition of problem	Worker, supervision, medical, safety, and labor relations
2. Attempt to transfer with existing physical defects	Worker, personnel, safety, and labor relations
3. More intensive appraisal of worker to determine his best points as well as disability	Worker, medical, and clinical psychologist
4. Referral to special group for placement	Worker, handicap committee supervision, medical, safety, labor relations, and psychologist
5. Retraining	Worker, occupational therapist, and safety

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Psychological Counseling

Mental illness is the number one problem of our society at this time. Statistically, one out of every ten individuals in the United States will be hospitalized sometime during their lifetime for treatment of mental illness. This leaves little doubt as to the impact of this problem on the field of safety. In this field there are a great many unknown and erroneous concepts concerning the emotionally ill and their relationship to the safety program. The chronic alcoholic who is generally thought to be a serious threat to the safety record is, in most instances, a careful worker because of his fear that an accident will lead to the discovery of his alcoholism and subsequent disciplinary action. Absenteeism is the real problem associated with alcoholism.

Another general concept concerns the acutely disturbed individual who has outward manifestations of emotional turmoil. His fellow employees are fearful that he might "blow up the plant," but surprisingly enough he is rarely associated with a serious occupational injury during this disturbed period of time.

Perhaps the most overlooked but most significant hazard is the man whose outward appearance is one of serenity, but who is harboring profound psychological problems which may manifest themselves in an occupational injury (Fig. 14.3). In a situation such as this it is frequently found that the injury and the subsequent disability play a very definite role in solving that particular man's problems. Many people fail to appreciate the role that the work situation plays in individuals with emotional breakdowns. Dr. H. Levinson, director of the Industrial Medical Health section of the Menninger Foundation, stresses that the majority of the industrial accidents occur in people who have these underlying emotional problems.[5]

Mental illness, which is not clearly black or white, is difficult to accept in many instances. Much more research is needed in this particular field as it applies to safety, but recognition that these factors do play a role in accidents and dissemination of this knowledge by the safety engineer may contribute to improvement in the safety record.

ACCIDENT PRONE

The phrase "accident prone" is a sad and tired quotation conceived many years ago by individuals who felt they could establish certain

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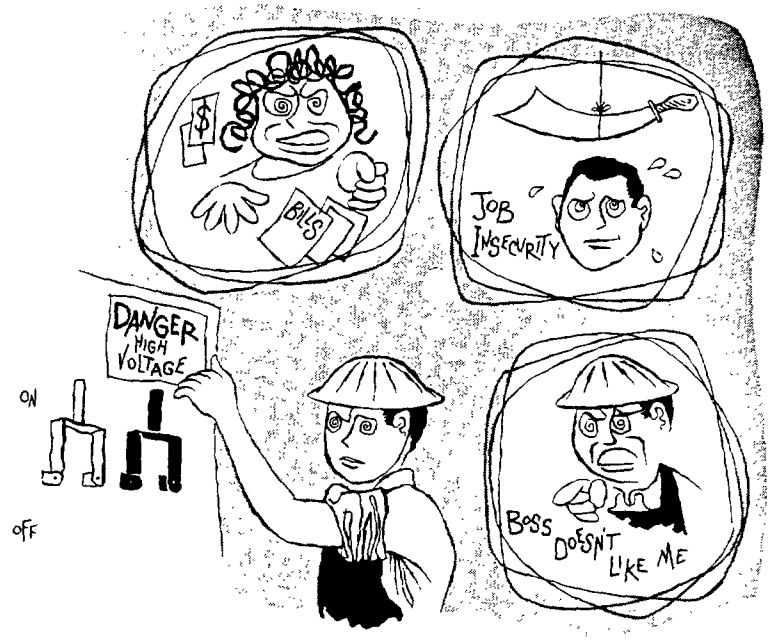

FIG. 14.3. Emotional anxieties.

criterion from past behavior and accurately predict accidents in the future. Unfortunately, a careful statistical approach by those who actually deal and treat accident cases fails to bear out these predictions. Psychiatrists and psychoanalysts who represent the highest degree of training in understanding the human mind almost always refuse to "go out on a limb" and predict definite future behavior in their patients. Realizing this, it becomes somewhat absurd to compile a few figures on numbers of minor injuries of an individual, stir it in the pot with some brief psychological testing, season it with some crystal ball gazing, and come up with a resultant diagnosis and stigma of "accident prone" on a workman.

An unpublished experience of the author involved an examination of the "accident prone" concept in a chemical plant with more than 8000 employees. The ten "thickest" medical charts (or those individuals who had reported the most injuries) were pulled and examined on the preconceived notion that these certainly must be the accident prone individuals because of the frequency of their medical visits. Their cases were reviewed by a physician, a clinical psychologist, and the individual's supervisor. A determination was made

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of the emotional stability of each case and the supervisor was asked his opinion as to the risk of serious injury in each case. The results were just the opposite of what would be expected. All of these individuals with frequent medical department visits were good, solid citizens with stable personalities. They were good workers. They were very consciously following the plant safety rules of reporting every injury to the letter. How unfortunate it would be to label these individuals "accident prone" as a reward for strictly adhering to company rules. It has been the author's experience that most individuals who have disabling injuries are relative strangers to the medical department. This experience certainly does not fit with the concept that most people in management have regarding the accident prone individual.[6]

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15

The Role of The Nurse in Chemical Plant Safety

Eleanor Mort, R.N.

Occupational health has been defined as "the application of public health principles, and medical, nursing, and engineering practice for the purpose of conserving, promoting and restoring the health and effectiveness of workers through their place of employment."[1] Safety programs are directed primarily toward the first of these aims—the conservation of health, while the health service personnel are chiefly concerned with promoting and restoring health. However, the health and safety personnel alone can only implement the kind of program management wants. They must have the cooperation of production supervisors and foremen, and through them the active participation of all employees in order to maintain a truly effective occupational health program.

The number and variety of personnel making up the occupational health team varies with the size of the industry. Some organizations have a large full-time staff of doctors, nurses, and safety and industrial hygiene specialists. In many places, however, there may be two or more full-time nurses and a number of full-time safety personnel; but the medical direction is provided by a doctor who has a private practice and spends only an hour or two a day at the plant. Relatively few of the nurses working in industry today have had any formal training in occupational health. This is also true of a great many part-time physicians. They both very often learn this different phase of their

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FIG. 15.1. The anatomy of chemical equipment should be as familiar to the plant nurse as the anatomy of her patients. Courtesy Rohm & Haas Co.

profession while working together to solve the problems and cope with the situations which arise. This is not the usual doctor-nurse relationship. Caring for ill people in a hospital, the doctor gives orders and the nurse carries them out. In the industrial environment, however, since the nurse has much more opportunity to become acquainted with the plant, the people in it, and the work hazards involved, the part-time physician must depend on her to a considerable degree for both information and communication. Since they are essentially dealing with healthy people, they establish a "collaborative relationship"[2] wherein they continuously work together to further the objectives of a good occupational program.

The industrial nurse who works without direct medical supervision a great deal of the time must be ever alert to the danger of assuming functions which either legally or by professional training belong to the physician. It is essential that she have specific procedures and orders written by the plant physician covering all the more common occupational and nonoccupational conditions with which she may be con-

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fronted. The nurse in a chemical plant has a special responsibility to insure that the procedure book contains an accurate and up-to-date description of all chemicals made or used in the plant including intermediate substances formed at various stages, and also possible by-products, with the circumstances under which they may occur—such as the possible formation and evolution of hydrogen sulfide from hydrolysis or acidification of sulfides or sulfhydrates; or phosgene from trichloroethylene on contact with heat or flame. The building or location in which each substance may be encountered should be noted. The signs and symptoms of both acute and chronic toxicity should be listed, along with modes of entry into the body. Engineering methods of control such as special ventilation or enclosure of process should be included, as well as safety precautions to be observed, as for instance all rubber clothing when working with hydrofluoric acid.[3]

FIG. 15.2. Industrial nurse participates in fire fighting practice session at the plant fire grounds. Courtesy Rohm & Haas Co.

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In addition to engineering and safety controls, medical restrictions should be enumerated. Asthmatics and people with other respiratory diseases should not work where they might be exposed to chlorine or other respiratory irritants. A small amount of chlorine in the air which might make the average person cough for a few minutes could irritate an asthmatic so severely that he would require medical treatment. Specific instructions by the plant physician for the first-aid treatment of the corrosive, irritating, or toxic effects of each chemical substance should also be included. Nowhere is the knowledge and application of prompt first aid more important than in a chemical plant. In the event of a chemical eye burn or body burn, whatever can possibly be done to lessen the severity of the burn must be done immediately. Nothing that anyone can do later can reverse the tissue damage which has already occurred if swift, thorough flushing with copious amounts of water has not been carried out. The beneficial effects of cold water on chemical burns, following the initial flushing, have been equally as dramatic as the spectacular results achieved with the cold water treatment of thermal burns—the effectiveness of which is in direct ratio to the speed with which the hypothermia is accomplished and the length of time it is adequately maintained.

Compiling a complete and accurate chart such as Table 15.1 requires the cooperative efforts of not only the medical and safety sections, but research and production personnel as well. Valuable information concerning the practical everyday problems of handling a specific substance can be learned by talking with the man who does just that for 8 hr a day. The completed data form a ready source of reference, and they are particularly valuable in the indoctrination of new people in both the medical and safety departments. For a doctor or nurse relieving for vacations or illness it is indispensable both for refreshing their knowledge and for bringing them up-to-date on any new chemicals or procedures.

Every contingency cannot be covered by a standing order. Most work forces consist of a cross section of the population and anything can happen to them that can happen to people anywhere. A nurse never makes a medical diagnosis, but since the occupational health nurse usually sees the ill or injured person before he is seen by a doctor, she must be capable of making a competent nursing diagnosis. If every person who came to the plant hospital were sent to a doctor, a great many manhours of work would be wasted—and there would be no need for a nurse.

In order to make a skillful nursing diagnosis the nurse must constantly use her eyes, her ears, and all her trained powers of observation.

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TABLE 15.1. Sample Reference Card for Chemicals

Chemical	*Bldg.*	*Mode of Entry*	*Toxic Signs and Symptoms*	*First-Aid Treatment*	*Methods of Control*
Benzene or Benzol		Inhalation (most dangerous)	Acute: Anesthetic headache excitement confusion hysterical symptoms Severe Cases: collapse unconsciousness death Chronic: Symptoms vary depending on susceptibility, degree and duration of exposure: headache, dizziness, irritability, restless sleep, tremors, dry mouth and throat, hemorrhages, progressive reduction RBC and WBC, severe, even fatal, anemia	Remove from exposure Bed rest Keep warm and quiet Respirations ceased Institute rescue breathing immediately If breathing—100% O_2 administered under 4 cm positive exhalation pressure 30 min periods every hour 3 hr Remove all contaminated clothing. Cleanse skin as soon as possible Usually complete recovery from single exposure Remove from exposure Require medical care	Engineering: isolation special equipment and design Enclosure adequate ventilation Prevent toxic and/or explosive accumulation Safety: employee education periodic vapor concentration test Medical: 1. Preplacement exam includes blood count No less than: WBC, 4000 RBC, 4,000,000 Hb, 12 gm/100 cc 2. Periodic blood examination
		Ingestion	Tablespoonful known to cause extremely acute symptoms, as above	Induce vomiting Prompt medical aid	
		Absorption	Very slight		

From: M.C.A. Chemical Safety Data Sheet SD-2, Benzene.[9]

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Even what may seem to be a simple request for an aspirin or something for an upset stomach can never be granted casually. Enough information must always be obtained to accurately evaluate the seriousness of the complaint. The response to just a few questions may indicate that the present distress was probably caused by overindulgence and lack of sleep. On the other hand, suggestions of a more deeply rooted disturbance may gradually emerge. A comprehensive history, plus a detailed report of all symptoms, and a record of all vital signs observed by the nurse can be of considerable value, both to the doctor in diagnosing the condition and also to the safety personnel in the case of a work-connected disability. In the modern-day chemical plant new materials are constantly being introduced. The full toxic effects on the human body of many of these substances are sometimes not known. Keen observation by the occupational health nurse combined with accurate recording could be of considerable significance in epidemiological studies.

In order to sustain an effective safety program directed toward the conservation of the health of the workers it is important that they first be physically capable of doing the required work. This necessitates a comprehensive health evaluation plan which should include preplacement, return to work, and periodic examinations for those exposed to toxic materials. There are also a number of other occasions when a health evaluation is desirable such as when transferring from one job to another or at retirement. The physician is responsible for the health evaluation program. Realistic, well-defined policies must be worked out with management concerning such things as the kind of examinations to be made and where, when, and how often; when the nurse may return a worker to his job after being absent due to illness or injury; and when he should be seen by the plant physician. Once agreed upon, all policies should be written down. Written policies concerning the health-evaluation program can also be of great value in enlisting union cooperation in protecting the health of members.

The nurse plays an important part in the health evaluation program. She frequently takes the preliminary health history and performs certain screening tests such as vision and hearing. She usually schedules the periodic examinations, and talks with the employee returning to work. Each of these health interviews affords her an excellent opportunity to add any pertinent information to his health record, establish rapport with the employee, convey to him her sincere interest in his health and welfare, and to either initiate or continue a health-education program with special emphasis on how to work safely with chemicals. If there can be said to be any one outstanding principle governing the

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FIG. 15.3. Industrial nurse checks blood pressure of employee. Blood pressure measurements have been used in studies of chemical exposure, as well as more routine index of health. Courtesy General Electric Co. Research Laboratory.

safe handling of chemicals it is cleanliness. This includes everything from good personal hygiene to careful work habits and good housekeeping. The importance of a thorough shower everyday and frequent changes of work clothes, including underclothing, cannot be stressed too often or too strongly. Some chemicals, if not removed from the skin or clothes by thorough cleansing, can be very irritating to the skin; while others may be absorbed into the body. Nothing affords greater protection from both chemicals and harmful organisms than a clean, healthy, unbroken skin surface.

Everyone working with chemicals must be impressed with the urgent need for proper skin cleansing and covering of any break in its continuity. According to a pamphlet published by the United States Department of Health, Education, and Welfare, and the United States Department of Labor, "Dermatitis is the most common occupational disease that attacks the working man. But if every workman could be brought to realize how important a healthy skin is to his well-being, there would be far fewer cases of skin disease. . . . In such heavily

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industrialized states as New York, Ohio, and Illinois two-thirds of all compensated occupational diseases are skin diseases."[4] Chemicals can be handled safely if they are handled properly. Lack of cleanliness and careless work habits are dangerous and should not be tolerated in a chemical plant.

The more knowledge the nurse in the chemical plant has concerning the various substances used and made, the processes involved, the work environment, and the engineering, safety, and medical controls necessary for the safe handling of each, the more effective she can be both in promoting the health of the workers, and also in aiding the safety department in their efforts to conserve health. Familiarity with the effects of a certain chemical and the prompt instigation of prescribed first aid can appreciably lessen the severity of an injury. A thorough acquaintance with toxic symptoms will help in the recognition

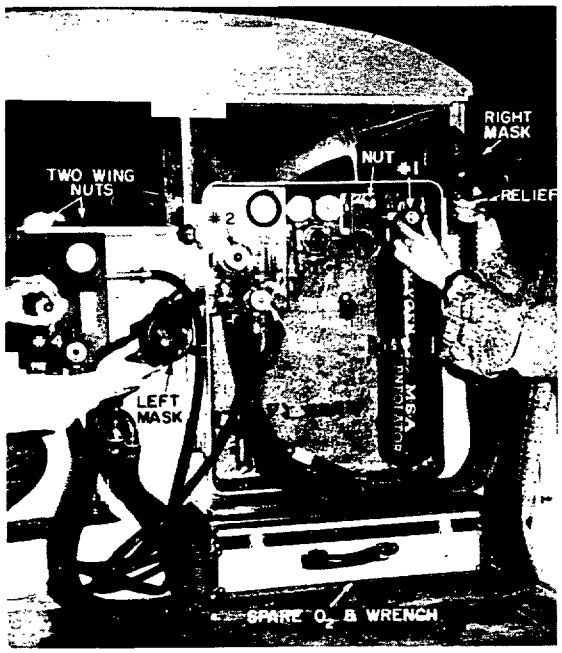

FIG. 15.4. Industrial nurse and safety engineer check the oxygen administration equipment installed in plant ambulance, which provides oxygen for two patients. Such equipment must be thoroughly understood by the nurse as well as by other emergency control personnel. Courtesy General Electric Co. Research Laboratory.

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of any early signs of trouble. In many instances this is the first indication the safety department has that there has been a break in the established safe-working procedure for a certain process, and the difficulty can be corrected before a more serious situation develops. In her day-to-day contacts with the worker, as she talks with him about his job, the occupational health nurse can better ascertain how well an employee understands and is conscientiously applying safe-working procedures if she is well informed concerning the hazards and problems involved, and the various engineering and safety measures used to control them.[5, 6, 7]

Formal first-aid classes are sometimes difficult to schedule in a busy plant, but a large number of the workers in all departments throughout the plant trained in proper first aid can be extremely valu-

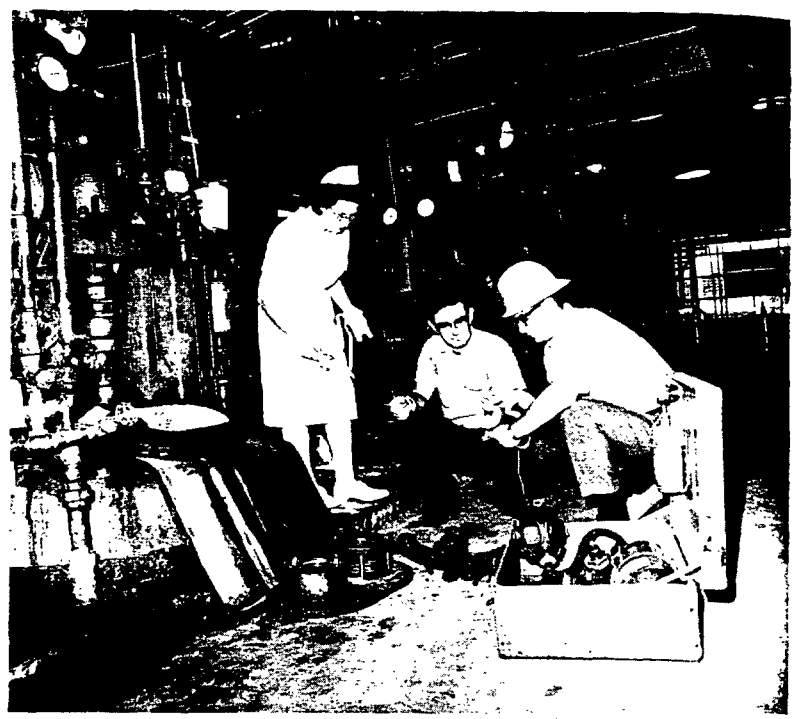

FIG. 15.5. Industrial nurse gives on-the-job instructions in the use of rescue kit designed to aid in rescue of man from a reaction kettle. Courtesy Rohm & Haas Co.

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able. It is well known that first aid training makes people infinitely more safety minded. Furthermore, when accidents happen, particularly involving chemicals, swift appropriate measures carried out by the people in the immediate area can appreciably lessen the severity of the injury—and even save lives.[8]

The tremendously rapid development and use of new chemical compounds in our modern environment presents a continuously greater challenge to the occupational health teams in today's chemical plants. As a member of the team, the nurse plays a vital role in helping to develop and maintain a program which is realistic in its recognition of the many production problems in this highly competitive industry; and yet is effectual in providing the means for "conserving, promoting, and restoring the health and effectiveness of workers."[1] The opportunity to participate in the exciting development and production of fascinating new materials and products makes nursing in a chemical plant one of the most stimulating in the whole field of occupational health.

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16

Effects of Toxic Agents

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The concept "safety" cannot be defined in a positive way, but only as the absence of its converse, "unsafety." Safety cannot be measured except as the risk, that is, the probability of injury, immediate or foreseeable. Safety has the same connotation regardless of the field of human activity under study. The means of achieving it and the results of failure of achievement, of course, will vary with the possible source of "unsafety."

This book is concerned with problems of the chemical industry. A major source of risk of injury lies in the chemicals used or made. The places in which risk may exist include all those in which a worker might come into contact with chemicals—the research laboratory, the control laboratory, the pilot plant, the major manufacturing plant in all areas into which chemicals can enter.

We emphasize laboratories as a site of risk of injury because in many years of industrial work, in visits of inspection to many chemical installations of widely differing programs and goals, we have, in general, found far less attention paid to safe practices in laboratories than in main production areas. Yet the laboratory is the place of birth of all new chemicals and the laboratory worker is the first to be exposed to any injury of which the new material might be capable.

In thinking back over our own chemical training in high school, undergraduate and graduate schools, we cannot remember ever receiving any warning about health hazards from chemicals or any instruction on safe procedures. In the many hundreds of original articles in

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English, French, or German, which we have read in all fields of chemistry, we cannot remember any specific warning except as to flammability or explosiveness.

Programs of safety in the manufacture of chemicals are relatively new. In this country many date only from the beginning of World War II. Yet the possibility of serious harm from chemicals was made known to the world by the newspaper reports of the first German "gas attacks" on the French and British armies in May, 1916. These accounts and similar reports of subsequent attacks, often exaggerated for propaganda, concerned chemicals affecting the lungs and the skin —chlorine, phosgene, and "mustard." These were the only known efficient "war gases." The horrendous newspaper tales still persist in public memory so that even today people are more concerned over incidents in which chlorine is accidentally released or could be released from cylinders or tank cars than in possibly greater hazards from other chemicals.

This general disregard of the health hazard from any but the "war gases" existed even as late as the beginning of World War II. All major nations engaged in the first great conflict conducted active research to find new chemicals with which to incapacitate the enemy or to deny him access to important terrain. Accidental exposure of military and civilian personnel to chemicals other than war gases gave much valuable information. But this was "classified" and never appeared in literature accessible to the public.

The United States Navy, from bitter experience with fires in gun turrets, knew of the dangers of gases and fumes generated from cordite burning in confined spaces and by research traced the hazard to nitrogen oxides from nitrocellulose. But this information was not readily available to physicians treating victims of the Cleveland Clinic fire in 1932. In that fire many patients, doctors, and nurses died after breathing oxides of nitrogen evolved from burning X-ray films (made with a nitrocellulose base) or a mixture of these oxides with carbon monoxide.

Even today many chemists do not realize the hazards of a carelessly operated nitration reaction, and many raise their eyebrows when told that hydrogen sulfide, that valuable simple reagent used even in high school laboratories in inorganic analysis, shares with carbon monoxide the record as the greatest chemical killer of all time.

Was this disregard of safety due to ignorance or to familiarity which "breeds contempt?" Was it thought that the relatively small quantities of individual chemicals used or stored in the laboratory reduced any risk to a negligible level? Why was it considered that only "war"

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gases were hazardous and the "peace" gases not worthy of consideration? Chemicals can injure in microgram quantities. A man can be killed by a shot from a 25-caliber pistol as easily as from a burst of a 16-in. shell.

This indifference to safety in chemical laboratories is diminishing. Perhaps this is because we are now waging war on insect pests and the chemists making new insecticides may suspect that a chemical which will kill an aphid or a red spider or a mosquito might not have a very salutary effect upon a chemist.

This chapter will indicate, with suitable examples, some of the risks inherent in chemicals if they are used carelessly and describe situations in which risk arises and outline general methods for its reduction.

This is not a chapter on toxicology. Safety in the use and making of chemicals is not assured by perusal of manuals on toxicology or detailed knowledge of ultimate medical effects of "unsafety." Luckily, safety can be attained by a much easier route, for existing texts on toxicology deal mostly with adverse effects of chemicals on laboratory animals, which are not necessarily the same as the effects on humans. They can consider only a small fraction of the many thousands of chemicals available and can seldom predict the possible physiological action of those yet "unborn."

We would emphasize that the function of a safety program is "prevention." No amount of knowledge, even if obtainable, on the ultimate disease pattern which might be produced by a chemical will necessarily insure safety in its use. The view so often expressed that it is difficult for a small company to insure safety because it cannot afford expensive toxicological studies is based on a fallacy. Currently hundreds and thousands of chemicals are made and used. All the toxicological laboratories in the world working around the clock on each day of each year could not accumulate more than a miniscule of knowledge on the toxicology of one per cent of them. And how is safety to be established while this minute amount of knowledge is being gathered?

As a group the chemical manufacturers of the United States have established a highly creditable record of industrial safety despite the paucity of detailed knowledge of toxicology.

Physical State a Factor in Exposure

Safety can be assured only by a carefully planned program which considers all conceivable ways in which the tools to be used, manual, mechanical or chemical, might offer health hazards, plus those factors

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in the work terrain which could accentuate the hazard or spread it to other parts of the work area or even beyond plant limits.

When the tools are chemicals this matter of terrain may be as important as that of the potential hazard at the point of their original use or production.

A carpenter's hammer is not expected, of its own accord, to drive nails into a plank or to crush the finger of the carpenter. An automobile is not expected, when standing on a level with the engine dead, to dart suddenly across the road into a traffic lane. But the user or maker of a chemical must expect it to move in all directions unless human agency is used to confine it. Gases and vapors diffuse everywhere. Dusts are spread by the slightest breeze. Liquids, uncontained, flow to lower levels or seep through the walls of inadequate containers. Solids may exert a vapor pressure and solids may diffuse through other solids.

This tendency of chemicals to move spontaneously unless adequately confined makes it inevitable that they may come into contact with or even enter the bodies of workers close to them. If the topography of the plant area allows, they may reach out to those not expected to be exposed or even to people living beyond the confines of the plant.

Most of the chemicals in use today or being newly made are strange to nature. The human body may not know how to handle them or may not be able to deal safely with the quantities to which it is exposed. The entry of foreign chemicals into the body may interfere with normal body functions, and so set up an opportunity for traumatic injury by mechanical tools, or it may lead to any degree of impairment of health, even to death.

Chemicals may come into contact with the skin, the outer covering of the eyes, the linings of the nose, mouth, throat, and the respiratory tract (bronchi, bronchioles, and the air sacs of the lungs), and the whole length of the digestive tract.

If presented in adequate concentration, the contacting material may act at the point of contact, or it may be absorbed into the blood stream and be distributed throughout the body. Some of the invading chemical may be destroyed by the body defenses. Some may be changed to derivatives which may be less harmful or more harmful. Some may be excreted through the kidneys and have a local action on the excretory tubules or the urinary bladder. Sometimes a particular organ may take a chemical out of the blood stream and store it, only to liberate it at a later date under stress of disease.

The possibility of contact of a chemical with any part of the body

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depends upon the physical properties of the chemical and the efficiency with which preventive measures offset these properties.

The possibility of injury at the point of contact depends upon the fundamental chemistry of the contacting substance *vis-a-vis* the chemistry of the body tissue on which it alights. All injury by chemicals, wherever it occurs, conforms to known laws of chemical reaction.

The possibility of entry of a chemical into the blood stream depends upon its solubility characteristics and the biochemistry of the surface with which it makes contact and of the tissues between this surface and the blood or lymph vessels involved in the circulation of fluids throughout the body.

The possibility of injury after invasion of the blood stream depends upon the specific chemical powers of the invader and the chemistry of organs or tissues to which it is transferred from the blood.

All these possibilities, other than that of the initial contact, can be summed up in a definition of *toxicology* as "the study of the conditions under which and the mechanisms by which a chemical, natural or synthetic, may, by virtue of chemical action, disturb function or structure of living tissues or organs and so impair health."

It is of the essence of a safety program in establishments where chemicals are used or made that initial contact with the human body be prevented or reduced to a minimum and that duration of any unavoidable contact be terminated as promptly as possible. A detailed knowledge of toxicology is not needed unless there has been failure of prevention.

Chemicals may appear in work areas as solids, of various particle sizes down to the micronic dimensions of fumes; as liquids, en masse or dispersed as mists or aerosols; and as vapors or as gases.

Solids, as large particles and at room temperature, present a physical rather than a chemical hazard. They may have sharp edges which cut or they may be ejected from machinery as missiles. The outstanding exceptions are the solid forms of the alkali metals, potassium and sodium and their hydroxides. By contact with moisture always present on the skin or the mucous membranes of the eyes and nose, these materials may cause severe injury by production of heat of reaction and concentrated alkalinity.

Solids finely divided as dusts and especially micronized dusts and fumes may be inhaled and pass down deep into the respiratory tract. Silicosis and berylliosis, the two most serious industrial lung diseases, result from breathing dust.

Liquids en masse confine their attention to the skin and the outer covering of the eye. As mists and aerosols they may enter the respir-

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atory tract. When ejected at high velocity, as may occur with hydraulic fluids, liquids can penetrate deep into the skin or the eye and cause severe injury by mechanical and chemical means.

Vapors and gases may have action upon the skin or eyes, but their usual route of hazard is the respiratory tract. Liquids, vapors, and gases may penetrate the skin and reach the blood stream. One notable exception is carbon monoxide.

Each of these states of matter requires its own consideration in a safety program aimed at prevention of contact of chemicals with any part of the human body in concentrations or total quantity capable of causing either immediate or delayed injury.

Chemicals and the Skin

Experience over many years shows that at least two-thirds of all industrial injuries due to chemicals are skin injuries. Dermatitis, whether of the simple contact type or due to allergy, while usually not of serious import, is unpleasant, uncosmetic, and may lead to much lost work time. If allergic, it may even make it advisable to change employment.

Despite the relatively mild nature of most cases of chemical dermatitis, *in toto* the result may be as great a loss of work time as that due to the common cold and a much greater disturbance of employee relations. At first thought this might seem to be an absurd situation. Men do not work naked. Is not the skin easy to protect?

Actually the most difficult problem of prevention of injury by chemicals arises when the chemicals used can act on or be absorbed by the skin. It is difficult, not so much because of lack of mechanical means of protecting the skin, as because of discomfort caused by some of these means and resistance to others.

Clothing will reduce contact with chemicals. The face and eyes can be protected by suitable masks or goggles. Many tasks can be carried out efficiently by wearing suitable gloves, many can not.

But chemicals can penetrate clothing or can be collected in clothing and form a reservoir from which they can diffuse toward and eventually reach the skin. In so doing not only do they contaminate the outer clothing but also the underclothing. The entrapment of chemicals, in particular hydrocarbon or chlorinated hydrocarbon solvents, between clothing and skin can cause severe burns.

Clothing impermeable to chemicals is also impermeable, in the reverse direction, by chemicals, in particular water, produced by the body. No man can work in completely impermeable clothing for

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more than about 20 min. Beyond this time he will suffer circulatory collapse.

Even if we solve the problem of protection of the major part of the body with clothing, we still face the problem of shoes. Leather has been the traditional material for shoes. Substitutes for leather must have one property which makes leather so suitable for foot covering. They must absorb or allow the outward passage of moisture. Nobody can long withstand failure of the removal of perspiration from the feet. Maceration of the skin, infection, and ultimately severe injury would follow any use of impermeable material for shoes. But leather can absorb many harmful materials, and leather shoes can build up and pass to the feet a dangerous reservoir of harm. Contaminated clothing, other than shoes, can usually be cleaned. But shoes cannot be decontaminated without risk of destruction. And they are too expensive to be thrown away when contaminated.

While it might seem that total prevention of contact of chemicals with the skin is not possible, it is possible to reduce to a minimum the risk of harm from that contact. The method is simple.

A program of daily showers, with change to clean underwear and clean outer protective clothing, reduces the time of contact of chemicals with the body and the possibility of absorption through the skin. This program requires adequate shower facilities as well as means for laundering discarded contaminated clothing.

This daily routine must be supplemented by more immediate action when there is spillage of strong acids which can destroy clothing, or of materials such as aliphatic and aromatic nitro- or amino-compounds, or some chlorhydrins which can very rapidly penetrate the skin, or of solvents which, when trapped between skin and clothing, can cause burns. Protection against chemicals which rapidly penetrate the skin can now be afforded by impenetrable clothing ventilated by a continuous flow of cooled air.

For many years much use has been made of "barrier" creams to prevent direct contact of chemicals especially with hands and arms. They are undoubtedly useful in many situations, but we have always had strong reservations against their unrestricted use. A barrier cream could actually become a reservoir of harmful substance from which some could reach and enter the skin. To be fully protective the cream must either be completely impermeable to the materials against which protection is desired, or it must render them inactive by strong adsorption or chemical reaction. There is, of course, a quantitative limit to the amount of contaminating chemical which a film of barrier cream can successfully repel. Further, the principle source of entry of mate-

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rials through the skin is from massage which forces them into hair follicles. No worker can refrain from handling tools or performing motions with the hands which, in fact, lead to massage of barrier cream plus any harmful chemical which it carries into the skin. A barrier cream, used without careful consideration of all circumstances of its use, may actually increase the risk of injury.

When barrier creams are used, workers often tend to think that their protection is assured. The cream, plus harmful materials it has trapped, is kept on the hands while eating, and it is allowed to stay on the skin beyond work hours. Quite often economy-minded men have allowed the cream to stay on their hands so that, at home, they can do dirty jobs such as cleaning cars or oiling and greasing mechanical tools. Thus they have not only prolonged their own possible exposure to harmful chemicals, but they have risked transferring contamination to their families and anything in their homes which they have touched.

Even if barrier creams are used, a daily program of showers and clean clothing is still an essential part of a safety program. The only certain means of preventing either direct or remote (after absorption) injury by chemicals which come into contact with the skin is the use of plenty of water aided by soap.

We emphasize *plenty* of water. The mere dipping of the hands for a second or two in a bowl of water or holding them under a stream from a faucet for an equally brief time is not adequate. This fact has a scientific explanation. With the exception of resinous materials, most chemicals can be removed from the skin by flowing water used in adequate quantity. Textbook figures on solubility in water apply only to small volumes, 100 ml or 1 l, and for these they express a saturation concentration. A forceful and continuous flow of gallons of water is quite a different matter.

Many chemicals dissolve in water with the evolution of great heat. If only a small volume of water is used to clean the skin, the heat of solution may be sufficient to cause a severe burn. But a large volume of water will absorb this heat by virtue of water's own high specific heat.

The chemical means of neutralizing or destroying chemicals on the skin should never be used. In addition to the dangers of heat of chemical reaction, there is the possibility of injury by the reagent used. We cannot successfully "back-titrate" a strong acid by an alkali without risk of injury by the alkali or a strong alkali by an acid without risk of injury by excess acid. A chemical reagent which will destroy the contaminating material may also destroy the skin.

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In rare cases it is best to remove the harmful material from the skin in two stages, first using a solvent and then following with soap and water and a final flushing with copious water. The initial cleansing with the solvent should be done quickly, and the water and soap stage reached as soon as possible. Many solvents useful in the initial cleansing may facilitate absorption through the skin, and if the contaminated area is large, sufficient material may be so absorbed in a short time to cause serious illness. A solvent alone should never be relied upon.

Protective gloves are frequently worn when chemicals are handled. Like other protective clothing, unless selected with due regard to their ability to resist the particular chemicals used, gloves may increase the hazard. Rubber gloves are protective against many acids and alkalies but not against other materials. Carbon disulfide and aliphatic and aromatic amines and nitro-compounds can either rapidly penetrate rubber, natural or artificial, or can be absorbed by it and eventually diffuse through the glove to the skin.

The best protective gloves are those which are cheap enough to be discarded when contaminated or which can be thoroughly decontaminated. Immediately after use they should be washed thoroughly, inside and out, and placed in an uncontaminated container. The careless habit of leaving gloves on dirty equipment, such as the top of a filter press, makes their use a harmful and deceptive gesture toward safety.

For a majority of chemicals, contact with the skin for a few minutes or even a few hours of the work day will be harmless if the daily routine of cleansing is employed. Others, if not promptly removed, may cause mild burns or reddening of the skin, and others may cause severe burns. But there are some compounds which without warning can react with chemical components of the skin to produce "allergens." Repeated contact for 5 to 10 days may be necessary or, in a few cases such as formaldehyde, a single severe burn might suffice. No abnormal reaction may be noted during this period of "sensitization." Then without any apparent warning, further skin contact with even a very small quantity of the chemical may lead to a violent skin reaction and even to general sickness.

Some dermatologists have held the theory that workers, initially made sensitive to chemicals such as tetryl, can be "hardened" by repeated contact. But this is not the case with many sensitizing materials, and too often it is necessary to remove workers from all possible contact with the material which has rendered them sensitive.

Chemical allergy can be a serious affliction. Treatment is often difficult. But *prevention* is simple—soap and plenty of water.

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Chemicals and the Eyes

The eyes are as vulnerable as other exposed parts of the body to chemicals in the work atmosphere. Gases, vapors, mists, and aerosols may come into contact with the cornea, the outer covering of the eye, and if irritant or corrosive may cause severe harm. But the greatest source of injury is liquid splashed into the eye, or solid particles of alkali metals or their hydroxides flying into the eye.

Actually there are very few chemicals which, except under very unusual circumstances, cause severe, permanent eye injuries. The most hazardous are strong acids and particularly strong alkalies. Sodium-hydroxide solutions are probably the major source of blindness in industry. Dimethyl sulfate is also a very dangerous material for the eyes.

As with the contact of chemicals with the skin, contact with the eyes can be successfully handled by washing the eye with flowing water. The washing should last at least 15 min. The stream of water used should not be forceful lest mechanical injury be caused. It should be emphasized that "copious" water should be used. Mere use, once or twice, of the "eye-cup" is not adequate. Currently a number of very practical eye fountains for industrial use are available, and these should be installed wherever risk of eye contamination exists.

As with the problems of chemicals and the skin, *prevention* is better than treatment. Safety glasses should be worn in any area in which chemicals are handled or stored. Suitable visors for special laboratory operations are available. Safety shields of laminated glass, tempered glass, or plastic should be placed between laboratory workers and any apparatus in which a reaction is carried out to diminish the risk of injury from explosion.

Chemicals and the Respiratory Tract

It is a fundamental fact of life that at each inspiration air is drawn through the nose and mouth and into the tree-like structure called the respiratory tract. This consists of the windpipe (the trachea), bronchi, bronchioles and the final air sacs (the alveoli). The bronchi and the smaller branching bronchioles spread like the branches and twigs of a tree and ultimately end in the leaves—the alveoli. In many ways the alveoli take on the part played by the leaves of a tree in the physical aspects of respiration. But respiration in the tree is from leaf to trunk, whereas in the human respiratory "tree"

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it is from the trunk (trachea and main bronchi) to the leaves (alveoli).

Any harmful material dispersed in the air breathed will obviously be drawn into at least part of the respiratory tract. It will come into contact at least with the lining of the nose (and perhaps the mouth) and the trachea. Its destination beyond the trachea depends upon its physical and chemical properties.

Of the usual routes of entry of chemicals into the body—through the skin, the respiratory tract, and the digestive tract—entry via the respiratory tract is potentially the most hazardous. While, for the average man, the total area of skin is not more than 2 sq m, the area of lung tissue exposed, at each inspiration, to chemical contaminants of the atmosphere may be of the order of 80 to 100 sq m. Whereas the skin is permeated with difficulty by most chemicals other than gases, the walls of the air sacs are permeated with ease by most materials and those chemicals which pass through the walls enter the blood stream and are distributed throughout the whole body.

At each inspiration about 500 cc of air reaches deep into the lungs. The volume may be increased by deep breathing during physical exertion and the frequency, per minute, with which the lung walls are exposed to this volume may also increase with physical labor.

The lining of the airway, the trachea and bronchi, is protected by two mechanisms. The surface in contact with the air is covered by a layer of mucus which traps particles and droplets entering the tract. Beneath this mucous layer innumerable cilia sweep mucus and the material it collects upward toward the mouth. By reflex action unusual quantities of mucus are coughed up and expectorated or swallowed.

It is fairly well established that particles or droplets of 5 to 10 microns diameter are dealt with by this mucus trap. Those of 3 to 5 microns are deposited on the walls of bronchi and bronchioles. Particles of 1 to 3 microns diameter are deposited directly on the walls of the alveoli. As particle size further decreases, deposition occurs less readily, and the contaminating material may be removed by simple exhalation. Small particles from $\frac{1}{10}$ to 1 micron do not easily settle out, but since they are subject to Brownian motion, they may come into contact with and be deposited on the walls of the airway and the alveoli.

Changes in the velocity and direction of air flow in the respiratory tract, and especially the turbulence produced at the numerous points of division of larger into smaller bronchi, may lead to impaction of

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even larger particles on the lining walls. In the smaller bronchi the velocity of air flow is greatly reduced, and large particles aspirated to this point may be deposited by gravity alone.

The depth to which gases, vapors, and mists may be drawn into the lungs depends to a great extent upon their solubility and ability to irritate. A highly irritant gas, such as ammonia, will react with the moist tissues into which it first comes into contact and produce such a reaction that the exposed worker will rapidly leave the contaminated area. If he is trapped and cannot leave, he may suffer acute laryngospasm and suffocate. Gases of moderate solubility may cause some irritation of the upper respiratory tract and so give warning of their presence even in low concentration. But in high concentration they may be drawn deep into the lungs in one or two breaths and have serious effects. An example is chlorine.

The most dangerous gases of all are those of low solubility and irritancy, such as phosgene and nitrogen oxides. They may be absorbed without immediate appreciable effect, but six or more hours later chemical pneumonia or pulmonary edema develops.

Recent interest in aerosols for medication has disclosed the fact that materials of even slight irritancy, inpinging on the linings of the nose or trachea, may lead to reflex constriction of the smaller air passages and a condition similar to asthma.

The term *solubility* which we have used here refers to solubility in water, but when applied to dust particles or vapors of organic solvents it may not have such a simple connotation. The respiratory tract is lined with living cells of complex chemical structure and architecture. Each cell has an outer bounding membrane composed, in its simplest form, of a "sandwich" of lipid material between two layers of protein. Passage through this membrane depends on many factors including solubility in the water of hydration of the protein and in the lipid layer of the membrane. An increase in the ratio of lipid to water solubility generally facilitates entry through the cell wall.

Inert gases, in general, easily pass directly to the alveoli and into the blood stream. The rate of absorption into the blood depends upon solubility in the blood plasma and the volume of blood flowing through the lungs in unit time. This latter factor will increase with physical activity. If these gases are taken up by any organs or tissues, absorption will go on until these tissues and the blood are saturated. No more gas can then be absorbed.

The process is reversed on removal to fresh, uncontaminated air. Gas in the venous blood flowing to the lungs is exhaled through the

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walls of the alveoli and, with depletion of saturation of the blood, gas taken up by the tissues is released into the blood stream. The complete removal of gas from the body may take many hours if it is very soluble in any body tissue.

Vapors of solvents, if they are not destroyed in the body, behave in general like inert gases. An interesting example of slow elimination is given in the writings of the renowned French physiologist, Claude Bernard. He conducted his research on many types of animals, including sheep. To increase his meager research funds, the carcasses of the sheep, after operation, were sold in the local meat market. This procedure was quite profitable for a time and then, suddenly nobody would buy the sheep. What was the reason? Bernard had changed the anesthetic used in his work from chloroform to ether. Very little chloroform was needed to anesthetize the sheep and that little rapidly left the body. But considerable quantities of ether were required, and the ether persisted in the fatty tissues and gave the meat of the sheep an objectionable odor and taste.

The problem of solubility also enters into the ultimate fate and action on the body of inorganic dusts. Materials, such as silica, considered by the chemist as highly insoluble, should, logically, not be passed easily through the alveolar walls. But here another body mechanism comes into play. The complex cellular structure of the wall contains "wandering" cells which act as scavengers and engorge foreign particles. These cells are able to pass through the walls of blood capillaries and lymphatics draining the lungs. They flow to the lymph nodes around the bronchi and here, by an action not yet explained, the silica, if it be of the correct type, can cause damage. The resulting disease, silicosis, is one of the most serious in industry. It is possible that materials such as silica are more soluble in the complex aqueous medium, cytoplasm, than in pure water. It is also possible that adsorption on the protein of enzyme systems might lead to chemical reactions which produce damaging silica complexes.

The problem of silicosis should warn against too complacent acceptance of "test-tube" insolubility as a basis for the assumption that a particular solid, as dust, provides no risk if inhaled.

It does not matter whether we are dealing with the problem of inhalation of an inert gas, such as helium, or argon, or of the vapor of a solvent of low chemical reactivity with the chemicals of living tissue, we must never forget the possibility of reduction of the oxygen content of the inhaled air to a point at which normal respiration is difficult. This is at about 16% by volume. While at this figure of 16% oxygen, serious injury would not be caused by breathing an inert gas,

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many workers might suffer from headache and dizziness and from changes in the circulation which might render them prone to injury if they are using tools or operating moving equipment.

Theoretically, prevention of inhalation of chemicals contaminating the air we breathe should be relatively simple. The mouth and nose, through which air first enters the body, offer only a few square centimeters of orifice. These could be covered by a suitable mask allowing the passage of air but not of dust, or a mask attached to a canister which adsorbs dusts or vapors. This method of protection is indeed available and useful but only under very restricted conditions. A filter mask which is capable of holding back small particles of dust necessarily offers some resistance to the passage of air and therefore may hinder the normal, unconscious act of breathing. The mask will be uncomfortable, especially on hot, humid days, and the filter material will eventually become saturated. A mask with a chemical canister will rarely hold back air concentrations of more than 2% by volume of a vapor or gas, and it will do this only for some 20 min. Such a canister mask is also uncomfortable to the wearer. It is never safe in an emergency when the concentration of the contaminant of the air is unknown, and it is never safe when the oxygen content of the air is below 16% by volume.

This simplest form of prevention of inhalation of harmful chemicals should be used only for very short-term activities in laboratories, when the possible concentration of the material against which protection is desired is known to be low, and it is certain that the filter material or contents of the canister will, in fact, hold back the harmful chemical.

In emergencies or for protection against concentrations above 2% by volume and for periods longer than about 20 min, that is under conditions in which canister masks are not adequate, personal protection is afforded by air-line respirators or by a self-contained breathing apparatus supplying compressed air or oxygen. Like the simpler canister mask, such apparatus must be used with care. It must be kept clean and in proper working order at all times. Whenever air is supplied, either directly to an airline from a compressor, or as precompressed air from a tank, this air must be free from contamination. A worker, who is calling for protection against, say, hydrogen sulfide, is scarcely helped by a supply of nitrogen to his airline respirator or by compressed air containing finely dispersed oil or carbon monoxide from the compressor.

This purely local protection of the points of entry of harmful substances into the respiratory tract is neither practical nor efficient for the hourly and daily demands of the laboratory or the manufacturing

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plant. The only satisfactory way to assure protection of workers is by ventilation.

In recent years state and federal laws and regulations, following on years of voluntary action by the chemical manufacturing industry, have required precautionary labeling of containers of hazardous materials entering the home or industrial plants. Whenever a chemical offers the risk of injury by inhalation, the container label must carry the phrase "use with adequate ventilation" or "use only with adequate ventilation." The word "adequate" is difficult to define. Since ventilation is required to control all physical forms in which contaminants appear in the atmosphere, we would suggest as a definition, "Adequate ventilation is such ventilation immediately around the worker that dusts do not settle on his unprotected skin of a type or in an amount which can cause harm and that at his mouth and nose level there are neither adequate concentrations nor total quantities of gases, vapors, mists, or dusts to cause injury when inhaled or swallowed." We would consider anything short of this to be inadequate ventilation.

This definition would appear to require knowledge of the minimal concentration or total quantity which could be harmful—knowledge which, as we have already explained is not available for more than a very few materials and is not available when a new chemical is first prepared in the laboratory. Further, since in both laboratory and plant the worker's exposed skin area, nose, and mouth are not fixed in space, the definition demands a system of ventilation operative at any point in laboratory or plant at which that exposed skin and that nose and throat may be located at any time during the daily work.

In the early days of protection by ventilation it was thought that the desired end could be reached by dilution. Volumes of fresh air were poured into the workroom in the hope of reducing the overall concentration of atmospheric contaminants to a level incapable of causing harm. This procedure was expensive, inefficient, and in the case of materials which might dust, it could actually induce a hazard which otherwise would not exist.

The modern method is to ventilate at the source of possible origin of any physical form of a harmful material and to ventilate by suction so that it could not approach the skin, the nose, or the mouth of the worker. Localized suction is applicable to any scale of operations in laboratory or plant. It requires less overall energy than the crude system of dilution and need be operated only at any particular site during the period of actual possible exposure.

In manufacturing plants, hoods and negative pressure can be installed over reaction kettles, filter presses, drying and flaking apparatus.

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and packaging equipment. In the laboratory this form of ventilation has been traditional in the chemical hood.

Whether in plant or laboratory, ventilation by removal at the source of origin of air contaminants is efficient only if the equipment used is kept in good operating condition and is used with intelligence. Since this phrase "used with intelligence" may seem unnecessary to some, we would illustrate it by observations on the use of the chemical hood.

The first acquaintance of any future chemist with the chemical hood or "fume cupboard" was probably made in high school. And some of the bad habits which later might plague him were also probably acquired there. The hood has always been a structure with a movable front sash and at its back there was a duct carrying a fan. It was used to store apparatus such as the old "Kipp" generator for production of hydrogen sulfide or for carrying out reactions in which this gas or other reactive gases were used. This storage function of the hood was necessary because the Kipp generator usually leaked and hydrogen sulfide was undesirable because of its odor of "rotten eggs" in the general laboratory area.

This habit of using chemical hoods as storage places has extended beyond the original purpose as storage for equipment continuously subject to leakage. In too many laboratories the hood is now the repository of reagents and equipment not currently in use which would "clutter-up" the laboratory bench.

The modern chemical hood usually has a baffle plate toward its rear with a clearance of an inch or so at the bottom or sides through which the fan, when operating, sucks air. As more and more reagent bottles and unused apparatus are placed in the hood for storage, two events occur. First, the movement of air back to the outlet duct is prevented, because much of the space between the bottom of the baffle plate and the floor of the hood is virtually closed by stored material. Second, the air drawn into the hood, that is, air which should be carrying contaminants away from the chemist working in the laboratory, is bounced off the bottles and other stored objects, and the turbulence resulting may actually force air out into the laboratory.

There are other common errors in the use of hoods which we would consider "unintelligent." Most hoods will not operate efficiently if the front sash is raised more than 4 to 6 in. A hood with the sash raised half-way or completely is very poor protection. Again, the turbulence caused by obstacles in front of the baffle plate can also be caused by the body of a chemist standing close to the front of the hood or by bulky apparatus erected just outside the front.

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Finally, if the hood is quite properly used to store equipment from which gases or vapors might leak, the habit of the economy minded, to turn off the fan at the end of the work day, may have very unfortunate consequences for the unwary who might later open the hood to set up apparatus or remove equipment.

In outlining the content of a sound safety program, we stated that it should consider "those factors in the work terrain which could accentuate the hazard or spread it to other parts of the work area or even beyond plant limits." It is unfortunate if, in installing ventilation to protect one group of men, another group is placed in jeopardy. Air taken from, say, a laboratory and carrying contaminating chemicals must be vented somewhere. Is the output stack of the ventilating system of adequate height and properly situated in relation to other buildings so that there is no risk of entry of its exhaust into neighboring buildings? Is the stack of sufficient height that, under conditions of high humidity and low wind velocity, harmful gases or vapors will not fall to the ground between buildings?

Under this heading of work "terrain" we would also include the more limited area of the laboratory or work room itself. Often the ventilating apparatus has been installed when very few obstacles, including the bodies of workers, were in the path of air flow. Changes in the placement of equipment, addition of permanent machinery or apparatus, and occupation of the work room by more people than originally intended or relocation of their work positions in relation to the air flow, could have the same general disturbing effect as we have described when discussing the "intelligent" use of a chemical hood.

Finally, cleanliness of equipment, of containers of reagents, and of even the walls of the laboratory or production area may be a factor in deciding success or failure of an apparently adequate program of protection.

Chemicals and the Digestive Tract

Risk of injury by swallowing chemicals is not usually considered important in industry. Yet it does exist and may actually be significant. In the laboratory careless use of pipettes is an obvious source of injury to the mouth. If the material pipetted has a high-vapor tension, vapor may be inhaled. In the more modern, more efficient laboratories, of course, pipetting is now mechanical.

In heavily dusted areas the larger particles of dust drawn into nose and mouth will be desposited there and, if they have no warn-

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ing local action, will be swallowed. Aerosols containing large droplets may also lead to swallowing.

In industry a serious risk of swallowing harmful substances exists if workers are allowed to eat lunches or snacks during the "coffee hour" without first thoroughly washing hands and face, or if they are allowed to take food, chewing gum, or chewing tobacco into contaminated work areas. This is a practice very difficult to control.

To produce serious injury by swallowing, greater concentrations or total amounts of chemicals are usually needed than are required to injure by inhalation. Many chemicals are not easily absorbed through the walls of the digestive tract unless they first injure those walls. Those which are absorbed into the blood stream pass through the liver in which important detoxifying mechanisms operate.

The digestive disturbances and loss of appetite, which are so often early symptoms in developing chemical poisoning, are not usually due to direct action on the operations of the digestive tract itself but rather to effects on the total body functions by chemicals which have entered the body by any route.

Again, prevention of injury depends upon control of movement of harmful materials into the work area and meticulous cleanliness of the worker. Water and soap again are potent tools for prevention.

Examples of Inadequate Protection

We have outlined major sources of risk of injury by chemicals in the laboratory and the manufacturing plant. We have also described in general terms simple means of reducing that risk. Unfortunately there are many sceptics in this field of safety with chemicals. To help convince them we cite a few examples of what follows failure to apply simple means of protection. These examples relate to the points in our general discussion.

Dermatitis, the most frequent form of industrial injury due to chemicals, can be prevented by cleanliness of clothing and person. Inadequate cleaning of clothing may perpetuate it.

Three workers were showered by a mixture of dilute hydrochloric acid and aromatic chlorine compounds when a still broke. They removed their outer clothes and were said to have cleaned them. But all suffered chemical dermatitis for 3 weeks. Their dermatitis disappeared promptly when *all* clothing worn at the time of the accident was very thoroughly cleaned and left to hang in fresh air to dry.

A worker handling a rubber anti-oxidant became sensitized and was apparently removed from all possible contact with the offending material. His

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dermatitis did not disappear. He was still wearing garters, the "elastic" of which was contaminated. When these were discarded, he recovered.

Clothing contaminated by chemicals should not be worn at home. It should be thoroughly cleaned either on the plant or by cleaners experienced in handling such materials.

The wife of an operator in a small dynamite plant complained to the plant manager that she and her children frequently suffered from severe headaches. The operator had "purloined" a discarded glove from the plant. The glove was of a type rejected by the plant because the palms were coated with rubber. The rubber had absorbed nitroglycerin. This chemical rapidly passes through the skin. The children played with the glove and the wife often handled it in her daily house cleaning.

Beryllium dust is the source of a very serious lung disease—berylliosis. Workers in plants handling beryllium are now well protected. But in one plant, at least, this protection was spoiled by shortsightedness. A worker was allowed to take home his contaminated work clothes. His wife laundered them and in doing so breathed sufficient beryllium dust to produce lung injury.

Gloves made of rubber or rubberized materials may not be good protection against liquids which can penetrate them.

The rubberized gloves mentioned above were discarded in the safety program of the dynamite plant because nitroglycerin will penetrate rubber.

An outbreak of painful dermatitis of the fingers among "doffers" in a plant making viscose rayon was found to be due to penetration of rubber gloves, used as protection against the acid-spinning bath, by carbon disulfide liberated from the regenerating viscose. The outbreak was halted by careful selection of the gloves after tests for permeability by carbon disulfide and the wearing of a light cotton glove beneath the rubber.

Barrier creams are useful when used with care under proper circumstances. Sometimes they can unexpectedly make matters worse.

An epidemic of dermatitis broke out in a plant making a synthetic fabric by impregnating cotton cloth with a plastic. The solvent was methyl ethyl ketone, which was recovered and re-used. The plant safety department advised use of a barrier cream but the condition of the workers using it became worse. A research chemist at the plant solved the mystery. Under the conditions of use, methyl ethyl ketone was partly converted to diacetyl. This compound, in contact with the skin, apparently polymerized to form a quinone which combined with proteins of the skin to produce the allergen which caused the dermatitis. This chemical process was facilitated by the alkalinity of the barrier cream. Diacetyl had apparently built up in the recirculated solvent to a significant concentration. Careful fractionation of the solvent before re-use eliminated the trouble.

Frequent washing of the hands with soap and plenty of water may remove a hazard caused by absorption of chemicals through the skin.

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In a military arsenal a group of women was engaged in weighing plaques of a propellant composed of nitrocotton impregnated with a high concentration of nitroglycerin. After weighing, they sewed the plaques together. The girls would work for a few days and then quit, complaining of severe headaches. The rapid labor turnover was threatening the work program. The difficulty was overcome in a very short time when the girls were required to wash their hands thoroughly at the end of each work hour.

When washing to remove contaminating chemicals, plenty of water should be used. When part of the function of water is to remove heat of reaction, flowing water from a hose or a shower is essential.

A plant using titanium tetrachloride was amply provided with showers at every point at which workers might be splashed with this irritant material. The workers were equipped, in some operations, with complete rubber protective clothing. They were also thoroughly indoctrinated in safety practices, including the use of water to remove any of the chloride which splashed on their clothing or bodies. A young, inexperienced worker was accidentally sprayed with a large volume of titanium tetrachloride. He panicked and, instead of using the shower close at hand, rushed to a large vat of water and jumped in. Titanium tetrachloride reacts with water with evolution of great heat. The still water of the vat boiled and the worker was severely injured. Flowing water from the shower would have taken up the heat of reaction and carried it away from the man's body.

An operator in a small chemical plant carelessly handled a drum of oleum. A defective bung fell out, and oleum poured down the man's leg and into his calf-high "cowboy" boots. Fellow workers at once turned a hose on him but he fought them off. Before they finally overpowered him, his right ankle and foot were severely burned and corroded by the acid. He had seen steam generated when spilled acid was diluted with water, and he did not know enough about the hazards from oleum to realize the usefulness of plenty of water.

Sometimes it is best to precede the use of water in cleansing contaminated clothes or skin by the proper use of a solvent. This must then be removed by soap and water.

Tetraethyl lead is a highly dangerous compound. It very rapidly penetrates the skin. All workers who may come into contact with more than minute quantities of this compound, during its manufacture or at blending plants, are thoroughly indoctrinated into procedures for handling spillage. The chemical is transported in tank cars and at blending plants it is transferred to storage tanks. At the point of transfer, workers are protected by proper clothing and two showers are provided, one delivering kerosene, the other water. In unloading a tank car the men work in pairs. The pipe from the tank car to the storage tank ruptured during such an unloading, and a worker was literally bathed in tetraethyl lead. He at once stepped under the kerosene shower and, assisted by his buddy, flushed the chemical from his clothes and body. He then stepped under the water shower and was thoroughly bathed with soap and plenty of water. This man, accidentally exposed

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to a large volume of one of the most dangerous chemicals known, was not injured to the least degree by this accident.

In contrast to this skilled handling of a potentially serious accident consider the following:

A gang of laborers was employed in digging a drainage ditch in a plant manufacturing tetraethyl lead. The foreman failed to note that an old drain ran parallel to the new one and that this old drain carried water contaminated with tetraethyl lead. Water from the old ditch seeped into the new. The feet of the laborers were not properly protected. Some acquired tetraethyl lead poisoning.

Copious flowing water is as valuable in cleansing the eyes of chemicals splashed into them as it is in cleaning the skin. Prompt washing of the eyes with flowing water for at least 15 min can, in most cases, prevent more than temporary eye irritation.

A driver whose car radiator was beginning to freeze drove into a filling station and asked for a methyl alcohol anti-freeze. An inexperienced attendant unscrewed the radiator cap and without waiting poured in methyl alcohol. There was a violent eruption and the hot mixture of radiator water and alcohol hit the face and eyes of the attendant. His eyes were immediately flushed with water, and he was sent for medical attention. The outer surface of the eyes rapidly became cloudy and were described as looking like "the white of a boiled egg." But, thanks to immediate removal of the contamination, damage was restricted to the outer layer of the cornea and within three weeks this subsided and the eye was restored to normal.

Canister masks may be very useful under limited conditions. But care must be taken that, even for these conditions, the canister is adequate to hold back the harmful vapors or gases against which protection is needed.

In a paper-making factory plans were made to kill slime in vats by use of a compound of diethyl mercury. It was planned to add this to the contents of a vat and mix by using air from a compressed air line.

Diethyl mercury is quite volatile and the agitation with air produced a harmful concentration of the vapor in the work area. The safety department of this plant had been informed, after careful inquiry from supposedly responsible sources, that an all-purpose canister mask would afford protection. It did not, and two serious cases of poisoning resulted. Apparently the advising "authority" was not aware that a canister which would absorb vapors of metallic mercury will not hold back vapors of alkyl mercury compounds.

Serious and often fatal accidents occur when the oxygen of the atmosphere of the work area is reduced below the concentration needed for normal respiration. This situation occurs in all major conflagrations,

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and can occur if high concentration of inert gases are liberated, produced or used where men work.

In past years public utility companies supplying electricity to large cities have had bitter experience in this problem. The transformers in large buildings were often in closets in sub-sub-basements. These transformers occationally overheated and power supply to the building failed. A service man was sent out and failed to return. When assistance was sent, the first man was found collapsed or dead at the foot of the transformer. In such cases the transformer fluid was an oil which, when overheated, absorbed all the limited supply of oxygen in the restricted volume of the closet. The service man walked directly into an atmosphere of nitrogen.

During a visit to the physiology laboratory of a famous university, the laboratory director volunteered to demonstrate effects of breathing oxygen-helium mixtures. After adjusting leads to various recording devices, he donned a face mask attached to a battery of gas tanks. At his signal an assistant turned a valve. He took one or two breaths, became blue in the face, and his heart beat became rapid. The mask was promptly removed and he quickly recovered. Someone, without warning his fellows, had replaced the tank containing oxygen and helium with a tank of pure helium.

Some of the recently developed saturated polyfluorinated aliphatic hydrocarbons are chemically and physiologically very inert. They are used as refrigerants, as propellants for aerosol bombs, and as solvents. High concentrations of these materials, as gases or solvent vapors, accidentally liberated have had the same effect on exposed workers as would high concentrations of inert gases, and by the same mechanism—reduction in available oxygen.

Cleanliness of work areas and of equipment handled in the course of the daily work may be a very important item in a program of safety with chemicals, especially if the materials involved can be absorbed through the skin. In some older chemical manufacturing plants, often for very specific reasons, parts of the work rooms may be constructed of wood or covered with wood. Wood, like leather, can absorb many materials deposited on it and in time these wooden structures become a veritable reservoir from which, if volatile, vapors can be emitted.

Some years ago, during a study of methods of protection of workers against inhalation and skin absorption of nitroglycerin in the manufacture of dynamite, surveys were made of atmospheric concentrations of the chemical in work houses under varying conditions of ventilation. The walls of these houses, for safety reasons, were of wood. Settling of dust containing nitroglycerin resulted in absorption of this chemical into the wood. During the work hours ventilation systems were adequate to maintain a safe atmospheric concentration of nitroglycerin vapor. But after the day's work was ended and the ventilating system shut off, vapors from the walls built up atmospheric concentrations beyond those considered physiologically safe. Spraying the walls with water would temporarily lower the vapor con-

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centration, but once the walls were dry, with ventilation still shut down, the process of evaporation from the walls started again.

The base beta-naphthylamine is very easily absorbed through the skin. It also can be a dusty material and can exert a significant vapor pressure. Beta-naphthylamine is not toxic, in the usual sense of the word. It has no action on most organs of the body. But, after absorption, it is concentrated in the urine and is absorbed by the walls of the urinary bladder. It is then converted into a hydroxy beta-naphthylamine which is a potent carcinogen. During a study of this compound, many pounds of it were used in a biochemical laboratory. As the study progressed methods of determination of beta-naphthylamine in the urine were attempted, using fluorescence as an indicator. Workers in this and other laboratories provided urine specimens, which were usually placed temporarily on the biochemical laboratory bench. We were much alarmed when all were found to give strong fluorescence, indicating excretion of considerable quantities of the naphthylamine. Some of the contributors of the specimens had worked with the chemical or with animals which had been fed the chemical. But others, so far as we could discover, had never been exposed to it. Yet their urine specimens, after standing in this laboratory, were positive for beta-naphthylamine. When the routine was changed and no urine specimens were allowed to enter the biochemical laboratory, none showed fluorescence. Apparently during the months of work with the amine this laboratory, especially the walls and ceiling, had become contaminated. A very thorough cleansing removed the contamination. If the problem under study, cancer of the bladder caused by beta-naphthylamine, had not been of such a serious nature, it is doubtful whether the possibility of contamination of a whole laboratory would ever have been given serious thought.

One of the rare effects of poisoning by trinitrotoluol is damage to the bone marrow. It appears to occur only in a few specially sensitive individuals, but in these it can follow absorption of much smaller quantities of the chemical than are usually considered harmful. Bone marrow damage was found in a worker in an explosives plant who, apparently, never was engaged in any plant operations which would involve TNT. He was the driver of a small locomotive on a light railway used to carry boxes of the chemical from the packaging area to the magazine or to the railhead. But he did occasionally help in loading these boxes on to the cars drawn by his locomotive. Chemical tests showed that the outside of these boxes was contaminated with TNT.

When a ventilating system is installed to prevent atmospheric contamination in one area, it is wise to study carefully the position of the output stack of the system lest protection of one group is obtained at the expense of another. We have described a number of examples of misplaced enthusiasm in an article, "Use Only with Adequate Ventilation" published in *Air Engineering* (Vol. 4, No. 6, pages 23–30, June, 1962). In these days of air-conditioned laboratories, great care must be taken that the mechanisms for removal of atmospheric contamination due to chemicals—the chemical hood or temporary exhaust

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systems—do not result in recirculation of chemicals via the air-conditioning system.

In these days of public concern over pollution of the atmosphere, everyone responsible for operating either a laboratory or a plant bears the burden of assuring that no harmful quantities of his chemical tools or harmful products or wastes can reach beyond the bounds of property under his immediate control. Even though his site of operations might be far from a residential area, and none but a few persons might ever be expected to approach areas around this site, conditions could sometimes arise to produce unforeseen risks.

An experimental nitration operation was being carried out in a small laboratory adjacent to a wooded area. For some unexplained reason the chemist decided to vent the nitrogen oxides produced by his reaction through a duct which passed through the roof of the hut and was then carried vertically downward parallel to the outer wall and opened a few inches above the ground. All went well for some time. Then came days of high humidity, mist, and small wind movement and that movement was directly toward the woods. Nitrogen oxides accumulated in high concentrations and lay close to the ground in the woods. Luckily, at that time, there were no wanderers in those woods, otherwise a serious situation might have arisen.

A small plant whose operation required the use of high concentrations of an alkali cyanide solution, carefully programmed the removal of cyanide-contaminated wastes from the operating area. The wastes were collected in a catch basin away from the plant and situated on the edge of a wooded gully. This small reservoir and attached pumping equipment was inspected daily. On a humid, misty day, with no wind movement, a worker inspecting the reservoir and pumping apparatus near it became dizzy and almost collapsed. Apparently hydrocyanic acid gas, which is always liberated in small quantities from cyanide solutions by the carbon dioxide of the air, which forms a stronger acid than HCN, had become concentrated in the mist to a degree capable of causing respiratory disturbance.

Whenever gases or waste solutions capable of evolving gases are discharged from a plant or may, by accident, escape from equipment anywhere on the plant, atmospheric conditions may lead to hazardous situations.

In the old "chamber process" for making sulfuric acid, sulfur dioxide from burning sulfur or pyrites was mixed with nitrogen oxides generated from sodium nitrate. The mixture of oxides with water vapor was pumped successively into a series of chambers. A leak occurred in a pipe line carrying the crude oxide solution at a time when the external temperature was well below zero. The solution rapidly froze and formed a small deposit below the point of the leak. When the spring thaw came, a craftsman was sent out to inspect the pipe line and repair leaks. He worked above the previously solid, but now thawing, mixture of oxides long enough to inhale nitrogen

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oxides in a lethal quantity. This same hazard of evolution of nitrogen oxides from frozen reaction mixtures was experienced in the manufacture of TNT during World War II in plants located where winter temperatures were very low.

EXPOSURES OF NONOPERATING PERSONNEL

Safety from injury by chemicals is a "freedom" and, like all freedoms, can only be assured by "eternal vigilance." It is not sufficient that a laboratory or a manufacturing plant establish on paper a program of operations which will protect workers. It must continually strive to educate those workers and search for the best means of reducing risks.

Many chemical companies and research centers have well-established safety programs, and a major item in them is the monthly, or sometimes even weekly, safety seminar. But who attends these meetings? Are they not, usually, confined to those who are actively concerned with the making or using of chemicals? Are clerical personnel also instructed in the hazards which chemicals may afford? Are guards or those who clean laboratories at night so instructed?

The chemical manufacturing industry of this country has built up a magnificent record of on-the-job safety and is continually improving it. But when, a few years ago, a comparison was made of the frequency of lost-time injuries incurred on the job to the frequency, among the same workers, of injuries sustained away from the job, it was found that the ratio of off-the-job to on-the-job injuries was 5 to 15. Safety education had apparently been focused on risks while at work and not on risks in general.

With rapidly increasing frequency the products of chemical laboratories and plants are being used in and around the home. A recent federal law has required labeling of containers of hazardous chemicals "intended or suitable for household use." But anyone who has been concerned with safety in the handling of chemicals knows that labeling may be ineffective for, too often, the chemical which has caused trouble has been removed from a properly labeled container and placed in one not labeled. The "purloining" of chemicals from laboratories or plants for home use is not infrequent and most often includes transfer of materials from labeled to unlabeled containers.

Some years ago an accident occurred on the West Coast which pointed up the danger of this practice. Two young men, workers in a chemical plant, took a large quantity of carbon tetrachloride from a drum. They went outside the town to a pit over which they could drive their car so that they could work on the transmission. They used the carbon tetrachloride to

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degrease the differential gear. They were found dead under the car. The drum from which they had taken the solvent was adequately labeled. The plant in which they worked conducted a good safety program, including frequent safety seminars. In fact, shortly before the accident, the subject of a safety talk had been carbon tetrachloride. *But the two young victims of carbon tetrachloride were not at the safety meeting because they were office workers.*

Some Chemical "Criminals"

While this chapter is not intended as a thesis on toxicology, we think that emphasis on a small group of chemicals, appearing frequently in the laboratory, the plant, and the home, and which in our opinion warrant the title of chemical "criminals," might round out our plea for continued caution. The four chemicals are *hydrogen sulfide, nitrogen oxides, benzol,* and *carbon tetrachloride.*

We have chosen these four for a number of reasons. First, they are frequently encountered in laboratories at all stages of chemical education as well as in chemical research. Second, they are such familiar items that they are treated with indifference and are used carelessly. Last, they have without doubt killed or injured more people in peace time than any other compounds, with the exception of carbon monoxide, which has been a prime chemical killer since the days of the charcoal burners and the first forgers of metals.

Hydrogen sulfide is the first gaseous chemical reagent which the student meets in his study of inorganic analysis. For his analytical work it is supplied to him either from the historic Kipp generator, or, in modern times, from tanks in which it is compressed to a liquid. Both generator and tanks are apt to be stored in the chemical hood. The Kipp almost invariably leaks. The tanks can leak if not carefully tended.

Traditionally, the one property of hydrogen sulfide well known to students is that it has the odor of rotten eggs. In such eggs the gas is produced by decomposition of organic sulfur compounds in the egg yolk. But, also traditionally, it is never explained to the student that this odor is perceptible only when the gas is present in low, unpleasant but harmless concentrations. Dangerous concentrations of hydrogen sulfide paralyze the olfactory nerves. This property is the cause of many accidents, some near misses, too many fatal. I fear this gas more than any other chemical, because of personal experiences and experiences of my friends.

Some years ago, while a chemistry student in the University of London, a fellow student and I went to the chemical hood intending to start a gravi-

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metric analysis working under the hood. My friend reached the hood first. The ventilating fan was not operating. He raised the front sash and put his head into the hood. He at once staggered back and collapsed. I dragged him to an open window. He was conscious but unable to speak or move for several minutes. When he recovered, he did not know what had happened. The usual Kipp generator was stored in the hood and, as usual, it leaked and filled the hood with a dangerous gas concentration.

Some years later my wife, as a pre-medical student, suffered a similar "near-miss." After class hours she decided to complete a Kjeldahl analysis for protein nitrogen. She planned to use the chemical hood since dangerous nitrogen oxides would be liberated. She opened the hood, but remembered nothing more until she found herself at the exit from the laboratory, struggling to get to her feet. She does not know how she reached the exit. It was Saturday and no other person was present.

The odor of hydrogen sulfide was noticed in the basement of a famous toxicology laboratory near to a room in which tanks of the chemical were stored, for use in a program of lead analysis. When the storage room was approached, with proper precautions, a janitor was found unconscious at the entrance. Inside the room the laboratory manager was dead, near a leaking gas tank.

Hydrogen sulfide is a frequent cause of deaths of workers on sewage repair. Usually they are multiple deaths. The companion of the first man to collapse goes in to rescue him. Ignorant of the properties of the gas, he fails to provide himself with the only respiratory protection adequate for the situation—a self-contained breathing apparatus delivering compressed air or oxygen. Sometimes man after man attempts the task of rescue and becomes a victim.

A person not adequately equipped should never try to rescue a worker felled by hydrogen sulfide. He may merely provide another fatality for, by almost instantaneous action, the gas paralyzes its victims so that they can neither help themselves nor call for help.

Nitrogen oxides are liberated whenever organic matter is heated with nitric acid. Nitration reactions are common in student laboratory work in both analytical and organic chemistry. They are equally common in research laboratories and in chemical manufacturing.

Nitrogen oxides are sometimes obvious as "brown fumes," but not always, and the degree of brownness is not related to the extent of the harm caused if they are breathed. The oxides may not give any warning, by irritating the eyes or throat, but within 6 or more hours severe lung injury may develop. We have already mentioned the fire at the Cleveland Clinic in which many patients, doctors, and nurses were killed by breathing these gases. A faulty heating apparatus started a fire in a basement in which X-ray films were stored. The films contained a nitro-cellulose base.

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Benzol is a useful solvent and was formerly a common constituent of metal polishes, plastic woods, and rubber cements. It is probably found in most laboratories and is not usually regarded with suspicion. High concentrations of benzol vapors are anesthetic, but a single heavy exposure, even if it leads to loss of consciousness, will seldom cause lasting harm.

The great danger with benzol lies in damage to the bone marrow which follows frequent breathing of low concentrations of the vapor. The disease produced is similar to leukemia and, like leukemia, is seldom curable.

Carbon tetrachloride is the last of our "criminals." It is a very useful solvent especially for removing grease from fine electrical equipment. Its careless use has caused much illness and many deaths. We have already cited the case of the two young office workers who used carbon tetrachloride to degrease the gearing of their car. Here is another case:

Toward the end of the fighting in Korea a large airplane carrying troops from Japan landed at a West Coast airport. The plane was badly needed so a crew was rushed to clean it, inside and out. The men working inside were given buckets of carbon tetrachloride, with a little water floating on the top, and were set to cleaning with swabs and mops. No ventilation was provided. Two of the men were overcome and died within a few hours.

Another hazard is added to that of the vapor if carbon tetrachloride is used in the vicinity of naked flames or very hot metal. A rather unusual situation invoked this hazard. The glassblower's shop in a large research center was supplied with oxygen piped in from tanks outside the shop. Whenever oxygen is used, great care must be taken to avoid grease on any part of the tank, valves, or pipes from the tank. The safety department decided to degrease the oxygen pipeline to the glassblower's shop and did so, using carbon tetrachloride. When the glassblower used the oxygen supply after the degreasing, he and his assistants were made very sick by phosgene produced in the flame of his torch. Nobody had thought to thoroughly purge the oxygen line of carbon tetrachloride vapor.

Summary

Chemical accidents hurt people. Careful, intelligent handling of chemicals will prevent accidents. Proper ventilation and protection of workers by clothing or individual breathing equipment will prevent chemicals liberated accidentally from coming into contact with the body of workers or from their breathing gases, vapors, mists, or dusts. If, in spite of such protection, chemicals do settle on exposed skin, immediate removal with the use of plenty of water will call a halt

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to direct injury of the skin or to absorption through the skin with possible general illness.

More than two-thirds of chemical injuries in industry are injuries of the skin. Water is the best "antidote" for a majority of industrial chemical injuries.

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17

Toxicity Vs. Hazard

H. H. Fawcett

"How toxic—how hazardous?" These two related thoughts are frequently combined into one compound question, yet in their practical aspects they may require entirely different answers. This discussion will point out some of the factors which must be considered in evaluation of the true *hazard* of a substance suspected of being *toxic*.

The word toxic has been loosely applied to many different effects, when actually it should be related to general, systematic effects of a substance in living animals or humans. Almost every substance will produce injurious effects in a living body to some degree (even "safe" substances like salt, baking soda, and sugar can produce serious illness when taken in excess). The key questions are: *how much* is needed to produce a toxic effect, and, of equal importance, *how likely* is this amount of material to enter the body where it can actually produce this effect? Substances differ widely in their relative toxicity, in their ability to enter the body, and in the effects they produce.

Toxicity, for this discussion, is defined as too much of a substance for the body to tolerate without injury. Toxicity is *not* a specific physical constant determined by standardized devices, such as used to determine specific gravity or melting point. Not a property of the substance itself, toxicity defines the degree to which the substance affects living cells. Figure 17.1 represents attempts to explain this concept.

However, living cells do not lend themselves to absolute standardization. The University of Texas recently observed wide variations

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even in "uniform" white rats bred and selected for experimental investigations—one rat drank 15 times more alcohol than another, and another traveled 6 miles while his less active brother was moving 150 ft. If rats bred and carefully selected for uniformity are such nonconformists, consider how much more humans differ from each other and from the standard curve. The problem of individual variation has been demonstrated many times in the field of toxicology, as well as in other phases of life. The time-honored expression, "One man's meat is another man's poison" aptly sums up man's experience in this respect. Just as there is no "standard animal," there is no "standard man"—animals and humans are subject to wide variations.

Toxicity cannot be measured at all until a definite *recognized* change has occurred in an animal or in a human. These changes may be very small and easily overlooked; such changes as impaired judgment and delayed reaction time may be involved at levels too low for the production of body damage.

Animals may react in a much different way than humans. Mules, for example, do not develop silicosis even when working beside miners who develop the disease. Crystalline penicillin G is essentially nontoxic in animals, with the exception of guinea pigs. Guinea pigs are peculiarly sensitive to penicillin (and to certain other antibiotics) and doses as small as 7000 units/kg may produce serious effects and finally death within a few days. Doses as high as 9,800,000 units, or 5.93 g/kg were tolerated in mice, while humans can tolerate tremendous doses (even daily doses as high as 86,000,000 units for a 28-day period), except for those who are allergic and then even small doses produce severe, and occasionally fatal shock. Animals may survive a relatively large or acute dose but die from smaller doses over a longer period; the rodenticide warfarin (3-a-acetonyl-benzyl)-4 hydroxycoumarin is an example of such a substance.

To illustrate how much information we need to complete the evaluation of a potential hazard (not merely citing toxicity alone), we should ask fundamental questions:

17.1. WHAT EXACTLY IS THE CHEMICAL COMPOSITION OF THE SUBSTANCE AS ACTUALLY USED?

It is futile to attempt any evaluation of hazard without specific and definite information on composition. To say a solvent mixture "contains mineral spirits" is to present completely inadequate information, since mineral spirits vary widely in composition, and also the per-

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centage of mineral spirits in the mixture may be very small or quite high. Other constituents in the mixture may be far more hazardous, such as benzene or carbon tetrachloride. If a proprietary-brand solvent or mixture is involved, the maker will usually reveal the complete formula on a confidential basis to a responsible person for the user, if given assurance that the information will not be used against his best interests or passed on to anyone else.

If the supplier will not cooperate, two alternatives are always suggested: (1) analyze the substance yourself; (2) locate a more cooperative supplier. Usually the supplier will cooperate if he realizes his business depends on cooperation, and this approach is usually faster, more accurate, and more economical for all concerned than analysis. With the new techniques, such as chromatography and infrared spectrography, however, analyses are much easier to obtain than previously, and nothing should deter us from obtaining the complete analysis if we are suspicious a hazard may be involved.

17.2. WHAT ABOUT TOXICITY IN ANIMALS?

Once we have learned *what* is involved chemically, we can turn to the literature in the hope that our substance has been investigated and published. At this point extreme care must be exercised, since toxicity values are by no means absolute; they can be considered only as yardsticks of activity. Spector[1] lists five conditions that influence the toxicity of any given compound.

DOSE. Generally the larger the dose, the more rapid the action.
RATE OF ABSORPTION. The faster the rate of absorption, the quicker the action of the drug.
ROUTE OF ADMINISTRATION. Toxicity is greatest by the route that carries the toxic substance to the bloodstream most rapidly. In decreasing order of speed, routes for most substances are:

intravenous (into a vein)
inhalation (breathing)
intraperitoneal (into the abdominal cavity)
intramuscular (into a muscle)
subcutaneous (under the skin)
oral (by mouth)
cutaneous (on the skin)

SITE OF INJECTION. With subcutaneous injections, toxicity may be affected by the density of the subcutaneous tissue. In intravenous

administration, the rate of injection, or the amount of toxic material injected per minute, will considerably influence the value of the toxic dose.

OTHER INFLUENCES. Disease, environmental temperature, habit and tolerance, idiosyncrasy, diet, season of the year—all may affect toxicity. The toxicity of chemicals will also vary with the species of animals used and sometimes with different strains of the same species. Within the same strain, the toxicity may differ with age, weight, sex, and the general conditions of the animals. The time to produce death, or the period of time for which fatalities are counted, may also be a factor.

There are several units in which the toxicity dose is expressed. The most frequently used are: LD or lethal dose (the amount which kills an animal), the MLD or minimum lethal dose (the smallest of several doses which kills one of a group of test animals), LD_{50} or lethal dose for 50% (the amount which kills 50% of a group of test animals, usually 10 or more), and LD_{100} or lethal dose for 100% (the amount which kills 100% of a group of test animals, usually 10 or more). Sometimes D is replaced by C in the above symbols, and the word "concentration" used instead of dose, as LC = lethal concentration, when referring to vapor concentration in air.

The usual form in which lethal doses of solids and liquids are expressed is in milligrams of substance per kilogram of body weight of the animal, or abbreviated as mg/kg or g/kilo. Since a 150-lb adult weighs about 70 kilograms, it might be expected that animal data could be translated into human data by multiplying the mg/kg dose by 70. This practice is filled with pitfalls, and it should be used as a "degree of magnitude" rough calculation. For reasons already mentioned, plus the important fact that there is no laboratory animal (except possibly the higher apes) which reacts like man, extreme care should be used in applying animal data to humans.

17.3. WHAT ABOUT HUMAN EXPOSURES?

The real value and ultimate test of toxicity data, of course, is what actually happens to humans. Here we see even clearer that toxicity is not a simple matter. Some substances highly toxic to young children (up to age 4 years) are relatively nontoxic to adults, because no adult would eat or drink them except by the highly unusual accident or a suicide measure.

Two common materials which cause serious poisonings in children are kerosene and aspirin. By chewing on cribs, windowsills, and toys

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Acute Inhalation Toxicity

for Rats in	PPM for Hours	
Acrolein	8	4
Allyl chloride	2,900	3
Thiophene	8,700	½
Nitroethane	30,000	1
DMF	Sat. Vapor	4
1, 1, 1-Trichloroethane	10,000	3

Toxicity Scale

Rating Term	Lethal Dose for Man
1. Extremely	Taste
2. Highly	Teaspoon
3. Moderate	Ounce
4. Slightly	Pint
5. Pract. Non-	Quart
6. Relat. Harmless	>Quart

Threshold Limit Values

Are
- Time-Weighted Average
- Day-After-Day Exposure
- Required Number of Factors in Deciding on Hazard

Are not
- Common Denominators
- Sole Criteria for Disease
- Air-Polution Values
- Permanent (Reviewed Yearly)
- "Toxicity" Data

A lead grinder forgetful named Peck
Parked his respirator south of his neck
'Twas a very poor notion
The lad lost all motion
For lead dust made him a wreck!

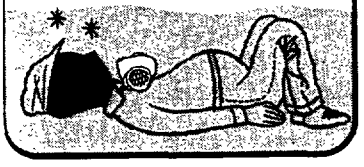
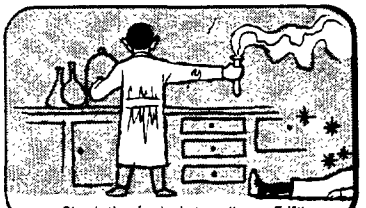


FIG. 17.1. Various attempts to explain toxicity.

"Concern for man himself and his fate must always form the chief interest of all technical endeavor; Never forget this in the midst of your diagrams and equations"

A. Einstein



"Check this for toxicity, will you, Ed?"

Skin Penetration Toxicity is Greater than by Mouth

Chemicals	*Times*
Fluoroallyl alcohol	43
Di-2-*n*-hexyl ether	30
5-Indanol	8
Formaldehyde	7
Tridecyl acrylate	7
Alkyl pyridines	6
Aliphatic amines	2-6
2-Ethylbutyric acid	4
Vinyl butyl ether	4
Substituted adipaldehydes	3
Butyl Cellosolve	3
1-Heptanel	7

	Vapor Pressure m.m. Hg.	(°C)	T.L.V. p.p.m.
Acetylene Tetrabromide	1	(65)	1
DMF	4	(25)	10
Nitroethane	20	(25)	100
Thiophene	60	(20)	—
1, 1, 1-Trichloroethane	100	(20)	350
Acrolein	213	(20)	0.1
Allyl chloride	400	(27)	1

FIG. 17.2. Four views of toxicity.

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painted with lead-containing paint, children may be poisoned with lead. A highly unusual case, reported a few years ago, developed from a teen-age boy chewing on a lead "sinker" which he used in fishing. Medications, especially aspirin and sleeping pills, are often eaten by young toddlers, occasionally with fatal results. The recent establishment of over 500 poison-control centers in the United States and Canada to advise the physician on an emergency basis the composition and recommended treatment in poisoning cases may help to make the public more aware of accidental poisoning cases, and hence to prevent accidents involving drugs and other chemicals.

Another practical problem encountered in evaluation of hazards is that much necessary data can only be obtained by experience. For example, some substances such as the isocyanates have a very low level of true toxicity, but in extremely small concentrations in air, they can cause bronchial irritation from sensitization. The irritating aspects of materials are not shown by animals. A mixture of diphenyl and diphenyl ether is a widely used heat-transfer agent, having a very low toxicity rating, but when accidentally sprayed in a man's face it causes serious, almost fatal, respiratory effects due to irritation. Hydrogen sulfide is an example of a gas which in higher concentrations soon paralyzes the nose so the odor cannot be used as even a rough estimate of concentration for this highly dangerous substance. Irritation varies with people—some people frankly say they like the odor of pyridine and of mercaptan while others are irritated, annoyed, and affected by the same concentration. Boric acid is an example of a chemical which has been used in the treatment of burns for many decades, but whose toxicity has been recently recognized as too high to justify its use in this application.[2]

Beyond the gross dosage problems, as reflected in poisonings, there is the practical day-to-day exposures encountered in industry. This is the real practical test of toxicity—what does the substance, either alone or in combination with other substances, do when breathed or absorbed in other ways at rates which will probably vary over wide limits during the day, for several hours a day for a certain period of time. To furnish a guide to the control of such exposures, Professor Warren Cook tabulated and published in 1945 recommendations of maximum concentrations permissible for many common substances. Since 1947, the American Conference of Governmental Industrial Hygienists has sponsored a committee which publishes an annual revision to the threshold limit values, formerly referred to as MAC or maximum acceptable concentration values. Nearly 300 substances are currently listed by the committee.[3] This list is not an official

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"standard," but many states have adopted it as the working limits for their labor or health codes, and it has been referred to in the Walsh-Healy Health and Safety Act, which applies to federal contractors.

Before using this list, however, it is wise to carefully read the preamble, in order to understand exactly what the list *is* as well as what it *is not*. These values are not a measure of relative hazard. The early values were established largely on the basis of safe level to prevent damage from chronic exposures. As more data became available based on actual experience, many values were lowered to reflect irritation and other transitory or acute changes. Recently, subacute levels have been introduced to reflect comfort levels. In addition to the threshold limit values, when evaluating hazards, we must consider the vapor pressure of the material which will determine the potential of attaining the MAC under given conditions of use, as well as other important factors which can relate to actual conditions of use.

Another source of information which is often helpful in evaluating the hazards of a substance is the manufacturer—a person who is truly interested in seeing that the substance is used without adverse effects. Both in published data sheets and in answers to specific inquiry by telephone or mail, the manufacturer will give practical recommendations as to the precautions he believes necessary. The more specific the inquiry, the more helpful will be the reply. Regardless of the quantity (a few grams may represent more hazard than a million gallons) the fundamentals are the same, and the manufacturer will usually supply the information if requested.

Another guide to safety information is open literature. Much is available for those who seek it. A two-part article in *Industrial and Engineering Chemistry*, points out several excellent sources of safety information not widely used.[4] The Manufacturing Chemists' Association[5] and the National Safety Council[6] both publish detailed information on many chemicals—information which helps in evaluating potential hazards. Hygienic Guides, published by the American Industrial Hygiene Association, now cover nearly 100 substances in considerable detail.[7] A reference librarian frequently can suggest many sources of specific information either in permanent volumes or in periodicals.

17.4. WHAT CLASS OF TOXICITY INCLUDES THE SUBSTANCE?

Ultimately we must decide on the degree of hazard presented by a substance. Classification of hazards goes far beyond toxicity, as

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illustrated by the excellent work of a National Fire Protection Association Committee chaired by James J. Duggan, which classified and labeled substances, especially larger amounts in barrels or storage tanks, for emergency control purposes. The N.F.P.A. Standard 704 M, which resulted from this work, includes toxicity (hazard to life), flammability (fire hazard), explosion hazard (probability of explosion), and chemical reactivity (possible reactions with other nearby substances, if spilled or ruptured), which, combined with other essential emergency would be most valuable to emergency personnel.[8]

Hodge and Sterner tabulate toxicity into six classes:[9]

TABLE 17.1. Toxicity Classes

Toxicity Rating	*Common Used Term*	LD_{50} *Single Oral*	*Inhalation 4 hr Vapor Exposure Mortality 2/6–4/6 Rats*	LD_{50} *Skin Rabbits*	*Probable Lethal Dose for Man*
1	Extremely toxic	1 mg/kg or less	<10 ppm	5 mg/kg or less	A taste, 1 grain
2	Highly toxic	1–50 mg/kg	10–100	5–43 mg/kg	1 teaspoon, 4 cc
3	Moderately toxic	50–500 mg/kg	100–1000	44–340 mg/kg	1 ounce, 30 gm
4	Slightly toxic	0.5–5 g/kg	1000–10,000	0.35–2.81 g/kg	1 pint, 250 g
5	Practically nontoxic	5–15 g/kg	10,000–100,000	2.82–22.59 g/kg	1 quart
6	Relatively harmless	15 g/kg and more	>100,000	22.6 g/kg or more	>1 quart

Another interesting and useful tabulation is the relative eye damage produced by 60 chemicals, classified into ten ratings.[10]

17.5. HOW LIKELY AM I TO RECEIVE A HARMFUL CONCENTRATION?

The old cliche of the sea states, "Not all the waters of the seven seas can sink a boat until it gets inside the boat." Toxicity is much the same. A chemical in a bottle, in a tank, or in a boat is harmless as long as it is fully contained. In evaluating the hazard, therefore, the basic consideration should be based on how much of the substance will be in the air, or where it will be so it may be eaten, or absorbed through the skin or the eyes. Once this is established, we can add the toxicity data, expressed as dose, or irritation, or maximum allowable concentration, or threshold limit value, and find some measure for the actual hazard.

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About ten years ago, a relatively new chlorinated hydrocarbon was introduced on the market, and widely promoted as a substitute for other solvents such as carbon tetrachloride. The new substance had many characteristics and properties of carbon tetrachloride—its vapor pressure, cleaning ability, and drying without residue were similar to carbon tetrachloride. Extensive animal exposure has established a firm basis for assigning this substance a threshold limit value of 500 parts per million in contrast to 10 parts per million for carbon tetrachloride. This limit has since been lowered to 350 parts per million—still a very wide margin over carbon tetrachloride. Although we agree this solvent is much safer than carbon tetrachloride, and we continue to recommend it for many applications, we must point out that at least three fatalities have resulted from its use. Such solvent fatalities usually involve a careless use in a confined unventilated space, while working alone. For example, a technician was believed to have been working at the bottom of the outer shell of a vacuum furnace, 38 in. in diameter by 49 in. deep, cleaning oil and grease from the interior surfaces with steel wool and rags saturated with the solvent. The tank was located in an open room and had one 15-in. and three 6-in. diameter ports 28 in. from the bottom. The solvent was being used from an open coffee can, and approximately a quart had been used when the technician was found dead, about 50 min after the supervisor had last checked the work. Such cases do not indicate the solvent is not relatively safe—it simply underscores again that *any* solvent must be used with respect. Use of any solvent in a confined space without adequate ventilation, especially by a man working alone or with only nominal, occasional supervision, is extremely unwise. In this connection, an advertisement used by some distributors that a solvent is "20 times safer than carbon tetrachloride" is highly misleading, and represents a use of threshold limit values in an entirely different manner than intended.

17.6. WHAT IS OUR EMOTIONAL APPROACH TO THE SUBSTANCE?

A few substances have come to be associated with high hazard in the public mind. If we consider "poisons" as synonymous with "hazards," we probably think of cyanide, lead, silica, arsenic, and carbon monoxide. Snake venom, curare, benzene, and carbon tetrachloride might be included on second thought. The strange enigma of beryllium and beryllium compounds and the surprising reluctance of intelligent persons to accept the facts about the substances, indicate that publish-

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ing data alone does not insure that everyone will be informed or will believe. Some of the older tonnage chemicals, such as aniline, nitrobenzene, and hydrogen sulfide, have not yet been widely recognized as hazardous, and there are many substances about which we know so little that it is impossible to even guess how safe or how hazardous they are in the intended applications. Recently, a university reported the death of three students who were working with several bicycloheptadiene derivatives, previously not considered hazardous. Animal investigations are underway to elucidate the hazard.[11]

Extreme fear and anxiety about hazards may actually create accident situations, just as may apathy and ignorance. Personnel may be so fearful that they will become nervous and supersensitive—perhaps even allergic. The reverse condition, lack of adequate and proper respect for a hazard, may also contribute to accidents by encouraging carelessness and lack of protective measures. Exactly how to present the degree of hazard to personnel in their specific use of the toxic or corrosive material, so they will actually react with respect and confidence *but not fear*, is one of the challenges of supervision. In addition, the emotional state of the man, his emotional stability and adequate adjustment to his job, his boss, his company, and his home life, all may be far more important in evaluating actual on-the-job hazards than toxicity data alone. In all cases, it must be the *man*, not the chemical, which is the center of our attention.

Another factor which may minimize the hazard of a substance is irritation ability. If a gas or vapor affects the upper respiratory tract sufficiently to cause sneezing, coughing, or extreme discomfort to the eyes or throat, the normal reaction is one of escape or repulsion, which tends to decrease the exposure. On the other hand, if the substance is not sufficiently irritating or objectionable, the practical danger is much greater, since the warning will be less or inadequate.

Summary

All chemicals, *per se*, are toxic (common usage meaning the ability of excessive amounts to produce damage to life).

Toxicity refers to the effect on living cells (usually animals or humans).

Toxicity data must be carefully screened and examined before extrapolating into human experience.

Chemicals, even "extremely toxic," may or may not be hazardous, depending on their use.

Until they reach and produce effects inside the body, toxic substances are not harmful.

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Our procedure should be to properly evaluate the hazard presented under the conditions of use, and then take precautionary measures to insure safety as needed by the circumstances and conditions developed.

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18

Safe Experimentation

H. H. *Fawcett*

Before developing the subject of safe experimentation, an explanation of the terms *safe* and *experimentation,* especially when these two are used together, is in order.

One definition of safe is "free from or not liable to danger of any kind." For our purposes, danger may be expanded to mean (1) physical hazards, such as flying glass, electrical shock, pressure, and vacuum; (2) chemical hazards, such as skin corrosion, dermatitis, and poisoning from fumes (inhalation), ingestion (eating), and skin absorption; and (3) fire and explosion hazards, such as undesired ignition of flammable gases, liquids or solids, or unexpected evolution of pressure-producing gases.

With these thoughts in mind, to use safe as an adjective modifying experimentation, which is "an act or operation designed to discover some unknown truth, principle, or effect," implies that we are able to prevent all dangerous situations which might arise in research. We concede that we probably will never be able to foresee all the booby-traps which may arise in scientific work, before we can completely understand what motivates a man to unsafe acts resulting in accidents. However, just as we can change the velocity of a reaction by modified conditions or by a catalyst, so can we decrease the dangers in experimentation by the catalysis of safety.

To illustrate how we might apply safety knowledge to research, let us imagine we are interested in the reaction:

$$X + Y \rightarrow Z.$$

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To make our example realistic, let us assume X is a gas at room temperature and atmospheric pressure; that Y is a liquid at room temperature; and that our product, Z, is believed a solid by analogy of its assumed molecular structure. We have never reacted X, the gas, with Y, the liquid, and can find nothing in the literature concerning the reaction. The problem then is to prepare a set-up in which the reaction may be studied without injury to personnel.

Since we have assumed that the two reactants are known chemicals, some of the physical and chemical properties should be available from the maker or supplier. We should not neglect to request safety data as well.

In the case of X, the gas, we might inquire:

1. Is it flammable with air; if so, within what range?
2. If flammable, what is the auto-ignition point?
3. If nonflammable, does it undergo decomposition into flammable or toxic products?
4. What is the vapor density compared to air?
5. What are the hazards of inhaling the gas?
6. What parts of the body are affected by inhalation?
7. What respiratory protection is required, such as a chemical cartridge respirator, canister-type mask, or self-contained air or oxygen breathing apparatus?
8. What first-aid treatments (both on the spot and by the physician or nurse) are recommended?
9. Can the gas be detected by odor, and, if so, at what concentration?
10. What analytical or instrumentation method is available for determining injurious concentrations of the gas in air?
11. What is the maximum allowable concentration for continual 8-hr exposure to the gas in air?

From a practical standpoint, it will usually suffice at the research stage to know the answers to the first eight items given above, questions nine through eleven are usually important only when pilot plant or experimental scale plant operations are reached.

With the answers to the first eight questions, we can decide how elaborate our care in handling should be, our care in transferring, and our care in reacting the gas, X. If it develops that the gas is relatively unreactive, such as nitrogen, the inert gases, sulfur hexafluoride, carbon dioxide, or the simple fluorocarbons, we need relatively little ventilation, shielding, protection against fires or explosions, and relatively simple specific medical procedures. However, if a gas such as hydrogen cyanide, fluorine, chlorine, diazomethane, hydrogen sulfide,

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hydrogen selenide, or arsine is involved, extreme care must be taken. All these gases are severe health hazards, and most are flammable or explosive under some conditions. Hence, it is imperative that the gas be handled at all times in an environment where ventilation will be adequate to remove escaping gas and to dilute it promptly below the levels which are toxic or flammable. Medical control should also be established. First-aid measures for on-the-scene and clinical treatment by the physician or nurse should be considered before actual work is begun. The question of periodic physical checks should be explored. Frequently, in this connection, the investigator, or some other interested party, can assist the medical personnel by calling attention to the problem and by reviewing the known and unknown aspects of its effects upon humans, to the extent such knowledge is available.

Turning now to our other raw material, *Y*, the liquid, an attempt should be made to assemble as much of its safety data as are available. Several important items are:

1. Purity, such as nature and amount of impurities;
2. Flash point and fire point, so relative degree of fire hazard can be established;
3. Boiling point at atmospheric pressure and stability of the liquid toward heating and distillating;
4. Freezing point;
5. Stability on storage, including possible effects of heat, light, water, and metals, by formation of dangerous by-products, such as peroxides in ethers, and on spontaneous heating as in drying oils;
6. Vapor pressure at room temperature and elevated temperatures;
7. Flammable range of the vapors in air;
8. Auto-ignition point of the vapors;
9. Vapor density, which determines ease of ventilating;
10. Effects of inhalation of the vapors, in both acute and chronic exposures;
11. Effect of both liquid and vapor exposures on skin and eyes;
12. Effect of ingestion (accidental intake).

Although all these items are important in the final control, it is doubtful whether they will all be readily available for the liquid under question. An active search should be continued, however, even to the extent of experiments to determine the effect of the liquid and its vapor on laboratory animals if the human exposures to the liquid or its vapor are to continue for long periods.

With the available data on reactant, *Y*, we can plan the degree of safe handling needed. If the liquid is relatively free of serious fire

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and health hazards, such as the higher alcohols, higher esters, and higher ketones, the normal care with which a conscientious experimenter treats all materials should suffice. If, however, serious health or fire hazards are present, as with ether, lower alcohols, lower aldehydes, ketones, nitro compounds, and many aromatic compounds, the handling procedures should include protection of personnel from excessive exposures to either vapor or liquid. This, of course, includes the necessity for closed-system work insofar as possible, as well as personal protective equipment such as gloves, goggles, face mask, apron, and respiratory protection. As experience is gained, the procedures should be changed to further increase safety as the necessity arises. For example, adequate protection may have been taken against fire and explosions, but experience may show that sufficient vapor is being released to the laboratory air to make personnel develop headaches, occasional dizziness, and upset stomach. Obviously, the set-up should be reviewed with the objective of decreasing the air-borne exposure in this case.

The actual experimental work is now begun, with the degree of care suggested by the study of *X* and *Y* and their probable interaction. Obviously, if the search for data on *X* and *Y* has yielded only partially complete information, additional precautions should be included to safeguard against unknown hazards.

At first, only small amounts of *X* and *Y* should be brought into contact, such as gram or sub-gram quantities, and the results observed carefully. Changes in temperature, in color, in viscosity, or in physical state should be noted. By varying concentrations, time, temperature, and pressure, the optimum conditions for the reaction can be established. Safe limits can now be imposed to insure that the reaction will not exceed the specified conditions.

When the product, *Z*, is first isolated, the usual elementary analysis will at least suggest possible structures. We know that certain groups in a molecule create explosive tendencies. Among these "plosophores" are:

$-ONO_2$ nitrate	Organic salts of the following types:
$-NH-NO_2$ primary nitramine	perchlorates
$-N-NO_2$ secondary nitramine	chlorates
$R-NO_2$ aliphatic nitro	picrates
$Ar-NO_2$ aromatic nitro	nitrates
	bromates
	chlorites
	iodates

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Less powerful, but often more sensitive compounds contain these groups:

$-N_3$ azide	—O—O—perioxide
—NO nitroso	=N—X halamines
—N=N—diazo	—C≡C—acetylides
—N=N—S—N=N—diazosulfide	

The presence of one or more of these in the molecule should serve as a warning of relative instability. Another safety evaluation is to consider the oxygen balance, if the molecule has combined oxygen within it. The closer the molecule approaches self-satisfaction by oxidation, the more powerful the explosive. As an example, three nitro groups on an aromatic ring, such as exists in tetryl, TNT, and picric acid, provide a source of readily available oxygen for the rapid burning or explosion of the molecule.

It is difficult to establish definitely when exhaustive (and admittedly expensive) investigations should be undertaken to develop the safety data on a new compound. Much depends on the amount of compound available, the forecast for production, and on the end use. If this compound, *Z*, is an intermediate which some company will use to produce a new end product and the processes are well-engineered, the minimum of such information will usually suffice. On the other hand, if the new compound, *Z*, is destined for wide use by the public, such as a food, cosmetic, economic poison, or container, extensive studies should be made to establish quantitatively such data as:

1. Impact sensitivity.
2. Stability on storage.
3. Melting point.
4. Acute and chronic dosage by various routes, such as injection into the blood stream, injection into the stomach, skin contact, eye contact, and dust inhalation.
5. Maximum allowable concentrations or threshold limit values for continuous 8-hr exposures.
6. Fire hazard, both from ease of ignition and from rate of burning.
7. Injurious vapors or gases from burning.
8. First-aid and clinical treatment for exposures.

Usually, a review of these items will be made during the transition from laboratory to pilot plant scale and at least some of this data should be available before plant personnel is involved. From this data should evolve a warning label which will serve to define the outstanding hazards of the compound and which should be displayed on every

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bottle, drum, or tankcar of the product which leaves the plant. The Manufacturing Chemists' Association has formulated definite rules for warning labels and increasing emphasis is being put on this warning procedure by federal, state and local laws.[1] In addition, the Interstate Commerce Commission, Bureau of Explosives, must classify the compound before it can be accepted for express shipment and the proper warning label must be attached to all shipments.[2] The producer must supply the data for this classification.

We have briefly discussed the role of "safety data" in research. The more that is known of a compound, including its effects on humans, before it leaves the laboratory or pilot plant, the more complete will be the insurance against unwanted experiences. If we remember that chemicals, like humans, have characteristics which may be either blessings or curses, depending on how they are controlled, we shall have progressed toward safe experimentation.

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Testing Reactions and Materials for Safety

J. S. Snyder

The chemical industry's property damage and business interruption losses in recent years have been high. The National Fire Protection Association, which makes an annual study of all large fire losses, classifies a large fire as a loss which exceeds $250,000. The N.F.P.A. reports that in 1961 the chemical industry had eighteen large fires, that killed fourteen persons, injured 314, and cost almost $8,500,000. In 1962, only four chemical industry fires (there were several others) exceeded both the loss of life and property damage of all eighteen in 1961. Each involved an explosion. The estimated property damage and business interruption costs for two of these four explosions were greater than $8,000,000 *each*. We experienced the worst "large loss" fire experience in 1963 with 488 such fires resulting in over $350,000,000 in damage.

A real problem exists, and if the present trend continues, the problem will become even more acute. The small, isolated pot-and-kettle installation is a thing of the past. Today industry is installing complex, automated processes. The reactions usually are fast because of the nature of the reactants, high temperatures, high pressures, and active catalysts. To complicate matters even more, many of the reactants and products are extremely toxic. An intelligent appraisal of the new risks must be made, and presented to management with recommendations for minimizing the probabilities of serious incidents.

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Chemists usually admit that in most organic reactions where compound *A* and compound *B* react to form compound *C*, 3 or 4 transitory compounds may be involved during the reaction. Not only the product is obtained, but varying amounts of other unwanted compounds as well. If the reaction is run every time exactly as the chemist describes, there will be routine operations, but, how close to or how far from an unstable situation the reaction may be, usually is not known. Ideally the parameters of safe operations for every step should be known, and procedures and equipment should be designed so that the limits will not be exceeded.

Knowledge as to what constitutes a potentially unstable condition, and why some compounds and mixtures behave in an undesired fashion, is relatively meager. Hence, the key to any determined effort to test for stability is the interest and backing of research management who must know it is important to find out how safe a reaction is as well as what is the yield. Most research chemists have not been trained or oriented in this direction.

No chemist would consider undertaking a new synthesis without a literature search; a good research chemist makes frequent use of the library. Unfortunately, the amount of safety information published in the chemical journals is very meager. Even standard textbooks on organic chemistry used in universities discuss dangerous reactions in a very routine manner. Hence, it is not difficult to understand why so many research chemists are not safety oriented. Perhaps another reason is that the consequences are minimal when instability is suddenly encountered in the laboratory. A reaction which could result in an explosion in a plant operation may merely cause one of the ground joints of the laboratory flask to be pushed apart or broken by materials frothing out over the bench. The chemist just does not equate the effect of the rapid gas evolution on a loosely connected glass system to the effect on tight steel equipment, containing large volumes, without the pressure-relieving capacity to take care of such a sudden surge.

Occasionally the feeling is expressed that it is an insult to professional ethics among chemists to warn that while a procedure described in the paper was being developed, variations in conditions resulted in misadventure, characterized by loss of reaction product to the ceiling or bench, or where flying glassware caused injuries. The research chemist is best qualified to recognize a potentially hazardous compound or reaction. No scale-up of laboratory to pilot plant or of pilot plant to factory should be permitted without adequate consideration being given to the stability of the compounds and reaction involved.

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To undertake such a study, the following steps are suggested:

First, although little may be located in the classical literature, an ever-increasing body of safety literature can be helpful. Some research work has been done, and papers have been written on stability of materials. Second, there are ways to confirm or allay some suspicions with simple tests.

The Manufacturing Chemists' Association, in their Chemical Safety Data Sheets,[1] and the National Safety Council Chemical Section Data Sheets,[2] contain some stability data on a limited number of common materials. The 1962 revision of National Safety Council Data Sheet 486, *Chemical Safety References,* gives an indication of the data available on a fairly large number of compounds. Volume One of *Case Histories of Accidents in the Chemical Industry,* issued by the Manufacturing Chemists' Association, contains an indexed compilation of nearly 600 accidents, and many of these illustrate the causes and results of unexpected instability. The Committee on Chemicals and Explosives of the National Fire Protection Association, Subcommittee on Hazardous Chemical Reactions, has published a directory to several hundred reactions which cause unwanted results if not controlled.[3] Two of the many National Board of Fire Underwriters Research Reports are especially interesting, namely, "Nitroparaffins and Their Hazards," and "Fire and Explosion Hazards of Organic Peroxides."[4]

The United States Bureau of Mines Explosives Research Laboratory has contributed much to the chemical stability literature.[5] Much of the Bureau's research has been on explosives and includes several important tests for evaluating explosives. These same tests can also be used for evaluating nonexplosives. (See Chapter 29.)

One source of information frequently overlooked is the manufacturer. When confronted with a compound of suspicious configuration, it is possible the maker has literature on stability or his research staff has unpublished data he will furnish on request.

The Department of Defense has authorized considerable research on test methods for propellants, and these tests have application to commercial problems. One publication that contains information on both common and exotic materials is *The Handling and Storage of Liquid Propellants.*[6]

A search through this literature and others cited at the end of the chapter, will assist the chemist in the art of recognition, which is the heart of the matter, even though it may not yield the specific reactants he plans to use. Certain types of compounds, mixtures, and reactions should always be suspected. Many may be familiar because they are difficult to handle, but the reactivity noted in the laboratory

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is amplified many fold in the closed pilot plant and factory equipment.

An explosion is a sudden release of pressure regardless of the source. For instance, a bursting steam boiler is truly an explosion even though steam is not an explosive.

An explosive is any substance that can produce in thousandths or even millionths of a second, high-pressure gas capable of destroying the surroundings. A detonation is the process in which an explosive undergoes chemical decomposition or oxidation—reduction, primarily within a high-pressure zone or shock wave that travels at greater than sonic velocity through the unreacted material. In other words, a true detonation is capable of almost instantaneous self-propagation once the reaction or decomposition is initiated.[6, 7]

The reactive chemicals to be considered are not explosives even though they may be capable of self-reaction. As compared to explosives they react very slowly and seldom produce shock waves of any significance. Usually the reaction can be controlled after initiating it, by cutting off feed rates, or by lowering temperatures or pressures. With an explosive, this is impossible.

Steele and Duggan, in their paper "Safe Handling of Reactive Chemicals,"[8] characterize a reactive chemical as a material which will vigorously polymerize, decompose, condense, or otherwise react with itself in the pure state, or in the presence of a catalytic amount of some other material, or which will react violently with water. Classes of compounds which react with themselves include those containing a vinyl linkage, such as vinyl chloride, acrylates, and styrenes. Some of these require only high temperatures to catalyze polymerization. Others polymerize in the presence of light, peroxides, caustics, and strong acids. Most of the monomers have to be inhibited chemically or at least refrigerated to prevent polymerization. Another group involves the carbonyl radical contained in materials such as butyraldehyde and acetyldehyde. These can condense with extreme vigor in the presence of bases and sometimes strong acids.

Certain conjugated unsaturated compounds, such as butadiene, acrolein, and acrylonitrile can polymerize violently in the presence of suitable catalysts or when heated. Epoxy compounds are also self reactants. Ethylene oxide is the smallest and most reactive member of this group, and is capable of violent decomposition.

Strong oxidizers such as chlorine dioxide, chlorates, perchlorates, permanganates, peroxides, and chromic acid are all capable of uncontrolled reactions. Compounds of this type are capable of the instability which causes many chemical-plant and laboratory explosions.[9, 10] It is essential that the chemist determine the parameters of safety both for

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these compounds and for any reaction system that contains these compounds. The chemist should deliberately determine at what temperature the reaction accelerates dangerously, which common compounds can inadvertently or by design catalyze the reaction, and at what concentrations and temperatures this becomes difficult to control.

Compounds that are reactive with water are included in this study, because the results of this mixing can be violent and destructive. Among compounds requiring extreme care in this respect are sodium metal, aluminum alkyls, chlorosulfonic acid, phosphorous trichloride, and calcium carbide, as well as the concentrated mineral acids, including sulfuric and nitric acid and their mixtures.

Acetylene and acetylenic compounds are notoriously unstable. Metal acetylides are sensitive to heat, shock, and abrasion, and some can be classed as explosives.

Nitrogen-containing compounds fall into a class by themselves, and they can be very confusing. Nitrogen gas is quite inert, and it is usually added to a reaction mixture to minimize the possibility of an explosion. Gaseous ammonia, although it will form a flammable mixture in air, is not usually considered an unstable compound. The ammonium ion, however, increases the sensitivity and reactivity of some compounds. For example, compare the stability of ammonium nitrate with sodium nitrate.

Amines are not reactive in the above context. Trimethylamine is a prime example, although it makes up for its apparent innocence with an obnoxious odor. However, the fact that nitrogen is present in the compound does require a certain amount of caution, because when it comes into contact with strong oxidizers, vigorous and even explosive exotherms are experienced. In contact with mercury, explosive fulminates are formed and reactions with hydrochloric acid will produce diazo compounds with distinct thermal instabilities. Hydrazine, which is just two amine radicals with a nitrogen—nitrogen bond, is an extremely reactive compound and a propellant. Its vapors are shock sensitive and can explode with extreme violence.

The commercial diazo compounds with the —N=N— linkage are not generally shock sensitive, usually because the molecule is quite large, but practically all will decompose exothermically and even explosively on heating, and they are sensitized by a variety of compounds. All the hydrazines and hydrazones are reactive and can form explosive compounds, but unless intimate knowledge of the chemistry involved is applied, predictions are risky. For example, hexamethylene tetramine is used in making explosives, but it is not particularly sensitive by itself although it contains a high nitrogen percentage.

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N=N bonded compounds are not explosives, but if another nitrogen is added to form an azide, $\overset{-}{N}-\overset{+}{N}\equiv$ or $N=\overset{+}{N}=N$, the molecule becomes sensitive. The azides are thermally unstable, and all explode when heated. Most are shock sensitive even at room temperature.

The oximes C=NOH are reactive but not really sensitive compounds, and neither are the nitriles with the C≡N (cyanide) linkage. The carbon—nitrogen bond is much more stable than the nitrogen—nitrogen bond. The isocyanates —N=C=O are not sensitive.

The nitrogen—oxygen bond is an interesting linkage. Nitro compounds with the —O—N=O linkage are usually strong oxidizers and can be thermally unstable at relatively low temperatures. Compounds with more than one nitro group form our common explosives; the more nitro groups the more sensitive the compound. But if the molecule is small enough even one nitro group can be enough to make the compound shock sensitive. For example, a few years ago, two tank cars containing nitromethane exploded. This substance was manufactured for many years and shipped in tank-car quantities, until one day the right conditions occurred and the contents detonated. There are other materials in the same category that may not yet be identified as such.

Nitroethane has not exhibited the sensitivity of nitromethane. However, by test we have determined that if as little as 5% by weight of *n*-butylamine is added to nitroethane, the mixture is as shock sensitive as some explosives.

The ability to sensitize relatively stable compounds is not easily predicted. Not enough is known about the chemistry involved to be accurate. By sensitization is meant not only the increase in shock or friction sensitivity, but the ability of one material to catalytically decrease the thermal stability of a compound or mixture, either by lowering the decomposition temperature or by causing a rapid oxidation. Naturally this includes compounds which are reactive, and, therefore, capable of being affected more easily and by a surprisingly wide variety of materials.

Some of the references contain lists of incompatible compounds, such as the Department of Commerce Research Report, "Explosives, Propellants and Pyrotechnic Safety Covering Laboratory, Pilot Plant and Production Operations."[11] Some of the hazardous mixtures include ammonia with chlorine, mercury, or calcium hypochlorite; chlorine with acetylene, petroleum gases and finely divided metals, cyanides, and concentrated formaldehyde, and hydrazine and ferric oxide.

An unusual highly exothermic reaction with relatively common materials may be of interest. The contents of a receiver tank con-

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taining a chloroform-methanol mixture were being transferred to a drum that had originally contained tetrahydrofuran. The operator filling the drum heard a hissing noise and warned nearby workers to leave the building. While the building was being evacuated the drum exploded causing relatively minor building damage. A few windows were broken, a door was blown off its hinges, but no injuries resulted. Investigation revealed that sodium hydroxide was being used as a stabilizer for tetrahydrofuran and probably some caustic remained in the drum.

Laboratory studies proved that when chloroform is added to methanolic sodium hydroxide, a vigorous reaction occurs. When 1 g of sodium hydroxide was added to a mixture of 1 ml of methanol and 1 ml of chloroform, an exothermic reaction took place which, after 5 min, became vigorous enough to bubble out of a 6-in. test tube. Aqueous sodium hydroxide also reacted in methanol-chloroform mixtures in the same way. Chloroform-tetrahydrofuran-sodium hydroxide mixtures did not react, thereby indicating that tetrahydrofuran was not responsible for the incident.

It should be noted that methanol plays the role of solubilizer by increasing the contact between base and chloroform. Other solvents which dissolve sodium hydroxide and are miscible with chloroform can be substituted as the solubilizer. The reaction products may be different, but the net effect will be the same. Potassium hydroxide and other alkalies may replace sodium hydroxide as a reactant in the solubilizer-chloroform mixture.

As a supplement to the recognition of reactive chemicals, the chemist should be alerted to certain types of reactions which utilize these chemicals.

All nitrations should be viewed critically. Many, if not most, of these reactions display thermal instability at certain temperatures and pressures especially if there is an excess of nitric acid. In many of the mixtures tested an excess of nitric acid will also cause the mixture to be shock sensitive.

Oxidation-reduction reactions using peroxides, chlorine, per acids, or per salts are notorious for explosions because of thermal instability or shock sensitivity. Included in this group would be the Wolff-Kishner reductions employing hydrazo compounds and even metal hydride or pure hydrogen reactions.

Condensations such as Friedel-Crafts, Claisen, and Cannizzaro types; polymerizations; Reppe chemistry reactions utilizing acetylenic compounds; and Grignards are examples. There are many more reactions and compounds which fit into these categories.

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Simple tests can be run that are adequate for continuing laboratory work. There are more elaborate tests which should be used if the work is carried further into pilot plant or factory size equipment, or if the first test reveals a dangerous condition.[12]

The initial testing for thermal stability is based on the fact that practically all hazardous reactions involve rapid exotherms and that the rates of all reactions increase with temperature. Experts have determined that even for the majority of explosives, initiation is thermal in origin. With very little experience this test is remarkably reproducible, and it will reveal exotherms in oxidation and polymerization reactions involving reactants of low volatility. Hundreds of determinations may have been made without incident, but we should still insist on a rapid pre-test to safeguard the tester. This pre-test involves dropping a small quantity, less than one-tenth of a gram, on a hot plate at above 300°C. If a sound is heard like a pop, bang, snap, or crackle, the barricading is brought into the scene. If the sample decomposes, chars quietly, or sizzles first because of the evaporation of liquids, the test is continued. It is absolutely essential that the compound or mixture decompose for this pre-test to be valid.

The simple thermal stability test makes use of a standard melting-point apparatus, as illustrated in Fig. 19.1.[13] The heating coil in the

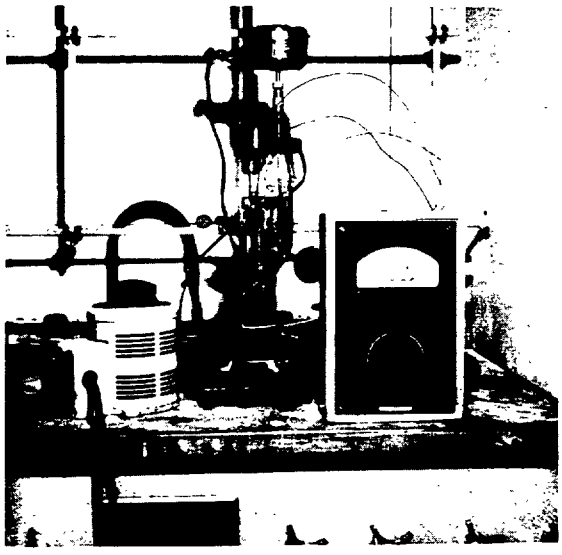

FIG. 19.1. Thermal stability test apparatus.

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silicone oil-filled cyclic bath is regulated by a variable transformer. The material to be tested, about 1 g of active ingredient, is added to a 15-ml pyrex, tapered bottom, centrifuge tube. A fine wire thermocouple with a melting-point tube as a corrosion shield is inserted to a point near the bottom of the sample. The centrifuge tube and a second thermocouple are inserted through a cork into the melting-point apparatus. The thermocouples should be at the same level. The test is run in a hood with the hood door closed. The variable transformer and the temperature indicator are located outside the hood.

The stirrer is turned on and heat is applied. The rate of heating is kept at 10° to 15°F/min. The oil temperature is not permitted to exceed the sample temperature by more than 25°F, preferably not more than 15°F. If it does, the rate of heating is slowed. For every 25°F increase in the temperature of the sample, the time, sample and oil temperatures, and transformer settings are recorded. Any change in the state of the sample is also recorded, as any evolution of gas, charring, melting, boiling, or fuming.

Particular note is paid to any rise in sample temperature above or approaching the oil temperature. If this occurs, readings are taken more rapidly. If the sample temperature even equals the oil temperature, the result of the test is considered to be positive. If an exotherm

TABLE 19.1. Temperature Readings—Thermal Stability Test

Reaction 1

3 Ml. Open-Tube Test

Time From Start, Min.	*Temperature, °C.*		*Transformer Setting*	*Comments*
	Sample	*Oil*		
0	29	29	60	
2	38	54	60	
4	52	71	60	
5	66	79	60	
7	79	90.5	60	
8	93	102	60	
9	102	107	60	Slight gassing
10	107	113	60	Gassing
13	121	126.5	70	Gassing
15	135	139.5	70	Gassing rapidly
17	149	151.5	80	Gassing rapidly
18	163	163	90	Gassing rapidly
18½	171	168	100	Gassing rapidly
19	204.5	188	110	Gassing rapidly
19½	215.5	193	Off	

ETC 03333

is not shown, heating is continued until the sample temperature reaches 600°F or until the sample is completely decomposed.

Table 19.1 is an example of one of the first tests. The exotherm experienced when this reaction got out of hand in large-scale equipment caused no injuries but considerable building damage. This explosion was the impetus that led to the development of the test. Note that the entire test took only 20 min to run. Slow bubbling was observed at 102°C. This bubbling increases with temperature and becomes quite vigorous. Note that at a bath temperature of 163°C the sample temperature equals the bath temperature and then begins to exceed it as the exotherm proceeds more and more rapidly. Incidentally, more precise tests that will be described, definitely showed that the exotherm begins at 90° to 95°C. Figure 19.2 shows the last 5 min of the test graphically.

Remember that this is a relatively crude test whose sole purpose is to uncover an exotherm and not to define precisely where it begins.

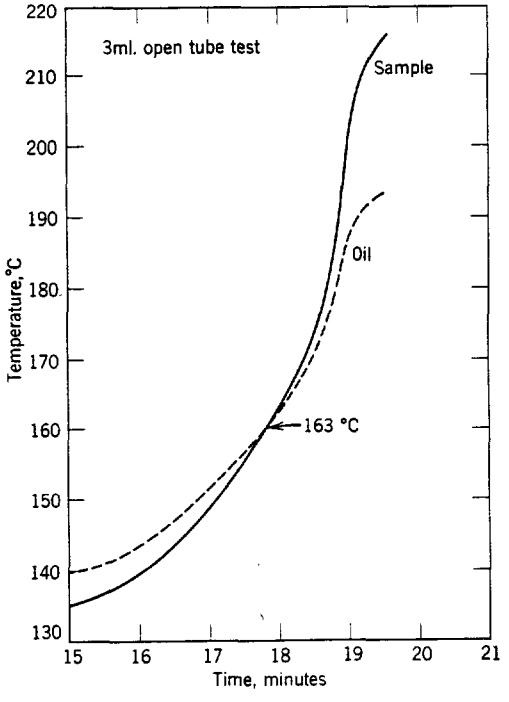

FIG. 19.2. Temperature curves—thermal stability test.

FIG. 19.3. Still buried 4 ft into the ground by uncontrolled reaction.

FIG. 19.4. Still after removal.

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The bubbling observed was a good indication, but not all exothermic reactions give off gases in the early stages. Whenever the sample temperature exceeds the bath temperature it is a sure indication that the reaction is exothermic, and in large-scale equipment this can be serious. To repeat, this test is most suitable for oxidation and polymerization reactions involving compounds of low volatility. Volatile compounds give erroneous results here but if the volatile is an inert solvent, not one of the reactants, the results can be meaningful to an experienced observer. Where two phases are involved agitation should be provided by bubbling nitrogen through the mixture, and it may also be desirable to use larger quantities here.

If an aging period is required to achieve a hazardous condition, such as in peroxide formation, this test will not discover the reaction.

Finally, since this test merely determines exotherms, we can expect to find a number of exotherms at very high temperatures which do not constitute a particular hazard. An experienced chemist, who knows the process involved and the meaning of this test, should be able to interpret the test results satisfactorily.

The reaction discussed previously was an oxidation by sulfuric acid. The mixture normally was heated to 90°C, held for ½ hr and then cooled. The reaction vessel was a 500-gal glass-lined reactor, rated at 90 lb and insulated. This time it was decided to heat it to 90°C and let it cool by itself. Unfortunately, the vessel maintained excellent adiabatic conditions. The slow and easily controllable exotherm at 95°C became uncontrollable with this result.

The still buried 4 ft into the ground is shown in Fig. 19.3. It penetrated an acid brick-covered concrete floor. The still after removal is shown in Fig. 19.4. Note that it was not badly distorted. This was not a detonation, and there was not any fire after the explosion. The hole in the roof about 20 ft directly above the vessel is shown in Fig. 19.5. The head of the still embedded in concrete 250 ft away is in Fig. 19.6. It reached a height estimated at 170 ft.

An indication appeared at 102°C showing there was some bubbling occurring, some slight exotherm. At 163°C it was confirmed in the test. Even if it is assumed there was no bubbling at 102°C, merely the reaction at 163°C, this should be enough indication that at some lower temperature, possibly 60° to 70°C lower, an exotherm can occur, and if this reaction is to be carried out in anything larger than a small laboratory flask a more precise indication should be obtained of where the exotherm begins and how rapidly it progresses.

The next test employs a Dewar flask, and it must be run in a barricaded area. A diagrammatic sketch of the flask is shown in

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FIG. 19.5. Hole in the roof, 20 ft above vessel.

Fig. 19.7. It is useful for getting a more precise indication of where an exotherm begins. It approximates, but by no means approaches, the adiabatic conditions that are possible in an insulated, jacketed, factory reactor. Here 100 to 150 ml of the mixture is heated under carefully controlled, remotely operated conditions. Usually the agitated mixture is brought to a predetermined temperature level and the heat turned

FIG. 19.6. Head of still embedded in concrete 250 ft from still pot.

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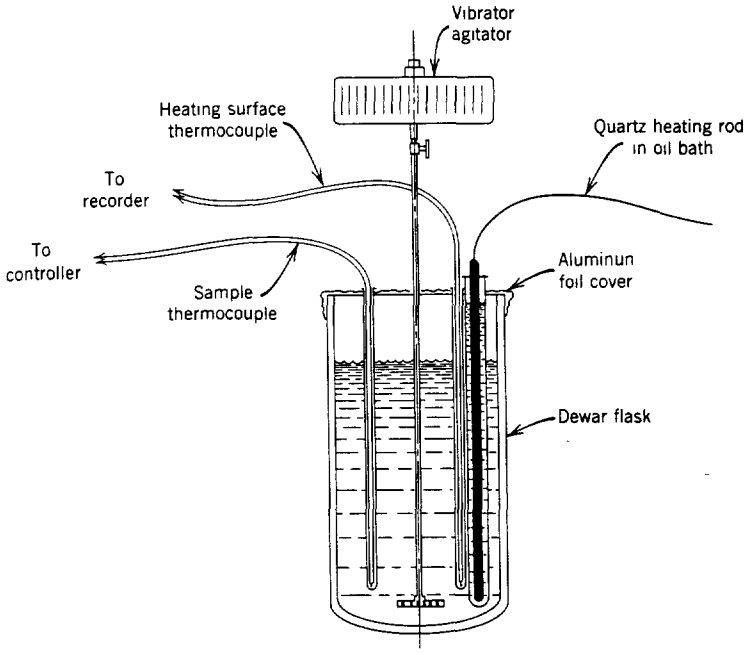

FIG. 19.7. Dewar flask test apparatus.

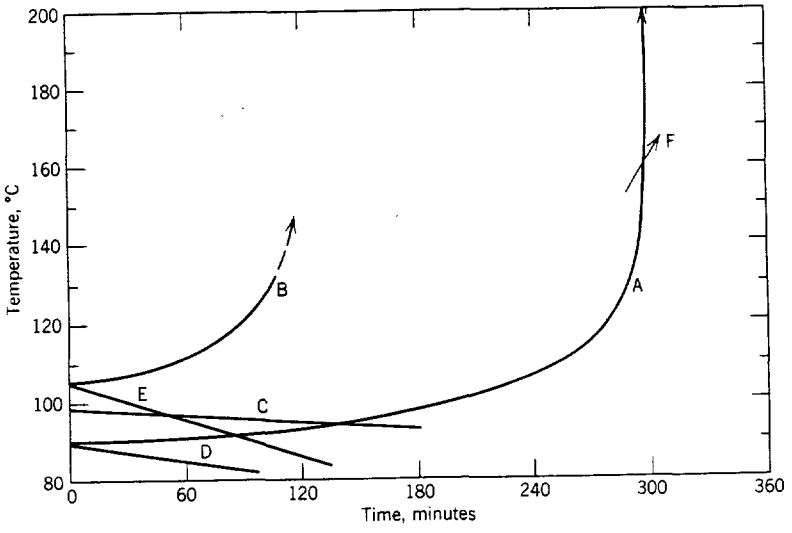

FIG. 19.8. Time, temperature curves for Dewar flask stability test.

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off. If nothing happens in 5 min heat is reapplied. The procedure is repeated to 300°C.

Let us return to the previous example and the Dewar flask determination in Fig. 19.8. Curve *A* shows the calculated time-temperature curve for a 500-gal jacketed and insulated reactor with only static air in the jacket. Curves *B*, *C*, and *D* show the curves for 125 ml of the reaction mixture in a 200 ml Dewar flask. Note how sharply the temperature affects the occurrence of an exotherm.

Curve *E* shows the Dewar flask curve for 125 ml of the reaction medium with the active ingredient removed. Curve *F* shows the rate of increase in temperature of 100 ml of reaction mixture at 160°C

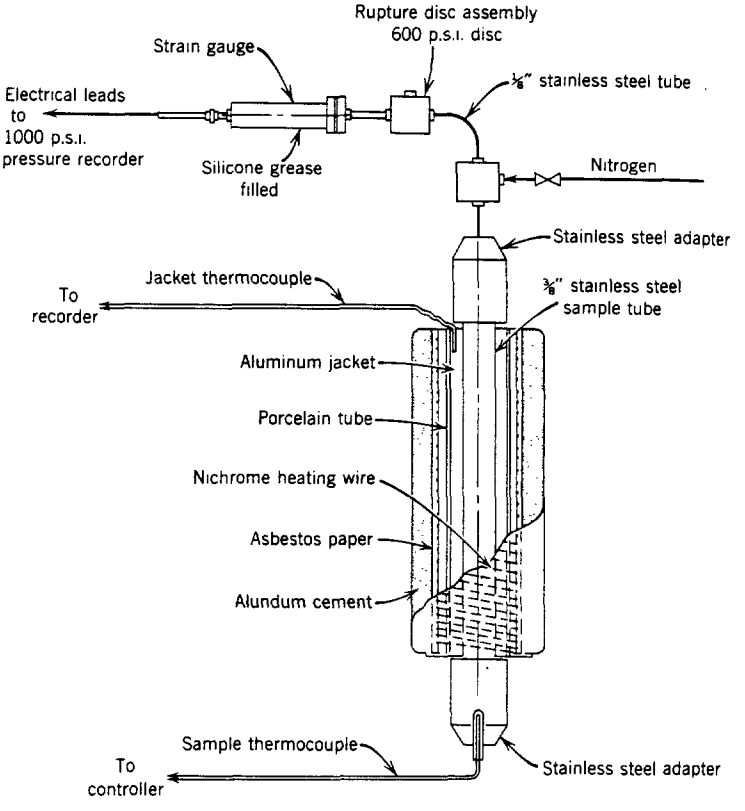

FIG. 19.9. Pressure tube test apparatus.

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in an uninsulated 250 ml round bottom flask. This rate is about 1°C/min as compared to about 40°C/min for Curve *A*, a factory reactor. A 10-ml sample in a test tube at 160°C will drop in temperature.

Incidentally, even though it could be demonstrated that the exotherm begins very slowly at 95°C, calculations indicate that with a 500-gal volume in this reactor and with full cooling water on, the reaction still could be controlled in the range of 130° to 140°C. With the Dewar flask test a combination of a rapid exotherm and substantial gas evolution is a sure indication that in factory equipment there would be an explosion.

Other tests are used in thermal stability studies. The pressure-tube test in Fig. 19.9 was developed by the Bureau of Mines.[12] The stainless-steel tube can be insulated as shown here or immersed in a heated oil bath. The heating-rate technique can be employed by observing the jacket versus sample temperatures, or the tube can be heated to a given temperature and the temperature increase observed over a 5 to 15 min period. This is a good precision method where noncondensable gases are produced. It would not detect polymerization, and it can be rather difficult to interpret the data received. This bomb must be barricaded.

The improved thermal stability bomb in Fig. 19.10 developed by Dr. G. A. Mead of the Air Reduction Company is fully described in the publication *Liquid Propellant Test Methods, Recommended by the Joint Army-Navy-Air Force Panel on Liquid Propellant Test Methods.*[14] This small bomb is immersed in a bismuth-lead alloy bath. An air vibrator agitates both the bath and the sample bomb. This is an excellent and precise tool. Exotherms on the order of 2° and 5°F can be detected. This entire apparatus must be barricaded, but it is possible to enclose it safely in an isolated laboratory.

Another interesting approach was developed by Dr. Joseph J. Martin when he was searching for the cause of the devastating 1953 explosion in a plant at Tonawanda, New York.[15] Tertiary butyl peracetate was the compound involved. It would not detonate when heated to dryness and would not detonate when subjected to the shock from an exploding blasting cap.

Dr. Martin discovered that if he inserted a 50-watt coil in the liquid and turned it on, the rapid heating of the sample caused it to detonate every time. Perhaps this phenomenon is due to compression of bubbles or to the localized high temperature which initiated the decomposition. The latter is very plausible because hot spots created

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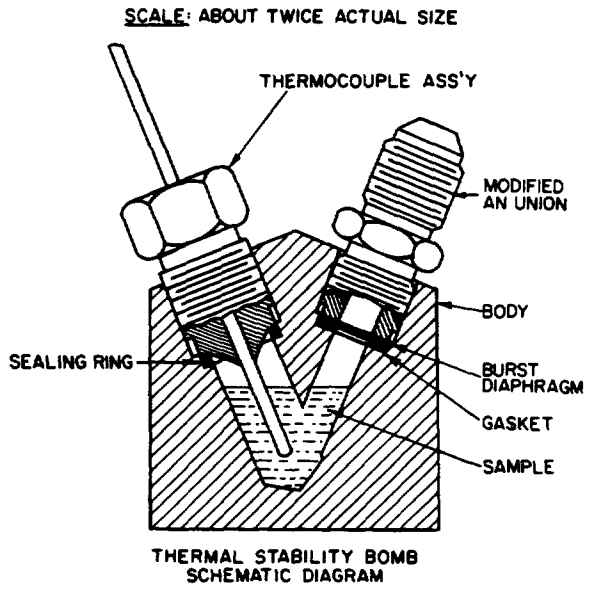

FIG. 19.10. Thermal stability bomb.

when the heat could not be dissipated rapidly enough to the surrounding liquid does cause decomposition, and presents a yield problem in factory equipment even with relatively stable materials.

The thermal stability tests are recommended because they are reproducible. Many modifications of closed vessel tests are being used with success. Particularly valuable are the ½ or 1-liter bombs used where the problem of high volatility is encountered.

The importance of thermal stability determinations cannot be overemphasized. If the various mixtures which can be reasonably expected are tested, the great majority of the possible exotherms will be revealed.

Where factory or pilot plant operations are contemplated, the more exact Dewar flask and closed vessel tests should be run on the most suspicious mixtures. If instability is observed at a relatively low temperature and if there is a possibility of mechanical instability—this means if a nitration is involved or peroxides, or diazo compounds —compounds and reactions where mechanical instability has been known, determinations should be made. There are organizations that will do this work, using apparatus such as the following:

In Fig. 19.11, an impact tester employs a fixed weight dropping at varying heights on a small amount of liquid in a precisely designed

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sample cup. The impact sensitivity is determined by observing a stainless-steel diaphragm. A hole in the diaphragm caused by a piston in contact with the diaphragm is positive. The mechanism of explosion of liquids in the drop-weight test is reported to be thermal ignition by compression of a bubble, followed by a normal deflagration process. A full description of this apparatus can be found in the previously mentioned *Liquid Propellant Test Methods*.[14] This tester will determine the ease of ignition through mechanical impact but not whether the ignition once initiated can be propagated. A further description of the meaning of this test and the next one (Fig. 19.12) can be found in the article "Evaluating the Explosive Character of Chemicals," by R. Van Dolah.[12]

The drop-weight tester requires that it be operated remotely but no real barricading is necessary. The card-gap test shown in this figure requires a true explosion-resistant test cubicle and an isolated location in order to avoid the consequences of the shock wave and the noise. This is truly a rigorous test for any compound or mixture, and it will

FIG. 19.11. Drop-weight tester.

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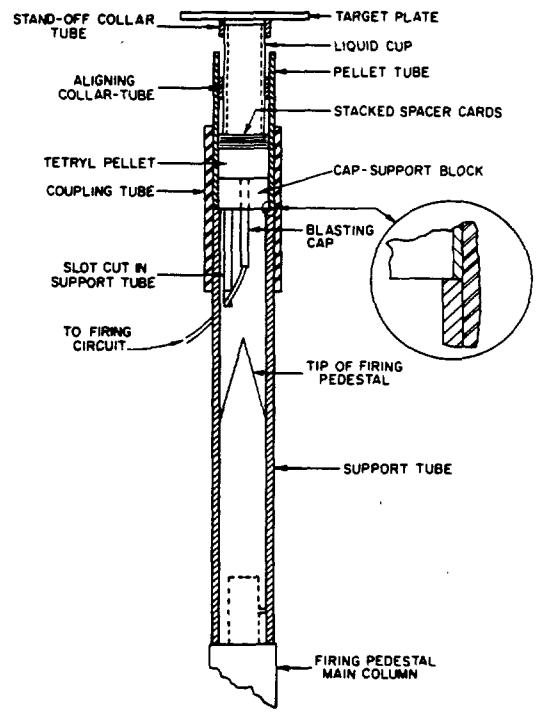

FIG. 19.12. Card-gap test apparatus for shock sensitivity.

determine whether ignition can be propagated to full detonation. We noted previously that nitroethane which by itself was not sensitive to shock when tested by card gap, was sensitive when 5% by weight of butylamine was added. It is probably true there is only a remote chance of encountering an initiator comparable to the 50 g of tetryl used in close proximity to the sample in this test. This test was run at room temperature with a small quantity of sensitizer. A process development chemist in the laboratory, or an operator's error can result in having a mixture at 50°C containing more sensitizer. Such a mixture could detonate from a much smaller shock, perhaps even dropping a flask on the floor. Knowing that the mixture is shock sensitive is essential in order to prevent these accidents.

In Fig. 19.13, the plate with the hole is similar to the hole produced

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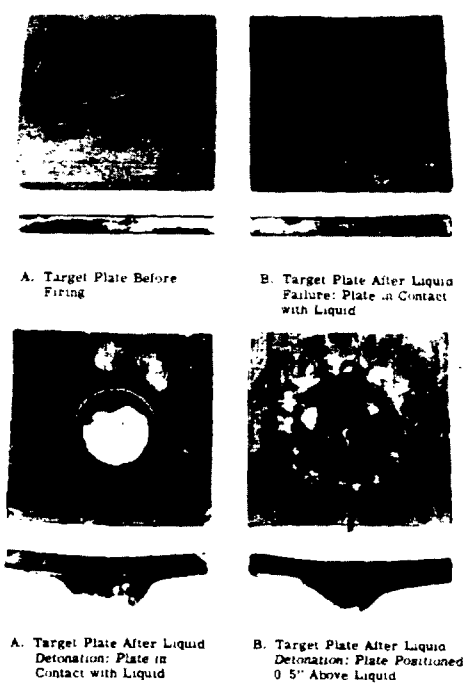
by the nitroethane-butylamine mixture. This plate is just resting on the sample cup when when the 40 cc of sample is shocked by a 50-g tetryl booster. The plate just cannot get out of the way fast enough, and the hole is blown through it.

It is most important to remember that a negative test does not mean a detonation is not possible. Low-order detonations of a type that can wreck a building may not show up here. The best procedure is to test at the highest temperature and under the worst conditions conceivable. Try to obtain a positive result. From there, usually enough inert diluents or desensitizers can be added, or the temperature lowered enough to pass below the threshold of detonation. Stability then is much more certain.

One last facet of this stability problem should be noted. If thermal decomposition at a relatively low temperature, or a rapid oxidation,



A. Target Plate Before Firing

B. Target Plate After Liquid Failure: Plate in Contact with Liquid

A. Target Plate After Liquid Detonation: Plate in Contact with Liquid

B. Target Plate After Liquid Detonation: Plate Positioned 0.5" Above Liquid

FIG. 19.13. Card-gap test apparatus, typical test results.

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or shock sensitivity has been discovered, the reaction may still be run safely. In many cases an inert diluent or a desensitizing agent is added.

For example, suppose an exotherm begins slowly at 100°C. A reaction in benzene is run without any problem. Since the benzene boils at 80°C, all the benzene must be vaporized before a higher temperature is reached. This could be a sufficiently good safety factor for a small scale supervised run with careful control of the reaction temperature, the quantity of reactants, the addition rates, and so on. Inert solvents also act as good desensitizing agents for shock sensitive systems. For instance, the shock sensitivity of nitromethane shows up very dramatically when tested in the card-gap apparatus. When 15% by weight of benzene is added to nitromethane, the mixture will not be shock sensitive by this test.

In conclusion: The tendency toward employing highly reactive compounds and mixtures must be recognized and dealt with.

The chemist's normal sources of information do not give proper attention to the possibility of instability, but there are other sources that could be of help.

The chemist should take the half hour necessary to use the melting point apparatus and from this simple screening test, determine if other tests should be run. The chemist is the one who has to prepare some of these potentially hazardous mixtures in order to run the test. He should start on a very small scale, in a hood, and keep himself protected at all times. Management should decide whether to run the other tests or have them run elsewhere. A final and most important word of caution on testing—there is no guarantee that an explosion will not occur. The art of testing is very new. Enough is not known of the various mechanisms involved in explosions to devise sufficient tests. The right contaminant or sensitizer or the right amount at the right temperature or the right pressure may not have been tested. But if testing is done intelligently reasonable assurances are obtained that the rumbling noise is just thunder or a jet plane.

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20

Shock Sensitivity and Its Evaluation

Robert W. Van Dolah, Ph.D.

Shock sensitivity or ease of initiation of detonation is another manifestation of chemical instability. In contrast to the relatively slow chemical changes that characterize the usual decomposition or oxidation reactions, exceedingly rapid chemical reactions may be initiated by shock waves in potentially explosive systems. The discussion that follows is limited to means of evaluating the tendency of materials to exhibit this type of instability.

The terms "detonation" and "explosion" are frequently misused or interchanged. "Detonation" is often applied to very violent explosions accompanied by loud noise or shock waves or to explosions causing very severe damage. Strictly speaking, the term "detonation" should be limited to processes in which an exothermic reaction takes place in a high-pressure wave that advances with supersonic velocity through the unreacted material; in contrast, flames or deflagration waves travel at less than sound velocity. Moreover, except during the buildup or decay of a detonation, the velocity of propagation ordinarily is constant and is defined by the physical (fluid-thermodynamic) variables of the system. The steady-state characteristic of a fully developed detonation provides a convenient means of recognizing this type of reaction, although the picture may be a little confused by the fact that two types of detonation exist. Normal detonation is characterized by high-wave velocities, ranging from 2000 to 3000 m/sec in gases and from about 3000 to 8000 m/sec in liquids and solids. Abnormal, or low-order detonation is frequently observed in liquids

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and has been occasionally reported in solid systems. In these reactions the velocity of the wave is only slightly supersonic with respect to the material undergoing decomposition, being of the order of 2000 m/sec.

Detonations are extremely damaging because of the accompanying high pressures. Even in gaseous systems, the reflected pressure, sensed by end-on collision with a wall, can be 40 to 200 times the original pressure, compared to 6 to 8 times in a typical deflagration. The detonation pressure developed by an explosive system is closely related to the density of the system. Thus, the detonation pressures of condensed-phase materials are exceedingly high. Liquid and solid explosives give detonation pressures that may exceed 300,000 atm in a high-velocity detonation and reach as much as 5000 to 20,000 atm in a low-velocity detonation. Consequently, an appreciation of the tendency for chemical systems to undergo these extremely violent reactions and of the corresponding initiation mechanisms is very important if disastrous incidents are to be avoided.

Gaseous systems are detonable over limits of composition that are somewhat narrower than the corresponding limits of flammability. A deflagration, or ordinary combustion, frequently undergoes transition to detonation, especially in a gaseous system confined in piping. This process can conveniently be pictured as follows: The pressure waves from the deflagration continuously catch up with those developed at an earlier stage until a shock wave forms. The shock increases in strength until it is capable of initiating reaction, but only after an induction period. Finally the reaction is completed immediately behind the shock wave which is thus supported by a constant input of energy that maintains a constant velocity. In condensed-phase systems, a detonation may be initiated by an identical situation if the materials are particularly sensitive to initiation or are very energetic. Primary explosives are placed in a separate class from other explosives because of their extreme tendency to go from deflagration to detonation. Some liquids can go from deflagration to detonation when confined, but the process is much more complex than that of solid systems.

Sensitivity to initiation of any decomposition reaction is too often interpreted as detonability, whereas frequently the event observed is a deflagration. With solid or liquid mixtures, the most widely used test is a drop-weight test in which the sample is hit by a hammer or falling weight, sometimes through an intermediate plunger or pin. In the more sophisticated versions, a constant weight dropped from varying heights serves to compare the sensitivity of various systems, larger weight-height products indicating greater stability. Ordinarily, this

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procedure does not lead to detonation except with very sensitive materials such as primary explosives. Generally, the result is an ignition, and little information is developed as to the potential consequences of this ignition. However, the limitations of this test should not preclude its use. It can and should be applied to any solid or liquid for which the estimated heats of formation and reaction (in the absence of air) suggest the possibility of an explosive reaction. The test is easy to carry out in the laboratory. A steel block, a few crystals or a drop of liquid, and a carpenter's hammer are all that is needed. A loud bang or even a pop, indicative of initiation, should warn the man at the bench that the substance warrants some care in handling.

Like most sensitivity tests, the hammer or drop-weight test is very much affected by extraneous factors. This is particularly true of solids and liquids, where the presence of inert diluents or solvents, especially water, can act as an effective heat sink and modify the test results significantly. The presence of bubbles may also have a marked effect on the sensitivity of liquids.[1] Sometimes impurities can act as sensitizers. Grit increases the sensitivity of solid explosives, and nitromethane is sensitized by amines.[2] Another limitation of the drop-weight test is that it does not characterize the energy released by the explosive reaction of a given substance which may vary widely for compounds that show equal sensitivities. Thus nitroglycerin and lead azide are rather comparable in sensitivity as evaluated by the drop-weight test, but the heat of detonation of nitroglycerin is about seven times that of lead azide (1500 vs 220 cal/g).[3]

The sensitivity of condensed-phase materials to initiation of high-velocity detonation is most frequently determined by means of a card-gap test, first developed almost simultaneously in Great Britain and the United States. This test has undergone a number of modifications and is now applied in several "standard" versions. Essentially, the sample is subjected to a shock wave derived from a specific high explosive charge and attenuated by passage through an intermediate barrier or gap. Originally, this barrier consisted of paper cards or wax, but now it is most commonly formed by stacks of plastic discs. Perforation of a steel witness plate placed above the sample indicates that a high-velocity detonation was initiated.

In the most common version of the card-gap test, the sample is contained in a cup formed by a 3-in.-long section of 1-in., Schedule 40, extruded, black steel pipe, both ends of which are faced in a lathe; the bottom is closed by a thin diaphragm of polyethylene or Teflon.[4] If the material to be evaluated reacts with ordinary steel, the pipe may be coated with Teflon enamel or replaced with a cylinder of aluminum,

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plastic, or glass. However, as these latter modifications may influence the test results, data obtained, for instance, in aluminum pipe should not be compared directly with those obtained in a steel pipe. The test is normally conducted at ordinary temperature and pressure, but when desired, elevated temperatures may be obtained by wrapping a simple inexpensive electrical heating tape around the sample cup. The booster (or donor) charge ordinarily used is a 50-g, cylindrical tetryl pellet, approximately 1 in. x 1⅝ in. in diameter, pressed to a density of 1.57 ± 0.3 g/cm^3. Although tetryl is not usually considered as unduly sensitive, it should be handled with great care. In addition, as it is quite toxic, precautions should be taken to avoid excessive contact with hands or other parts of the body.

Tetryl is sometimes difficult to obtain; in this case it can be replaced by pentolite (50-50 pentaerythritol tetranitrate-trinitrotoluene). A variable gap is built up from 1.625-in. diameter discs punched from .010-in.-thick cellulose acetate sheet. For gap thicknesses greater than 0.5 or 1 in., it is convenient to substitute a single thick disc or cylinder of polymethyl methacrylate (Lucite or Plexiglas) for an equivalent thickness of cellulose acetate discs. The witness plate or target is a cold-rolled, mild steel plate, 4 x 4 x ⅜ in. thick, placed directly above the sample cup (Fig. 20.1) and supported at a standoff distance of 1/16 to ⅛ in., usually by means of a tightly fitting cardboard collar on the cup. The sample cup, card gap, and donor charge are aligned on a common axis. A paper mailing tube may be used for this purpose with some additional spacers to center the acceptor and donor. A No. 8 commercial electric blasting cap, or a more powerful cap known as an Engineer Corps Special, is used to initiate the donor. These blasting caps are hazardous, and every possible precaution should be taken to avoid premature initiation; special emphasis should be placed on gentle handling and protection from electrostatic charges that may accumulate on personnel conducting the test.

This test, which may involve 100 to 130 g of explosive partly confined in a fragment-producing container, requires that substantial protection for personnel be provided to shield against blast or fragments. This protection can consist of a reinforced concrete enclosure, all-steel chamber, or some more elaborate structure. It is important to realize that fragments of the test set-up may travel a considerable distance; any open-faced barricade should be located in an area where no one will come within range of projected fragments. If reinforced concrete is used, an additional lining of boiler plate backed with wood is recommended to protect the concrete against damage from fragments. Another point to be considered is that a positive result (explosion or

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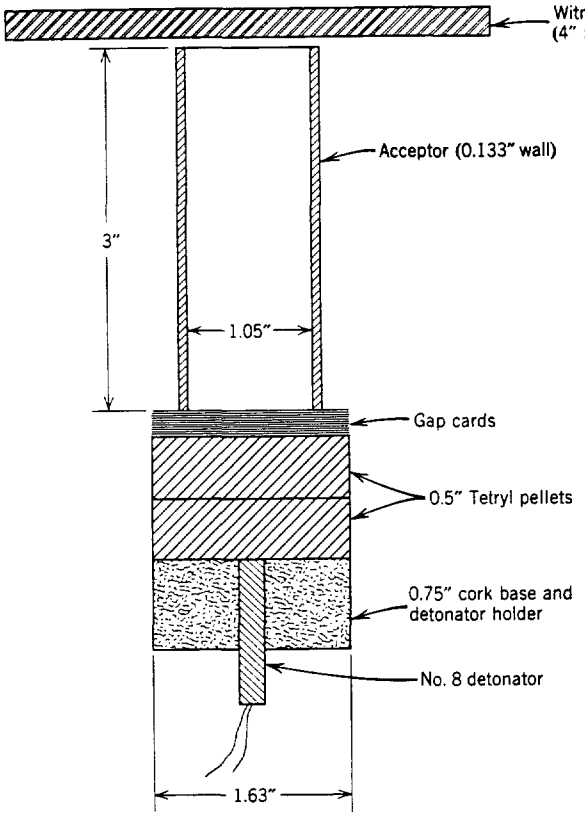

FIG. 20.1. Schematic of 3-in. card-gap test.

detonation) can be accompanied by considerable noise which may lead to complaints from occupants of adjacent areas.

Only personnel who have been fully instructed in the safe handling of explosives should attempt to conduct the card-gap test. A standard operating procedure should be followed to prepare and fill the sample cups, align the donor, insert the blasting cap, and place the charge in the bearing chamber. Some positive means must be provided to control the firing circuit. A locked safety box is normally used, and the person who places the detonator in its final position and connects the leg wires of the blasting cap to the firing line should be the sole possessor of the key. A siren, horn, or buzzer should sound a warning before the shot is fired. It is good practice to check the continuity of

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the firing circuit with a galvanometer of a type designed specifically for this purpose and available from explosives suppliers. When the test is positive, the resulting detonation may produce toxic fumes. If it is negative (no detonation), unexploded material that can nevertheless be explosive or toxic may be scattered in the enclosure; serious accidents have resulted from accidental initiation of undetonated materials in bombproofs. Therefore, the area must be decontaminated; the means selected for this purpose depend heavily on the nature of the substances being tested.

Following the shot, the witness plate is examined to determine the nature of the result. A clean hole in the plate indicates a high-velocity or normal detonation, although a very hard plate may be broken by such a reaction. If the plate is completely undamaged, it may be assumed that there was no initiation of detonation. A dome or some other distortion of the witness plate indicates an intermediate reaction. In general, a bulge or rip in the plate is evidence of a low-velocity or incompletely developed detonation. The significance of such results is discussed later, but as the test is usually run, a low-velocity or incomplete detonation is considered to be a negative result. The usual experimental design seeks to define the gap thickness at which there is a 50% probability of a high-velocity detonation. This 50% point may be conveniently determined with a minimum number of shots, using the Bruceton up-and-down technique.[5] The result is expressed either as the number of standard .01-in. cards or as the equivalent thickness in inches. Some typical card-gap data are given in Table 20.1.

Other versions of the card-gap test have been developed to meet special needs. Frequently in research programs, suspect materials are available only in small quantities. For such cases, the Naval Ordnance Laboratory has developed a small-scale card-gap test[6] in which the donor is a 1.4-in.-long, 0.2-in.-diameter RDX column loaded in a 1-in.-diameter brass cylinder. The sample is loaded into a similar brass cylinder; the gap material is Lucite or Plexiglas. The result of the test is determined by the depth of dent in a steel witness plate.[7]

Also, the Naval Ordnance Laboratory uses a larger-scale card-gap test to evaluate propellant materials. A 5½-in.-long acceptor is contained in a 1.437-in.-id, 1.875-in.-od, cold-rolled steel tube; the donor is a 2-in. by 2-in. tetryl or pentolite charge. Cellulose acetate cards or Lucite cylinders are employed as before in the gap.[8] A 6 x 6 x ⅜-in. mild steel plate is again used to determine the result of the test.

In yet another version, the Bureau of Mines employs charges long enough to allow insertion of pressure-sensitive or ionization-sensitive probes. Used in conjunction with counterchronographs or oscillo-

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TABLE 20.1. Typical Card-Gap Results

	Density, g/cm³	Gap value, inches
Nitromethane	1.13	0.27
Nitromethane-ethylene diamine (90/10)	—	2.3
Nitroethane	1.05	< .0
Nitrobenzene-nitric acid (30/70)	—	> 5.0
NG-EGDN (steel cup)[3]	1.6	[1].4
NG-EGDN (aluminum cup)[3]	1.6	1.2
Dinitrotoluene (solid)	1.27	.90
Dinitrotoluene (liquid)	—	[2]< .0
NH_4ClO_4 (200 mesh)	1.39	1.23
NH_4NO_3 (200 mesh)[4]	1.20	< .0
NH_4NO_3 (200 mesh)	.41	1.46

[1] Low-velocity detonations have been obtained at gaps as great as 110 in.
[2] Liquid dinitrotoluene has a critical diameter of many inches.
[3] Mixture of 50% nitroglycerin—50% ethylene glycol dinitrate.
[4] Ammonium nitrate at this density has a critical diameter well over 1 in.

scopes and simple electronic circuits, these probes make it possible to measure wave velocities. This test arrangement (Fig. 20.2) has proved effective as a means of distinguishing low-velocity detonations from unstable (accelerating or decaying) detonations which all affect the witness plate in the same way when shorter test charges are used. Steady low-velocity detonations destroy the entire length of the pipe, produce a dome or other substantial damage in the witness plate, and yield wave velocities of approximately 2000 m/sec. With a decaying detonation, only the bottom portion of pipe next to the gap is destroyed and wave velocities, measured by pressure-sensitive probes, are in the sonic range. An accelerating detonation should reach normal velocity in the long charge and should cause a hole in the plate.

Low-velocity or low-order detonations are extremely important in assessing the potential hazards of explosive systems. However, it is only very recently that any comprehensive understanding of their nature has been achieved. Earlier investigators reported propagation velocities equal to, or slightly above, the velocity of sound, but because of the difficult experimental and theoretical problems posed by these reactions, they were little studied. It is now known that such detonations are associated with the breakup, or cavitation, of liquids caused by an interplay of shock and rarefaction waves, some of which are derived from the walls of the container.[9] The very anomalous results for nitroglycerin shown in Table 20.1 can be attributed to the relative

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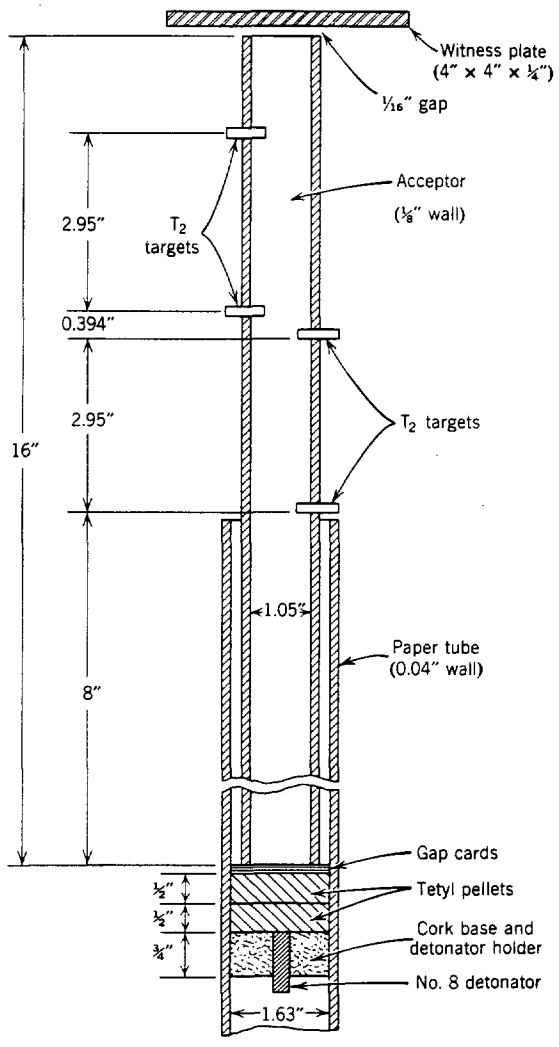

FIG. 20.2. Schematic of instrumented card-gap test.

ease of initiation of low-velocity detonation in the two kinds of metal containers. The threshold of the shock amplitude necessary to initiate such detonations is exceedingly low. For example, nitroglycerin has been initiated to undergo low-order detonation in the 1-in.-diameter card-gap test with a gap of 110 in. of Lucite. In fact, this type of

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detonation has been initiated in nitroglycerin by a donor weighing as little as 1 g, across a barrier of about 5 in. of brass, known to be a more effective shock attenuator than Lucite.

In addition to the error in evaluation that low-velocity detonations can introduce into the card-gap test if only a witness plate is used as criterion, further misinterpretation may result if the critical diameter for detonation of the material tested is greater than the actual diameter of the acceptor. This critical diameter may be defined as the minimum charge diameter which will allow steady-state propagation of a detonation. It is related to the rate of chemical reaction, or energy release, and to the rate of energy loss through expansion of the products and associated rarefaction waves. Critical diameters may be as little as a millimeter or less in the case of nitroglycerin and nitric acid-nitrobenzene solutions, and as much as 15 in. or more for fertilizer-grade ammonium nitrate.[10] For solid materials they are strongly dependent on particle size and density as illustrated by the data on ammonium nitrate in Table 20.1.

Thus, if prilled ammonium nitrate is ground and sifted into a container to form a very low-density charge it can detonate reliably at ordinary temperatures for diameters as small as 1 in. Similarly prilled nitrate, heated above 140°C, can be initiated across about 1.5 in. of plastic to yield a stable detonation in a 1-in.-diameter charge, as the critical diameter decreases with increasing temperature for both solids and liquids. This behavior is very frequently useful when dealing with insensitive systems. In some cases, materials that have large critical diameters can be evaluated as smaller diameter acceptors if the test is performed in very heavy-walled containers. This technique is frequently applied to solid explosive materials. It has limitations when applied to liquids because low-velocity detonations seem to develop most readily, and from the weakest shocks, in heavy-walled containers. Finally, materials that have large critical diameters may still be tested by using powerful donors and short charges. The reaction is sufficiently overdriven to result in some threshold pressure at the far end of the sample even though the detonation is decaying. This approach has been used to study the sensitization of ammonium nitrate by organic materials.[11]

There is a rather widespread tendency to deprecate the results obtained with explosive-driven shocks. It is frequently argued that in actual practice no explosives are present to provide similar shocks. However, quick-acting solenoids, gear pumps, cavitating impellers, and "water hammer" in liquid-filled lines can readily result in shocks of comparable amplitude that can initiate deflagration, as well as low- or

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high-order detonation, or can at least produce incipient reactions leading to one of these catastrophic reactions. In the case of solids, impact, friction, or electric sparks may initiate a deflagration reaction which, in the more sensitive systems, may undergo a transition to detonation before the pressure resulting from the deflagration is dissipated. The maximum possible pressure on a system is frequently, but mistakenly, thought to be only the hydrostatic pressure. However, when a reaction is very rapid and energetic, the pressure is determined by the inertial mass of the reacting material or of its confinement. In the case of a pile of solid material, this pressure is related to the acceleration imparted to the material as follows:

$$P = \rho h a$$

where ρ is the density, h is the height of the pile, and a is the acceleration. In the case of a liquid in a pipe, the maximum pressure may similarly be determined by the inertial mass of the liquid to be accelerated, or by the dynamic strength of the pipe. For example, Schedule 80 seamless-steel tubing requires a pressure of about 10,000 psi to burst under dynamic loading.

In conclusion, when evaluating the potential hazards of a system, it is not enough to consider only those incidents that are likely to occur and to seek reassurance by assuming the absence of strong initiating shocks. On the contrary, it is essential to assess the true explosive potential of the system and to assume that the conditions for the initiation of a reaction leading to a catastrophic explosion may be realized if suitable precautions are not taken. The card-gap test provides a useful technique for making such assessments. However, it should not be regarded as the only one—other experimental and analytical methods are available for evaluating energy potential, the tendency to decompose under thermal shock, the decomposition temperature, and other important factors. These should not be neglected in determining the stability of materials that may be hazardous under conditions of manufacture, storage, or use.

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FIG. 23.24. Although this photo was posed, similar misuses of respiratory protective devices have actually been observed—even in highly toxic atmospheres.

parachutes, life lines, and other devices which permit no compromise if human life is to be considered worth preserving.

Training is a highly important aspect of respiratory protection, and it is the one phase of the respiratory protective program where the greatest improvement is needed if we are to derive maximum efficiency from existing equipment. Putting on a mask or apparatus for a few minutes once or twice a year is not adequate training. The United

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States Bureau of Mines Health and Safety Activities, through its district and subdistrict offices, conducts training courses in first aid, and also in the use of various emergency breathing apparatus. These courses can be modified to meet special needs on request. Addresses of offices which offer these courses may be obtained by contacting the Assistant Director, Health and Safety, United States Bureau of Mines, Department of the Interior, Washington, 25, D. C. This service of the Bureau is available to the mineral and allied industries, as well as to governmental agencies. The Bureau has mine-rescue equipment at each of its District and Subdistrict Health and Safety field offices.

During training, breathing apparatus should be worn for relatively long periods, in dark and confined spaces, climbing hills or stairs, duplicating all manual labor expected, and in smoke-filled atmospheres while performing work by hand-carried or other portable lights. Smoke generators are commercially available which will quickly fill a room, a basement, a tunnel, or small building with a smoke that is

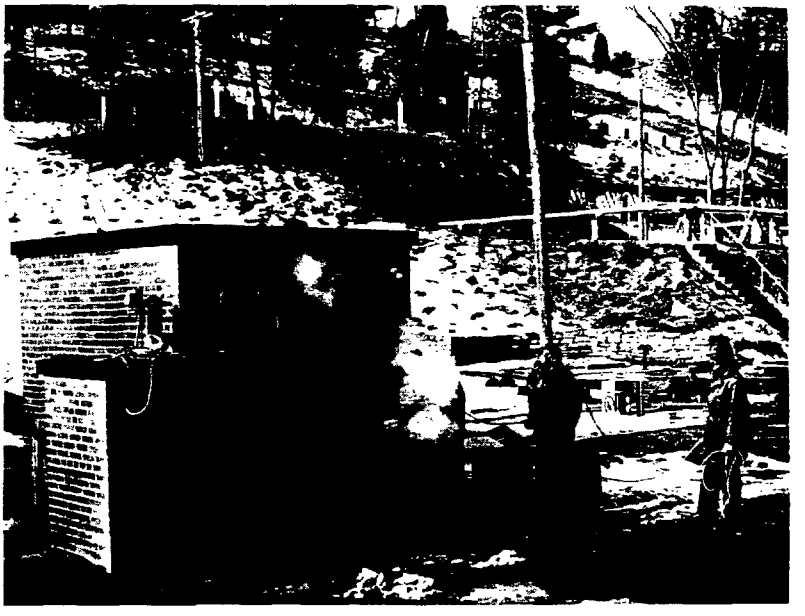

FIG. 23.25. On-the-job training using simulated smoke from smoke bomb develops confidence and experience in use of breathing apparatus. Training and retraining are vital to insure proper use in emergency.

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realistic but relatively harmless, and it can be ventilated out without damage or residue.[22]

Smoke bombs, which contain hexachlorethane, zinc oxide, calcium silicate, and potassium nitrate, are usually not injurious if used outside. However, in confined spaces they can be lethal. Forty-six fatal exposures are on record; one was a 35-year-old fireman who attempted to extinguish the smoke bomb with a fire extinguisher. The bomb had been ignited at the bottom of a depression a few feet below ground level and surrounded by buildings on three sides. The zinc chloride smoke, which is extremely caustic to the mucous membranes, caused acute interstitial fibrosis resulting in death 18 days later.

The "buddy" system and team drill should be practiced as in a real emergency. The use of life lines should be a part of this training whenever possible, and it should be a standard part of any underground, tank, or smoky operation. Signals are used to communicate by mine rescue teams to the team members who are outside by prearranged pulls on the hand lines. In the simple form, a code based on the word *OATH* in which *O* means OK, signal by one pull; *A* means advance or feed in more line, signal by two pulls; *T* means take up line, signal by three pulls; *H* means help, send aid, signal by four pulls. Stand-by men should already be masked and ready for entry in case the team in the mine or confined space calls for help. This same philosophy, of having stand-by personnel ready to go, should be encouraged in any emergency use of respiratory protective equipment. As mentioned previously, voice amplifiers and two-way radios may greatly aid in the communication problem, but any electrical device used in an atmosphere which may contain flammable gases or vapors, should have a "permissible" rating by the Bureau of Mines or the Underwriters' Laboratory for the gases or vapors expected.

The need for proper physical examinations and medical control for persons wearing emergency breathing equipment is obvious, but it has been neglected in some instances in the past. A regular program of physical check-ups with particular attention to the respiratory and circulatory system, as well as the general mental and physical condition, probably would have prevented some cases where inhalation of smoke combined with physical exertion, without or with respiratory protection, has produced serious illness. Stable pulse rates before, during, and after exercise, good general physical condition, moderate weight, good eyesight, and, where mouthpiece breathing is involved, proper teeth alinement, are all considered vital requisites to pretraining by the Bureau of Mines instructors. A practice of not permitting persons to return unprotected or alone to smoke, fumes, vapors,

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or gases after they have been seriously affected or overcome and revived, would help prevent more serious inhalation effects. Such restraining action may require physical force to implement in practice, since a "patient" who is partially recovered from fume or smoke inhalation may display highly irregular behavior. One recommendation is that persons sufficiently exposed to fumes, gases, smoke, and/or carbon monoxide to require treatment should not return to active duty in less than 4 to 6 hr, while those who have been rendered semiconscious or unconscious should rest 24 to 48 hr. Since chronic carbon monoxide poisoning is considered by some medical authorities to be a fact, and since carbon monoxide is not released by the blood as quickly as previously believed, the implications for fire fighting should be obvious.

Conclusion

The field of respiratory protection is dynamic—there is need for wider application of existing knowledge, proper use of existing equipment, as well as research and engineering, to produce even better and more adequate devices, training aids, and basic and applied information. It should be stressed that properly designed and carefully maintained breathing equipment, if used with full appreciation of its limitations, by healthy persons, properly and adequately trained, could eliminate most fume, gas, vapor, and smoke disabilities in the future. The ideal breathing apparatus for all applications has yet to be developed, and may never be developed until there is sufficient demand for it, backed by the willingness of the user to pay the cost, and this demand transmitted to developers and engineers who are both technically competent and have a zeal to improve the quality of breathing in man's complex life.[26] Of all our human needs, none is more vital than the next breath.

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24

Eye Safety in Chemical Processing

Joseph Guelich

If we wear glasses there is a good chance that they are safety glasses with hardened lenses. If we have a small child who wears glasses, they may be safety glasses. If we have children in chemistry laboratories in high school or college, the schools may have a rule that the students must wear safety glasses. If we wear glasses and engage in such activities as squash racquets, the chances are that we have equipped ourselves with safety glasses. These are all indications that today there is a clearly discernible trend toward universal eye protection, off the job and on. Of course, a complete eye protection program in chemical processing neither begins nor ends with a safety-glasses program. We have, you might say, four lines of defense: preventing the accident, preventing the injury, guarding the person, and minimizing the injury.

24.1. PREVENTING THE ACCIDENT

One of the most familiar examples of preventing the accident is something learned in high school chemistry, to the effect that sulfuric acid should be added to water and not vice versa. There are many examples. One user of caustic soda found that he was having trouble making up caustic solutions by adding solid caustic to water. Despite repeated admonitions, the operators would add the solid caustic too fast and the heat of solution would cause the vessel to spit and boil over. They found an acceptable solution by replacing purchases of

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21

Safe Handling of Flammable Materials

William S. Wood

21.1. INTRODUCTION

Flammable liquids and gases are extremely important to our modern way of life and constitute a major volume of present-day commerce. Billions of gallons of highly flammable motor fuel are manufactured and marketed to the motoring public annually with a high degree of safety. On the other hand many fires with accompanying injury and death result from improper storage and use of flammables, especially in and around the home or small business. The difference lies in appreciation of the hazards of the materials and the application of safe procedures.

Flammable materials are utilized in a high proportion of processes in the chemical and petrochemical industries. Benzene, olefins, and ethers are indispensable raw materials in organic syntheses. They also may be used as the vehicles in which reactions occur or as solvents to effect separations. Cleaning operations utilize large amounts of flammable liquids, and the fuels used to supply process heat may be volatile hydrocarbons.

Flammability is one of the hazardous properties that must be evaluated and dealt with in order to utilize these valuable materials with a minimum of injury and loss. It is important that the user learn to evaluate the physical and chemical properties that will be pertinent to the environment and the application of each material.

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21.2. THE COMBUSTION OF FLAMMABLES

Although combustion is one of the oldest known chemical reactions, its mechanisms are imperfectly understood and erroneous concepts are held by many who work with flammable materials or fight fires in which flammables are involved. This discussion is an attempt to guide in the recognition of valid hazard criteria, in the selection of safe environmental conditions, and in the emergency action needed when an accidental release occurs.

The Anatomy of Fire

Minimum requirements for a flame or the propagation of a flame front are often represented in terms of the "Fire Triangle." Fuel, oxygen, and heat are shown as the three sides in Fig. 21.1. In relation to flammable liquids and gases the three requirements are more accurately described as shown in Fig. 21.2.

1. Gas or vapor within certain limits of concentration.
2. Air containing a minimum concentration of oxygen.
3. An ignition source of minimum temperature and energy.

A fire results when all three sides of the triangle are in place. However, any two of the above requisites can co-exist without a fire as long as the third is not added. Since an oxygen-bearing atmosphere surrounds nearly all normal activities, the problem usually consists in keeping flammables separated from all possible ignition sources.

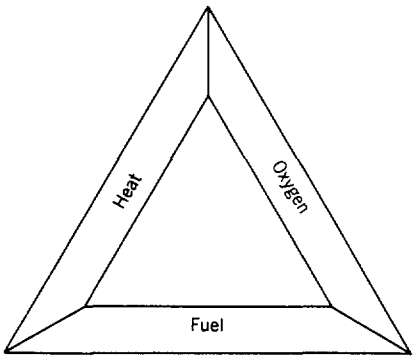

FIG. 21.1. The fire triangle (complete).

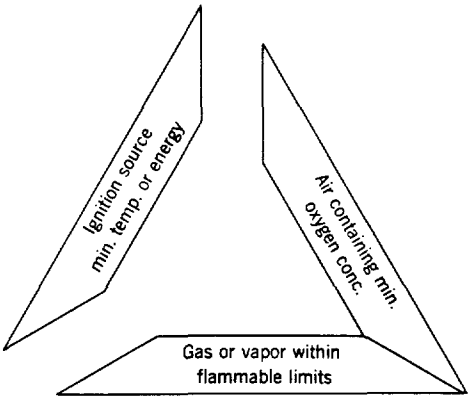

FIG. 21.2. Fire triangle (incomplete).

The Fuel

If even a small flame is passed over a pan of methanol, ignition occurs promptly in the vapor above the surface. The same flame over glacial acetic acid or naphthalene at ambient temperature would not ignite either material. If, however, the acetic acid is heated only slightly, enough vapor will be generated to permit ignition and, with further heating, the naphthalene also could be burned. Liquids and solids do not burn as such. They give off vapors and gases which mix with air and can be ignited when a combustible mixture is attained.

Obviously volatility is a primary factor in determining the conditions under which an ignitable mixture can occur. Classical expressions of volatility such as vapor pressure and boiling point, while definitive, do not of themselves relate directly to flammability. The flash-point determination is an empirical but highly satisfactory method of determining the minimum temperature at which an ignitable mixture exists above the surface of a liquid.

The American Society for Testing and Materials has standardized a number of methods for determining flash point. The tag closed tester (ASTM D56)[1] is used for testing liquids with flash point below 175°F. The Pensky-Martens Closed Tester (ASTM D93)[2] is used for materials (mostly fuel oils) with flash points 150° to 230F°. The Cleveland Open Tester (ASTM D92)[3] is used for high-flash materials.

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On the basis of volatility expressed as flash point and boiling point, NFPA 30, 1963 defines flammable and combustible liquids as follows:[4]

		Examples:
Class IA	Flash point below 73°F Boiling point below 100°F	Pentane Ether
Class IB	Flash point below 73°F Boiling point 100°F or above	Benzol Ethanol
Class IC	Flash point 73° to 99°F	Amyl Acetate
Class II	Flash point 100° to 130°F	Acetic Acid Decalin
Class III	Flash point 140° to 199°F	Aniline Naphthalene

Caution is recommended in relying too heavily on flash point as the major criterion of flammability. Liquids atomized into a fog or mist can be readily ignited far below the flash point of the material. Froths can likewise be flammable. Combustibles absorbed in porous materials such as insulation can ignite under surprisingly mild temperature conditions.

Reid vapor pressure (ASTM D323)[5] is a specification measurement of volatility applied to gasoline and jet fuels. Its units are pounds per square inch gage at 100°F. While originally intended as a performance specification, it is a useful indication of volatility in storage and handling.

The fact that a "safe" material has been heated in processing above its flash point and thus become readily ignitable may be overlooked by the casual operator. Also a small amount of volatile material in a relatively high boiling mixture will drastically lower the flash point and render the whole volume dangerous.

Finely divided dusts of combustible solids can constitute a severe fire hazard. Sulfur, carbon, polymers, and many other solids form explosive suspensions in air. Sometimes a minor explosion or other disturbance disperses dust that has accumulated on flat surfaces for long periods of time. The result may be a severe explosion (see *NFPA* 654–63, "Prevention of Dust Explosions in the Plastics Industry").[6]

The Atmosphere

Most situations involving flammable-material safety occur in the presence of normal air (20 to 21% oxygen). Atmospheres are sometimes enriched by increasing the oxygen content, possibly to 100%

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oxygen. Ignition is more easily accomplished and combustion is much more rapid in pure ogyxen or in oxygen-enriched air.

Air deficient in oxygen can occur naturally from decay or fermentation of organic material. Dilution with inert gas such as nitrogen or carbon dioxide may be intentional in order to inhibit combustion. For each flammable material there is a concentration of oxygen below which a flame will not be propagated. For many substances the minimum oxygen content required to support combustion is approximately that required to sustain life in the human being (approximately 12%).

Other oxidizing agents such as chlorine, fluorine, nitrogen oxides, and hydrogen peroxides, while unusual in most industries, could be encountered in the chemical plant as well as on the launching pad. Many such oxidizers are much more vigorous than oxygen and require special safety precautions.

21.3. IGNITION OF FLAMMABLE MIXTURES

The autogenous ignition temperature is the temperature at which a small amount of a substance will spontaneously ignite in a given atmosphere and burn without further heat input. It is likewise a useful guide to the maximum safe temperature of any surface in contact with vapor mixtures above the flammable liquid.

The ignition temperature may be determined by a number of different procedures, and widely differing results may be obtained on the same material by different methods. One useful procedure is ASTM D286–58T, which is applicable to many flammable and combustible liquids. Ignition temperatures of many compounds as determined by the above and similar methods are listed in NFPA 325.[7]

Kindling temperature is a term applied to solids to express the temperature to which a portion must be raised to initiate flame. Many factors such as size, shape, and purity affect the value for a given material.

Spontaneous ignition of dry phosphorus or of drying oils is well known to the chemical industry. Recent additions to this category are the aluminum alkyls, certain boranes, and some silanes. Aluminum trimethyl ignites immediately upon exposure to air and this property has been utilized by injecting the alkyl into jet engines to re-ignite the fuel after a flame-out. Aluminum triethyl usually flames instantly upon exposure to air at rather low ambient temperature, while aluminum triisobutyl only fumes copiously and does not ignite unless the temperature is about 100°F.

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Hypergolic ignition of such mixtures as hydrazine-hydrogen peroxide are becoming commonplace in space vehicle systems. The characteristics of each such system should be determined prior to any plant design or operation.

Flammable mixtures may be formed and exist harmlessly so long as no source of ignition is present within the system. The combustion process must be initiated by the introduction of a finite amount of energy. Ignition sources include hot surfaces, hot filaments, flames, hot gases, electric sparks, and adiabatic compression of the mixture itself.

Hot electrical filaments such as heaters and broken electric lamps are effective igniters if a minimum energy of about 2 millijoules is available. Van Dolah et al[8] showed that the temperature required to ignite a large volume of flammable substance decreases with increase in wire diameter.

Husa and Runes[9] showed that large metal surfaces must be considerably hotter than the accepted ignition temperatures in order to initiate a flame. Absence of confinement and attendant convection currents possibly account for the higher temperatures.

Electrical sparks are well known as ignition sources particularly in gasoline engines or oil burners where they function in a "friendly" situation. However, high-tension sparks are not very likely to occur in the plant environment unless such an ignition system is faulty. Studies have shown[10] that a spark with minimum energy of about 0.2 millijoules can ignite a flammable mixture near the stoichiometric proportions in air.

Break sparks occur when open relays or switches are operated or a commutator is exposed. Adequate energy is present in most such systems to ignite a flammable mixture. Obviously a welder's arc would be a most effective igniting device.

Friction sparks of a steel tool striking a stone or sparks from a grinding wheel have been proven rather ineffective ignition sources. While nonferrous tools made of beryllium-copper have long been considered necessary to avoid spark ignition of hazardous atmospheres, experience has shown that few if any fires have been caused by the use of steel tools. The American Petroleum Institute no longer insists that nonferrous tools be used in the presence of flammable hydrocarbons. Nonsparking tools are still used extensively in the chemical industry, and may have advantage particularly in the case of impact tools used in digging.

Pumping of relatively clean organic materials can cause a static accumulation to be concentrated on the liquid surface in the receiving

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tank. Klinkenberg et al.[11] demonstrated that high-velocity pumping of jet fuel resulted in explosions in the vapor space above the liquid. A dangerous static charge exists when the liquid contains enough impurity to allow the collection of charges but not enough contamination to make the liquid sufficiently conductive that the charge can bleed off rapidly. Many common liquids are sufficiently low in conductivity that this dangerous situation obtains. Slow pumping and subsurface discharge aid in controlling the static buildup. Additives to "contaminate" the product and hasten static bleed-off have been offered but are not widely used. Floating-roof tanks or inerted tanks are commonly used to eliminate the vapor-air space above sensitive materials. The United States Bureau of Mines has recently studied this problem extensively under a contract with the American Petroleum Institute.

Acetylene welding (and oxy-acetylene cutting operations) are among the most common sources of ignition. Not only the flame itself but the white-hot metal shower may reach and ignite flammables. Plasma jets, lasers, and masers, while still largely experimental, may soon become sufficiently commonplace to be credited with being ignition sources.

Fuel and Oxygen

It has been stated that only gases and vapors are capable of entering into the combustion while liquids must be vaporized and mixed with air before they can burn. The stoichiometric mixture representing the ideal composition for combustion is calculated after writing the chemical equation for burning pentane in air.

$$C_5H_{12} + 8\,O_2 + 30\,N_2 \rightarrow 5\,CO_2 + 6\,H_2O + 30\,N_2$$

1 mole pentane vapor + 38 moles air $\rightarrow$ 5 moles CO_2 + 6 moles H_2O + 30 moles N_2.

Thus, 2.6 volume % of pentane vapor in 97.4% of air provides the theoretical fuel-oxygen balance for combustion.

Flammable Limits

If the concentration of vapor is reduced below the stoichiometric mixture it is termed "lean," and a concentration can be reached at which a flame will not propagate. At such a low concentration there is sufficient distance between fuel molecules for the intervening air to quench the flame front. The lowest concentration of vapor at which

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a flame can be propagated is called the lower flammable limit (or lower explosive limit). For pentane this is 1.5% of vapor in air as experimentally determined.

If on the other hand the vapor concentration is increased above stoichiometric, the mixture can become so "rich" that there is insufficient oxygen to support combustion. The highest concentration of vapor in which a flame can be propagated is the upper flammable limit (upper explosive limit) 7.8% for pentane. The concentrations between the two values for a given material constitute the "flammable range." Coward and Jones[12] published the most comprehensive list of these data available.

Figure 21.3 illustrates the relationship in another way. In an adiabatic closed system the temperature (and pressure) will increase when a flammable mixture is ignited. The temperature (or pressure) rise will be maximum at or near the stoichiometric, and it will be

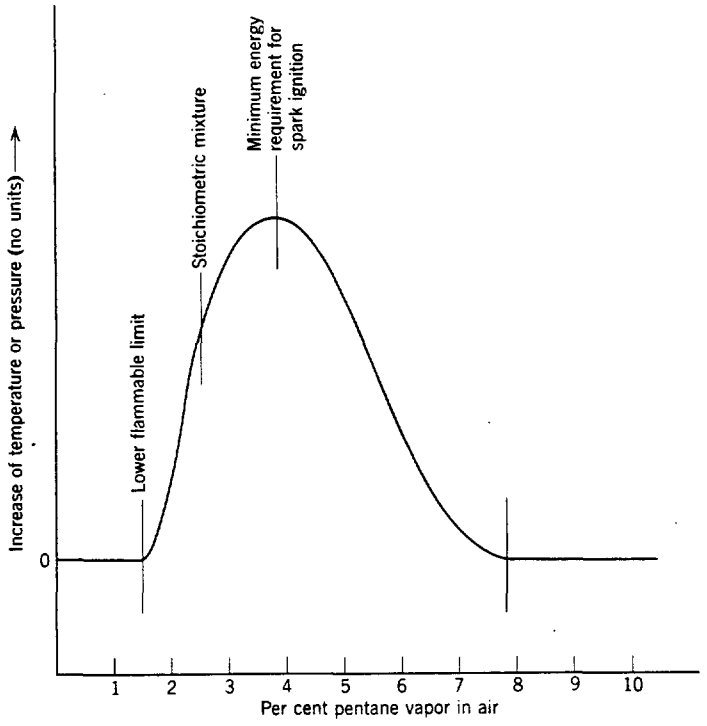

FIG. 21.3. Energy vs mixture for pentane.

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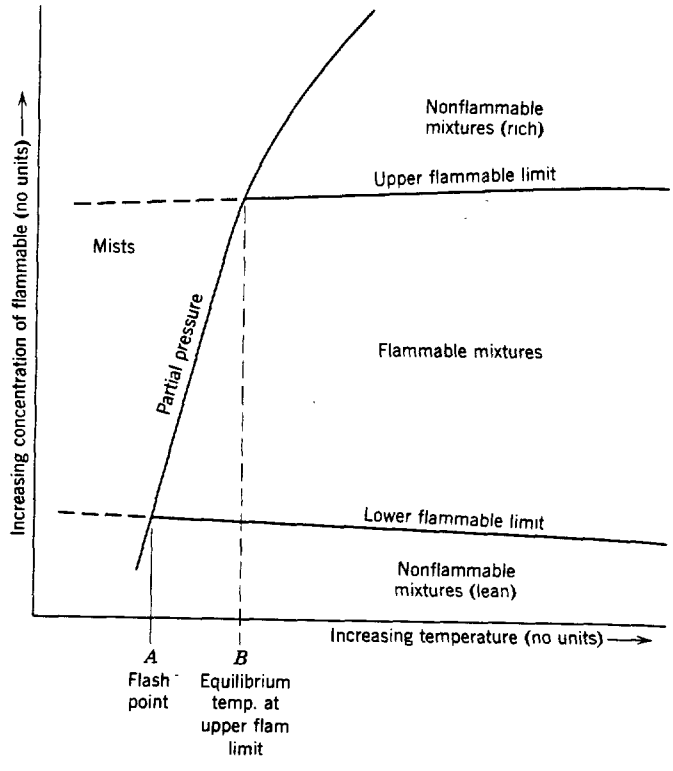

FIG. 21.4. Relationship of partial pressure, flammable limits and flash point.

less at both higher and lower concentrations. The temperature rise would become zero at the lower flammable limit and at the upper flammable limit.

It has been shown experimentally that the flammable range becomes wider with increasing temperature,[13] doubtless because of increasing molecular activity or enthalpy of the mixtures. Figure 21.4 illustrates how the UFL concentration increases slightly with temperature, and the LFL line descends as temperature increases.

These coordinates can also be used to plot the vapor pressure of the substance with increasing temperature. The intersection of the vapor-pressure line with the lower flammable limit line at *A* is where air above a liquid contains just enough of the vapor to allow a flame to propagate. The temperature at *A* can be experimentally determined as the flash point.

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While not usually designated or susceptible to experimental determination the temperature at intersection B is of interest and can be estimated rather easily. Below this temperature a mixture cannot possibly be too rich to burn. In other words, between these two temperatures, A and B, a tank having air above the liquid would always have a flammable zone. At temperatures above B the mixture will be nonflammable if vapor-liquid equilibrium actually exists, but may be flammable if equilibrium is not achieved or if air is drawn into the tank. (A more extensive treatment of flammable limits and ignition temperatures is presented by G. W. Jones in a chapter he wrote in Patty, *Industrial Hygiene and Toxicology*, Vol. I, Second Edition, pp. 511–546, Interscience, New York, 1958.)

21.4. ATMOSPHERES OTHER THAN AIR—EFFECT ON FLAMMABLE LIMITS

Enrichment of air with oxygen increases the value of the upper flammable limit, but it does not appreciably affect the lower flammable limit. Flammable limits in pure oxygen have been determined for many common materials (Fig. 21.5).

Dilution of the air with nitrogen, carbon dioxide, or other inert gas

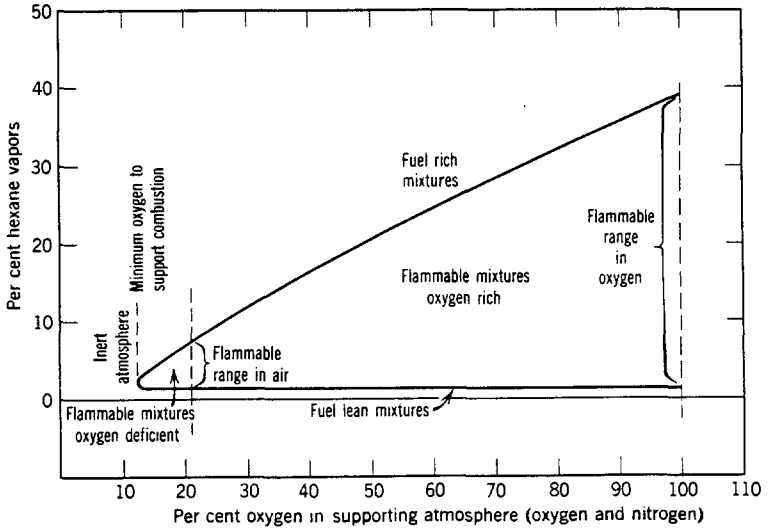

FIG. 21.5. Limits of flammability of hexane in oxygen—nitrogen atmospheres.

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serves to decrease the upper flammable limit. If sufficient diluent is added, no flammable zone exists, since insufficient oxygen is present to support combustion.

Flash Point and Fire Point

Flash point is the minimum liquid temperature at which a flame can be propagated across the surface of the liquid when a standard ignition source is applied. The liquid does not continue to burn at the flash point but, if the liquid is further heated, a temperature will be reached at which the liquid flashes and continues to burn. This is the fire point, and it will be 30° to 50°F higher than the flash point. Fire point is sometimes confused with ignition temperature but there is no direct relationship between the two.

Detection of Flammable Vapors and Gases

Accurate, reliable detection of flammables in the air is vital to the prevention of fire or explosion. Simple, inexpensive instruments are readily available but judgment and experience are needed for proper interpretation of tests.[14]

The "hot wire" type of meter is the oldest and most commonly used. The wiring diagram of a battery-powered portable unit is shown in Fig. 21.6. The sample passes over the heated test coil (but not the heated reference coil). Combustibles burn on the incandescent wire and raise its temperature, therefore its resistance, and the imbalance of the Wheatstone bridge is read on the meter. The usual instrument is calibrated to read the percentage of the lower flammable limit of a calibration substance such as hexane. A more sensitive device operating on the same principle has an additional range reading 1000 ppm full scale.

In a vapor concentration less than LEL the needle will be on the scale. In a vapor concentration between the LEL and the UEL the needle will remain off scale above 100%. At concentrations above the UEL the needle will swing rapidly off scale and then drop back to zero. Atmospheres deficient in oxygen result in unreliable low readings. These vagaries emphasize the need for skill in manipulation and interpretation. Such tests usually precede evaluation for "hot" work and issuance of a permit.

Similar instruments are designed for continuous sampling and may be set to sound an alarm at any desired percentage of LEL. One to sixteen points may be sampled by a single device.

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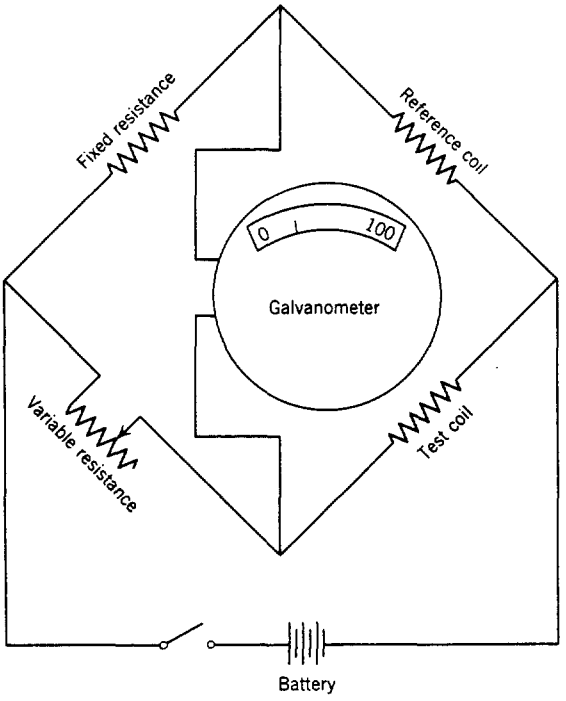

FIG. 21.6. Simplified wiring diagram—hot wire flammable gas detection instrument.

Other principles used to detect the presence of flammables are: thermal conductivity, diffusion rate, specific gravity, and infrared spectrum. While such instruments are relatively new they are finding acceptance for solving special problems.

21.5. CODES, REGULATIONS, AND INFORMATION

Federal, state, and local government agencies have sought to protect the public by enacting laws and issuing regulations setting forth minimum requirements for shipping and storage of flammables. Federal and state labeling laws require warnings on packages of hazardous material but do not apply to those handled in bulk. However, laws or regulations, no matter how well written or enforced, cannot achieve an adequate level of industrial safety. Informed and in-

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terested management with the aid of a competent safety staff can institute and enforce an effective program.

A basic knowledge of factors relating to flammability and kindred phenomena is essential to an effective fire prevention program. Voluntary adherence to recognized cooperative standards has proven effective in reducing loss from accidents involving flammables.

The National Fire Protection Association, by utilizing the services of hundreds of experts on its committees, has published dozens of codes covering all facets of this subject. Similar information is published by the National Board of Fire Underwriters, Factory Mutuals, American Standards Association, Underwriters' Laboratories, and many other organizations.

Much of the research and testing of flammable materials has been carried out by the United States Bureau of Mines and published in its reports. The National Academy of Sciences in its *Fire Research Abstracts*[15] publishes information on new studies and data.

Shipment of flammable liquids is regulated by the Interstate Commerce Commission as set forth in Tariff No. 15 by T. C. George.[16] Approved containers and tank vehicles are listed and placard requirements are spelled out. Local jurisdictions such as the Port of New York Authority regulate the movement of flammables as well as corrosive and explosive materials through tunnels, over bridges, over turnpikes, and through towns. Shippers should make sure the proper route is chosen to avoid delays.

Municipal and suburban volunteer fire fighters are concerned over the burgeoning truck transportation of chemicals. Too often the fire service called to a truck accident, spill, or fire must act with little or no information as to contents and properties. Enlightened chemical manufacturers are beginning to teach and train these men to enable them to avoid exposures and work more effectively. The Chem-Card program developed by the Manufacturing Chemists' Association is a step in this direction.

Prevention of Ignition

Whenever a flammable liquid or gas is being transferred from one vessel to another, the two should be electrically bonded in order to equalize electrostatic potential and prevent a static spark. Permanently affixed or temporary bonding lines may be provided to establish the metal-to-metal connection. Clamps or clips must be applied carefully to be sure that paint, scale, and corrosion are penetrated and

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contact is made with bare metal. Pumps, mixers, process vessels, tanks, and drum racks should be adequately grounded to drain off stray electrical currents. Pipe systems are unreliable as conductors unless all joints are welded, soldered, or jumpered.

NFPA 70,[17] the National Electrical Code requires that all electrical equipment and wiring conform to Class I, Group D requirements where flammable gases or vapors may be present at any time. See Chapter 6. Explosion-proof equipment is designed with physically strong cases and vents so that an internal explosion would not rupture the case and the flame would be effectively quenched in the vents. Wiring in hazardous areas is enclosed in conduit, and seals prevent passage of gas or vapor into operating cases. The Underwriters' Laboratory publishes periodic lists of electrical equipment tested and approved for hazardous exposures.

Certain relaxation is permitted where the flammable is in a closed system and vapors would be released only in extraordinary circumstances. Even in this Division 2 area, sparking devices are prohibited except in approved enclosures. Intrinsically safe electrical equipment has been suggested for certain uses,[18] particularly for instruments. These have not been approved by the codes but as their development expands, code consideration is inevitable. Purged or inerted instruments and cases offer economies when justified by an adequate engineering study.

Equipment in which flammables are to be utilized must be located with careful consideration for geographical relationship to ignition sources and possible vapor pockets. Vapors of nearly all flammable liquids are appreciably heavier than air (methanol, the outstanding exception). In still air, vapor tends to hug the ground and can travel considerable distances on the level or downhill, reach an ignition source, and flash back to the origin as a sheet of flame. Collection of vapors in a low place has been illustrated dramatically by the accidental breaking of an electric light bulb in a service-station lubrication pit. Dikes built around tanks to prevent spread of a liquid spill can retain a blanket of flammable (or toxic) vapor.

The Flammable Liquid Code, NFPA 30,[19] specifies the minimum distances for tanks of various sizes from property lines, roadways, and other tanks. Minimum vent diameters are specified to prevent overpressure under the worst fire exposure conditions. Floating roof tanks, widely used in the petroleum industry, have the advantage of eliminating vapor space above the fluid—important when vapor-liquid equilibrium results in flammable mixtures at ambient tem-

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peratures. Tanks having free space above the liquid should be fitted with conservation vents and flame arrestors to prevent ignition of the vapor mixture.

Emergency Action

While flammables are often handled in closed systems, spills can and do occur. Open dumping of drums and similar hazardous practices are still a part of chemical manufacturing. Vapors released from such planned or unplanned operations can spread for considerable distances and blanket large areas with unseen flammable vapors.

Operating error, process abnormality, equipment failure, or faulty maintenance are some of the causes of the release or spill of substantial quantities of flammable materials. Whether such a release results in a disastrous fire or explosion depends upon many factors, few of which can be controlled once the emergency exists. Location of the release, temperature conditions, wind direction and velocity, slope of the ground, proximity of furnaces or welding operations, as well as properties of the material released, influence the probability of ignition. Fires involving flammable materials take a heavy toll of both lives and property, are often quite spectacular, are frequently difficult to approach and extinguish, and too often lead to financial collapse of the owners.

There are three steps to follow in case of an emergency release of flammable liquid or vapor: (1) immediately shut down all flames and sparking equipment in the area, particularly downhill and to leeward, (2) shut off the source as quickly as possible, and (3) vacate personnel from the affected area. Supplementary steps are: (4) get meters and technicians to monitor the area, (5) call the fire department for stand-by coverage, (6) mobilize guards or police to barricade the area and reroute all traffic. When tests show that little vapor remains undispersed, repairs may be made and fires relighted.

Fighting Flammable Liquid Fires

While fire fighting is covered in Chapter 28 it is well to consider a few points concerning flammable liquid fires and their extinguishment. It is important to keep equipment, especially supporting structures and tanks, cooled by water streams if extinguishment is likely to be time consuming.

Carbon dioxide and dry chemical extinguishers are effective on nearly all flammable liquid fires of limited scope. Steam may be used

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on smaller fires and water fog on some larger ones. Foam, either chemical or mechanical type, is the workhorse for larger flammable liquid fires. Polar compounds such as alcohols, ketones, and ethers require a special foam compound which must be applied with utmost skill and care.

Horizontal tanks, whether stationary or mobile, present an unusual hazard when they are involved in a fire. When these tanks rupture, because of inadequate relief of internal pressure, the failure almost invariably occurs at the ends. Fire fighters who value their lives will approach such vessels for cooling and extinguishment from the *sides,* not the ends.

Summary

Recognizing the ever present danger with flammable materials, anyone involved with their handling should:

Know the hazardous properties of the flammable material involved in the operation.
Store and transfer safely in a closed system if possible.
Avoid (or control) ignition sources in areas containing flammables.
Plan and rehearse emergency action.
In case of vapor release prevent ignition if possible. Evacuate and monitor the area.
Remember the fire triangle. Air is usually present. Keep flammables from contacting an ignition source.

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22

Radiation—Controllable Energy

H. H. Fawcett

Radiation is the process of emission, transmission, and absorption of energy. Radiation is of several types. Some radiation, such as radio waves and television waves, as well as visible light rays, are part of our daily life, and are called nonionizing radiation. Other types, such as X-rays and gamma rays, are not obvious to us under normal circumstances and are called ionizing radiation, because of their ability to react with matter to release electrons. The wide area covered by the electromagnetic spectrum is noted in Table 22.1.

The properties and physiological effects of radio frequency and microwave radiations have been well summarized elsewhere.[1, 2, 3, 4] Light, including ultraviolet and infrared, is well documented.[5, 6, 7] Laser beams have recently introduced unique problems because of coherent monochromatic nature of the light emitted.[8, 9, 10, 11]

The purpose of this chapter is to survey briefly the shorter wavelengths and particles, usually referred to as ionizing radiation, and to supply references for a more complete study.

Ionizing radiation has been in the environment since the formation of the earth,[12] but man has only recently learned of its potential for beneficial use. See Table 22.2.

Centuries ago we learned to control and reap benefits from fire. More recently, we have learned to control ionizing radiation and to benefit from its availability and use. From a practical viewpoint, radiation is used only if the unique properties present methods for

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TABLE 22.1. The Electromagnetic Spectrum*

Type of Wave		*Wavelength*
Radio, Standard AM and international bands		100 km to 10 meters
Shortwave, Television channels, 2–13, and FM		10 meters to 1 meter
Ultrashortwave and TV channels 14–83		1 meter to 10 cm
Microwave (radar)		10 cm to 0.5 mm
Infrared		0.5 mm to 7700 angstroms (Å)
Far	500μ to 10μ	
Intermediate	10μ to 1.3μ	
Near	1.3μ to 7700 Å	
Visible light		7700 Å to 3900 Å
Red	7700 Å to 6300 Å	
Orange	6300 Å to 5900 Å	
Yellow	5900 Å to 5500 Å	
Green	5500 Å to 4900 Å	
Blue	4900 Å to 4500 Å	
Violet	4500 Å to 3900 Å	
Ultraviolet		3900 Å to 100 Å
Near	3900 Å to 3000 Å	
Middle	3000 Å to 2000 Å	
Extreme	2000 Å to 100 Å	
X-rays		100 Å to 0.1 Å
Superficial Therapy	5 Å to 0.9 Å	
Diagnostic	0.9 Å to 0.1 Å	
Therapeutic	0.1 Å to 0.3 Å	
Gamma rays		1 Å to 0.001 Å
Cosmic rays		0.1 Å to 0.0001 Å

* Band separation is not clearcut and overlap occurs.

Source: Journal of the American Medical Association, Vol. 187, No. 11, page 846, March 14, 1964. "The Biological Effects of Laser Radiation," by M. S. Litwin and D. H. Glew.

more efficient or more refined techniques. Understanding and appreciation of its benefits for many uses,[13] mundane (as in locating leaks in underground piping) to exotic (as in nuclear power sources to supply energy to space vehicles) will doubtlessly encourage wider interests and applications. Atomic power from nuclear reactors is already economically attractive; power from thermonuclear fusion has been demonstrated publicly.[14]

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TABLE 22.2. Body Tissue Dose Rates Due to External and Internal Irradiation from Natural Sources of Radiation in "Normal Regions"*

Source of Irradiation	*Dose rates in mrem/year*		
	Gonad	*Haversian canal*	*Bone marrow*
External irradiation			
Cosmic rays (including neutrons)	50	50	50
Terrestrial radiation (including air)	50	50	50
Internal irradiation:			
K^{40}	20	15	15
Ra^{226} and decay products (35% equilibrium)	0.5	5.4	0.6
Ra^{228} and decay products (equilibrium)	0.8	8.6	1.0
Pb^{210} and decay products† (50% equilibrium)	0.3	3.6	0.4
C^{14}	0.7	1.6	1.6
Rn^{22} (absorbed into bloodstream)	3	3	3
Total	125	137	122

* UN (1962).

† Pb^{210} in excess of that expected from Ra^{226} and decay products in 35% equilibrium.

Source: Environmental Radioactivity, by M. Eisenbud, McGraw-Hill Book Co., New York, page 170.

For definition of units of radiation, see Section 22.2, pages 354–356.

22.1. RADIATION SOURCES

Ionizing radiation sources may be broadly classed as nuclear sources and electronic (or machine) sources.

Principal Forms of Ionizing Radiation. All are particles of matter with the exception of X-rays and gamma rays, which are electromagnetic waves. The deuteron consists of a proton and a neutron; the alpha particle, of two protons and two neutrons. Some of the mass of the constituents of deuterons and alpha particles are transformed into the energy which binds them together.

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This table lists the Principal Sources of Ionizing Radiation.[15]

Nuclear Sources	*Electronic Sources*
nuclear reactor	high-voltage transformer
gaseous-fission products	impulse generator (capacitron)
spent-fuel rods	Van de Graaff generator
liquid-reactor fuel	resonant transformer
fission products (solutions or separated, such as Cs 137 and Sr 90)	linear accelerator
	betatron
natural radiation sources (such as Ra, Th, U)	cyclotron
	bevatron
man-made radioactive isotopes (such as Co 60)	other particle accelerators

Table 22.3 summarizes the properties of principal forms of radiation.

TABLE 22.3. Properties of Radiation

Ionizing Radiation	Symbol	Mass	Charge
Electron	○	1	−
Proton	●	1,836	+
Neutron	○	1,839	○
Deuteron	●○	3,671	+
Alpha particle	●●	7,296	++
X-ray or gamma ray	~~~→	0	○

Source: Scientific American, 201, p. 76 (1959)

Properties of Radioactive Sources

The most widely used sources of radiation are radioactive isotopes. Isotopes are forms of elements which have identical chemical properties, but because of the different number of neutrons in their nucleus, they have different atomic weight. Many isotopes are not radioactive. Eighty of the 103 known elements have at least 1 stable isotope; some have as many as nine. A total of 280 stable isotopes has been discovered. Sixty-six naturally occurring radioactive isotopes (or species) have been identified.[16] Over a thousand known

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TABLE 22.4. Available Radioisotopes Listed According to Half-Life

	*Half-Life**	*Radioisotopes***	*Radiation*	*Half-Life**	*Radioisotopes***	*Radiation*
	24.2 s	Silver-110	β,γ	43 d	Cadmium-115*m*	β,γ
	30 s	Rhodium-106 (Ru^{106})	β,γ	44.3 d	Iron-59	β,γ
	72 s	Indium-114	EC,β^-,β^+,γ	44.6 d	Hafnium-181	β,γ
	2.6 m	Barium-137*m* (Cs^{137})	IT,γ	45.4 d	Mercury-203	β,γ
	17.5 m	Praseodymium-144	β,γ	50 d	Indium-114*m*	IT,γ
	12.47 h	Potassium-42	β,γ	50.5 d	Strontium-89	β
	12.5 h	Iodine-130	β,γ	57.4 d	Iodine-125	γ
	12.82 h	Copper-64	EC,β^-,β^+,γ	59.1 d	Yttrium-91	β,γ
	13.6 h	Palladium-109	β,γ	60.9 d	Antimony-124	β,γ
1	14.2 h	Gallium-72	β,γ	64 d	Strontium-85	γ
	15.05 h	Sodium-24	β,γ	65 d	Zirconium-95	β,γ
	19.0 h	Iridium-194	β,γ	71.3 d	Cobalt-58	EC,β^+,γ
	19.2 h	Praseodymium-142	β,γ	74.2 d	Iridium-192	β
	24.0 h	Mercury-197m_2	EC,IT,γ	75.8 d	Tungsten-185	EC,β,γ
	24.0 h	Tungsten-187	β,γ	84.2 d	Scandium-46	β,γ
	26.8 h	Arsenic-76	β,γ	89 d	Sulfur-35	β
	35.55 h	Bromine-82	β,γ	115.1 d	Tantalum-182	β,γ
	38.7 h	Arsenic-77	β,γ	119 d	Tin-113	EC,γ
	40.3 h	Lanthanum-140	β,γ	119.9 d	Selenium-75	EC,γ
	46.8 h	Samarium-153	β,γ	129 d	Thulium-170	β,γ
2	53.5 h	Cadmium-115	β,γ	165.1 d	Calcium-45	β
	64.4 h	Yttrium-90	β	246.4 d	Zinc-65	EC,β^+,γ
	64.8 h	Gold-198	β,γ	249 d	Silver-110*m*	IT,β,γ
	65 h	Mercury-197	EC,γ	285 d	Cerium-144	β,γ
	66 h	Antimony-122	β,γ	371 y	Ruthenium-106	β
	67 h	Molybdenum-99	β,γ	1.3 y	Cadmium-109	EC,γ
	75.4 h	Gold-199	β,γ	2.07 y	Cesium-134	β,γ
	88.9 h	Rhenium-186	EC,β,γ	2.5 y	Promethium-147	β,γ
	4.53 d	Calcium-47	β,γ	2.78 y	Antimony-125	β
3	5.00 d	Bismuth-210	β	2.94 y	Iron-55	EC
	5.27 d	Xenon-133	β,γ	3.57 y	Thallium-204	EC,β
	7.5 d	Silver-111	β,γ	5.24 y	Cobalt-60	β,γ
	8.05 d	Iodine-131	β,γ	10.27 y	Krypton-85	β,γ
	11.06 d	Neodymium-147	β,γ	10.7 y	Barium-133	EC,γ
4	12.0 d	Barium-131	EC,γ	12.46 y	Hydrogen-3	β
	12.8 d	Barium-140	β,γ	12.7 y	Europium-152	EC,β,γ
	13.7 d	Praseodymium-143	β	16 y	Europium-154	β,γ
	14.3 d	Phosphorus-32	β	28 y	Strontium-90	β
	16 d	Osmium-191	β,γ	30 y	Cesium-137	β
	18.68 d	Rubidium-86	β,γ	125 y	Nickel-63	β
	27.8 d	Chromium-51	EC,γ	5.57×10^3 y	Carbon-14	β
	32.5 d	Cerium-141	β,γ	2.12×10^5 y	Technetium-99	β
	34.3 d	Argon-37	EC	3.08×10^5 y	Chlorine-36	β
	35 d	Niobium-95	β,γ	1.56×10^7 y	Iodine-129	β,γ
	39.7 d	Ruthenium-103	β,γ			

* s, second; m, minute; h, hour; d, day; y, year.
** The radioisotope in parenthesis is the one under which the listed radioisotope is cataloged.

DECAY ALLOWANCE

Decay Allowance for isotopes with half-lives of less than 15 days is shown by brackets in half-life column. Allowance calculated from 8 A.M. on day of shipment.

1—One Half-Life
2—One Day
3—Two Days
4—Four Days

Suppliers of radioisotopes include:

Oak Ridge National Laboratory, Isotopes Division, P. O. Box X, Oak Ridge, Tennessee.
General Electric Co., Vallecitos Atomic Laboratory, P. O. Box 840, Pleasanton, California.

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radioactive iosotopes (also called radionuclides) have been produced artificially. Of these, nearly one hundred radioactive isotopes are commercially available from several sources in the United States and Canada.

Radioactive isotopes (or radionuclides) tend to become stable as they give off radiation, much as a mechanical clock tends to "run down" as the energy in the spring is expended. The time required in radioactive materials for half of the atoms to emit their radiation is called the half-life. Each radioactive isotope has its own unique half-life, which may be from a fraction of a second to billions of years (Fig. 22.1). During this decay, radioactive isotopes emit one or more forms of energy. These include:

1. *Alpha particles* (mass number 4, charge plus 2), which are helium nuclei evolved from decay of elements of high atomic number, such as thorium, radium, polonium, and plutonium. As decay occurs, the parent alpha-emitting element acquires an atomic number of two less and a mass number of four less than the parent. Because of their relatively large mass, alpha particles have relatively little penetration power. As a practical matter, paper will stop alpha particles, and even the most energetic alphas are attenuated or dissipated by less than 3 in. of air or 0.002 cm of aluminum. Alpha emitters are not without potential hazard, however. While they pose little hazard from an external radiation standpoint, they do present serious problems as internal radiation sources, and this, together with the long

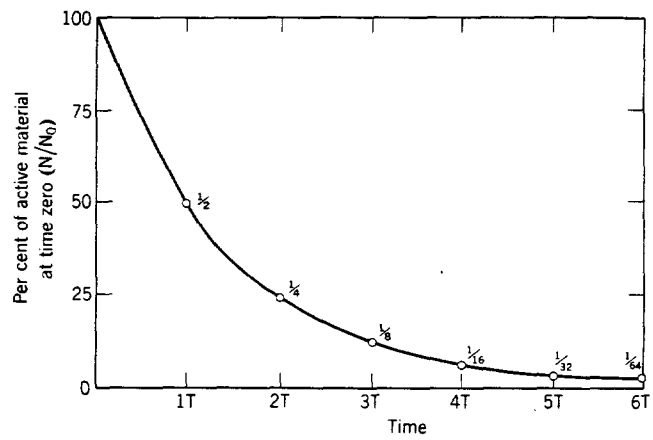

FIG. 22.1. Radioactive decay, illustrating concept of half-life.

half-life and intrinsic toxicity of the metals themselves, make it mandatory to prevent the possible entrance into the body by ingestion, inhalation, or other routes.

2. *Beta rays* (or particles) are electrons. They are the only negatively charged ionized particles of direct interest in the study of radiation effects. Since their mass is very small, they can penetrate deeper than alpha particles can penetrate. The electron acts an an ionizing particle when liberated from the atom, either by particulate or electromagnetic radiation. The energy of the electron determines the amount of secondary ionization, which greatly contributes to the total ionization or damage occurring in any cell. Ionizing particles have almost two-thirds of their energy carried away and distributed throughout the environment by these secondary electrons.

The relative energy of the electron has a significant effect on the shielding required to protect personnel who may be in the area. Glass, plastic, and aluminum are often used for shielding of betas or electrons, but glass and many plastics discolor and become brittle in high-radiation fields. With low-energy electrons, iron, copper, concrete, or concrete blocks are used as shields. The beams of high-energy radiation, such as fast electrons from accelerating machines, have found application including the modification of polymers to improve physical properties, such as tensile strength, food preservation, drug sterilization, and other uses. Typical electron accelerators include the Van de Graaffs, producing electrons of 1 to 6 mev (million electron volts, or mev, is a measure of the energy of a particle or wave); resonant transformers producing 1 to 3.5 mev electrons; betatrons producing 6 to 30 mev electrons; and linear accelerators yielding 3 to 25 or higher mev electrons. Both low-voltage electrons, also called cathode rays, and high-energy electrons, may be emitted by a heated filament (cathode) in a vacuum tube.

3. *Gamma (and X-) rays* are electromagnetic radiations analogous to light but of shorter wavelength. They differ from each other fundamentally only in their frequency (wavelength) and in their source. X-rays are frequently called Roentgen rays in honor of their discoverer, Professor W. Roentgen. Both X-rays (usually supplied by a machine employing a tube, such as the Coolidge tube) and gamma rays (usually from a radioactive isotope or radionuclide, such as Cobalt 60) may be used for clinical radiotherapy in humans, for radiography in the inspection of welds or flaws in pipes, vessels, and other metallic forms, or for many other uses since it is the characteristic of the ray which gives it utility. In deciding whether to use a machine-produced or radioactive source-produced ray, such factors

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as convenience, cost, ease of control, absoluteness of control, and precision of manipulation are often considered.

Neutrons are not emitted directly from radioactive isotopes, but they are essential to the production of most radioactive isotopes. One theory considers them the fundamental building blocks of all elements. Neutrons are electrically neutral, have very high penetrating power, and exhibit no electric interactions. Nuclear reactors are the most practical peacetime source of neutrons. By their ability to convert or transmute other elements by entering their nucleus (a process known as neutron capture), neutrons produce most of the man-made radioactive isotopes (or radionuclides) from stable atoms introduced into the reactor. The flux inside one reactor has been estimated to be a mixture of:

Thermal neutrons	$1.1 \times 10^{12}/cm^2$ sec
Neutrons ($\geq$0.1 mev)	1.4×10^{11}
Neutrons ($\geq$0.5 mev)	6.7×10^{10}
Fast neutrons ($\geq$1 mev)	4.2×10^{10}
Gamma-photons (av. 1 mev)	$\sim 5 \times 10^{11}$

The General Electric Test Reactor has peak flux as follows:

core position
3×10^{14} nv thermal, and 6×10^{14} nv fast
pool position
1×10^{14} nv thermal, and 3×10^{13} nv fast

22.2. UNITS OF RADIATION

For radiation sources, the fundamental unit of activity is the curie, named for Madame Curie. The curie is that amount of any radioactive material in which 3.700×10^{10} nuclear disintegrations occur per second. The millicurie (mc) is one-thousandth curie; the kilocurie (kc) is one thousand curies. Many experiments or operations are performed using less than a millicurie of a radioactive isotope. Sources of one to several kilocuries are used routinely for medical therapy, while food sterilization may require several hundred kilocuries. Stronger sources require the most meticulous care to prevent excessive exposures. Preplanning of a facility, careful selection and use of equipment, standardized procedures, and adequate education and training of personnel are important aspects of a radiation program, especially where large sources are involved.

The effect of radiation exposure depends upon the quantity of radiation, the type and amount of interaction of the radiation with matter,

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and on biological differences. A unit, the roentgen, has been established which defines the ionization effect in air by X-rays or gamma rays. It is defined as the quantity of X- or gamma radiation such that the associated corpuscular emission per cubic centimeter or 0.001293 g of air produces, in air, ions carrying one electrostatic unit (esu) quantity of electricity of either sign. One roentgen or X- or gamma radiation will result with the absorption of about 87 ergs of energy per gram of air. (The associated corpuscular emission referred to in the definition are electrons produced by the interaction of X- or gamma rays with air. All ion pairs produced are considered if we wish to account for the entire amount of energy.) Because it is defined in terms of air and refers to X- or gamma radiation, the roentgen must be converted to more useful units to be practical. For X-rays used in radiation therapy and for soft tissue, 1 roentgen yields an energy transfer of about 97 ergs/g of soft tissue. The energy per gram for other types of radiation and for other materials will differ significantly.

Since it is the actual energy transferred to and reaction with tissue or materials which produce effects, the "rad" was developed as a unit of absorbed dose. The rad represents the absorption of 100 ergs of nuclear (or ionizing) radiation per gram of the absorbing material or tissue. It is a valid unit of radiation dose for any type or energy of radiation and for any material with which the radiation interacts.

Equally absorbed doses produced by different types or different energies of radiation produce different biological effects. The quality of the radiation, the intensity or rate of delivery, and continuous versus fractionated administration have been identified as important variables. These differences have led to the concept of relative biological effectiveness, or RBE, in which various ratios have been established for the relative effectiveness of various types of radiation. These include:

Radiation	*rads*	*RBE or rems*
X-rays, gamma rays, electrons, beta rays, and nuclear weapon neutrons	1	1
Fast neutrons and protons up to 10 mev	1	10
Thermal neutrons	1	4 to 5
Heavy recoil nuclei	1	20
Naturally occurring alpha particles (from Ra, Po, Th, U)	1	10 to 20

By incorporating these RBE ratios into the previous definition of a rad, the "rem" has been evolved as an indication of the extent of the

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biological injury (of a specific type) which results from absorption of nuclear radiation, and is calculated by the formula:

$$\text{dose in rems} = \text{RBE} \times \text{dose in rads}$$

The rem is a dose unit of *biological* effect, whereas the rad is a unit of *absorbed energy dose*, and the roentgen (for X- and gamma rays) is a unit of *exposure* or total dose. Another term, linear energy transfer (or LET) is the energy released by the radiation per unit length of the absorbing tissue.

Measuring Radiation

Since radiation can not be observed with the normal physical senses, measurement is a prime prerequisite of radiation control.[17, 18, 19] An awareness of why radiation must be measured is essential for safe use. Important reasons for radiation measurements and records include:

1. To maintain a cumulative record of exposure to radiation of every individual exposed. (This has become increasingly important, both legally, and because of the interest in cradle-to-senior citizen documentation of the medical aspects of each individual.)
2. To measure over a short period the exposure of individuals carrying out specific operations during which the radiation level is abnormally high. For example, if a source is manually moved or physically transferred from a shielded storage location to a work station, or a radioactive isotope solution is removed from its shipping container and checked for identity and activity, a certain exposure is practically unpreventable, but it can usually be kept within recognized limits as repairable by the body. Measurements are essential to control such exposures.
3. To survey the flux or radiation level in all parts of the facility to detect areas of unnecessarily high radiation levels. For example, a bottle or drum of radioactive waste solution may have been temporarily stored with other chemicals under circumstances in violation of standard operations and procedures. Prompt discovery of this error by survey aids in restoring proper control.
4. To locate radioactive contamination on the benches, floors, and other surfaces, or, when necessary, in the air. Spills will occasionally occur, even in the meticulous operations, and unless careful surveys and clean-up (often referred to as decontamination) are instituted promptly and effectively, radiation can spread and eventually result in unnecessary exposure to a wide area and involve other personnel.

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5. To monitor contamination on hands, feet, hair, skin, or clothing of personnel who are working with or have contact with radioactive materials. (In large operations where this is a part of normal daily routine, special instrumentation may be available for self-monitoring of feet, hands, and body, located in a locker or wash-room area; in smaller operations, a readily available survey meter may suffice. For removal of radioactive material from the skin, special cleaners are available which combine chelating agents with surface-active detergents. Shower facilities or other methods of thorough washing of the whole body, including the hair, should be readily available for emergency decontamination and medical control of chemicals and radioactive materials, even if showers are not used routinely.)
6. To establish legal protection for the employers and employees, in compliance with local, state, and federal codes and other laws controlling radiation.

Radiation surveys and services are not glamorous occupations. However, they do require the same type of intelligence, patience, time, initiative, and a degree of dedication, as other accident prevention work. The seriousness, the moral and legal responsibility of the position, and the accountability must be fully appreciated if the job is to be done properly on the required routine basis.

Radiation Instrumentation

Film Badges. Photographic film of the proper type when processed will respond to radiation much as it does to visible light, and this fundamental fact is the basis for the film badge dosimetry—the device of choice by many individuals for measuring and subsequent recording of accumulated radiation exposure. Low cost, convenient size, capability for integrating doses over relatively long periods of time, and the permanent nature of the record are advantages which are possessed uniquely by film badges. Film badges detect from a minimum of about 10 mr to hundreds of roentgens of exposure from low-energy X-rays and beta rays to very high-energy gamma and neutron radiation. Film badges will not detect radiation from alpha particles, since alphas are stopped by the paper necessary to shield film from exposure to light.

Film badges consist of small sheets of sensitive photographic or X-ray type film supported by a plastic or metal frame holder. The holder may contain small discs or pieces of metals of different density,

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positioned in front of the film to intercept part of the impinging radiation. Aluminum, copper, silver, cadmium, and lead are frequently used to aid in discriminating different energy levels and types of radiation. Normally the badge in its holder is worn on the lapel or shirt pocket, and it is used as an indication of total body exposure. Where fingers and hands may have more direct exposure, as in the use of X-ray diffraction equipment, smaller film badges may be worn on the fingers to measure hand and finger exposures. If the forearm and hands are likely to receive exposures, a film badge may be worn on the wrist or lower arm to indicate exposures to such local areas.

Where exposure to neutrons may be encountered, an additional sensitive film is placed behind the beta-gamma film. Since cadmium has a high cross section for the absorption of slow neutrons, only fast neutrons penetrate the cadmium shield, producing recoil protons which leave tracks in the film, while thermal neutrons leave proton tracks in the areas of the film where no cadmium shields the neutrons. Slow neutrons, faster than thermal but slower than 0.5 mev, will not leave tracks. On the developed films, the tracks are counted using a microscope.

Badges are usually worn for a week or 10 days and are returned to the service supplier for processing and reporting of results. Since a few days normally lapse between returning the badges and receipt of the exposure report, emergency processing and reporting service should be available on a 24-hr basis, so any badge may be immediately processed when received, and the results telephoned or telegraphed to aid in determining whether an unusual exposure has actually occurred. This is important both clinically and legally, since high exposures must be immediately reported to medical and regulatory agencies. In addition to regular reports listing all badges used during the period, separate reports for each individual may also be obtained, showing totals for the previous period, for the past quarter year (or thirteen weeks), and for the total accumulated exposure for the individual since the inception of the badge service.[20] Although badges do not give immediate information and are not self-reading, they represent an excellent radiation control device, if they are supplied, processed, and reported by a reputable service. Quality of control in processing and reporting is of extreme importance to insure accuracy of results and records.

A new approach to analysis of minute concentrations of uranium uses tracks from fission particles in solid state media.[21] See Fig. 22.2.

Ionization Chambers. Ionization of air or other gases by radiation provides a method of measurement based on the movement of electrons

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FIG. 22.2. "Fossil" particle tracks produced in minerals by uranium atoms which underwent natural fission. Courtesy General Electric Research Laboratory.

from one part of the wall to an electrically charged plate or post. Since a single alpha particle from radium, for example, produces 137,000 positive ions and an equal number of electrons when it is completely absorbed in air, the consequent electric current can be measured with the aid of an amplifier. The ions formed in a gas (ions of nitrogen and oxygen molecules in the case of air) are usually exceedingly reactive; they often undergo chemical change during the time required to collect them at an electrode. The total electric charge, however, is not thereby altered. For this and numerous other reasons the ionization method of detection has proved remarkably trustworthy. Ionization chambers are widely employed to count energetic particles and to determine their individual energies. If the instrument is properly designed, with thin walls and high sensitivity, beta rays as well as X-rays and gamma rays may be measured.

The ionization effect is used for personnel monitoring in small, pocket ionization chambers, which are devices about the size and shape of a fountain pen. When charging the device initially with an auxiliary charger to a known potential, such as 150 v, the change in the capacitor due to discharge by ionization may be noted by reading the residual charge on a reader device. Another type, not unlike the other in external appearance, is a combined electrostatic ionization chamber and a fiber electroscope. The quartz hair-like fiber is charged with an external battery to read scale zero. As the radiation produces ionization, partial discharge occurs, and the fiber moves across the scale. Its location may be immediately observed by viewing the scale

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through the lens built into one end and observing the shadow against a light.

Both types discharge as the dose accumulates, and they may be read as frequently as desired. One style, designed for civil defense application, may be used also to indicate rate of exposure by exposing the device for a specified number of minutes, and then interpreting the dose per unit time as a rate (such as roentgens per hour).

One disadvantage to the pocket ionization chambers is their relatively high sensitivity to shock, which may be inaccurately interpreted as radiation exposure, if the device is accidently dropped. For this reason, pocket ionization chambers are often worn in pairs.

For higher levels of radiation, other types of dosimeters are available. Phosphate glass dosimeters measure doses in the range of 10 to 600 r, which is a critical range for determining probable survival of any individual exposed to high levels of radiation. (Single doses in the range of 25 to 100 rems over the whole body will produce nothing other than blood changes; doses of 100 to 200 rems will result in a certain amount of illness, but will rarely be fatal; for doses between 200 and 1000 rems the probability of survival is good at the lower end of the range but poor at the upper end.) The special glass contains traces of silver and other metals as activator and, after exposure to radiation, it becomes fluorescent under ultraviolet light.[22] Another type, the chemical dosimeter, utilizes the principle of the color change produced when an acid, such as hydrochloric, is liberated from chloroform or other chlorinated hydrocarbons, in the presence of an organic dye indicator such as methyl red or methyl orange. Indicators of this type may be dissolved in wax or a paraffin, and they are used to study penetration of the radiation by observing the color changes at various depths. The Fricke dosimeter, developed by Hugo Fricke, is based on another chemical reaction, the oxidation of ferrous sulfate dissolved in sulfuric acid, to give an accurate measure of absorbed energy.

The principle of ionization, when incorporated into the appropriate electronic circuitry, is used as a dose-rate meter. Available in a wide range of types and incorporating several scales to accommodate various intensities, from less than 1 mr/h to 5 r/h and with a movable shield in some models to permit discrimination between beta and gamma radiation, ionization dose-rate meters are widely used for survey purposes.

Geiger-Mueller Counter. The Geiger-Mueller counter is a count-rate meter, in which a thin-walled tube reacts with radiation to produce electronic pulses which are amplified so they can be displayed on a

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meter and heard on a speaker or earphones. It employs high voltages to break down the gas, once a passing particle has supplied an initial requirement of ions. Such a device yields a burst of current strong enough to be observed without amplification. Depending on the type and how the tube is housed and shielded, the Geiger counter can be very specific in pinpointing local radiation areas on contaminated floors or benches, or contaminated clothing or skin, especially if a sensitive end-window detector tube is used. Useful for counting large numbers of ionizing particles, the Geiger counter cannot determine their energies. Some Geiger-counter scales are calibrated in counts or pulses per minute, while others read milliroentgens per hour.

Scintillation Counters. Another method of detection rests on the emission of light by excited molecules. When an atom is excited, it must lose its excitation energy and return to its lowest energy state by emitting one or several photons. Since few atoms exist in isolation, the excitation energy is usually dissipated by collisions with other atoms or molecules and diverted to forms of energy such as heat. Although few molecules emit light when irradiated, special substances are available in which the excitation energy is not degraded, but they emit light under irradiation. Inorganic phosphors, such as zinc sulfide, and organic substances (usually aromatic polycyclic compounds), serve as scintillating media, and the light is picked up by a sensitive photo cell and amplifier that converts the burst of light into an electrical signal.

Alpha Detection and Measurement. Where alpha sources are used, an alpha-detecting instrument is required for check and control. Except for the scintillation counter, the instruments described previously will not perform this service. The typical alpha-detecting instruments have a very thin plastic-covered window which permits the alpha particles to enter the field of a relatively large probe, and the resulting pulse is translated directly into the circuitry, or, by ionization of a gas such as propane (in the gas proportional counter type), it produces secondary effects which then are amplified and indicated on a meter. Such meters read in counts per minute over a wide range, by choice of several scale multipliers, and must be calibrated for the particular alpha energy to be surveyed.

22.3. BIOLOGICAL EFFECTS OF RADIATION

The biological effects of radiation have been widely publicized in connection with nuclear weapons to the extent that it is difficult to

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approach the subject in the proper scientific manner, because of the high emotional content of much that has been written. The recent attempts to place radiation into its proper perspective will require an induction period before knowledge replaces fear in the minds of many. We live in a world in which radiation exists, and it is impossible to avoid some exposure.[23] See Fig. 22.3.

It is also true that the body can, within certain limits, repair the damage from radiation, whatever its source. At what point excessive or over-exposure to radiation is harmful to individuals depends on many factors. It is known that the different types of ionizing radiation differ greatly in their ability to penetrate the skin and body and in their relative effectiveness, a concept which is expressed in the RBE or relative biological effectiveness previously discussed.

The effects of ionization may be direct (localized within the cells directly affected, as a skin exposure), or indirect (since the action on one organ or group of cells, such as the bone marrow, may be transmitted to other cells remote from the bone by the blood). Effects may be immediate or delayed, depending on intensity, type, and other factors characteristic of the radiation involved. The effects may be reversible (repairable by the body through normal repair and replacement processes) or irreversible.

Certain body cells have been found to be more sensitive to radiation than others.[24] In decreasing order of sensitivity to radiation, some of these may be listed:

1. Lymphocytes, or white blood cells formed by the tissues of the spleen and lymph nodes. Because of their sensitivity, complete blood counts at frequent intervals following a suspected exposure to a large area of the body may reflect any serious damage and outline the recovery cycle which may be occurring. Reliable and accurate pre-exposure counts are essential for comparison purposes, since only by comparisons are such blood counts meaningful.
2. Granulocytes, or white blood cells formed in bone marrow. These are needed in proper ratio to combat bacterial infection.
3. Basal cells, which originate complex and specialized cells of the gonads, bone marrow, skin, and the alimentary canal.
4. Alveolar cells of the lungs, which are essential in oxygen-carbon dioxide exchange of the body.
5. Bile duct cells.
6. Cells of the tubules of the kidneys.
7. Endothelial cells, which line the closed cavities of the body, such as the heart and the blood vessels.

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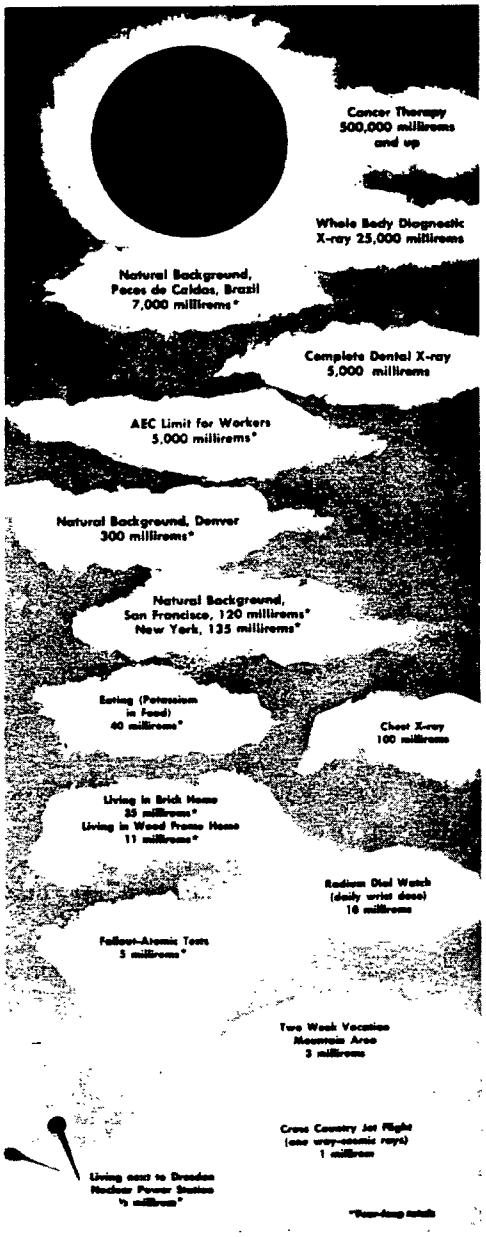

FIG. 22.3. Pinheads to planets—a comparison of radiation exposures of various kinds. Courtesy of General Electric Company.

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8. Connective tissue cells, which are structural cells of the tissue supporting the organs and other specialized tissues of the body.
9. Muscle cells.
10. Bone cells.
11. Nerve cells.

The relatively short life span which require blood cells to continually reproduce may explain the reason for their radiosensitivity. The life spans for typical blood cells are:

Cells	*Source*	*Life span*
Erythrocytes	Bone marrow	17 weeks
Granulocytes	Bone marrow	3 days
Lymphocytes	Lymphatic tissue	8 to 24 hours
Platelets	Bone marrow	3 to 6 days

In considering internal radiation, in which various radioactive materials, either naturally occurring or man made, may be inhaled, ingested, or otherwise gain entry into the body, it is interesting to note that certain radionuclides or isotopes tend to concentrate in a few vital organs, especially the lungs, kidneys, liver, and bone. This property, coupled with the known biological half life and the excretionary rate (at which the material is known to be eliminated from the body), makes it possible to use monitoring of exhaled breath, urine, and other body wastes as an indication of body burden or total amount of the substance actually in the body. In addition, whole body counters of great sensitivity have been used to measure the total radiation emitted from the whole body because of internally deposited radioactive materials. Some isotopes known to concentrate in certain body organs include:[16]

Lungs	*Kidneys*	*Liver*
Nickel 63	Chromium 51	Manganese 56
Radon 222	Manganese 56	Nickel 59
Polonium 210	Germanium 71	Cobalt 60
Uranium 238	Arsenic 76	Copper 64
Plutonium 239	Rhodium 105	Silver 105
	Ruthenium 106	Cadmium 109
	Rhodium 106	Silver 109, 111
	Technetium 127	
	Tellurium 129	
	Iridium 190, 192	
	Gold 198	
	Uranium 238	

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Bone	*Bone (cont.)*
Beryllium 7	Promethium 147
Carbon 14	Samarium 151
Fluorine 18	Europium 154
Phosphorus 32	Holmium 166
Calcium 45	Thulium 170
Vanadium 48	Lutecium 177
Zinc 65	Tungsten 185
Gallium 72	Lead 203
Strontium 89 and 90	Radium 226
Yttrium 90 and 91	Uranium 233
Niobium 95	Thorium 234
Molybdenum 99	Plutonium 239
Tin 113	Americium 241
Barium 140	Curium 242
Lanthanum 140	
Praseodymium 143 and 144	
Cerium 144	

Control of Exposures to Radiation

Regardless of the source (nuclear or electronic) or type of ionizing radiation, a few fundamental control measures are appropriate. No unnecessary exposure should be permitted, and the risk of exposure should always be balanced against the importance of the results to be obtained. Every operation or activity involving ionizing radiation should be preplanned, and, if possible, rehearsed with a "dry run" to insure that the desired operation can be accomplished in the minimum amount of time with the least practical exposure. This should not be understood to mean that all exposures should be avoided at all times, but, rather that exposures should be controlled and measured, so they can be kept within the limits which have been established. Obviously, amounts of activity (in the case of nuclear sources) or voltages and times of exposures (in the case of X-ray and other electronic sources) should be kept at a workable minimum. From a practical view, most exposures are controlled by the application of three principles: time, distance, and shielding.

Time. Radiation dose is directly related to the time of exposure—this elementary fact is one of the keys to radiation control. For this reason, every individual action or activity in the radiation field or area should be preplanned so no delays or other complications require unnecessarily long exposure. The formula:

$$\text{Exposure dose} = \text{rate} \times \text{time}$$

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is fundamental, since time is the easiest factor which an individual controls for himself. Stop-watches, clocks, or calendars thus become important instruments in the radiation control program, and the importance of time should not be minimized. All other factors equal, the same total dose is less likely to cause biological damage the longer the period of time over which it is accumulated.

Distance. Next to time, distance is probably the fundamental concept in radiation control. Radiation follows the same Inverse Square law as does light, namely, the intensity decreases as the inverse square of the distance from the source. A radiation flux or level of unity at a unit distance will be only ¼ unity at twice the distance, since $1/2^2 = 1/4$.

To illustrate further: if a source has an intensity of 100 mr/hr at 1 ft distance, the corresponding intensity for other distances up to 10 ft may be tabulated:

Intensity in mr/hr	*distance*	*ratio*
100 mr/h	1 ft	1
25 mr/h	2 ft	1/4
4 mr/h	5 ft	1/25
1 mr/h	10 ft	1/100

In practice, distance may be used to advantage by remote-handling aids, such as tongs, long-handled wrenches, cranes, and remotely operated mechanical hands. Viewing aids, such as mirrors, telescopes, closed-circuit television, and windows made of leaded glass installed so they may be filled with water solutions of heavy-metal salts, permit visibility from a distance without unnecessary complications.

Shielding or Filters. Any matter or mass placed between a radiation source or beam and the point of exposure will screen or decrease the exposure to at least some extent. As noted previously, even air produces some shielding effect. Whether or not shielding of a particular type is adequate for a given situation depends on specific considerations. The man who, half seriously, planned to construct a fallout shelter from cream puffs so he could eat his way out as the outside radiation level decreased due to the decay of the fallout radiation may have had originality and imagination but little scientific information. If fallout were all alpha activity (which, of course, it is not), if the eating rate matched the decay rate of the alpha, and if the sheltered did not breathe or eat any of the alpha-contaminated air, water, or food, the cream-puff shield might be adequate, just as paper or thin

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aluminum shelters would be. Unfortunately, beta and gamma rays of the energy levels associated with fallout would not be attenuated or stopped to any significant extent by the mass or density of cream puffs.

Each type of radiation is most effectively controlled by a particular shielding material. The type and energy must be considered in choosing the kind and type of shield required to cut levels of radiation down to acceptable limits. Shielding may be constructed of several different materials. Lead and the other heavy metals are excellent shields for radiation, but their cost is high. Concrete mixed with iron ore or heavy mineral aggregate (to increase the density) is effective but expensive and bulky. Poured walls or precast concrete made with iron ore or heavy aggregates in walls and ceilings or solid concrete blocks laid into wall form are the most common shielding materials.

The concrete thickness estimated to reduce radiation levels to establish limits for personnel near a one-million-volt electron beam generator is 2.5 ft, and, for a generator of 2 million volts, 4 ft. These numbers are estimates, and exact thickness will depend upon the voltage and kilowattage of the electron-beam generator, size of room, room geometry, and occupancy of adjacent areas. An alternate scheme is to construct two walls of timber and planking, filling the space between with poured sand as a barrier. Such a barrier is easily erected and dismantled, and the materials of construction may be reclaimed. However, the lower density of the sand as a barrier requires that its thickness be about 70% greater than the equivalent concrete shielding, thus requiring a greater overall floor area. The suggested floor plan used for facility planning purposes for a 1-mev electron beam unit is shown in Fig. 22.4.

A frequently used approach is to locate a machine or source in a pit or depression underground, so that the earth acts as a natural shield on the sides and bottom. Deep pools of water are also used as shielding material if the material is not adversely affected by water. In this connection, it has been reported that the radiation exposure to personnel aboard an atomic-powered submarine when submerged is less than that to a person on land near the same area, because of the shielding of the cosmic and other background radiation by the water.

Limits of Exposure

Any attempt to outline exposure limits must be predicated with the statement that exposure to radiation should be kept at the lowest

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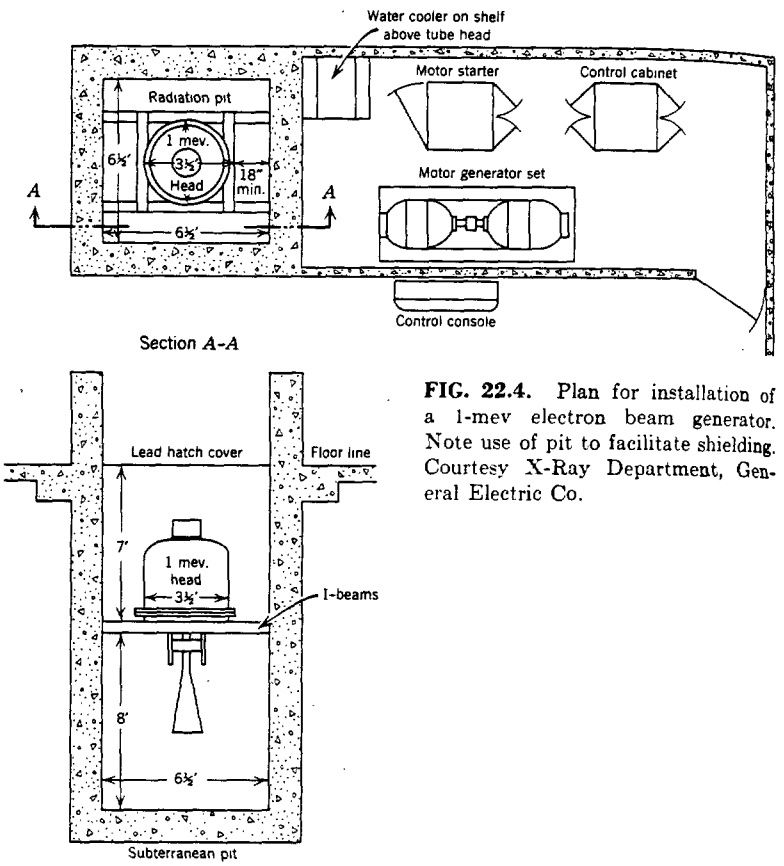

FIG. 22.4. Plan for installation of a 1-mev electron beam generator. Note use of pit to facilitate shielding. Courtesy X-Ray Department, General Electric Co.

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levels which are practical to achieve necessary results, always balancing the benefits to be gained from the exposure with the potential hazards, and recognizing the established limits. As in many other phases of life, the risk and gain should be weighed to achieve an understanding for the necessity for the risk.

External Dose Limits. The permissible limits for external radiation exposure are:

Site of exposure	*Dose for 13 consecutive weeks in rems*	*Accumulated dose*
Whole body, head, and trunk, blood-forming organs, gonads, lens of the eyes, and other organs	3	5 (N-18) rems*
Skin of the whole body	10	30 rems/yr
Hands and forearms, feet and ankles	25	75 rems/yr

* N is the age in years, greater than 18.

Internal Dose. Since the main route of entry of radioactive materials normally is by breathing, the control is to limit the average rates at which materials are breathed. For drinking water and foodstuffs, the permissible concentrations are also recognized. For further information on this subject, the reader is referred to Handbook No. 69, *Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure,* published by the National Bureau of Standards, United States Department of Commerce, Washington, D.C.

Permissible Limits for Nonoccupational Exposure. For external radiation exposure, the maximum permissible dose for nonoccupational exposure to the whole body, head and trunk, active blood-forming organs, gonads, or lens of the eye should not exceed 0.5 rem in any year. For internal exposure limits, refer to the Handbook No. 69 referred to above.

Summary

The material presented in this chapter is intended to serve as a beginning, however inadequate, to an understanding of radiation as a controllable hazard. Perhaps more than any other field of scientific knowledge, even in the scientific community itself, radiation

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is inadequately understood and even feared. The plea of Madame Curie is still unanswered in the popular mind:

Nothing in life is to be feared;
It is only to be understood.

The references attached furnish a key to this understanding, and the reader is urged to consult them in detail.[25, 26]

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23

Respiratory Hazards and Protection

H. H. Fawcett

Pure air, essential for breathing by humans as well as for the health of plants and animals, is a relatively rare commodity. No American or Canadian standard exists for breathing air. Yet, without this gaseous mixture, which is normally colorless, odorless, tasteless, and so ubiquitous it is taken for granted, life, as we know it on this earth, would cease in minutes. Since the average adult breathes about 16,000 quarts of air each day, air purity is a vital matter.

Many impurities in the air are the result of natural forces, such as moisture from rain or dust from the winds on dry soil, while others are caused by the activity of man, from his breathing, his industry, or his misadventure. When impurities are in low concentrations, we say the air is "clean," but when the variations, either alone or in combination, exceed human tolerance, we say the air is "polluted" or "impure." No simple yardstick exists to aid in measuring with precision the exact point when air ceases to be "clean," and each situation must be judged independently before valid conclusions may be drawn as to the relative safety or hazard of an environment.[1, 2, 3, 3a]

For routine industrial purposes, with which we are concerned, a guide is available in the *Threshold Limit Values* published after annual revision by the American Conference of Governmental Industrial Hygienists (see Appendix).[10] This guide lists several hundred substances, elements, compounds, and mixtures which have been studied in sufficient detail to suggest threshold limit values of time-weighted average concentrations in air for repeated normal work exposures. It

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is strongly recommended that anyone who consults this guide carefully read the introduction, which plainly states what the values are and are not intended to denote. To relate these values to a given environment requires analyses and interpretation by a person with specific knowledge and training.

"Community air pollution," as defined by the Interdepartmental Committee on Community Air Pollution of the United States Government, "is the presence in the ambient atmosphere of substances put there by the activities of man in concentrations sufficient to interfere directly or indirectly with his comfort, safety or health, or with the full use and enjoyment of his property. In general it does not refer to the atmospheric pollution incident to employment in areas where workers are employed, nor is it concerned with airborne agents of communicable disease, nor with overt or covert acts of war."

Increasing emphasis has been placed on the role of impurities in even low concentrations when breathed for long periods of time. Federal, state, and local agencies are active in the study of this problem, and much legislation has been proposed and enacted; some of it is even enforced. For a more complete description of the general air-pollution problem, which is beyond the scope of this chapter, the reader is referred to cited references and to the air-purity control agencies active in local areas.[4-9]

Another guide, *Maximal Acceptable Concentration*, has been furnished by the American Standards Association in the standards which that group issues for toxic substances in the air. This term is based on the premise that levels exist to which a person may be exposed without known ill effects or discomfort. These concentrations in themselves do not represent a scale of relative toxicity, but they do represent the concentration in air below which it is unlikely that ill effects will occur, except to hypersusceptible individuals.

Knowing the permissible allowable concentration of a substance is only part of the problem. The physical state, effects of temperature, volatility, flammability, explosibility—these and other factors must be considered. A highly toxic liquid of low volatility may be less dangerous than one of lesser toxicity but highly volatile. A substance that is toxic by absorption must be handled differently than one that is toxic only by inhalation or ingestion. Some substances are synergistic in that their toxicity is increased many fold in combination. Odor is no criteria of toxicity as some pleasant-smelling substances (such as hydrogen cyanide) may be quite deadly, whereas other disagreeable odors such as pyridine may be comparatively innocuous irritants. With hydrogen sulfide and with several other gases, the sense

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of smell is quickly deadened, and hence the nose is not a reliable indicator of concentration.

23.1. DETECTION

Substances such as acrolein, ammonia, bromine, chlorine, fluorine, formaldehyde, hydrogen chloride, hydrogen fluoride, ozone, and sulfur dioxide are easily detected by their irritating odor. It may be dangerous to include fluorine and hydrogen fluoride in this category because of their quick corrosive effect on respiratory tissues. Many others can be detected by their characteristic odors, but arsine, hydrogen cyanide, nitric oxide, phosphine, and stibine may be present in concentrations above the permissible limits of exposure by the time their odor can be detected.

Carbon monoxide is odorless, and for practical consideration, so is hydrogen sulfide. Even in permissible concentrations, which produce no irritation of the eyes or systemic discomfort, the olfactory nerves are paralyzed and the sense of smell lost within minutes, so the characteristic odor of rotten eggs no longer is recognized. In sudden high concentrations of H_2S, the odor is not detected at all, so the sense of smell is not dependable for the detection and recognition of it. Both of these gases can be detected by chemical means and by instrumentation. In the past, and even in modern installations, canaries and Japanese waltzing mice have been used as a positive means of detection and warning. They cannot fail to respond to lethal concentrations of CO or H_2S. Their use as detecting agents in mines is well known but their practical use to protect man has been questioned.[9a]

Certain gases may be difficult to detect by any known means within the required range. Phosphine (PH_3), for instance, has an odor threshold well above its Threshold Limit Value of 0.3 ppm, and the lower limit of detection of instrumentation is its TLV.

An excellent manual of air sampling equipment is available.[8]

23.2. PROTECTION

To prevent or reduce dangerous exposure to toxic materials, they should be confined insofar as possible, and releases should be vented *outside* buildings and away from work areas and other populated areas. Exhaust ventilation should be provided to remove emissions, and/or personal protective clothing and equipment can be worn.

In dealing with such gases as the phosphine mentioned above, where the toxicity is so high, and the detection and warning so difficult, con-

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finement is very important. If it is necessary to work with such a highly toxic gas inside, the building air probably should be changed every two minutes, with auxiliary equipment to double this air change in case of emergency—especially if the gas is also as flammable and explosive as is phosphine. In addition, suitable respiratory equipment should be worn, or at least it should be readily available so it may be donned in seconds. Time wasted while seeking a breathing apparatus, removing it from the box, inserting a canister (if required), and making certain it is properly working, may easily mean the difference between emergency control and disaster; and every effort should be made to be certain the breathing apparatus is of the correct type, that the wearer is properly trained, and can have the device in actual operation in as few seconds as possible. Half-hour or hour breathing apparatus in boxes requiring time and gymnastic activities of a superman to put on, and a high degree of training to insure they are properly working, have only limited value in operations where *immediate* control is needed. The apparatus should be of the size, type, and simplicity commensurate with practical and realistic needs. A more complete discussion on the limitations of various breathing devices is found later in this chapter.

To determine whether or not a hazard exists in an environment, a survey may be made, samples taken and analyzed, and the results correlated with the clinical observations of the persons exposed. It must always be remembered, as has been pointed out, that the atmosphere could be purple with pink dots, and yet no injuries may occur as evidenced by the only true criteria, namely, the humans involved. If a hazard is judged to exist, however, appropriate measures, such as process modifications, substitution of materials, revised work practices, changes in shift schedules, better ventilation, or other controls may be recommended. The use of respiratory protective devices, such as respirators, filter masks, or similar devices, for a long-term solution to a respiratory problem, has seldom been satisfactory.

Before reviewing respiratory hazards and protection, a brief listing of the classes of airborne substances may be useful:

Aerosols

Based on their physiological effects, aerosols may be classed:

1. *Nuisance and Inert.* Nonfibrosis-producing and nontoxic, but may be harmful in high concentrations
   examples: calcium carbonate, magnesium carbonate, and gypsum

2. *Inert Pulmonary Reactions.* Produce nonspecific pulmonary reactions
   examples: silicates, carbon, and aluminum
3. *Minimal Pulmonary Fibrosis-Producing*
   examples: barium compounds, tin, and iron oxides
4. *Extensive Pulmonary Fibrosis-Producing*
   examples: silica and asbestos
5. *Chemical Irritants.* Produce inflammation or ulceration
   examples: acids, fluorides, chromates, and chromic acid
6. *Toxic Systemic Poisons.* Produce pathological reactions
   examples: *a.* lead, manganese, antimony, arsenic (not considered significantly more toxic than lead)
   b. arsenates, organic phosphates, cadmium, radioisotopes, and beryllium (considered significantly more toxic than lead)
7. *Allergic Manifestations.* Produce allergic reactions
   examples: pollens, and dust of certain exotic woods
8. *Fever-Producing Reactions.* Action unknown or allergic
   examples: metal fumes, hemp, cotton, jute, bagasse

Aerosols (also called dispersoids or particulate contaminants) are substances present in the air as minute particles (dusts), as fumes (metal fumes), or as mists (chromic acid mists). In grouping these, it is recognized that they may be physically filtered, screened, or absorbed from the air with properly designed filters.[11] Aerosols may range in size from 150 microns to 0.001 micron in size (1 micron equals 39.37 millionth of an inch, or 1×10^{-4} cm). In considering the health hazards of dusts, it must be remembered that many dusts are also fire and explosion hazards.[16, 17, 18]

Pneumoconioses is a group of lung conditions which result from the inhalation of certain dusts or mists. Silicosis is one of the most common types of pneumoconiosis, and it is caused by the inhalation of "free" or uncombined silica, such as quartz, opal, flint, and cristobalite. Many other dusts may produce other types of lung involvement, such as carbon, iron, and barium (the last of which is also toxic). Other dusts cause chemical irritation, such as acids, alkaline substances, fluorides, and chromates. Allergic reactions may be caused by nuisance dusts such as pollens, some synthetic resins, certain plastics, felt, fur, gums, spices, tobacco, paper, rubber, exotic woods, starch, flour, and wool.[13] In referring to respirators for exposure to dusts classified above, the United States Bureau of Mines groups these as pneumoconiosis-producing and nuisance dusts.[20]

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Another classification refers to "toxic dusts." The Bureau uses lead as the reference, and says that listed dusts, for this purpose, are not significantly more toxic than lead, feeling that a difference between 0.1 and 0.2 milligram per cubic meter as a toxic concentration is not significant. Among dusts more toxic than lead are chromates, organic mercury compounds, yellow phosphorus, picric acid, selenium, tellurium, and calcium arsenate.

Respirators approved for all the above mentioned dusts (both toxic dusts and pneumoconiosis-producing and nuisance dusts) are called "dust" respirators.

"Fumes" include aerosols formed by the condensation of vapors from heated metals. Melting, cutting, and welding of zinc, lead, cadmium, and other metals produce such fumes.

"Mists" and "sprays" include liquid droplets formed when liquids are carried into the air or are formed by a reaction with the moisture in the air. An interesting example is that 0.3 ppm sulfur dioxide with water in the presence of sunlight may form as many as 20,000 particles per cubic centimeter of sulfuric acid mist.

The availability of filters with pore sizes from 10 millimicrons (approximately the size of the polio virus) to 5 microns (the size of common contaminants in liquids) has greatly improved and speeded up analyses of aerosols such as acid mists, metal fumes, smokes, and radioactive particles.[15]

In recent years, study and measurements of even smaller particles in air than previously observed, known as condensation nuclei, have contributed to our knowledge of the nature and number of particles in air. Particles on which water will condense are called condensation nuclei; under natural conditions only the larger particles are so affected. When the air is sufficiently supersaturated, however, apparently any particle will serve as a condensation center. Particles from such diverse substances as platinum, silver, stearic acid, glycerin, and lubricating oil will form droplets at a sufficiently high supersaturation of water vapor. Practical methods are now available to measure or count the number of aerosol particles in free air. Wider use of such techniques will doubtlessly throw much light on many air pollution problems, as well as lead to further improvements in our knowledge of aerosols, and hence respiratory hazards and protection.[14]

Respirators and masks intended specifically to furnish protection against pesticides, which are found by tests to give adequate protection against dusts, mists, and low-vapor concentrations of certain pesticides, are listed by the United States Department of Agriculture.[21] It should be noted the service of the United States Department of

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Agriculture differs significantly from the service offered by the United States Bureau of Mines. The two services are not parallel or even analogous.

Gases and Vapors

In this class may be included most of the air contaminants which are not classified as aerosols.

Irritant gases or vapors are those which produce inflammation of tissue, such as the skin, the eyes, and the respiratory tract membranes. They are divided into two general groups:

1. Action is limited to irritation (such as hydrogen chloride).
2. Action extends to systemic effects (such as the oxides of nitrogen).

Some of these gases and vapors have pronounced odors, but the nose cannot be depended upon as a reliable method of estimating concentrations, or in forcing persons to escape. Lacrimators or tear gases are ordinarily harmless to life in the concentrations usually obtained when used in open air. However, chloracetophenone, one of the tear gases used by the military and law-enforcement agencies, fired in shells or grenades, has caused two fatalities. In one case, a forty-year-old man locked himself in a room and successfully resisted all attempts to eject him. The police were called and they injected tear gas to drive him from his stronghold, but they were not able to enter for an hour and a half; during this time the man was exposed to the chemical fumes. He was found unconscious, and taken to the hospital where he died two days later from the inflammation of the air passages.

In another instance, a twenty-eight-year-old male barricaded himself in a bedroom of his house after refusing to leave as requested by law officers. A tear-gas grenade was tossed into the bedroom through a transom, and the man forcefully removed at a time estimated between 10 min and a half-hour. He expired in the hospital less than 18 hr later. It has been estimated that 0.82 ounce of tear gas per 1000 cu ft of air is a lethal concentration for a 10-min exposure. Prompt entrance by trained rescue personnel wearing respiratory protection, approved for this type and level of exposure, should be considered whenever such gases are deployed in confined space. Brombenzyl cyanide, which has an odor like sour fruit, is also used as a lacrimator. Lung irritants, such as chlorine, phosgene, and chlorpicrin, have had military application. Vesicants (skin irritants) such as mustard gas, lewisite, and the nitrogen mustards are also respiratory

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irritants. Sternutators (sneeze gas) such as diphenyl chlorarsin and adamsite (diphenylamine chlorarsin) produce effects designed to destroy morale, and they are not used for their lethal action. Nerve gases, which inactivate the cholinesterase, and cause acetylcholine accumulation in the central and peripheral nervous system, produce spasm and vision disturbances in very low concentrations, and more serious effects involving the respiratory system in higher concentrations.

Asphyxiants are substances which deprive the body tissues of oxygen, causing hypoxia or oxygen starvation. Two modes of action are known:

1. *Simple Asphyxiants* (such as nitrogen, hydrogen, helium, and methane) dilute or replace the partial pressure of oxygen in air.
2. *Chemical Asphyxiants* such as carbon monoxide, aromatic nitro compounds, and aromatic amino compounds (such as aniline, nitrobenzene, and chemically related molecules), hydrogen cyanide, hydrogen sulfide, acetonitrile, and other substances which combine with the hemoglobin of the blood or otherwise interfere with the oxygen-carbon dioxide exchange. Carbon monoxide has 210 times the affinity of oxygen for the blood. The rapid action of the above substances, once they have entered the blood, pleads for extreme respect.

The above discussion in no way minimizes the respect due the simple asphyxiants, for the insidious nature of their action is little appreciated. Nitrogen and other simple asphyxiants give almost no warning between the time breathing air is replaced with the asphyxiant and unconsciousness overtakes the breather. Under proper medical supervision, pure nitrogen may be breathed for several seconds, and this technique has been used clinically by Himwich and others. A loss of mental facilities begins within a few seconds, and unconsciousness may occur shortly after with no warning. The brain is the first organ of the body to be seriously affected by oxygen want, and the subject "blacks out" quickly. Mention is made of this little-appreciated phenomenon, not only because asphyxiants can be released in a room or tank with inadequate warning from the action of a fixed carbon-dioxide fire-extinguishing or inerting system, from a large spill of a liquefied gas (such as liquid nitrogen, liquid hydrogen, or liquid helium), from a leaking gas system, from an inert-gas generator (entrance into a tank car or other confined space which has been inerted with gases for refrigeration or to replace oxygen in the air), or from leaking cylinders.

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Even more insiduous but no less serious is the occasional use of a plant compressed-air supply for respiratory purposes without recognizing the hazard. If a cross connection is made which would permit an asphyxiant, toxic, inert, or flammable gas at a higher pressure to enter the compressed-air system at any point in the system, the results can be fatal. Two separate incidents have occurred within the past decade where nitrogen gas had been deliberately introduced into an air supply to maintain pressure for pneumatic instruments, and in both cases men, who were not aware of this change in operations, were overcome and expired before help could arrive. The importance of a separate system for breathing air cannot be overemphasized. It may also be noted that the United States Bureau of Mines approval for air-supplied breathing equipment stipulates that the quality of the breathing air is the responsibility of the user. A separate air supply, supplied by a compressor which cannot evolve carbon monoxide, carbon dioxide, oil mist, moisture, or other impurities, or compressed air from which the impurities have actually been removed, or from cylinders of tested known purity, should be used for air-supplied respirators, hoods, suits, and self-contained breathing apparatus which uses compressed air. The supply system should include pressure relief valves, filters, regulators, and absorbents as recommended by the manufacturer of the respiratory protective equipment and the United States Bureau of Mines.

This problem has become increasingly important with the rapid growth of interest in self-contained underwater breathing apparatus (SCUBA) as well as air-supplied, self-contained, and hose-line breathing equipment.[23]

An interesting incident, which illustrates that even "plant air" can create difficulty when not attached to breathing apparatus, occurred in a radio parts firm. Fourteen of 200 women employees were taken to hospitals when an odor, apparently of overheated oil, filtered from machines powered by compressed air, because of an overheated air compressor. The plant air lines apparently distributed these fumes to all parts of the plant. It is especially fortunate no one was wearing any breathing equipment attached to such a system.

Anaesthetics

Anaesthetics are gases and vapors which act primarily to induce the symptoms of anaesthesia when inhaled in sufficient quantities. They include the classic anaesthetics diethyl ether and chloroform but they also include most halogenated hydrocarbons, such as methyl

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chloroform (1,1,1-trichloroethane), trichloroethylene, ethylene oxide, nitrous oxide (laughing gas), and many other organic compounds.

As well as having physiological effects, these materials alone or in combination may produce decomposition products in a fire or when they are otherwise subjected to elevated temperatures. Even relatively harmless substances such as nonflammable refrigerants with low toxicity will evolve irritating decomposition products if heated above their decomposition temperatures. This has occurred where fluorocarbons were used as cleaning solvents for metal parts. After cleaning, the parts were heated over a flame to dry and to remove excess solvent. Several persons were hospitalized with pulmonary congestion. A similar problem can occur with trichloroethylene. Trichloroethylene vapor degreasers, when properly installed, maintained, and operated, are usually safe, but the failure or misuse of these degreasers has created serious problems, including both fire and toxicity hazards. Trichloroethylene is not completely nonflammable. Mass hysteria and unconsciousness because of the little-appreciated anaesthetic action of the trichloroethylene can occur in seconds; in one incident, seventy-two persons were overcome, and in another, twenty-six persons. Fortunately, all recovered after removal to fresh air and oxygen inhalation. The hazards of carbon tetrachloride mixtures in fire fighting, and of carbon tetrachloride in other applications, have been documented. It is hoped that in a few years, the vaporizing-liquid type extinguisher will be found only in historical collections and that alternate cleaning solvents will have replaced it for "bucket cleaning."

Substances Producing Other Effects

This class includes several substances whose action differs from previously mentioned substances. Included in this group are mercury vapor, white phosphorus, tetraethyl lead, tetramethyl lead, nickel carbonyl, arsine, phosphine, the boron hydrides, including diborane and pentaborane, hydrogen sulfide, and military "nerve gases." The initial action of these gases and vapors is primarily on the nervous system with respiratory arrest following. Arsine is the only gas which dissolves red blood cells.

If the above classification appears complicated, it should be noted that air contaminants seldom occur alone, and that even less is known about the combined action or synergistic effects of two or more substances, especially if they are classified in different groups. Even if the particles dispersed in air are nontoxic by themselves, they may

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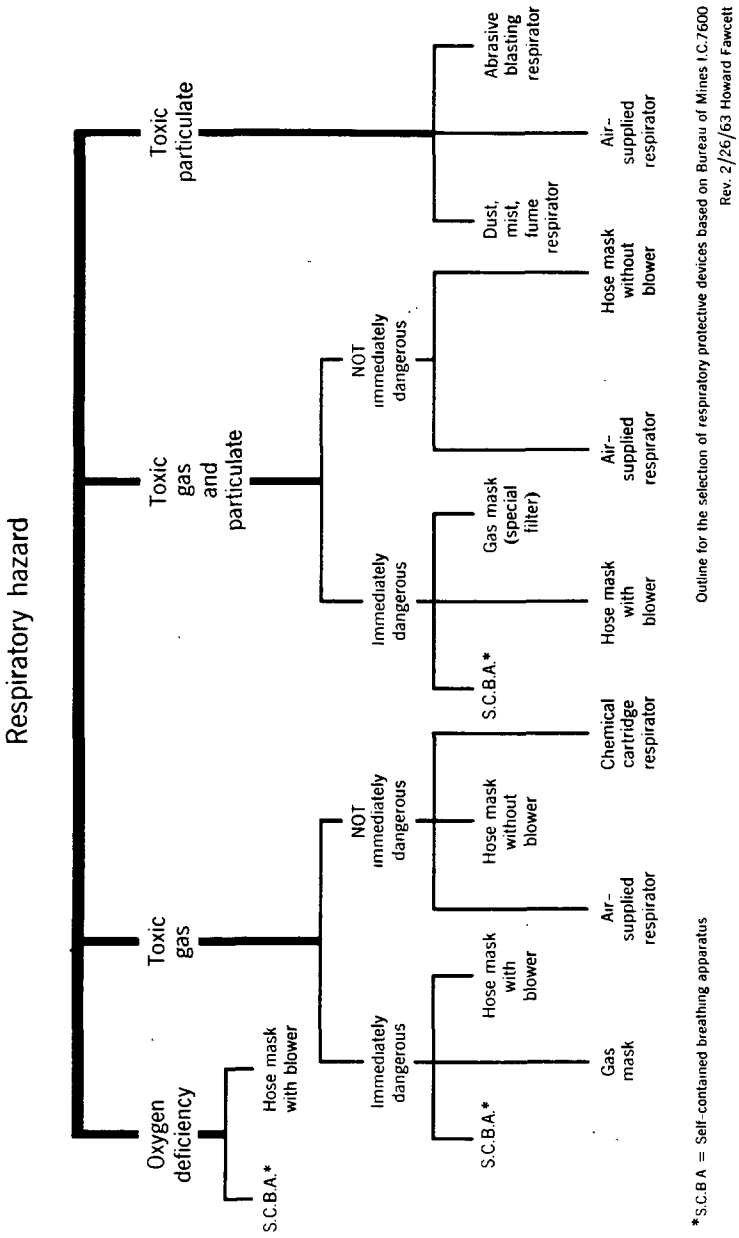

*S.C.B.A = Self-contained breathing apparatus

Outline for the selection of respiratory protective devices based on Bureau of Mines I.C.7600
Rev. 2/26/63 Howard Fawcett

FIG. 23.1. Selection chart for respiratory protective devices.

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act as carriers of condensable toxic vapors. Formaldehyde, for example, can have its toxicity increased five-fold by the presence of an inert aerosol. Hence, it is suggested that respiratory protection can become highly complicated, and that the practical application of respirators, gas masks, and self-contained breathing apparatus (each with its limitations), even by persons thoroughly trained in their use (who may or may not actually use them properly), is not a simple problem. Inadequately trained persons in an emergency situation, the nature of which is not fully known at the time, are in especially vulnerable positions, regardless of the availability of quality equipment.

Types and Applications of Respiratory Protective Devices

AIR-PURIFYING RESPIRATORS

The fundamental limitations of any air-purifying respiratory device are that the air must be within the limits for which the respirator was designed (for example, the oxygen content must be over 16%), that the unit will protect only against the specific substance or combinations in certain concentrations for which it was designed (for example, aerosol filter-type respirators will afford no protection against gases and vapors), and that the canister or filter must be maintained in proper working condition attached to a properly maintained facepiece which fits snugly enough to exclude leakage of contaminated air.

Aerosol filter-type respirators require frequent changing in filters when breathing resistance becomes uncomfortably high when worn in areas containing excessive dust, mists, or fumes. Chemical cartridge respirators will safely protect only against the specific gases and vapors in nonemergency situations where no more than 0.1% concentrations are encountered. Extremely toxic materials, such as acrolein, acrylonitrile, aniline, dimethylaniline, arsine, bromine, carbon disulfide, dimethylsulfate, hydrogen cyanide, hydrogen fluoride, hydrogen selenide, hydrogen sulfide, iodine, methyl bromide, methyl chloride, nickel carbonyl, iron carbonyl, nitrobenzene, nitroglycerine, nitromethane, the oxides of nitrogen (nitric oxide and nitrogen dioxide), ozone, phosgene, phosphine, phosphorous trichloride, stibine, sulfur chloride, diborane, pentaborane, and other substances are too toxic even in very low concentrations to rely on a simple cartridge-type respirator.

Chemical cartridge respirators should not be used against gases which are odorless, or whose odor threshold is high, since odor is the

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FIG. 23.2. One respiratory facepiece may be used with several different filters for a variety of exposures, underscoring the need for selection of the properly designed filter for each particular exposure.

only warning of failure of the canister, facepiece leakage, or of concentrations which are above the design limits of the respirator. Methyl chloride is an example of a gas whose warning properties are inadequate for practical warning purposes. Substances which are highly irritating to the eyes, such as sulfur dioxide and ammonia, require eye protection (such as gas-tight goggles, an air-supplied hood, or a mask with a full facepiece). Several lacrimatory (tear-producing) substances, such as benzyl chloride, are in the same classification, and a respirator alone is clearly inadequate. Carbon monoxide cannot be stopped by a chemical cartridge, except of the type used in the canister of the Type N universal gas mask and the miner's self-rescuer, both of which contain Hopcalite. This mixture of oxides of manganese, copper, cobalt, and silver catalyzes the oxidation of carbon monoxide to carbon dioxide, provided it is properly activated, dry, and the carbon monoxide concentration is not excessive. These qualifications have been the cause of much misunderstanding in the past.

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Ammonia cartridge respirators will safely protect against ammonia vapors up to 1000 ppm, while eye irritation from ammonia begins about 70 ppm. Mercury cartridge respirators are effective against concentrations of mercury vapor normally encountered at ambient temperatures and pressures, but service life is proportionally reduced where higher concentrations of mercury from elevated temperatures and pressures are present. Specially designed vacuum cleaners for use in cleaning mercury spills (ordinary vacuum cleaners in this service create more hazard than they correct), and highly portable mercury vapor survey instruments have aided greatly in reducing this hazard. No Bureau of Mines approval schedule has been established for chemical cartridges to protect against other than organic vapors. Combination cartridges have the limitation of a shorter service life when used with one particular type hazard than the equivalent specific single purpose cartridges would have for the same hazard.

Many respirators use a "half-mask" or oro-nasal (mouth and nose) facepiece, while gas masks use both half-masks and full facepieces. Only full facepieces on gas masks are approved by the United States Bureau of Mines, since it has been found difficult to achieve a tight fit with a half-mask. Recently, the self-rescue or "pocket" respirator,

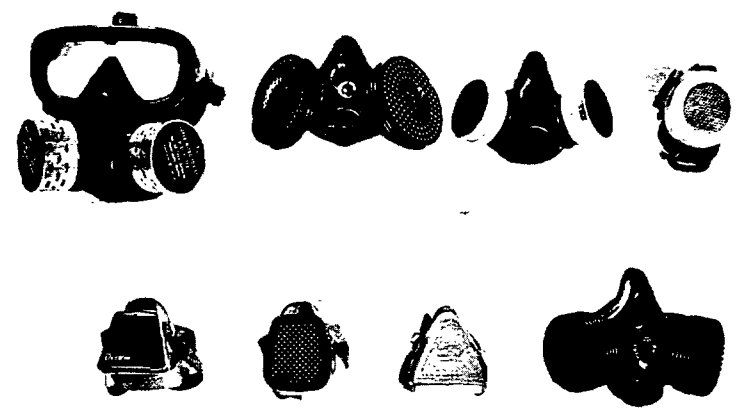

FIG. 23.3. The variety of respirators, designed for a wide range of exposures (from toxic airborne particulate to heat), mandates careful selection and control.

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normally used with a cartridge containing Hopcalite with a dryer and designed for escape from mines, has been extended into other cartridges. The mouthpiece of this style respirator is held tightly by the front teeth of the wearer, and the breathing is accomplished through the mouth, since a nose clamp blocks off the openings of the nostrils and prevents inhalation of contaminated air and irritation of the membranes of the nose. A neckband and a belt-pocket holder permit the respirator to be worn ready for instant use. Car-

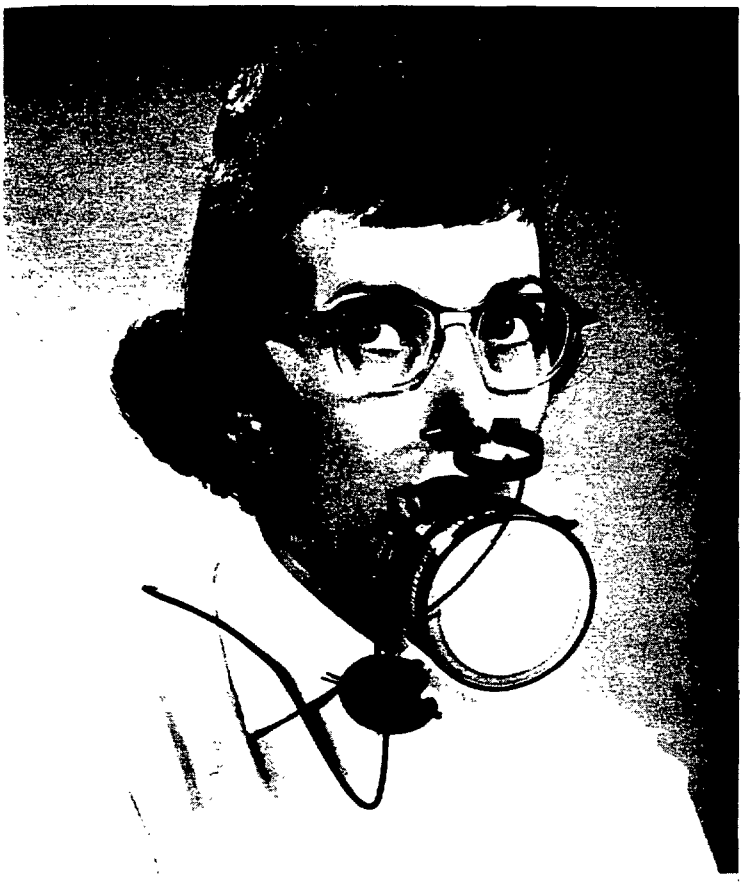

FIG. 23.4. Mouth-style respirator (with nose clip) may be used with different cartridges for several types of exposures, and is especially appropriate as an escape device.

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tridges for twelve different applications will fit the basic holder and mouthpiece.

Industrial canister-type gas masks, with canisters designed for specific substances or specific combinations, have the same limitations in general as chemical cartridge respirators, except that they are effective in concentrations of any specific gas or vapor, or members of the group of gases or vapors for which they are designed, of not more than 2% concentration in air or a 2% total concentration for a mixture of gases or vapors for which the canister is designed. The industrial-type ammonia canister is approved for 3% ammonia.

Depending on the size of the canister and the service for which it was designed, the service time varies. Protection against a combination of various gases and vapors, such as acid gases, organic vapors, and ammonia can all be obtained in one canister, but the service life of such a combination is shorter in the combined canister when used with one substance, than is the life of an equivalent canister designed for the specific substance alone.

The only warning that a canister or cartridge is "exhuasted" or spent is sensory detection of vapor or gas passing through the canister or cartridge. For carbon monoxide, which is odorless, canisters have a timer or window indicator. It is obvious that the "self-rescuer" type does not even have this warning aspect, since the nostrils are closed off. In other words, unless we have a complete knowledge of the actual concentrations which are experienced, there is a false security in using canister-type or cartridge-type gas masks and respirators which have caused many users to question the place of such devices.

Persons who need corrective lenses in order to work properly when wearing respiratory protection, especially full facepieces, may be interested in three methods of incorporating lenses inside a facepiece. One method consists of wire frames which fit around the circumference of the facepiece sight lenses and hold a 50 mm round lens. A second method suspends wire-frame goggles with short bows between holders molded into the facepiece. A third method consists of a center post built inside the mask, on which can be attached 40 mm rimless glasses. Such arrangements seldom encourage perfect alinement of the prescription lenses to the viewer's eyes, but, with adjustment, a sufficiently accurate fitting can be achieved for most persons to wear for reasonably long periods. Contact lenses offer a possible solution to this problem, but the hazards of contact lenses in increasing or aggravating a chemical burn to the eye, especially if the lenses are not immediately removed before irrigation with water, must be recognized.

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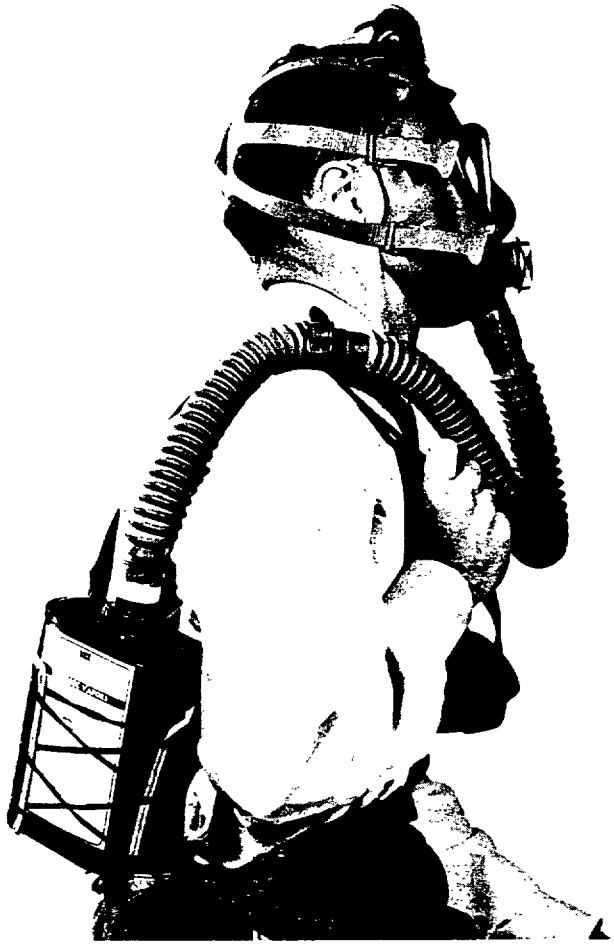

FIG. 23.5. Canister-type gas mask designed for organic vapors, with canister worn on back to minimize exposures. Useful in rodding of tanks and in other situations where face would be close to high concentrations.

The Type N universal gas-mask canister (which is not really universal in spite of the name) is constructed of several layers of chemicals and filters which are intended to protect against 2% acid gases, organic vapors, other gases, or 3% ammonia. Carbon monoxide is converted to carbon dioxide by this canister. The exact composition

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of the canister, its construction, and its limitations, varies with the individual manufacturer, who should be consulted for details. In general, the Type N universal gas mask may be used for protection against smoke and gases which do not exceed 2% by volume total, where adequate concentration of oxygen is present. Usually 16% oxygen is cited as the practical minimum for the use of the Type N mask, but life is not actually in danger until somewhat lower concentrations are reached, depending on what the other gases present are, the activity of the wearer, the altitude, and other factors. If the mask has a timer, which is used to count the number of inhalations and indicate total use of the canister, the canister should be discarded at least as soon as the pointer on the timer has completed one revolution, if not sooner. One authority recommends that Type N universal canisters be weighed immediately on receipt from the manufacturer, and that they be discarded as soon as they gain 45 g for the normal size canister. The 45-g limit was imposed since it represents the limit of the dessicant layers to keep the Hopcalite layer dry.

All manufacturers build an "indicating window" into at least one model of the Type N universal canister to indicate remaining protection against carbon monoxide. The indicator is the color change from blue (dry) to pink (wet) of a piece of specially treated paper, which warns of the excess moisture which prevents the Hopcalite from properly operating; hence, if the indicator shows pink the canister will no longer furnish protection against carbon monoxide. In addition, a one-way inhalation valve has been added to the canister top to prevent moisture or water from entering the canister from above. The maximum shelf-life of the Type N universal canister, once the canister has been attached to the facepiece, is one year, if stored with the bottom seal in place, even though the mask has not been used. If stored with both top and bottom seals unopened, as received, the shelf-life is considered by some to be three, and by others, five years. The manufacturer should be consulted and his recommendations followed, including whether the canisters should be stored vertically or on the side.

There is a growing conviction among safety and medical personnel in large laboratories, especially where a wide variety of substances may be encountered in unknown concentrations, that self-contained breathing apparatus should replace all canister-type masks—whether industrial or universal Type N. The writer agrees that no canister-type masks should be used for emergency control where the concentrations and identity are in doubt. From a practical viewpoint, this includes nearly all chemical spills and fires.

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With any respirator or gas mask, the problem of proper fitting of the facepiece is critical, and it becomes even more important the more toxic are the materials of concern. There is no universal facepiece which will fit all faces perfectly. An excellent discussion of this problem will be found in the AIHA-ACGIH Respiratory Protective Devices Manual.[19]

As part of its chemical, biological, and radiological warfare defense program, the Office of Civil Defense of the Department of Defense

FIG. 23.6. Light-weight facepiece attached to military-type canister. This mask is intended for civil defense protection and is not designed for industrial or fire gases.

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has stockpiled a mask designated as CD V-800 organizational mask for use by Civil Defense personnel. The canister on this chin-style mask is the same as used on the United States Army Assault Mask. This mask is reported to give "excellent protection" again CW (chemical warfare) and BW (biological warfare) agents, as well as against the inhalation of radiological particles, or CBR (chemical, biological, and radiological). Designed to be used in conjunction with a detection kit (which will detect and distinguish between the nerve gases and the mustard gases), the V-800 mask is designed specifically for war gases (including nerve gases) and will not protect against carbon monoxide, ammonia, and other industrial gases. The Army Chemical Corps has designed and developed a new mask, the M-17, for troops. It is designed to give complete protection against the inhalation of war gases, biological warfare agents, and airborne radioactive particles,

FIG. 23.7. Military masks were not designed for fire fighting or industrial gases. In addition, long storage may result in damage to rubber and metal, as shown here. Thousands of such masks are surplus and obsolete, and their use by uninformed persons constitutes a threat to life.

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FIG. 23.8. Two misuses of a gas mask: (*a*) wrong type and (*b*) improperly worn. Such masks were never intended for fire fighting or industrial gases.

but, of course, it does not actually protect against direct radiation effects. The M-17 mask does not have the protruding canister used in previous army masks, since it uses a new light-weight pliable gas-aerosol filter material. Pads of this material are enclosed within cavities molded into the rubber facepiece of the mask. Lower breathing resistance, superior vision, better speech transmission, and greater comfort are claimed. It should be emphasized that no gas mask should be used for purposes for which it was not designed. After both World Wars, several instances were reported where "surplus" army masks were used for protection against gases for which they were not designed, with serious consequences. It is vital that gas masks are not misused.

AIR-SUPPLIED RESPIRATORS

Since the simplest solution to respiratory problems is to supply clean air to the breather, the use of an air supply from some remote source where the air is not contaminated is both simple and logical.

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For many applications, air-supplied equipment has real advantages, but this equipment, like all other, has definite limitations. The simplest type is the Type B hose mask, which is a facepiece to which is attached a large-diameter (1-in. Inside Diameter) hose without a blower. The hose must extend to a respirable air source.

This mask depends on the breathing action of the wearer to move the air. For this reason, a maximum length of 75 ft of hose has been established for the hose mask without blower. However, such a unit should not be used in atmospheres immediately harmful to life, or from which the wearer can not escape without the device.

Low-pressure blowers, operated either by hand or by power (power blowers do not have Bureau of Mines approval at present), are used to supply Type A hose masks up to 300 ft. All hoses must originate at the blower. A respirable source of air must be assured, and a safety man with a full understanding of his duty must be present at the blower at all times. A sturdy harness must be provided to which a life line may be secured. Fouling of the hose must be avoided since this may cut off the air supply. The exit route must be the same as the entrance route. Hose masks can be used safely only if the above precautions and limitations are observed.

Air-supplied Type C respirators are divided into two classes: the continuous-flow type and demand- or pressure-demand-flow type. The continuous-flow type is usually used with a powered compressor or blower, while the demand-flow type is usually supplied with breathing air from large cylinders. The use of such equipment in atmospheres immediately hazardous to life is not recommended, since failure of the air supply or fouling of the hose would be serious, and further, it is vital to have respirable air of unquestioned purity. It is recommended that a separate air system be used exclusively for breathing air. Depending on the pressure available and the diameter of the hose, there is a limit to the length of hose which is practical for the continuous-flow type. Wherever possible, such systems should be piped as closely as possible to the outlet so possibility of fouling the hose and cutting off the air supply will be minimized. Exit from areas where air-supplied respirators are used must, of course, be the same as the entrance route.

If an air compressor or air from a cylinder is used, sufficient pressure relief and regulators must be available to protect the wearer against pressure in excess of that prescribed for the equipment. If a plant air compressor must be used for breathing air, it should be equipped with a temperature cut-off or carbon monoxide alarm, and a conspicuous sign placed at the compressor site to indicate it is used for breathing air.

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FIG. 23.9. Air-supplied respirator supplies breathing air from airline or cylinders. Type pictured is of continuous flow and is usually used with a compressor system; another type includes a demand regulator which supplies air only when inhalation is desired to conserve air supply from cylinder.

Air helmets, air hoods, and air-supplied suits have the same general limitations as air-supplied respirators. An interesting development is the increasing interest in the use of air-inflated or conditioned suits for protection of the whole body against hazardous materials, such as radioactive aerosols. In one form, a large impervious plastic tunnel

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or tube permits a man to work in one room while using slight air pressure from another room to supply both breathing air and inflation to the suit. The front of the suit is tailored into a facepiece and arms and gloves are attached. Mobility is reported good within the obvious limits imposed by the length of the tunnel attached. In another more mobile form, a complete suit with built-in arms and legs is supplied with air for inflation, and a hood, also air-supplied, is used for head,

FIG. 23.10. Light-weight plastic air-supplied hood for light exposures. Note hood does not touch head or face, since it is inflated with air.

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FIG. 23.11. Air-supplied hood for heavy-duty sandblasting.

face, and respiratory protection. Depending on the particular fabric, plastic, or composition used in its construction, this suit permits extended work inside tanks, reaction vessels, and other confined space which still contains a hazardous-to-life atmosphere. Properly used, together with safeguards to insure that the wearer's air supply and life line are always in proper position and working order, this suit has increased the safety and decreased operating costs in maintenance work inside vessels containing materials which are corrosive or are

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easily absorbed through the skin, such as aromatic amino and nitro compounds. The same general limitations noted above for air-supplied respirators should be observed.

A recent development in ventilation of protective clothing and respiratory breathing equipment is the application of a vortex tube for both cooling and ventilation to air-supplied suits, hoods, and masks. This simple light-weight device has no moving parts, and it operates on

FIG. 23.12. Air-supplied helmet with vest.

ETC 03427

FIG. 23.13. Plastic tunnel leading into next room permits worker to avoid exposure to airborne aerosols in front of him because of the impervious nature of the plastic. Breathing is through high-efficiency filters. Photo courtesy Hanford Atomic Products Operation, General Electric Company.

high-pressure air which is cooled at one end of the tube and heated at the other. The cooled air temperature (around 50°F) distributed to various parts of the suit and to the helmet, prevents excessive perspiration, and permits longer work periods in hazardous atmospheres (Fig. 23.14). Special suits, which include provision for wearing self-contained breathing apparatus inside the suits, have found application in

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(*a*) (*b*) (*c*)

FIG. 23.14. M-S-A Cool Flow System Employing Vortex Tube for Cooling and Ventilation. (*a*) Vortex tube mounted on rear of protective suit. (*b*) Suit, showing small internal tubes for distribution of air. (*c*) Vortex tube supplying cool breathing air to helmet-vest combination. Many other combinations are possible. Photo courtesy Mine Safety Appliances Co.

missile fueling operations and in handling highly reactive chemicals such as fluorine. One such suit system employs a back pack which uses liquid air to supply both breathing air and air for cooling (Fig. 23.15).

Regardless of the type "respirator" used, a definite program of education and control is necessary to insure that the device is actually worn properly, properly maintained, and that it is effective in achieving what is expected. After the Canadian Chalk River atomic reactor incident, respirators were used to prevent inhalation of radioactive contaminants. This program was successful only after a respirator officer was appointed to control their use and maintenance. Regular urine samples were analyzed to indicate the degree of effectiveness of the program, and an improved respirator, which was proven more effective, was made available for use.

Before considering self-contained breathing apparatus, a brief discussion of emergency situations which require the use of such equipment may be useful.

For emergency situations, where entry is essential for the conservation of life and property, there are neither fixed guides nor sufficiently accurate and foolproof instrumentation. In situations that may exist in firefighting, in the escape of vapors or gases, or where an oxygen deficiency may develop, the prudent approach is to assume conditions

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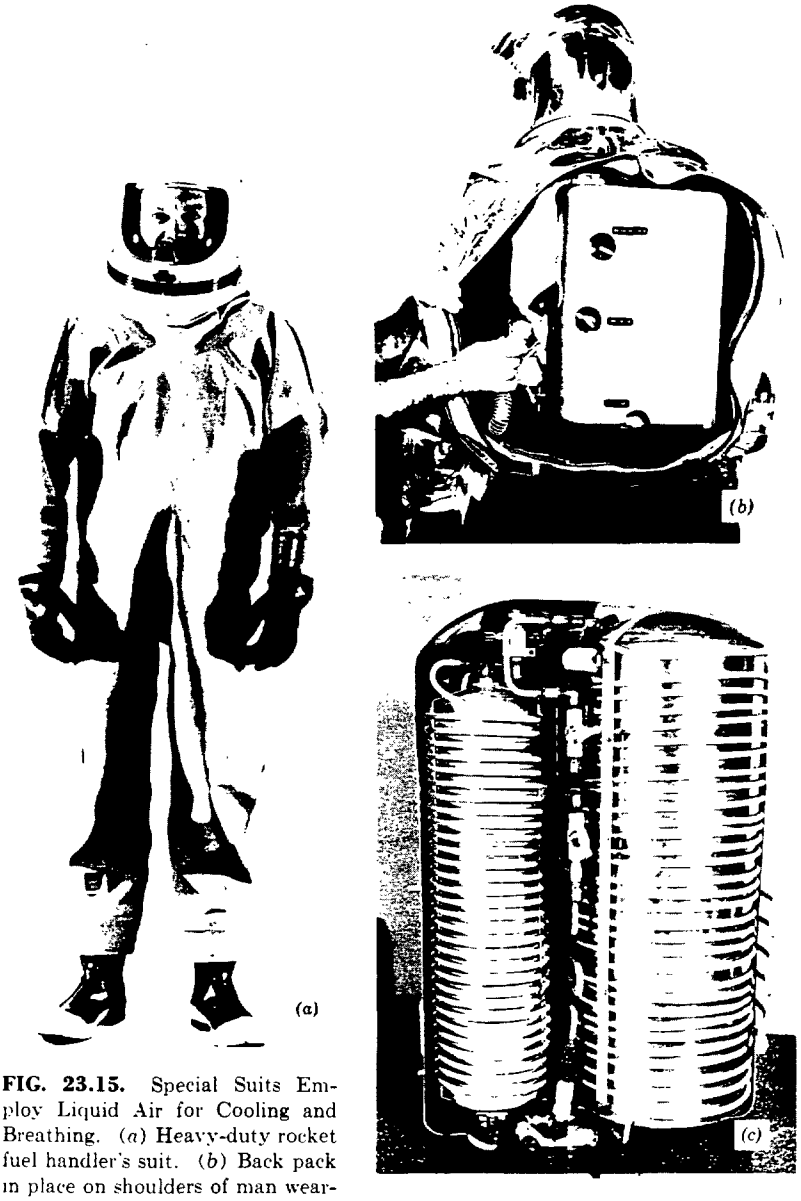

FIG. 23.15. Special Suits Employ Liquid Air for Cooling and Breathing. (*a*) Heavy-duty rocket fuel handler's suit. (*b*) Back pack in place on shoulders of man wearing fire proximity suit. (*c*) Back pack with cover removed showing large cryogenic vessel for liquid air storage, and smaller gas accumulator tank for gaseous air. Photos courtesy Aro Safety Products.

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are serious, and to use respiratory and other protection which will most adequately meet expected conditions. A preliminary appraisal of the situation must be made, and an arbitrary decision made at once by the qualified authority (usually the fire chief, the ranking police officer, the safety engineer, or the medical officer), to:

1. Retreat or approach.
2. Specify the objectives (personnel versus property).
3. Specify the procedures.
4. Order the use of required personnel and equipment.

Records of the fire services contain many instances where emergency personnel made an unnecessary sacrifice of their own lives under conditions where little or nothing would have been achieved by approaching the emergency scene. To cite a few specific instances, ten firemen died from injuries received as they approached an outdoor aluminum storage tank, which erupted with such force that three were killed by fragmentation, and seven by fumes and skin burns from the chlorinated hydrocarbon mixture. A chemical reaction of the Friedel-Crafts type had occurred between the aluminum tank and the stored solvents, which built up excessive pressure. No fire whatsoever was involved, and ten lives were sacrificed without any advantage.

In a more recent case, four firemen died in an explosion while fire fighting in a tractor-trailer truck during unloading of a cargo of organic peroxides, even though the identity and the hazard of the cargo was known. Another instance occurred when a train derailment caused a tank car of propylene, which was intact, to be weakened by the impingement of a small fire from another tank car which was leaking. The hazard was known, and all personnel were warned, but nineteen hours after the derailment, the work crews believed the hazard was over, and were at work moving and repairing the damage. Without warning, the propylene tank car exploded, soaring through the air several hundred feet. Numerous members of the work crew and fire services were killed and injured, because of the general disregard for the danger warning such an extended time after the derailment. Virtually all the fire personnel and emergency equipment in Texas City, Texas were destroyed and over six hundred lives were lost, when two ships containing a fertilizer grade of ammonium nitrate exploded.

Conservation of human life, including that of the emergency personnel, must always take precedence over the conservation of property. Fire services and police are not alone in the disregard for their own safety. Safety engineers, physicians, nurses, and management person-

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nel have encountered serious personal injury where, in the excitement and their concern for personnel and property, they ignored their own needs for protective equipment. A graduate chemical engineer, who was superintendent of a phosgene-production unit gambled that he could enter a building in which an operating error had been made, to control the emergency which threatened the loss of several tons of phosgene. Either his respiratory protection was inadequate or not properly worn, for he was so seriously exposed that, although he brought the emergency under control, he died from phosgene poisoning a short while later. The supervisor of health and safety in a chemical plant died in an attempt to aid several other persons overcome with hydrogen sulfide, which had formed from an emergency in which sodium sulfhydrate contacted acid in a drain.

Other analogous instances could be cited. The point is that such situations are especially pernicious, since the increased breathing because of the excitement, coupled with violent physical exercise, tends to drive gases and vapors deeper into the lungs and to accelerate the action of the substance. If a rescuer can remain calm, however, and breathe very shallow so that only tidal air is being moved, a much higher probability of survival can be expected. This skill has been observed in experienced nitration operators who learned to control their breathing so carefully that they were considered "immune" to oxides of nitrogen in concentrations which caused serious, and sometimes fatal, lung damage to their less-wise associates.

Objectives to be achieved in the emergency action must be carefully stated and fully understood by all involved before a decision is made to advance. If the prime objective is search and rescue of persons who may be trapped or otherwise unable to escape, it should be executed with all dispatch, and a systematic search plan ordered to conserve vital time and to reduce possible duplication of effort. If there are other objectives, such as the opening or closing of valves, switches, pumps, or controls, extreme care must be exercised to insure that the full consequences of such operations are known. To operate an ordinary domestic electric switch or motor starter in an explosive atmosphere, as in a spill of a flammable liquid or a leak of flammable gas, may supply the ignition source that will result in disaster.

Any equipment which must be worn or carried in an emergency operation will, by its weight or bulk, hamper or reduce efficiency. Against this hard fact must be balanced the benefit, both in safety and in efficiency, of having the proper equipment at the time and place it is needed. Rubber coats, boots, and hard hats have been accepted by the fire services and other emergency personnel. Records of many large

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and small fires prove that fire gases, especially when accompanied by heat, are often more lethal than fire itself. Anyone doubting this statement should read a detailed narration of the Cocoanut Grove Nightclub Fire in 1942, and study the research report on fire gases published by the National Fire Protection Association.[12]

In general, three conditions, which produce environments immediately dangerous to life, require the proper use of adequate respiratory protection for even a short entry. These include:

1. *Oxygen deficiency,* in which the oxygen in air is reduced to less than 16%.
2. *Toxic gases and vapors,* such as hydrogen sulfide, chlorine, phosgene, and the oxides of nitrogen, in which serious effects may result from breathing less than 100 ppm for less than a minute.
3. *Toxic gases and particulates,* such as produced in fires involving ordinary combustibles, wood, paper, textiles, and plastics, as well as in the fumes from welding or other high-temperature metal operations.

A brief discussion of each with a specific example will be given:

Oxygen Deficiency

If a tank is not ventilated after purging, or rusting occurs in a closed vessel, the oxygen concentration in the air will drop. Although light work is possible for several minutes when the oxygen concentration in air is less than 16%, a person breathing such low-oxygen air exhibits symptoms ranging from increased volume of breathing to unconsciousness and death. This condition is far more common than generally realized, in tanks, pits, caves, mines, wells, underground pipes, the holds of ships, and in burning buildings. It is the cause of suffocation by infants where blankets and plastic bags exclude air; it continues to take a toll of young lives where doors have not been removed or rendered inoperable on discarded refrigerators, ice chests, and deep freezers, used as hideaways during unsupervised play by children.

An example of a condition which may lead to oxygen deficiency is given in the following case history:

A motor transport company carries a variety of chemicals. It was necessary to clean the tanks whenever a change of chemical cargo was contemplated. A tank had contained sodium sulfide. After filling the tank with water and draining, an employee entered the tank to check for cleanliness. All the access ports of the tank were uncovered, but no air movers or forced ventilation was used. In a few minutes, a co-worker noticed the employee unconscious in the tank, made the rescue, and successfully applied artificial respiration. The cause of the accident was exposure to irrespirable gases, which were judged either oxygen deficient or to contain hydrogen sulfide from

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the action of the water on the sodium sulfide. Respiratory protection was not being used. In oxygen deficient environments, only two types of respiratory protective devices are recommended: the self-contained breathing apparatus, and the hose mask with blower. Of the two, the self-contained breathing apparatus permits much greater freedom of movement. The hose mask with blower requires an operator or attendant for the blower, restricts the wearer to 300 ft of hose, and requires exit by the same route as the entrance.

Toxic Gases

The second major circumstance immediately hazardous to life is the release of toxic gas or vapor. Such incidents may occur with little or no warning, and immediate steps must be taken, as noted previously, to identify both the nature of the emergency and what action is indicated. Three major sources of such gases and vapors may be listed:

1. Permanently installed equipment and processes, such as storage tanks, process piping, and reaction vessels.
2. Mobile equipment, such as cans, drums, cylinders, tank trucks, tank cars, barges, and tanker ships.
3. Chemical reactions out-of-control.

A tank car had been filled with chlorine 24 hrs previously, and was awaiting pick-up on a rail siding. A crack developed in the metal shell of the tank, permitting the 30 tons of liquid chlorine to leak on the roadbed within an hour. Police and fire personnel responded promptly, and, wearing self-contained breathing apparatus, aided in evacuation of eighty-nine homes down wind from the leaking car. Several persons were hospitalized for observation, and treated for chlorine inhalation. All recovered without residual effects. It should be noted this is the first spontaneous fracture in a railroad tank car containing chlorine, although rail shipments of chlorine have been made since 1909.

Another incident involved evacuation of approximately 13,000 persons in four towns when about 350 tons of anhydrous ammonia escaped between midnight and 2.30 A.M. following rupture of a 4-in. discharge hose above a dock where a river barge was being unloaded, and the operator failed to immediately stop the transfer.

An operator was adding muriatic (hydrochloric) acid to a reaction vessel. Noting a back flow into the charging tub, he investigated, receiving a high concentration of hydrogen sulfide gas directly in his face. Becoming light-headed and dizzy, he closed the valve to the charging tub, and headed for a stairway to the second-floor control

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room. Half-way up the steps, he collapsed and fell. Fortunately, his foot caught between the stair treads, which prevented his falling backward down the remaining steps. Regaining consciousness, he pulled himself to his feet and proceeded up the stairs, where help was obtained. Treated at the dispensary, he returned to work without further ill effects. The cause of the accident was because of the level of the solution in the kettle being greater than the height of solution in the tub, permitting a surge of hydrogen sulfide-saturated solution into the tub when the valve was opened to add the acid. Among the preventative measures, and revised operating instructions, was the request to furnish a 5-min self-contained breathing apparatus to be worn like a canteen during this part of the operating cycle, ready for instantaneous use in an emergency. This recommendation would put breathing apparatus in the same class with eye protection, head protection, and safety shoes as devices to be actually worn on the job—not to be frantically sought out in an emergency.

Toxic Gases and Particulates

Whenever a fire burns in ordinary combustibles, or in situations where the combustion process is less efficient than stoichiometry would suggest, toxic gases plus particulates are evolved. As suggested by the Fire Gases Research Report previously cited, it is impossible to predict in advance what may be encountered in a fire, especially when objects of composition unknown to the firemen are involved, and ventilation is not possible.

As a case in point, which also illustrates wasted manpower because of the improper use of respiratory protection, the following is cited:

> The fire was located in a drying-storage room of steel construction, measuring 8 ft by 50 ft by 30 ft, closed by an asbestos curtain at one end. There was no possibility of ventilating. The room was located on the sixth floor of a factory, and contained a large quantity of "wood flour" (pulverized sawdust) contained in 100-lb bags, used in casting ornaments. Fire was started by an electric motor in the rear portion of the room. The fire had smoldered for some time, and this room was heavily loaded with smoke, carbon monoxide, and carbon dioxide. The alarm was sounded when heat finally built up sufficiently to activate a sprinkler head, which transmitted an A.D.T. alarm. Since very little smoke was visible external to the drying room, the first firemen went in without any respiratory protection. They were quickly overcome. Members of the rescue company followed closely behind wearing universal Type N canister gas masks. These masks functioned well on the sixth floor outside the drying room, but inside, one of the five firemen was overcome. The other four heeded the warning sign of "overbreathing," and retreated to fresh air before being overcome. In all, thirty firemen were over-

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come in this multiple-alarm fire, multiple only because all men from the first companies were overcome and adequate respiratory protection was not ordered in the beginning. Fortunately, all recovered.

The incident cited should not be interpreted that the canister-type gas mask has no application. Unfortunately, these masks have been used often under conditions for which they were not designed. The term "universal service" is very misleading. Before entering *any* area with *any* mask, some reasonable assurance should be obtained that the concentrations of oxygen, toxic gases, vapors, and particulates are within the limits of the respiratory protective device to be used. If any doubt exists, a self-contained breathing apparatus should be used—not a canister-type gas mask. Even with self-contained breathing apparatus certain substances, such as hydrogen cyanide, phenol, aniline, nitrobenzene, and ethylene imine, may be absorbed through the intact skin in sufficient amounts to be toxic. For such exposures a complete protective suit of impervious clothing, plus respiratory protection, is mandatory. Such suits are now commercially available, designed specifically for various hazardous exposures. (Note comments on such suits under air-supplied respirators.)

Self-Contained Breathing Apparatus

Self-contained breathing apparatus is designed to supply complete respiratory protection in any concentration of toxic gases or in an oxygen-deficient atmosphere. However, as previously noted, certain gases and vapors will also cause systemic poisoning by skin absorption, and these require the use of complete skin protection of an impervious type in addition to respiratory protection.

The early self-contained rebreathing apparatus, which was imported from Europe, had serious deficiencies. Loss of life was reported by users in this country; nineteen accidents were reported involving twenty-six fatalities between 1911 and 1940, because of equipment failure and partly because of improper use of the equipment. Where life lines and standby rescue squads were employed, as recommended, the apparatus was generally satisfactory in the hands of well-trained users.

The first self-contained breathing apparatus to be approved by the United States Bureau of Mines was the 2-hr rebreathing type. The oxygen rebreathing apparatus is relatively heavy (39 lb for the 2-hr type), and it is bulky. The models in general use today require mouth breathing with a nose clip to seal the nose, but a full facepiece for these devices has been approved. The United States Bureau

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FIG. 23.16. Two-hour self-contained apparatus of the recirculation type. Originally designed for mine rescue work, these masks require a high degree of training and maintenance but are highly efficient if properly used.

of Mines requires 20 hr initial training in the 2-hr rebreathing apparatus before certification of the wearer as skilled in its use.

The self-generating oxygen breathing apparatus is much simpler in design, but it still requires a high degree of training and practice if it is to be used safely. It has been found to be extremely important that the training be repeated at frequent intervals for the self-

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generating oxygen breathing apparatus. No formal schedule of initial or follow-up training has been established by the Bureau of Mines for this type apparatus, but it has been often observed that the retraining was not adequate to insure the safety of a wearer in an emergency.

Breathing apparatus of the air and oxygen-demand type is available in half-hour, quarter-hour, 10 min, and 7½ min rating. Since the

FIG. 23.17. Self-contained demand breathing apparatus typical of types approved for 30 min using compressed cylinders (40 cu ft capacity) on back.

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Bureau of Mines has no approval schedule for any self-contained apparatus designed for less than a half-hour service, only the half-hour demand (air or oxygen) devices are approved. Although the schedule of work for the Bureau's half-hour rating is exhausting, the fact remains that large men under extreme stress and exercise have exhausted an expected half-hour (40 to 43 cu ft) cylinder in significantly less than a half-hour. Other wearers, under less exertion, may obtain up to 45-min service from a similar quantity of air or oxygen.

Differing only in whether it is supplied with compressed air or oxygen, the demand apparatus weighs nearly 30 lb for the half-hour type with a cylinder worn on the back. It is relatively awkward to put into service, and it restricts motion in confined or congested spaces. With practice, it may be put on and placed into operation from a mounted backboard in less than 20 sec, but pre-use checks, as recommended by the manufacturers and the Bureau of Mines, should never be neglected. Approximately a minute is required to put the device in full service from a carrying case. The back position of the cylinder makes it difficult to crawl under equipment. Climbing in and out of small openings, such as manholes and areas where obstructions, pipes, and conduits are present, requires special caution. Operation of a motor vehicle is awkward when wearing a cylinder on the back. The demand devices with shorter life overcome some of these objections since the cylinder or cylinders may be worn in front or in a side pack or knapsack. Since they may be worn for extended periods "ready to use," they can be put into instant service for escape or emergency control.

The purity of the air or oxygen with which the cylinder has been charged should always be questioned whenever a cylinder is filled or refilled, since other gases, such as pure nitrogen, acetylene, carbon dioxide, and mixtures of gases other than air have been found in "breathing-air" cylinders. Errors in compressed air used for breathing may be rapidly fatal, and every newly filled cylinder should be checked to insure that it actually contains "breathing air," regardless of the general reputation of the source of supply. Unless the user has his own compressor producing air of an unquestioned purity, no cylinder should be used for breathing purposes until the contents have been checked for purity. Several relatively simple instruments are available for oxygen analysis, for carbon monoxide, and for carbon dioxide analysis.

Any high-pressure cylinder may leak, and frequent inspection is necessary to insure that the air or oxygen is actually available for use

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FIG. 23.18. Ten-minute escape-pack demand air device. Note the battery-powered light, useful in emergencies by freeing hands for other tasks. No approval schedule exists for such devices under Bureau of Mines at present.

in an emergency. High-pressure valves, gages, and demand regulators, along with hoses and rubber parts, must be maintained in top operating condition by inspection and a regular preventative maintenance schedule as recommended by the manufacturer and the Bureau of Mines.

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As noted above, under conditions of extreme exertion or exercise, a large man may require air at rates in excess of the air supplied by some regulators in demand apparatus. The situation can be improved only by adjustment or modification of the regulator so air can flow at a faster rate, and such modifications should be attempted only by the

FIG. 23.19. Ten-minute breathing apparatus with two small air cylinders and regulator carried in side-sling bag. This device is ideal for quick entry and survey, since it can be placed into service in a few seconds while enroute to the scene. No approval schedule exists for such devices at present.

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manufacturer. It will not help, as some sources suggest, to enrich the oxygen partial pressure (or percent) of the breathing air. Where synthetic air (made by mixing nitrogen gas and oxygen gas from cylinders of each) is used, it should always be checked to insure that correct percentages of the gases have actually been obtained.

If demand-type apparatus is worn in environments where pressure above 1 atm is present (as in caissons or tunnels under pressure), the service time is reduced as the pressure increases. This is also true of the underwater use of the regular demand-type apparatus; a special modification of this equipment is available for use underwater. Peculiar effects have been reported when demand and closed-circuit oxygen breathing apparatus were worn under pressure. The use of oxygen in atmospheres above 2 atm absolute pressure, except under clinically controlled conditions, should be avoided, since oxygen produces a toxic effect of convulsions in some people under such conditions. A new technique, known as high-pressure oxygenation, or HPO, is being developed experimentally and clinically to aid in critical diseases and ailments by saturating the blood with oxygen. For periods up to 12 hr at normal atmosphere pressures, however, oxygen may be used without ill effects by healthy persons. A person in questionable physical condition should *not* wear any emergency breathing apparatus unless a physician has approved his use of it as not being contraindicated. Persons who do not have such specific approval should stay away from contaminated air and from water. Highly important in the underwater use of breathing apparatus is the necessary continuous breathing during the ascent—at no time should the swimmer hold his breath, and he should ascend no faster than the air bubbles ascend.[23]

When the supply of air or oxygen has been depleted, the supply in the normal demand-type apparatus cuts off abruptly, and the facepiece must be removed immediately or asphyxia can occur. In recently engineered devices, warning bells or physical restriction to breathing have been built into the device to indicate the approach of the end of the air or oxygen supply.

The seal around the facepiece must be absolutely gas tight in a toxic atmosphere, since in certain demand-type apparatus the facepiece is under slightly negative pressure momentarily during the beginning of the inspiration phase of the breathing cycle. A recent revision in some equipment eliminates the negative pressure phase of the cycle. Certain demand masks have supplementary attachments with a separate regulator and facepiece carried with the main mask for administering resuscitation to an overcome person on the spot while still in the toxic atmosphere, where removal to fresh air is not immediately

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possible. Another mask has a built-in battery-powered light, which frees the hands from carrying lanterns frequently necessary in emergencies.

In actual use, demand-breathing apparatus of the approved types have certain limitations and disadvantages.

1. Time is required to remove the apparatus from the carrying case and to put it into service (this may be reduced drastically by wall mounting of the unit so that the wearer can back into the harness, attach it, and have the unit in operation in less time).
2. The weight and bulk of these devices make movement difficult in confined spaces, and in areas where obstructions, such as pipes, wires, and beams are present.
3. Cylinders are difficult to refill "on the job." The need exists for adequate reserves of spare-filled cylinders, or large tanks or compressors of air, or oxygen for refining used cylinders if large scale use of the equipment is necessary.
4. If oxygen is used, extreme care must be observed to prevent contact with grease, oil, and other combustibles.
5. Pure oxygen inhalation may have complications.

Air should never be replaced with oxygen, either in a breathing apparatus, in a ventilation technique, or for any other purpose, without full consideration of the increased potential hazards from spontaneous fire when the oxygen concentration is increased above the 21% in air. Oxygen-enriched air is no substitute for adequate flow rates of air. Cylinders that have been used for air should never be used for oxygen. A flammable vapor-oxygen mixture requires only about one-thousandth the spark energy to ignite it as does a corresponding flammable vapor-air mixture. The resulting fire or explosion is many times more violent. Failure to appreciate these facts and to apply the necessary precautions have caused many serious injuries. For this reason, it is as important to actually analyze a suspected atmosphere for elevated oxygen concentration as for oxygen deficiency. Obviously flammable vapors and toxic gases should be checked also. Oxygen analyzers of the direct reading type are available, and are sufficiently accurate for practical control purposes. Such analysis for oxygen (which will reflect inert gases) should be combined with a check for flammable vapors and gases, and a check for whatever toxic gas or gases is suspected.

The second type self-contained breathing apparatus is the oxygen generating breathing apparatus. Now available in two models, one approved for 1 hr and one approved for a half-hour, both devices

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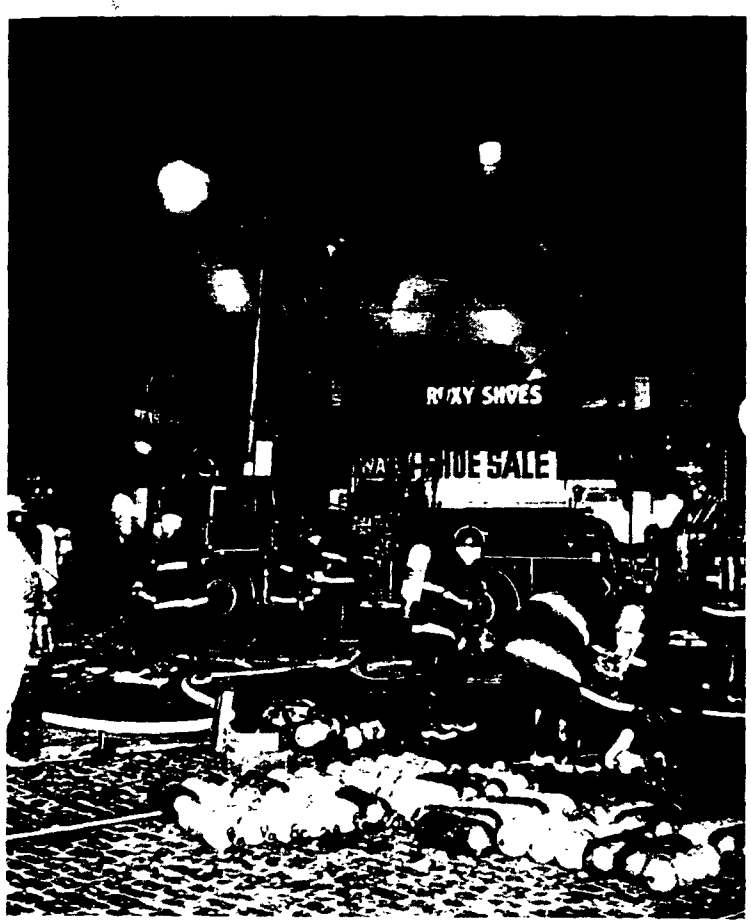

FIG. 23.20. Adequate reserves of filled cylinders must be maintained if large-scale emergencies are to be safely controlled. Forty empty cylinders may be counted in this scene. Photo courtesy Toronto Evening Telegram.

produce oxygen from a chemical reaction between the exhaled breath and the potassium superoxide in the canister. The oxygen which is evolved from this reaction is stored in a breathing bag and is made available to the facepiece on demand.

The water vapor and carbon dioxide are absorbed and reacted in the canister. These self-generating masks have a decided advantage over the demand air or demand oxygen masks insofar as weight and

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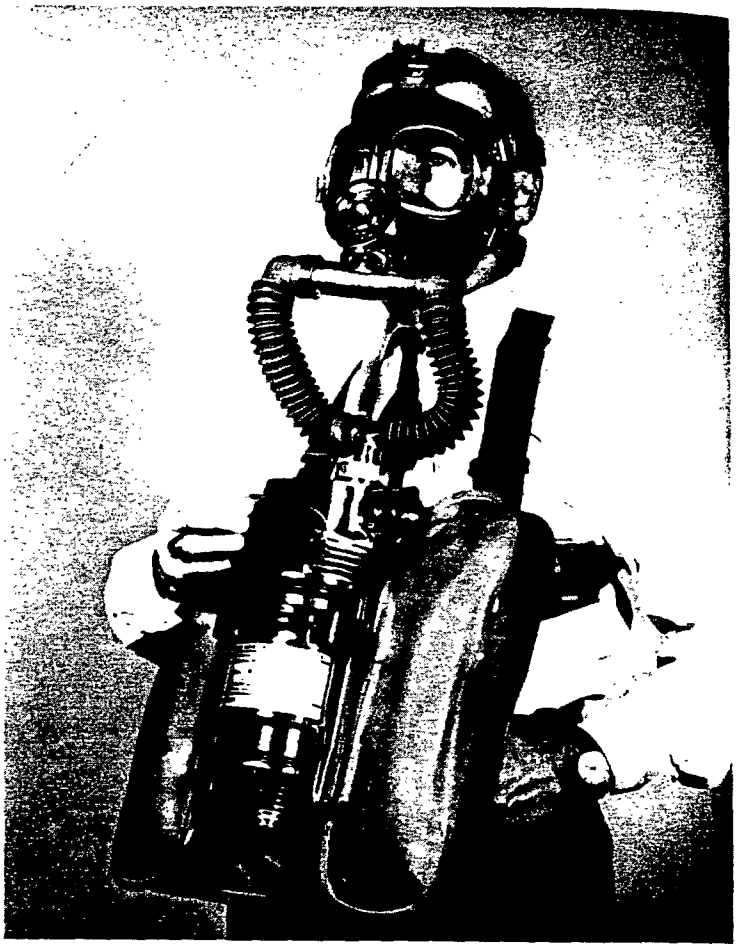

FIG. 23.21. Thirty-minute approved self-contained breathing apparatus of the oxygen generating type. Device has a self-starting oxygen candle activated by striking plate on which wearer has placed fingers.

bulk are concerned. In addition, obviously the 1-hr device has a longer service life than the 30-min demand mask. The temperature of the self-generating canister surface may reach 250°F, which is equivalent to the hazard presented by unshielded incandescent lamps, hot plates, and unlagged steam pipes in such an atmosphere. When worn in hot areas, or while working vigorously in the heat, the oxygen generated

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may expand to a volume which requires occasional "dumping" or deliberate release of surplus oxygen to maintain comfort.

The self-generating apparatus requires care in starting, especially in subfreezing temperatures. For this reason, it is considered good practice that both the apparatus and the canisters be stored inside a heated building, or in a heated truck cab or automobile, and that the apparatus be thoroughly started above freezing temperatures. Once started completely, the heat generated internally makes it possible to wear the mask in below zero temperatures. Unless the starting is complete, the wearer may be aware of insufficient oxygen and an excess of carbon dioxide during the first few minutes, by a feeling of light headedness and overbreathing, coupled with difficulty in coordination. If such a condition is noted, he should immediately seek fresh air, deflate the breathing bags, and restart the apparatus, until the breathing rate and the generating rate balance.

In the one-hr apparatus, care must be exercised to insert the canister in the correct orientation, and to avoid injury from the torn metal from the top seal. The canister must be brought securely into place after it has been punctured by the sharp point designed into the apparatus for that purpose. The facepiece should not be put on until the canister is completely seated. *A fresh (unopened) canister should always be used.* Once opened, a canister will continue to evolve oxygen even after removal from the canister holder. In view of the relatively high cost of these canisters, the temptation to re-use it is great, but re-use even for training must be avoided, and canisters must be promptly destroyed according to instructions on the canister, to protect the safety of the next wearer of the mask.

The timer on both models of self-generating apparatus is completely independent of the breathing, unlike the timer on the universal Type N canister gas mask which measures breathing. The timer must be manually set into operation, and it will ring a warning bell when the time has expired, a sign that the canister is approaching the end of its cycle. *The disposal of the self-contained oxygen-generating canisters must be performed exactly according to instructions on the canister.*

Oil, grease, gasoline, other flammable or combustible liquids or solids must be kept from the canister mouth to prevent an ignition or explosion. In a fire, oxygen-generating canisters will explode. Only clean water in large quantities should be used to destroy a canister. The canister must be promptly destroyed to insure that it will not be re-used or accidentally contact combustibles or flammables.

For reasons noted under demand-type breathing apparatus, the self-contained oxygen generating breathing apparatus should not be worn

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under pressures greater than two atmospheres absolute. Although the oxygen generating masks have significant advantages, certain disadvantages are recognized.

1. Frequent training is necessary, since these masks are really an extension of the human breathing system, not an auxiliary piece of equipment. Mechanically simple, they are psychologically more complex.
2. Longer time is required to put these masks into full operation, since the canisters are stored separately and must be inserted into the devices, and the starting ritual must be properly and thoroughly followed for absolute assurance. The starting problem has been simplified on the half-hour model only, by the addition of a small self-starting cartridge, which is an oxygen candle permitting immediate oxygen generation for the first few minutes breathing, while the main canister begins to generate.
3. These devices must be started in uncontaminated areas unless the self-starting feature mentioned above is used. If caught in an area which is contaminated (without the self-starter), the wearer should retreat to fresh air before starting the mask. The apparatus and canisters should be stored and completely started at above-freezing temperatures.
4. Adequate inventory of canisters, similar to adequate inventory of filled cylinders for the demand type, must be maintained. Used canisters must be carefully disposed of exactly according to instructions on the label.
5. Canisters are a one-use device. No attempt should be made to reuse canisters even after a short use, since there is no way to "turn them off," and no way to measure how much oxygen is remaining in a canister. Wearers have collapsed on the floor while wearing a mask with a used canister during practice sessions.

Speech Transmission

Inserting any material or membrane between speaker and listener affects the quality of the voice signal received, and the facepiece of a respiratory protective device is no exception. Measurements have shown that the standard speaking diaphragms cut down greatly on the ability to communicate effectively.[25] Recently small battery-powered amplifiers with microphone inside and the speaker outside the facepiece, have become available, and further developments in

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FIG. 23.22. Amplifier with microphone near nose and speaker behind plastic grill greatly improves communications when wearing masks.

this field may be expected to greatly simplify the speech transmission problem (Fig. 23.22.) A voice-powered two-way telephone system, using wires, has been available for use with certain breathing apparatus for several years. Further refinements in short-range two-way radio devices may make it possible for widespread use of such methods of communication by wearers of masks, and this would be especially valuable in situations where the wearer was not in obvious sight, because of smoke, fumes, darkness, or complexity of the area.

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Maintenance, Training, and Medical Aspects

The maintenance of the respirator, mask, hood, suit, or apparatus in first-class condition is extremely important. An emergency permits no time to attempt repairs or maintenance. Metal parts of apparatus wear, tarnish, or corrode; screws, nuts, and bolts loosen; rubber parts slowly "age" and eventually crack. Facepieces will take a "set" during storage, and they will eventually reach a point where they can be adjusted properly only with difficulty, if at all. Cylinders, regulators, and valves on demand-type apparatus must be checked frequently for leaks and cracks in welds, joints, and connections. Canisters on industrial or universal Type N or chemical cartridge respirators must be replaced whether or not they have been used. Canisters from self-generating oxygen breathing apparatus must be disposed of properly and promptly as noted above. Washing the facepiece with an antiseptic solution or soap, rinsing in clear water, and drying will insure sanitation and cleanliness, as well as prolonging the useful life of facepieces. Proper storage conditions and frequent checking for deterioration are so important that respiratory protective equipment should be on the same schedule with fire extinguishers,

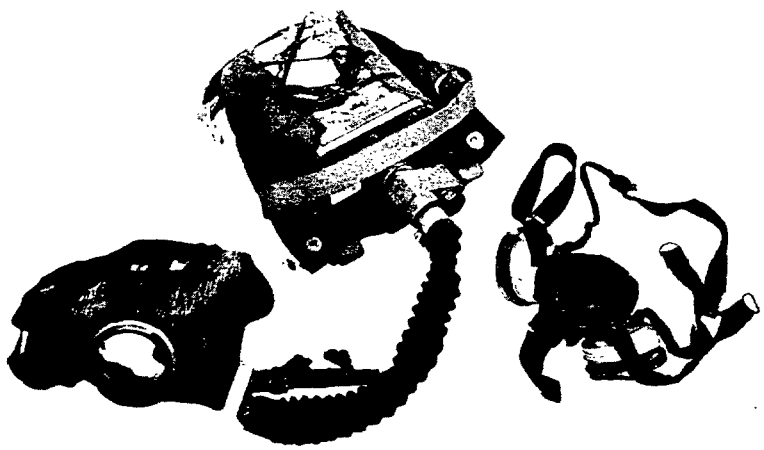

FIG. 23.23. Respirators and masks in poor condition must be destroyed and not used.

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FIG. 24.1. Full protection is needed during transfers.

solid caustic with liquid caustic. While there is a hazard from heat of dilution of 73 or 50% liquid caustic, the hazard is not anywhere near so great as the heat of solution produced by suddenly dumping large quantities of solid caustic into water.

In preventing accidents which involve the eyes in chemical processing, one fairly good rule of thumb is that the chemicals you cannot see are usually the safest. An example would be in filling containers. If the fill pipe ends at a point above the top of the container, the liquid is available to the eyes—that is, it can splash or bounce or in other ways be diverted from the container to the face. On the other hand, if the fill pipe extends into the container there is considerably less chance that the chemical running out of the pipe can reach the face (Fig. 24.1).

Prevention of eye accidents in chemical processing does not stop at chemicals themselves. Let us take the simple example of a pipe rack. Where are we going to put it? If it is in the middle of the yard and open at both ends, pipes sticking past the end of the rack present eye hazards to passers-by and to anyone who is getting pipe from the rack. You can automatically reduce this exposure by 50% by the simple expedient of locating one end of the rack against a building or fence. This hazard can be eliminated to passers-by by completely enclosing the rack, so that the exposure is limited to those who actually enter the enclosure for the purpose of obtaining pipe.

We can see that any consideration of new processes or even reviews of present processes can profitably include the query, "What are the potential eye hazards and how can they be reduced or eliminated?"

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24.2. PREVENTING THE INJURY

When we consider the prevention of injury to the eyes we must assume that the accident has occurred or will occur, and that our endeavour is to keep injurious chemicals out of the faces of our employees. In most instances this consists of imposing a barrier between the accident potential and the individual. A familiar example would be the window in a laboratory hood. Indeed, right here we might discuss the hood window, as it is one of the most abused objects in chemical processing. We have all seen hood windows that for all practical purposes were inoperative. Perhaps they were badly etched from months and years of HF determinations. Maybe the glass was old and opaque. Maybe services to the hood, such as nitrogen, were introduced from outside the hood through lines that entered at mid-hood levels (Fig. 24.2). All of these things preclude the proper function of the hood window, which is to protect the person and confine the fumes except when an operation is actually being performed in the hood. If a study were made of what this work consists of we would probably find that in an 8-hr day not more than half an hour is spent by the chemist in standing with his hands in the hood. But if

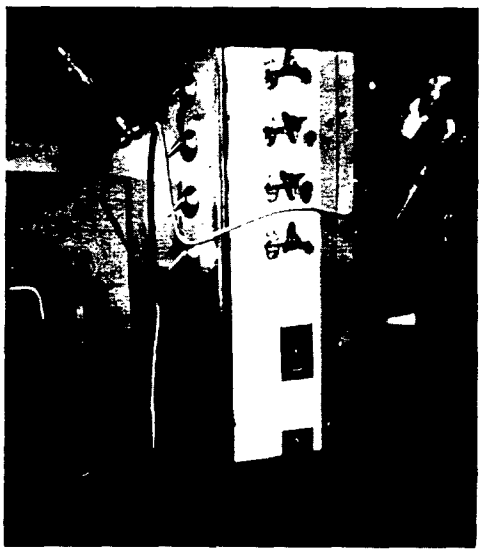

FIG. 24.2. Hood services, if not brought in at bottom sill, keep window from being closed.

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the conditions we have just reviewed are present the hood window will remain open the other 7½ hr.

Lately there is a new trend in hood design which protects the eyes and indeed all of the body except the forearms during the time the chemist is actually working in the hood. This design consists of transparent panels which slide horizontally on an overhead trolley and overlap in front of the hood (Fig. 24.3). The chemist is able to thrust his arms around the edges of the panels, which are not secured at the bottom, and do his work much as he would in a glove or dry box.

Remembering that we are talking about preventing the injury, which means imposing a barrier, this barrier can very often be simply part of the process equipment itself. Consider a gage glass on a tank. Let us assume that for some reason this is a gage glass which cannot be guarded, which is fragile, and which is installed at eye level. This clearly constitutes a hazard to the eyes. Now where are we going to put this glass on the tank relative to the area? Usually we would imagine that the gage glass would go at a spot most available to the operator who needs it, which would mean at the point of heaviest travel, such as an aisle. If the glass is put in this position it constitutes a potential hazard not only to the operator but to everybody that passes the tank. If we put the gage glass on the opposite side of the tank it is harder for the operator to read it, but it constitutes practically no hazard to anyone but the operator.

FIG. 24.3. Horizontal panels for hoods can provide eye and face protection even while working in hoods.

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In investigation reports on eye injuries in chemical processing, perhaps one of the commonest phrases is a variation of, "He turned the wrench and acid squirted out." The chemical industry has learned that this type of accident, which we call a line-breaking accident, is very nearly 100% preventable, because we can impose barriers. A barrier can be as simple as an old vinyl raincoat. The bolts are loosened on the flange a quarter turn or so and then work is continued with a raincoat or rubber sheet between the worker and the wrench and the flange. If the product in the line squirts out it is going to be deflected by the barrier.

Another barrier can be as primitive as a bucket of water. How many of us realize that something as simple as a plug cock, taken off a process line, can still constitute an eye hazard. If we examine drawings of plug cocks or many other different types of valves, we will notice that in the closed position in a line considerable product is contained within the valve. If the line is drained and the plug cock removed, the product goes right along with it. If the valve is subsequently opened, as for example in the act of working on it in the machine shop, the product can squirt out. One simple method of preventing this type of accident is by insisting that the valve be in an open position before it is removed from the line, and that it be immersed in a bucket of water and opened and closed several times before further work is done upon it.

24.3. GUARDING THE PERSON

The next line of defense in eye protection to some degree resembles the second, that of imposing a barrier. In guarding a person we provide a barrier on the person himself. This consists of something in front of his eyes such as safety glasses, mono-goggles, face shields, or masks. The eye-protection program of the Allied Chemical Company works very well, and it could be easily adopted by almost anyone interested in preventing eye injuries in the chemical processing industry. The program is based on one simple rule, which calls for the wearing of safety glasses by everyone all the time. These safety glasses are conventional frames without side shields and are plano for those people not requiring prescriptions. For people wearing prescription glasses we provide prescription safety glasses. All these glasses are provided at no cost, and we have no limitations on the number of glasses per person per year.

We think there are some very definite advantages to this program,

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even though we accept the fact that safety glasses provide only about 90% protection as compared to cup goggles or face shields. We also use face shields and cup goggles, and they will be discussed later. We think that safety glasses when worn all the time dispense with two serious objections to cup-goggle programs. No workman can be expected to wear cup goggles, mono-goggles, or face shields eight hours a day. In plants which rely upon this type of eye protection, some system must be evolved to determine when the workman must wear goggles. This determination seems to have taken three separate courses: the concept of an eye protection area, the decision of the employee's foreman, or the decision of the workman himself.

In a so-called "goggle area" signs are usually posted to inform that goggles must be worn in this area. However, this does not protect the people working or passing adjacent to this area, and historically people have suffered eye injuries when they have entered the area, as they put it, for a short time.

Programs which depend on the foreman or the worker to determine whether goggles should be worn really place too much responsibility on the foreman or workman. Probably neither of these individuals is competent 100% of the time to say whether a significant eye hazard exists. Furthermore, this type of program leads to arguments between management and the workman, usually with agreements that are only temporary.

The introduction of a 100% safety-glasses program is not something which can be done overnight. One usable method is to begin by announcing to the supervisory staff that at a future date safety glasses will be introduced, first on a permissive basis, and later on a mandatory basis. At this time request the foremen to begin wearing safety glasses and to equip wearers of prescription glasses with prescription safety glasses. Even at this early stage you will encounter some resistance from the foremen. This resistance can be met in many ways, such as pointing out the frequency of eye accidents in your company, and comparing safety glasses with other safety equipment commonly in use, such as rubber gloves, aprons, and gas masks.

When the workmen are equipped with safety glasses resistance and high initial cost will be encountered. The cost will come from the fact that employees are simply not used to wearing safety glasses and will break them, lose them, or leave them at home. We should be prepared to replace these glasses and initially there will be a need to carry a comparatively large inventory. Later on supply problems will diminish considerably, as the employees become accustomed to wearing glasses all the time. Glasses which are worn on the nose do not get lost or

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broken. The way glasses get lost or broken is by being sat on, falling out of the pocket, or getting knocked about in a tool box.

Eventually some unexpected dividends will be found in a 100% safety-glasses program. One of them is the psychological reaction of the workman who wears safety glasses. By the very act of his equipping himself with a protection device he becomes more safety conscious and will perhaps unconsciously consider other hazards in the plant more closely. Furthermore, a workman who wears safety glasses is inclined to kid a fellow workman who for some reason has left his glasses off. Another dividend consists in a reduction of off-the-job eye injuries. As workmen become used to safety glasses and convinced of their value they will wear the glasses off the job when doing things that carry a degree of risk to the eyes. This is particularly true on do-it-yourself projects. There are frequent testimonials from workmen who say that their eyes were saved by their glasses in accidents involving power tools in their own work shops.

A good eye safety program does not stop at safety glasses. Some operations require more complete protection. For example, in line breaking operations the minimum requirement should be a full face shield. This should be worn over safety glasses in order to protect the eyes when the shield is removed or momentarily raised (Fig. 24.5). Chipping, welding, and other high-hazard jobs likewise require additional protection such as mono-goggles or cup goggles. These additional requirements are best spelled out in safety manuals or posted in high hazard areas. Full hoods may be necessary (Fig. 24.4).

FIG. 24.4. Be prepared in line-breaking jobs.

FIG. 24.5. Change face shields before they become opaque.

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I would like to say a word about the future of eye protection programs with relation to safety glasses. Better glasses can be made. They can be better fitted, and delivery schedules can be improved. It is obvious that some standardization of safety glasses is needed. At the present time not all safety glasses parts are interchangeable. For example, there are 3, 5, and 7 barrel hinges, and variations in the shape of lenses. In a large chemical plant there may be two or three different brands of glasses, and the lack of standardization makes it difficult to replace broken parts. As for delivery schedules, these are not a problem on plano glasses, but delivery promises, so far as prescription glasses are concerned, have to be taken with a grain of salt. We are within our rights to insist upon minimum periods between placement of orders and delivery of prescription glasses.

Concerning the fitting of safety glasses, it is obvious that the better they are fitted to the individual the more likely he will wear the glasses all the time and the more comfort he will enjoy. There is a trend toward initial fittings by oculists or other members of the profession. These services cost money but they increase eye protection and additionally they relieve the busy safety engineer from the purely mechanical job of fitting and dispensing glasses.

24.4. MINIMIZING THE INJURY

We come at last to the important subject of treating the eye injury after it occurs. In a chemical plant the answer, which is deceptively simple, is water. The first-aid measures for a chemical injury to the eye consist solely of the application of water, lots of water, and for a long time. The best place to administer this water is as near to the scene of the injury as possible. This calls for lots of hoses as a minimum, many safety showers as a medium, and adequate eyewash fountains as an ideal. (We personally like home-made eye-wash fountains.) A simple design consists of three conventional shower heads each mounted 90° apart and at about waist level (Fig. 24.6). Such an eye-wash fountain takes care of the entire face and the position of the face relative to the ground is such that it provides for a maximum of dilution and run-off.

There is an excellent arrangement which protects bench workers. This consists of nothing more or less than a kitchen type of hose spray on a reel, with a spring-loaded nozzle at the end. If materials are accidentally introduced into the eyes the bench worker need only reach for the nozzle, pull it toward him, and direct the stream into his face.

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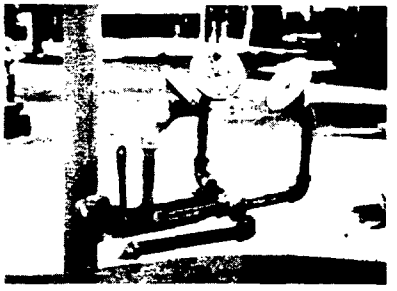

FIG. 24.6. Home-made eye-wash fountains can be cheap and reliable.

Following the use of water at the point of injury it is usually necessary to continue eye irrigation in the first-aid room. Very often other parts of the body are involved, and many first-aid rooms use tubs for immersion washing. These tubs should include spray hoses similar to home-shampoo hoses so that the eyes and head may be irrigated at the same time.

Some workers may be exposed to chemical burns of the eyes away from your plant. Examples would be truck drivers and those performing services at customers locations. Trucks should carry supplies of emergency water, in the glove compartment or in 1 or 5-gal cans kept in the cab of the truck. Lately an ideal place to keep water has been found—in acid tank-truck transports. These transports are equipped with roll-over bars. The bars are actually hollow compartments, which can be filled with water and fitted with a nozzle. As for work at customer locations, your people should be instructed to look for emergency sources of water as soon as they enter the location, and to report to you if such sources of water do not exist. It has been found sometimes that customers receiving products do not have safety showers near the point of unloading, and also found that uniformly the customer has been cooperative in providing such showers when requested.

Eye-wash fountains and showers should be periodically tested and a record of such testing maintained. No valves should be permitted in these lines. Fountains and showers in cold climates can be protected against freezing in various ways, such as using warmed circulating water, installing the piping below the freeze line, or using dry pipes from a warmed building (Fig. 24.7). Showers and fountains should be marked with signs and distinctive painting, and it is a good idea to use a green light at each shower. Some companies are using "drills" because it is probably against instinct to get under a shower with your clothes on. We have seen many instances in which a man

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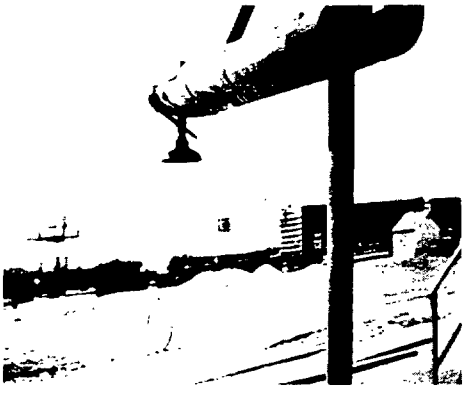

FIG. 24.7. Testing showers is encouraged by shut-off chains. Note freeze protection.

contaminated with a chemical splash would use a hose or even a basin instead of an easily available safety shower. Drills, which might take the form of getting under a shower just before quitting time, will condition the workman to use a shower when he needs it.

A final word is necessary relating to water substitutes and the fight we must make against them. In almost any plant individuals are found who feel that certain types of chemical burns are best treated not with water but with special solutions. For example, some people want to treat acid burns with sodium bicarbonate solutions or weak ammonia. There are serious deficiencies in these routines. For one thing, the so-called special solutions are never as readily available as water, or in the large quantities necessary to flush away the offending chemical. Even more important, the so-called neutralizer very often produces a secondary injury in that in the process of neutralization a new chemical product is formed in the ocular tissue. This not only increases the injury but makes the treatment more complicated as the physician who ultimately sees the patient will find it necessary to remove the chemical which has been formed before he can treat the injury.

Chemicals splashed into eyes can enter behind contact lens and do grave damage before the lens can be removed. Dr. D. J. Kilian, of Dow Chemical, has demonstrated this mechanism in experiments using fluorescein stains. Workers should be forbidden to wear contact lens when exposed to chemical splash; alternatively, they should wear cup goggles.

To summarize the modern concept of eye protection in chemical processes, we have four lines of defense: to prevent the accident, to

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prevent the injury, to guard the person, and to minimize the injury. These lines of defense are interdependent and each must be carefully planned for maximum eye safety.

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25

Other Personal Protective Equipment

H. H. Fawcett

In addition to previously discussed respiratory protection and sight conservation (eye protection and care in the broader sense), several other types of personal protective equipment play important roles in safety with chemical operations. As with other "safety devices," it must be emphasized that although these items do not reflect the true spirit of "accident prevention" (for if the accident or unwanted incident were completely prevented, no protection would be needed for the individual), they are an important "second-line" of defense, whereby the injury or exposure is either prevented completely, or is minimized in its severity. Whenever an unwanted incident or accident does occur, the presence in place of personal protective equipment of the proper type, designed, manufactured, sold, and accepted by the wearer through adequate training, may easily determine whether or not injury occurs.

Since the need and application for personal protective equipment are even more varied than the wide diversity of the equipment itself, this chapter will outline a few fundamentals and limitations, with the intent of encouraging the reader to an independent analysis in depth, in relating the equipment, with its inherent limitations and advantages, to his specific needs. It should be pointed out that the impeccable integrity both of the salesman and the manufacturer whose products he represents are of paramount importance in specifying, discussing,

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scheduling, purchasing, or applying such equipment. Unlike the respiratory protective devices (many of which are covered by test schedules of the United States Department of the Interior Bureau of Mines and the United States Department of Agriculture, which assure at least minimum standards have been met by the devices), no generally accepted schedules or testing by impartial agency cover these devices. This statement is made to emphasize that, while certain American and government standards exist for many of these devices, the potential user must accept the word of the manufacturer that they meet these tests, or conduct tests at his own expense. Control by some recognized completely independent agency or testing group is critically needed, especially in certain phases of personal protective equipment.

Head Protection

For chemical operations, especially in facilities with extensive overhead piping, tanks, columns, and other equipment which occasionally leaks or ruptures, some form of head protection, preferably including a wide brim or visor-peak, is indicated and frequently used. This protection may range all the way from a felt hat or a leather cap, both of which give considerable protection from chemical splashes, to bump caps and hard hats especially designed to furnish head protection. (The term bump cap is used to describe a relatively new head protector which furnishes much less protection against falling objects, but gives a satisfactory protection against many objects, such as pipes, conduits, and other obstacles encountered in a complex environment. Since the bump cap is difficult to distinguish from a hard hat by superficial observation, the reader is encouraged to consult the manufacturer on this point.)

At one time hard hats usually referred to a specific type of headgear, either of laminated fiberglass or of metal, but in recent times a bewildering variety of hats and caps have appeared. To further complicate the field, a few years ago the engineering department of a highly respected university reported tests they had conducted on a few hard hats, with conclusions that evoked considerable discussion about the efficiency of the hats. A wide variety of plastics are now available which have a high resistance to impact, such as the polycarbonates, and these are being used to make hard hats, bump caps, baseball caps, and firemen's hats. Further appeal is given by the rainbow of colors, which can be used practically to designate the craft, working group, or security clearance to which the wearer has been

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assigned. In selecting hats for use in a chemical operation, it is suggested that some of the less glamorous and subtle aspects of hats should be explored, such as the exact distinction between hard hats, bump caps, and their applications, that the electrical conductivity be fully explored (nonconductive hats should withstand 15,000 volts AC, 60 cycles, for 1 min with leak-through and leak-over not in excess of 8 milliamperes, while insulating hats should not fail below 20,000 volts), the reaction between the chemicals and mixtures of chemicals to which the hat will be exposed (no plastic or metal is completely inert to every chemical in all concentrations), as well as the design and construction of the suspension mounting, and, if the hat is to be worn in cold weather, the possible ease of attachment of ear muffs or wind barricades to prevent frostbite.

Ear Protection

Several states have recently awarded workmen's compensation benefits for partial loss of hearing, allegedly caused by occupational noise. This is only one manifestation of a growing awareness of noise in our complex civilization, as radio, television, stereo, PA systems, outboard motors, power mowers, jet engines, rocket blasts, and supersonic booms compete for our attention. The chemical industry is not without noise problems, although compared to other industry, it is relatively quiet. Agitators, grinders, mixers, pulverizers, compressors, fans, blowers, and other equipment produce noise; at what point this noise is objectionable or harmful requires careful analysis. The analysis and control of noise frequently requires an acoustics engineer (who supplies fundamental information), an industrial hygienist (who makes the measurements using equipment specified by the acoustics engineer), and the plant physician or a consultant specialist who can interpret this information into meaningful terms as it relates to the employees.

Where possible, noise should be reduced or eliminated at the source using engineering methods which have been proven. This would include attenuation by isolation or baffles and other means. However, for the many operations where it is economically or technically impossible to control the noise at the source, some form of ear protection may be considered by the physician, using the knowledge and data to aid in determining each problem in terms of the specific employees who will be affected. At the same time, the medical department might institute a regular program of audiometric testing, which can be used

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to periodically determine whether or not a hearing loss is or is not occurring, either from occupational or nonoccupational causes.

Once a program is decided upon, the medical department still has a key role—the proper fitting of devices (ear plugs, ear muffs, helmets, or the combination) so they are exactly matched to the individual, who must understand their importance. This is highly important if the program is to succeed. It should be noted that ear plugs, which are

FIG. 25.1. Ear protectors attached to hard hat. (Note compatibility with safety glasses.)

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the simplest and least expensive control measure, have only a limited ability to attenuate sound, and for higher sound levels, they are often supplemented by specially designed muffs, and, in extreme levels, by a helmet with built-in muffs. To facilitate voice communication with muffs and helmets, built-in earphones and attached microphones permit the use of telephones or radio equipment (Fig. 25.1).

The field of hearing protection is highly technical, and the reader is encouraged to seek specialized assistance from acoustic, medical, and industrial hygiene specialists who have specialized in this field, before embarking on any program of evaluation or control. Interest in this field doubtlessly will continue to increase.

Gloves, Aprons, and Specialized Clothing

Since many chemicals are corrosive to the skin and/or toxic by skin absorption, an effective barrier between the skin and the chemical introduces a highly desirable "second-line" of protection. As with other items, the more complex the device the more resistance may be expected in having it actually used, but an understanding of *why* is often the secret to securing acceptance. In this brief discussion, the virtues of various devices will be assumed, and the less-appreciated aspects mentioned.

Not all rubber or plastic used in gloves, aprons, or other clothing are suitable to the exposure from the specific chemical which may be encountered. In investigating gloves, aprons, or other clothing, the manufacturer should be consulted and asked to submit in writing the recommendations and suitability of the material for protection against the chemicals in the concentration, combination, and temperatures which will be encountered. Many manufacturer's tests are unbelievably incomplete and misleading: to recommend a glove for "sulfuric acid" is meaningless unless the concentration of the acid is specified, for battery acid and concentrated sulfuric acid differ widely in their action on gloves, although both may properly be listed as sulfuric acid. Temperatures, at which the gloves, aprons, and clothing will be used, as well as the temperatures of the chemicals to be contacted, should be questioned. Some rubber and plastics are unsatisfactory at extreme temperatures, both cold and hot, within the ranges actually encountered in use.

Gloves, aprons, and other clothing are made in a wide range of sizes and styles. Unless an item fits properly and permits the proper work actions, including the highly important finger dexterity, they may actually introduce additional hazards. This is especially true

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if impervious plastic or rubberized cloth is used for clothing which prevents normal body "breathing," and hence becomes so hot and humid that working efficiency is reduced drastically. For this reason, the air-ventilated suits, which introduce supplied air both for cooling the suit as well as for respiratory use, and the more recently introduced ventilating suits, inspired by the astronaut suits, in which liquid air (*not* liquid nitrogen or liquid oxygen) is used in a similar manner, may be of great practical significance as they are developed further and as their widespread need would suggest. (In this connection, it may be noted no Bureau of Mines schedule currently exists for air-supplied suits or for the liquid-air breathing systems. In view of the difficulty which has been encountered in the past in controlling the exact composition of "liquid air," it is hoped considerable care would be employed before these become widely used.)

Maintenance of gloves, aprons, and clothing must be of a high order, just as with respiratory protective equipment. For example, a small pin-hole leak (too small to note visually on casual observation) may permit entrance of sufficient amounts of corrosive or toxic agent to cause injury. This has been demonstrated many times with dilute (10 to 20%) hydrofluoric acid, which has no immediate warning property, but whose delayed effects may be noted several hours after the unsuspected contact from the defective glove. Checking of rubber or plastic gloves by inflation with air, immersing in clear water, and noting the air bubbles which indicate a leak, should be a frequent inspection procedure with gloves used with acids and other harmful substances. To use a defective glove is to have a false sense of security. Talc sprinkled into the gloves after each use will prolong the life as well as comfort of the glove.

Safety Footwear

Safety shoes and safety boots have become an accepted part of many chemical operations, perhaps because the intrinsic value of the steel safety cap, which weighs only an ounce, has been so dramatically demonstrated. In addition, safety shoes and boots have become attractive and comfortable, and they represent an excellent value. Part of this attractiveness has created some discussion in that shoes which offer somewhat less protection for heavy use (such as safety shoes with webbing and open stitches) are sometimes used where regular standard safety shoes are indicated. In spite of this, the major shoe manufacturers have continued to develop an ever-widening acceptance. Of special interest to chemical operations are safety shoes known as

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"powder shoes" which have no magnetic metal in their construction and hence cannot make a spark due to frictional impact, "conductive shoes" which have sufficient built-in electrical conduction that they permit static electricity accumulated on the body and clothing to bleed harmlessly to ground (assuming the floor or ground is sufficiently conductive to permit this), and acid-oil shoes, either all specialized rubber construction or with special oil-acid-moisture resistant soles and heels, especially made to be worn in liquid-contaminated areas.

Since shoes are the one item of safety clothing which may be worn by nearly everyone (unfortunate high-fashion designers have yet to produce safety shoes for ladies which are acceptable to their vanity), availability of safety shoes is of importance in securing acceptance. Recently, the "shoemobile" method of marketing was introduced successfully, which permits even small plants in relatively isolated areas to be serviced regularly by a wide variety of off-the-shelf shoes, with no inventory problems for the plant. This selection, coupled with payroll deduction permitted in many plants, and the fact that safety shoes are a deductible item for federal income tax purposes, as well as the need for foot protection in domestic situations, such as power lawn-mowers, has stimulated interest in safety shoes as desirable additions to the "second line" of defense.

Conclusion

Personal protective equipment has a place in any comprehensive safety program, but the success of its use will be the degree of acceptance. Unless it is actually worn in place at the time of the unexpected incident, it is worthless. For this reason, it requires extreme care in selection, maintenance, and, most important of all, sufficient understanding by the wearer so it will be used at all times for its intended purpose.

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Permit Systems

Jeremiah J. O'Driscoll

The repetition of accidents and injuries in performing certain tasks or under certain conditions emphasizes the need for a positive control of the operation and the spelling out of necessary actions to accomplish the work safely. Permit systems have been developed as the most satisfactory method for insuring the proper control and safe performance of repeated operations which have been proven to be hazardous.

Maintenance or repair operations which involve separate sections of a plant, or when different supervisory areas could be affected, must include a positive system of notification and approval by all concerned personnel to be accomplished safely.

The permit system, or a form of licensing and documenting in writing, is a convenient method of preparing a basic standard operating procedure, spelling out the task, personnel, equipment, method, location, the precautions to be taken, and the time for an operation to be performed.

The permit system offers one of the best methods to meet all the various conditions required for making difficult operations safe to perform. Several types of permit systems have been developed to various degrees of detail over a period of time by different industries depending on their particular needs and experience.

Frequently, it is practical to combine the requirements of several permits on one printed form to reduce the number of forms needed and to simplify the administration for a comprehensive permit system.

The use of permits has several advantages that could not be obtained

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with certainty in any other manner. They provide written information and instructions on hazards to be avoided in the operation, and these items must be reviewed by the person responsible for doing the work. They can insure that proper tests and preparations are made prior to to starting the work. They can restrict the performance of the work to personnel who are known to be adequately trained. They can insure adequate notification of all parties interested in the operation prior to its starting. They can clarify the responsibility for the operation; and the signing of the permit insures that the person is satisfied the proper conditions are being met. All persons signing the permit have their responsibility for the safety of the operation emphasized. They also provide a written record of the operation, including those who were involved in authorizing and supervising it. In general, they can provide an unusual degree of control over the operation to be performed. The many advantages possible from the permit system would seem to warrant its continued expanding use as an important device to improve the control and safety of normally hazardous operations.

The numerous types of permit systems that have been developed emphasize the large variety of operations that can be improved by their use. In general, all of these permits fall into one of several general types of permits such as *hazardous operation permits, hazardous work area permits, special hazard permits,* and *equipment operating permits.* The most generally used permits are for hazardous operations such as "hot work": welding and cutting, or the use of open flames; and for "tank entry": the opening and entering of tanks, voids or vessels by personnel. There are numerous additional types of specialized permits which have been developed in various industries to improve the performance of operations that are particularly hazardous.

Permit systems frequently used may be grouped in the various general types of permits:

Hazardous Operation Permits
Hot work (welding, cutting, open flame)
Tank entry (vessels, voids, closed spaces)
Line breaking (opening)
Disposal operations
Testing operations (explosives, propellants)
Excavations
After-hours operations

Hazardous Work Area Permits
Explosives building work

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Acid-area work
Flammables-area work

Special Hazard Permits
Toxic materials
Matches and lighter

Equipment Operating Permits
Material handling equipment or vehicle operating (vehicles, fork lift trucks, hoists, graders, etc.)
Sprinkler-valve closing permit

26.1. HAZARDOUS-OPERATION PERMITS

Hazardous-operation permits usually cover those operations which are repeated occasionally by various personnel and have repeatedly proven to be unusually hazardous if certain precautions and measures are not taken before starting the work.

Hot Work (welding, cutting, open flame)

Fire has been the greatest universal hazard to which chemical operations are exposed. Numerous times uncontrolled welding and cutting operations have been the source of fire in all types of industrial operations. These activities can be closely controlled by an effective permit system.[1, 2, 3] There are many areas where smoking, open flames, and welding and cutting operations are prohibited during normal operations because of the nature of the exposure or the large damage potential of the area. In these areas a permit system can provide for the controlled use of heat or open-flame sources.

The approval and granting of a "hot work" permit is usually restricted to a senior supervisor of the area involved and for a limited time period. Most of these permits actually require inspection of the area and approval by the plant safety supervisor, the fire chief, or their representatives, and the local area supervisor.

Figure 26.1 is a sample of a "hot work" permit form. The issuing of the permit is usually the responsibility of the area supervisor, who must inspect the area and verify that the following measures have been taken:

1. The equipment has been emptied and cleaned and all flammables, combustibles, or toxic materials have been removed from the area, and those items that cannot be removed have been shielded or wet down.

HOT WORK PERMIT No. 001

Supervisor _____ is authorized to conduct hot work as follows:

Location _____ _____ Room Building Area

Equipment _____

Work to be done _____ (burning welding other)

Start Date _____ Time _____

Expires Date _____ Time _____

Required Actions:	To be done	Done
Fire Department notified		
Combustibles removed		
Area wet down		
Fire watch assigned		
Hose line laid and connected		
Adjacent sewers covered		
Fire extinguishers present		
Forced ventilation needed		
Connections broken and blanked		
Equipment cleaned/flushed		

Special measures to be taken:

_____

_____

_____

Area to be inspected and approved before work by:

Safety Supervisor _____

Fire Department _____

Approved _____ (Safety Department)

_____ (Fire Department)

Authorized By _____ (Area Supervisor) _____ (Work Supervisor)

Area has been inspected at completion of work and is in a safe condition

_____ (Fire Watch)

_____ (Supervisor)

Note (Return completed form to Area Supervisor)

FIG. 26.1. Hot work permit form.

2. The area and equipment have been inspected by the safety or fire-department personnel, and adequate tests have been conducted, if necessary, to insure that there are no flammable or explosive atmospheres present.

The foreman or supervisor of the work crew inspects the area. When satisfied that the area is in proper condition and the permit has been properly completed and signed, he assigns a "fire watch" and then

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signs the permit and authorizes the work to be performed. Upon completion of the work, the area is inspected by the worker and the "fire watch" to insure that there are no smouldering or incipient fires started in the area. They then sign the form certifying the work has been completed safely and return it to their supervisor. He, in turn, forwards it to the area supervisor and to the plant engineer's office or the safety department.

Work postponed beyond the period of the permit usually requires reissue or extension of the permit after a review of the area and conditions by specified personnel. Fires, or significant changes of conditions in the area during the work, usually voids the permit and reissue is required.

Tank Entry (opening or entering vessels, voids, or closed spaces)

The numerous serious or fatal incidents involved in tank entry operations have emphasized the urgent need for close control of these operations.[4, 5, 6] (See also Chapter 23.) The approval and granting of a "tank entry" permit is usually restricted to a senior supervisor of the area involved and for a specified time.

Figure 26.2 is a sample of a typical "tank entry" permit form. Prior to approval and use of the "tank entry" form, the area supervisor must insure that the area and equipment have been inspected and that the tank has been emptied, washed, and flushed, and that all lines and drains have been disconnected and blanked off. All equipment, such as agitators or mixers, must also be disconnected or locked out.

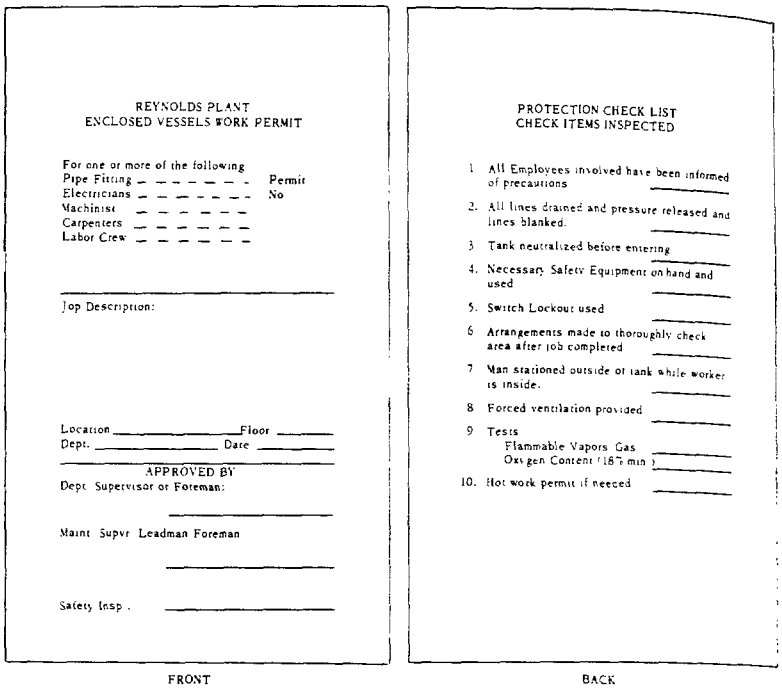
The work-crew supervisor is also responsible for inspecting the area and equipment and must insure that the following items have been accomplished:

1. Adequate tests have been made of the residue and atmosphere to insure that it is safe for entry. These tests usually include tests for flammable gases or vapors, oxygen content determination (minimum of 18%), and toxic materials exposure. Tests should be repeated at intervals to determine if an unsafe condition develops while work is being performed.
2. Personnel are properly equipped and clothed for work in the tank, and adequate forced ventilation has been provided. (Several air changes per minute are desired.)

   Equipment may include:

   Air line masks or self-contained breathing apparatus

   Life lines



REYNOLDS PLANT
ENCLOSED VESSELS WORK PERMIT

For one or more of the following
Pipe Fitting _ _ _ _ _ _ _ Permit
Electricians _ _ _ _ _ _ _ No
Machinist _ _ _ _ _ _ _
Carpenters _ _ _ _ _ _ _
Labor Crew _ _ _ _ _ _ _

Job Description:

Location _____ Floor _____
Dept. _____ Date _____

APPROVED BY
Dept. Supervisor or Foreman:

Maint. Supvr. Leadman Foreman

Safety Insp. _____

FRONT

PROTECTION CHECK LIST
CHECK ITEMS INSPECTED

1. All Employees involved have been informed of precautions
2. All lines drained and pressure released and lines blanked.
3. Tank neutralized before entering
4. Necessary Safety Equipment on hand and used
5. Switch Lockout used
6. Arrangements made to thoroughly check area after job completed
7. Man stationed outside of tank while worker is inside.
8. Forced ventilation provided
9. Tests
   Flammable Vapors Gas
   Oxygen Content (18% min.)
10. Hot work permit if needed

BACK

FIG. 26.2. Enclosed vessels work permit form.

Acid suits or protective clothing
Explosion-proof lights (extension lights should be low voltage)
Rescue equipment

3. A safety watch or observer is assigned and is familiar with his duties and the proper actions to take in an emergency. The "safety observer" should be stationed in a position outside the tank to observe the personnel in the tank at all times.

When the responsible supervisor is satisfied that all of the appropriate items above have been accomplished, he then signs the permit and authorizes the work to start. Figure 26.3 is a combined form of a "hot work" and "tank entry" permit.

Line Breaking (opening)

The breaking or opening of pipe lines, pumps, or attached equipment has been a continuous source of serious injury and incidents in chem-

ETC 03479

HOT WORK AND TANK ENTRY PERMIT No 001

Issued to _____

Location _____

Work to be Done _____

_____

_____

Circle Equipment to be Used

Gas Torch Welding Date _____

Grinder Impact Wrench Time Start _____

Air Drill Sandblasting Time Finish _____

Other _____

	Not Applicable	Yes	No
1. Has equipment been flushed with inert gas?	☐	☐	☐
2. Atmospheric Test?	☐	☐	☐
Type _____ Results _____			
Time _____ By _____			
3. Have all connections been blanked off or broken out?	☐	☐	☐
4 Has equipment been thoroughly steamed?	☐	☐	☐
5. Has equipment been flushed with water?	☐	☐	☐
If connections have not been blanked off or broken out, list special provisions			
_____			
6. Have breakers to electrically operated equipment been padlocked off?	☐	☐	☐
7. Is equipment free and clean of all flammables?	☐	☐	☐
8. Have all surrounding conditions been inspected and are they such as to permit doing the work safely?	☐	☐	☐
9. List special precautions and protective garments			
_____			

10. Signatures (Please do not use initials)

Tank Entry	Hot Work Permit
Shift Supervisor _____	Shift Supervisor _____
Inspector _____	Inspector _____

For special permits: Process Supv. _____

Plant Superintendent _____

Accepted by Maintenance Supervisor _____

(In case of fire or spill, permit is void until countersigned)

FIG. 26.3. Combined hot work and tank entry permit form.

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ical operations.[5] All of these operations should be subject to a permit system to insure careful supervision and safe performance. Figure 26.4 is a sample form for a "line breaking" permit.

All lines to be worked on should always be assumed to be loaded and under pressure. The following measures are usually followed in issuing these permits:

1. The issuing of a permit should be limited to the supervisor of the area who is completely familiar with the system, and who has verified the proper line to be opened and that all steps possible have been taken to drain and vent the line and any connected pumps, valves, and tanks. All pumps on the line should be locked out and all gages and sight glasses should be checked for zero readings.
2. The personnel assigned to do the work should be properly equipped and clothed completely with protective equipment as if the line were going to vent or spray when broken. The nearby area should be enclosed with a barrier rope and signs to exclude personnel not involved in the operation.
3. The procedure for actually breaking the line should be reviewed with the persons who do the work. The placement of a deflector of lead or a suitable material over the flange joints is usually required for the initial cracking of corrosive or toxic material lines. Adjacent nuts and bolts are loosened first, slowly, and in the most accessible position where they can be retightened quickly if necessary.
4. Emergency equipment and materials should be checked and available in the immediate area. Safety showers, hose lines, fire extinguishers, neutralizers, or other emergency materials should be on hand and ready for use. Emergency actions to be taken should be reviewed by the supervisor with the personnel involved.
5. Removed sections and involved valves or parts should be handled carefully until they are inspected for trapped material or residues and are flushed. Lines that have caked or contain residues that cannot be cleaned immediately should be tagged with warnings identifying the contaminant or condition until they can be properly decontaminated.
6. Broken lines remaining in place should have all openings blanked off to prevent later drips or spills.

Disposal Operations

The disposal of hazardous waste materials is frequently the source of accidents and injuries. This is probably because of the general

ETC 03481

LINE BREAKING PERMIT No. 001

Mr. _____. Supervisor. Foreman is authorized to break open the _____ Inch. _____ Line. located
(Size) (Type)

At: _____

_____

time _____ AM PM. on _____
(Date)

The following checked actions are to be accomplished before the work is started:

	Needed	*Done*
Area wet down	_____	_____
Area Barricaded and Posted	_____	_____
Hose lines laid and connected	_____	_____
Neutralizing agent _____. on hand	_____	_____
Spark Proof Tools	_____	_____
Protective Equipment Needed		
Complete Acid Suit	_____	_____
Hoods	_____	_____
Face Shields	_____	_____
Gloves	_____	_____
Boots	_____	_____
Goggles	_____	_____

Hazards of material and special measures needed.

_____

_____

_____

_____

The line and system have been cleared/emptied/drained. all valves have been closed. and all equipment has been locked out.

_____
(Area Supervisor)

All work has been completed and the line is:

Ready for testing and return to service _____

Broken and all openings are blanked _____

The area has been cleared and work completed satisfactorily.

_____
(Work Supervisor . Foreman)

(*Note: Return completed form.*)

FIG. 26.4. Line breaking permit form.

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feeling that it is a simple operation not requiring supervision and can be done in the most convenient manner. The frequency of serious injuries in these operations emphasizes the need for adequate supervision, careful planning, and development of safe procedures which take into consideration all the characteristics or peculiarities of the materials involved.[4] Requiring a permit for these operations can insure that only trained personnel are used and that adequate forethought has been given to the methods and facilities to be used in disposing of each material.

The permit form (Fig. 26.5) usually specifies the number of personnel involved and the manner in which each material is to be disposed. It can also be used as a standard operating procedure in spelling out specific measures to be taken at the site. These may include:

Fire-equipment standby and the checking of water or phone connections.
Flying of warning flags or the sounding of warning signals.
Notification of security, fire, or administrative department personnel.
Inspection of the area for intruders and perimeter control.
Inspection of the area at the conclusion of the operation and shutdown.

Testing Permit (explosives and propellants)

Testing operations involving explosions or possible explosions, fires, the release of toxic materials, high-noise sources, or other possible hazardous reactions can be effectively controlled by a permit system. The permit can insure adequate warning of nearby personnel and that proper procedures are followed to reduce the hazards involved to the absolute minimum. The form and requirements of the testing permit are usually similar to those for the disposal of hazardous materials. Testing operation permits may also be expanded to include a Standard Operating Procedure, when tests are of a similar nature and are repeated frequently. The addition of the Standard Operating Procedure to the permit form greatly improves the effectiveness of both measures and insures that all responsible personnel are familiar with all requirements and procedures.

Excavation Permit

In plants with numerous underground systems, such as pipelines and power conduits, or where soil conditions are unstable or possibly contaminated, digging or excavation operations are frequently controlled

ETC 03483

DISPOSAL PERMIT No. 001

Mr. _____, foreman, is authorized to dispose of the following materials in the manner indicated:

	Method	Location
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

The procedures posted at the burning ground and disposal area must be followed in detail during these operations. Personnel Authorized # ____

Time _____ Date _____

_____
(Supervisor)

FIG. 26.5. Disposal permit form.

by a permit system.[7, 8, 9] An "excavation permit" can be used to insure that any of the following desirable measures have been or will be taken:

1. The drawings of the area have been checked for existing lines and the plant engineer's office agrees to the operation.

2. The soil has been checked for contamination by flammable or toxic materials.
3. The area is properly posted and barricaded or roped off.
4. Proper shoring materials and methods are going to be used if the excavation exceeds a certain minimum depth, usually 5 ft.

Figure 26.6 is a sample "excavation permit" form.

After-Hours Operation Permit

Two instances when a permit system can prevent difficulties or complications are when unusual operations are conducted after normal working hours, or when equipment must be operated unattended overnight.

The permit can provide information as to the responsible parties and spell out emergency actions to be taken if necessary. It can also spell out any unusual hazards involved such as flammable or toxic materials.

The permit form should provide a copy to be placed on or attached to the equipment and a copy to be sent to the guard force for information. Before approval of the permit by the area supervisor, it is usually desirable to have a review of the setup by safety personnel. Figure 26.7 is a sample form for an "after hours operation permit."

26.2. HAZARDOUS WORK AREA PERMITS

Work areas where hazardous materials are processed or stored are frequently restricted to operating personnel only. Repair and maintenance activities in these areas can present an undue hazard to some operations as well as to the maintenance personnel unless necessary measures are taken to eliminate or isolate the potential hazard.

Several types of "Hazardous Work Area Permits" have been developed by organizations to provide a means of controlling all operations in high hazard areas other than the normal production activities.

All "hazardous work area permits" will require the approval of the area supervisor, who must also certify that all hazardous materials have been removed from the work area and that any necessary decontamination procedures or tests have been accomplished.

When the planned work includes hazardous operations such as hot work or tank entry, which in themselves require a "Hazardous Operation Permit," these permits should also be approved by the area supervisor.

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EXCAVATION PERMIT No. 001

DATE _____

EXCAVATION FOR: _____

_____

_____

_____

LOCATION: _____

_____

_____

CAUTION: Contained with the excavation area are:

_____

SPECIAL MEASURES TO BE TAKEN:

Area to be barricaded and marked.

Shoring required if 5' depth exceeded.

_____

_____

Authorized By

_____

Plant Engineer

FIG. 26.6. Excavation permit form.

ETC 03486

AFTER HOURS OPERATION PERMIT No. 001

FROM _____ TO _____
(Time-Date) (Time-Date)

LOCATION: _____

OPERATION: _____

_____

_____

_____

EMERGENCY INSTRUCTIONS: _____

_____

_____

POTENTIAL HAZARDS: _____

_____

RESPONSIBLE PERSON: _____

HOME PHONE NO. _____

ADDRESS _____

OPERATION SET UP MUST BE APPROVED BY:

SAFETY SUPERVISOR _____

Approved _____
(Safety Supervisor)

FIRE DEPARTMENT _____

Approved _____
(Fire Dept. Rep.)

OPERATION AUTHORIZED BY:

_____ _____
Date Area Supervisor

Note: One copy of permit to be attached to equipment.
One copy to filed with guard force office

FIG. 26.7. After hours operation permit form.

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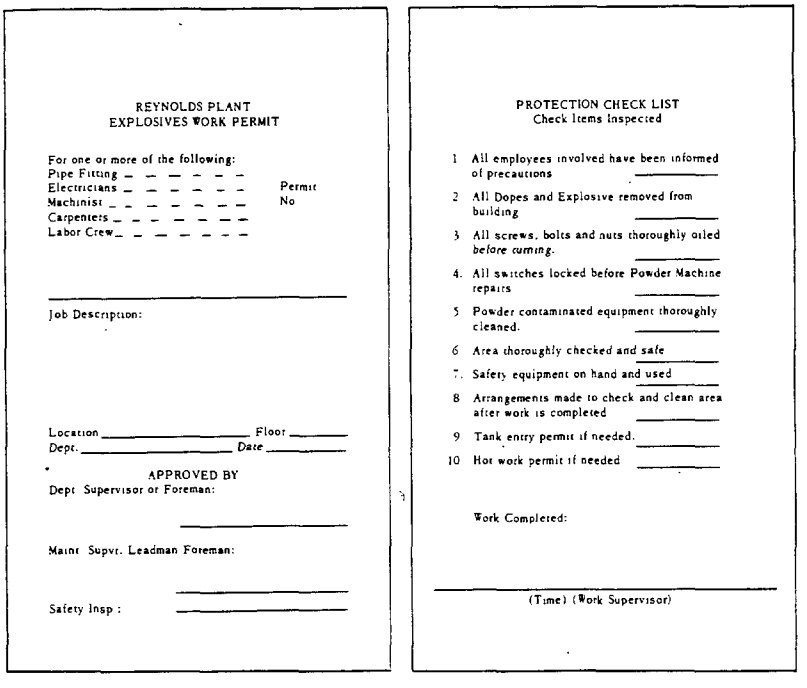
Explosives Building Work Permit

Maintenance or repair work in buildings or equipment which have contained explosives, propellants, or pyrotechnic materials obviously will present serious hazard situations if close controls are not present to insure that adequate measures have been taken to guarantee the safety of the operation.

Figure 26.8 is a sample form of a work permit used to help insure consideration of and completion of all the necessary actions to remove all unnecessary hazards from the area. The granting of a work permit for such operations is usually restricted to the area supervisor, who is usually required to insure that the following preparations have been completed.



REYNOLDS PLANT
EXPLOSIVES WORK PERMIT

For one or more of the following:
Pipe Fitting _ _ _ _ _ _
Electricians _ _ _ _ _ _
Machinist _ _ _ _ _ _ _
Carpenters _ _ _ _ _ _ _
Labor Crew _ _ _ _ _ _ _

Permit
No

Job Description:

Location _____ Floor _____
Dept. _____ Date _____

APPROVED BY
Dept Supervisor or Foreman:

Maint Supvr. Leadman Foreman:

Safety Insp :

PROTECTION CHECK LIST
Check Items Inspected

1 All employees involved have been informed of precautions _____
2 All Dopes and Explosive removed from building _____
3 All screws, bolts and nuts thoroughly oiled *before cutting.* _____
4. All switches locked before Powder Machine repairs _____
5 Powder contaminated equipment thoroughly cleaned. _____
6 Area thoroughly checked and safe _____
7. Safety equipment on hand and used _____
8 Arrangements made to check and clean area after work is completed _____
9 Tank entry permit if needed. _____
10 Hot work permit if needed _____

Work Completed:

(Time) (Work Supervisor)

FRONT BACK

FIG. 26.8. Explosives building work permit form.

ETC 03488

1. All hazardous materials have been removed from the buildings or danger area, thorough decontamination or cleaning has been accomplished, and any necessary safety tests have been made.
2. Precautions have been taken to prevent the reintroduction of hazardous materials into the area until completion of all repair and maintenance operations.
3. It is also frequently required that the normal building foreman be present while all repair or maintenance work is performed.
4. Adequate information is given to the supervisor of the work crew as to any unusual conditions or hazards that may be present or develop during the operation, and the proper action to be taken in an emergency.

The supervisor of the work crew also is usually responsible for inspecting the area and accomplishing the following items before approving the permit and starting the operation:

1. Inform all employees of the operation to be done and explain all precautions and emergency actions to be taken.
2. Obtain any specific "hazardous operation permits" needed during the course of the work, and taking all measures needed to prepare the area for the work to be performed such as wetting down, locking out controls, and posting or marking the work area.
3. Insure that all necessary safety equipment, emergency equipment, and fire fighting equipment is on hand, and that personnel know its location and are trained in its use. The testing of local hose lines and safety showers should also be performed by one of the crew members.

   Equipment needed may include:
   Neutralizing materials
   Protective clothing
   Air-line masks
   Gas masks
   Gloves
   Fire extinguishers

4. See that all the necessary tools, parts, equipment, and supplies are on hand for the work to be done.
5. See that after completion of the work, the area is inspected to insure that it is in proper condition, that all spills have been flushed or neutralized, and that all tools and work equipment or scrap have been removed.

ETC 03489

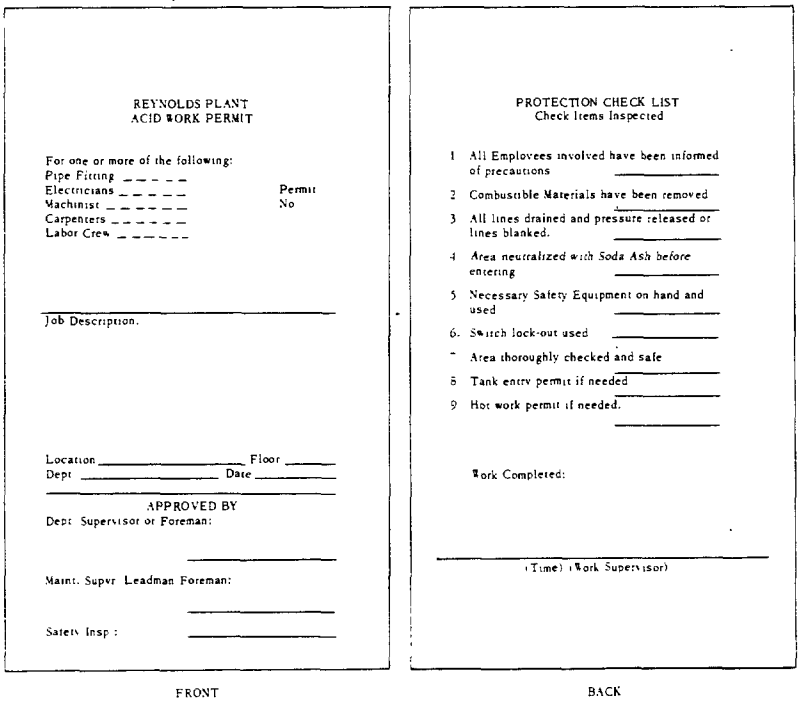
The permit is then usually signed in the space certifying that the work has been properly completed and returned to the area supervisor for acknowledgment and forwarding to the plant engineer.

Acid Area Work Permit

Maintenance and repair operations in an acid manufacturing or processing area can contain an unusual number of hazardous situations, making use of a permit system very desirable or necessary. Figure 26.9 is a sample form of an "acid area work permit" form.

The area supervisor, in authorizing a work permit for the acid area, is usually responsible for insuring that the following actions have been taken:

1. The work area has been inspected, all necessary safety tests have been made, and any unusual hazards or conditions are marked



REYNOLDS PLANT
ACID WORK PERMIT

For one or more of the following:
Pipe Fitting _ _ _ _ _
Electricians _ _ _ _ _
Machinist _ _ _ _ _
Carpenters _ _ _ _ _
Labor Crew _ _ _ _ _

Permit
No

Job Description.

Location _____ Floor _____
Dept _____ Date _____

APPROVED BY
Dept. Supervisor or Foreman:

Maint. Supvr. Leadman Foreman:

Safety Insp.:

FRONT

PROTECTION CHECK LIST
Check Items Inspected

1 All Employees involved have been informed of precautions _____
2 Combustible Materials have been removed _____
3 All lines drained and pressure released or lines blanked. _____
4 *Area neutralized with Soda Ash before* entering _____
5 Necessary Safety Equipment on hand and used _____
6. Switch lock-out used _____
7 Area thoroughly checked and safe _____
8 Tank entry permit if needed _____
9 Hot work permit if needed. _____

Work Completed:

(Time) (Work Supervisor)

BACK

FIG. 26.9. Acid area work permit form.

ETC 03490

and made known to the supervisor of the work crew. He should also verify the identification of the specific equipment to be worked on.

2. All necessary measures have been taken and any specific "hazardous operation permits" needed have been issued.
3. Operating personnel, in the area or in adjacent effected areas, have been notified, and any necessary safety measures have been taken to prevent complications in the operation.
4. Adequate information is given to the work-crew supervisor concerning any unusual emergency actions necessary to protect the facility.

The supervisor of the work crew is usually also responsible for inspecting the area—and accomplishing the following items before approving the permit and starting the operation:

1. Informing all employees of the planned operation and explaining all the precautions and emergency actions to be taken if necessary.
2. Obtaining any specific hazardous operation permits needed during the course of the work and taking all measures needed to prepare the area, such as removing combustibles, and posting and roping off the work area.
3. Insuring that all necessary safety and emergency equipment is on hand and that a hose line is connected and available. He should also satisfy himself that personnel assigned are trained in the use of emergency equipment, know its location, and have tested the safety showers and eye-wash stations in the area.

   Equipment needed may include:

Gas masks	Explosimeter (H_2)
Acid suits	Neutralizing materials
Air line masks	Life lines
Face shields	Fire extinguishers
Acid hoods	Danger signs
Gloves	Testing instruments
Boots	

4. Seeing that all necessary tools, parts, equipment, and supplies are on hand for the work to be done.
5. Seeing that after completion of the work, the area is inspected to insure that it is in proper condition, that all spills have been flushed or neutralized, and that all tools and work equipment or scrap have been removed.

ETC 03491

The permit is then usually signed in the space certifying that the work has been properly completed and returned to the area supervisor for acknowledgment and forwarding to the plant engineer.

Flammables Area Work Permit

Operations not a part of normal production activities in areas where large amounts of flammables are processed or stored are often subject to a permit system to limit the fire or explosion exposure of the facility. Normal maintenance and repair activities can be a serious threat where accumulations of flammable liquids, vapors, or gases may be encountered.

An effective work permit system for these operations can greatly reduce the probability of accidental ignitions or fires, and greatly reduce the results of accidental fires by insuring the presence of adequate equipment. The "flammables area work permit" form (Fig. 26.10) is usually originated by the area supervisor who must authorize all work done in the area, and must certify that the following pertinent precautions have been taken:

1. The work area has been inspected and all necessary safety tests have been made; all hazardous materials or conditions have been removed or corrected, and, where impossible to remove, have been marked and made known to the supervisor of the work crew.
2. All necessary measures have been taken, and any specific "hazardous operation permits" needed have been issued.
3. Operating personnel in the area or adjacent areas which may be affected have been notified, and all necessary safety measures have been taken to prevent causing complications in the operation.

The supervisor of the work crew is usually also responsible for inspecting the area and accomplishing the following items before approving the permit and starting the operation:

1. Informing all employees of the planned operation and explaining the precautions and emergency actions to be taken if necessary
2. Obtaining any specific hazardous operation permits needed during the course of the work, and taking all measures needed to prepare the site, such as wetting down, removing combustibles, posting and roping off the work area.
3. Insuring that all necessary safety and emergency equipment is on hand and that a hose line is connected. It may also be required that the plant fire department be notified. He should

ETC 03492

FLAMMABLES AREA WORK PERMIT No. 001

Mr _____ and personnel under his supervision are authorized to perform the following operations in the _____ area, on _____ (Date).

Job Description:

_____

_____

_____

_____

_____

These operations are to be performed after completion of the following checked actions:

Combustibles removed _____

Area wet down _____

Area barricaded and posted _____

Hose lines laid and connected _____

Atmosphere tested for flammable vapors or gases _____

Following emergency equipment on hand _____

Fire Entry Suit _____

Fire Extinguishers _____

(Dry Chemical/Foam)

Fire Department notified _____

Special precautions to be taken

_____

_____

_____

_____

Area to be inspected after completion of work _____

_____ (Work Supervisor) _____ (Area Supervisor)

Work Completed _____ (Time) (Work Supv.)

FIG. 26.10. Flammables area work permit form.

ETC 03493

satisfy himself that the personnel assigned to the job are familiar with the emergency equipment provided.

4. Seeing that after completion of the work, the area is inspected to insure that it is in proper condition and that all tools and scrap have been removed.

After completion of the work, the permit is usually signed in the space certifying that the work has been properly completed and returned to the area supervisor for acknowledgment and forwarding to the plant engineer.

26.3. SPECIAL HAZARD PERMITS

Special hazard permits are particularly useful when certain materials that are normally forbidden, or are to be restricted in use, must be handled.

Special hazard permits are usually valid for a considerable period of time, depending on the circumstances under which the controlled items are needed, and frequently the permit restricts the items to a particular location or area. The permit can also insure that all necessary conditions have been met, and it can be used to identify the specific persons or person authorized to handle the material. In cases where the material is particularly hazardous, the permit may not be issued until the personnel involved have been trained and have passed tests on their knowledge of the hazards involved, and the proper procedures and details of the standard operating procedure.

Toxic Materials Permit

Operations involving particularly hazardous materials or highly toxic compounds are usually spelled out in detail in a standard operating procedure or operation manual. In such operations a "toxic materials permit" can be used to control the locations and the personnel involved in such operations.

The issuing of a "toxic materials permit" is usually limited to the senior supervisor in charge of the operation involved. The criteria for issuing the permit will vary, depending on the circumstances and the degree of control or limitation desired. Qualifications of personnel and test requirements may also be spelled out. When operations are to be limited to a certain room or area, any special conditions or requirements, such as control of access, marking, ventilation control, or structural requirements may also be spelled out.

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TOXIC MATERIALS PERMIT No. 001

Mr. _____ is hereby authorized to possess

_____ (Amount) of _____ (Material) for use in _____

_____ (Room/Building/Area)

For _____ (Purpose).

Subject to the requirements checked below.

This permit is valid until _____ (Date)

_____ (Supervisor)

1. Material will be stored in:
   - Shipping Container _____
   - Safety Containers _____
   - Locked Storage _____
2. Material may be handled only by the following personnel:

   _____

   _____

   _____
3. Material after use will be disposed of by:
   - Evaporation _____ (Disposal Area)
   - Burial _____ (Disposal Area)
   - Burning _____ (Burning Ground)
   - Dilution & Sewer _____
   - Neutralization & Sewer _____
   - By Disposal Permit _____
4. Special Instructions _____

   _____

   _____

   _____

   (Protective clothing, equipment, measures)

FIG. 26.11. Toxic materials permit form.

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Although the forms will vary considerably, Fig. 26.11 is a sample form for a "toxic materials permit."

Match or Lighter Permit

Matches, lighters, or other flame sources, are items that are frequently forbidden in certain areas or entirely forbidden in chemical or petrochemical plants.

When these items must be carried or used by certain responsible personnel in such operations, it is customary to require that they obtain a "match permit" similar to one shown in Fig. 26.12. The limitations or requirements for use of matches or lighters may also be spelled out on the form.

26.4. EQUIPMENT OPERATING PERMITS

Equipment operating permits are frequently used to restrict the use of certain specialized vehicles or equipment to personnel who have been specifically trained in their operation and whose work requires their use.

MATCH OR LIGHTER PERMIT

Mr. _____ is hereby authorized to carry matches/lighter on his person in _____ _____ room/building/area.

This permit expires on _____
(Date)

_____
(Supervisor)

FIG. 26.12. Match or lighter permit form.

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Equipment operating permits may also be used in controlling such critical operations as interrupting fire main systems and the closing of sprinkler control valves.

Vehicle Operating Permit

The restriction of the operation of vehicles to certified personnel is usually necessary because of the specialized nature of the equipment and the large variety of operating controls involved. The proper operation of specialized equipment such as fork lift trucks, payloaders, graders, bulldozers, and transporters requires a considerable amount of training for operating personnel.

The training course usually involves complete familiarity and knowledge of the operating rules, local traffic regulations, and proving actual operating ability by successfully completing a standard obstacle course.

The permit is usually valid for a fixed period of one to two years with renewal requiring a refresher course and retesting. Figure 26.13 shows a permit in card form to be carried by the operator on his person.

VEHICLE OPERATING PERMIT No. 001

Mr. _____ is hereby authorized to operate the following equipment: _____

_____

_____

RESTRICTIONS: _____

This permit expires one year from date of issue.

_____ Date of Issue

_____ Supervisor

FIG. 26.13. Vehicle operating permit form.

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SPRINKLER VALVE CLOSING PERMIT No 001

Mr. _____ is hereby authorized to close sprinkler valve no. _____ controlling building no. _____ at _____ A.M./P.M., on _____ (Date), after completion of the following actions. _____ (In charge of Fire Protection)

The following actions have been taken before closing the valve.

1. Supervisors of building affected have been notified. _____
2. Local fire department has been notified. _____
3. All hot work or open flame operations have been stopped or removed from the building. _____
4. Emergency equipment is on hand (Plugs and caps, fittings, hose lines) assigned _____
5. Fire extinguishers are available and filled. _____
6. Special precautions taken

_____

_____

7. Copy of permit attached to valve _____

_____ A.M./P.M. _____ _____
(Time) (Date) (Person closing valve)

Valve No. _____ was opened at _____ A.M./P.M., on _____ (Date) Drain test was satisfactory and permit returned to Plant Engineers office.

_____
(Person opening valve)

FIG. 26.14. Sprinkler valve closing permit form.

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Sprinkler Valve Closing Permit

The operation of fire-main valves or sprinkler-system valves by unauthorized personnel, or without specific authorization, can seriously jeopardize the fire protection system for the entire activity. Many insurance carriers require notification of any anticipated interruption of fire mains or sprinkler systems.

The use of a permit system for the closing of sprinkler or fire-main valves can insure that adequate measures have been taken to reduce the hazards because of interruption of fire protection. Figure 26.14 is a sample permit form for closing sprinkler valves.

The issuing of these permits is usually limited to the plant engineer, who will be required to insure that the following items are accomplished by responsible personnel:

1. The insurance carrier is notified.
2. Equipment is on hand for emergency restoration of the service, such as plugs, caps, and fittings.
3. Supervisors of the area affected are notified, and the local fire department or fire brigade is informed.
4. Fire hazardous operations are stopped or removed from the area.
5. Fire watch personnel are assigned to insure immediate discovery of fire or other serious developments during the period of interruption.
6. The system is inspected and all valves are opened after completion of the work or interruption.
7. The insurance carrier is notified of the return to service of the system.

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27

Proper Maintenance Prevents Accidents

David T. Smith

Maintenance in the chemical industry differs from other industries because of the nature of the materials, processes, and types of equipment used. Since much chemical work involves the movement of fluids, gases, and powdered solids from one piece of equipment to another, many pipelines, conveyors, fork-lift trucks, and other material-handling devices are used. Containers are more likely to be tanks, drums, or some form of closed container than in other industries.

Much of the chemical-reaction equipment involves mixing, "cooking," cooling, and stirring under widely varying levels of temperature and pressure in sizes from one-quart laboratory autoclaves to huge columns that loom against the sky like grain elevators. Disassembling and reassembling in itself requires special rigging and millwrighting techniques. Specialized problems such as high corrosion rates, flammable liquids, and toxic or noxious materials are peculiar to this industry. Therefore a high quality of work is more necessary for safety of operation than in most other industries. Leaking pipes, equipment improperly reassembled, and so on expose personnel to hazards..

The cases where the process line was connected into the stair-pipe railing, where steam was connected into the toilet, and where the electronic recording instrument began to play radio programs are part of the folklore of chemical maintenance. If they did not happen, they should have, because they are so typical of the many "boners" that

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are possible as a result of inadequate identification of pipes, wiring, and equipment.

Records show many serious injuries and even deaths from mistakes such as connecting inert or toxic gases into air lines supplying air for humans to breathe or connecting piping so that wrong materials were added to reactions with resulting fires, explosions, and emission of toxic gas. Connections have been left open which allowed the escape of dangerous materials to expose personnel. Relief devices have been left inoperative or removed with vessels and systems to rupture from overpressure.

A second source of hazard to personnel and property from improper maintenance is the failure of equipment during either normal or abnormal operations. For example, leaking acid pipes can drip on persons, escape of flammable gas may result in fire or explosion, and loss of sulfide liquors to an acid stream will result in formation of deadly hydrogen sulfide gas. Even broken steps and stair rails take their toll of injuries every year.

In summary, in no other industry is high quality of maintenance, workmanship, and proper identification as important to safety as in the chemical industry.

Preventive Maintenance

By inspecting, repairing, and replacing equipment on an intelligently planned schedule, we can prevent failures from occurring, for the most part. There are tremendous cost advantages to this type program as well as safety advantages. Breakdowns during manufacturing operations result in loss of production, inefficient use of manpower, and increased repair cost because of overtime and other emergency penalties. These factors cost far more than the investment in a planned preventive maintenance program. The advantages to safety are obvious because of the reduction of exposure to emergency conditions and the ability to plan and provide safe procedures and equipment. The advantages to quality and quantity of production are not to be overlooked.

Preventive maintenance essentially is the system of determining the probable frequency of failure of a device or system, and inspecting, repairing, or replacing it before it fails. We can draw a curve showing the probability of failure of a given device against time, and it will appear as the "normal probability" curve (see Fig. 27.1). There is a very low probability that it may fail very early, then there is a rapid rise of probability of failure to an average value, then the curve

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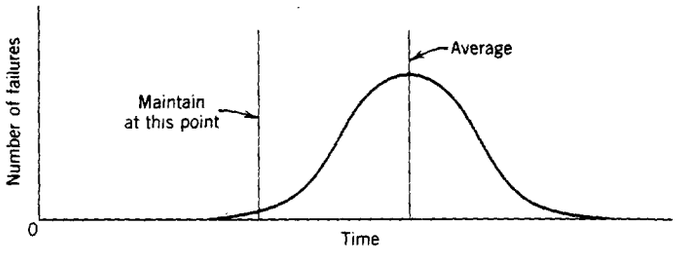

FIG. 27.1. Selection of periods for preventive maintenance.

drops again. There is a very low probability that failure will be deferred until long after the average time. The shape of the curve will appear as a bell, with the peak as the average. Our job is to schedule maintenance so that we are confident that we take action before the likelihood of failure is 2%, or some other chosen figure. In other words, we would be confident that 98% of the time we will have applied maintenance before a failure occurs.

It is obvious that this requires a knowledge of the average length of time before breakdown of the particular device under the specific conditions of operation. Often this is not easy to determine. Past experience in similar operations, studies of rate of deterioration, and other means of analysis can be used. Knowledge of how the device or system can fail, and of the most likely ways for it to fail can help to determine the frequency of failure.

Needless to say the ability to match optimum maintenance dates and time with availability of equipment (release by operations for shut down), availability of materials, maintenance facilities and manpower are required. To accomplish this, planning ahead, using schedule sheets, and keeping everybody informed, appear to be key points. It is important to control *all* equipment from a preventive maintenance standpoint by making schedules for every piece, even if the frequency is as long as once every ten years.

An example of the working of preventive maintenance in a typical plant follows.

Pumps P-16 through P-22 in Building A310

STEP 1. Area-maintenance engineer and operating-department supervisor agree on frequency of inspection and removal of pumps to pump

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shop for overhaul. Spare pumps will be installed. Frequency is annual and one pump is scheduled to be replaced each month, January through July.

STEP 2. Shut-down dates and times are entered in production control schedule to coincide with down time for other mechanical work.

STEP 3. Maintenance engineering group enters dates and times on work-order control-system cards.

STEP 4. Monthly maintenance work-order schedule shows dates and times.

STEP 5. Work order is issued one week in advance by maintenance engineering group. Time and date are agreed on again by operating supervision. Instructions are issued to operating personnel on readying equipment.

STEP 6. Work procedures are reviewed with maintenance foreman and men. Men, equipment, and materials are lined up.

STEP 7. Work done.

STEP 8. Results are recorded on equipment maintenance record of the pump, and next overhaul date is scheduled.

Proper maintenance to prevent accidents means more than achieving freedom of failure of the equipment and buildings maintained. It means protection of people while doing this maintenance. This can be considered in three phases:

First, protection of operating personnel from temporary environmental hazards caused by maintenance work. For example, roping off temporary openings, keeping areas cleared below overhead work to protect against falling objects, keeping discarded parts and tools from being a stumbling hazard on floors, shielding of welding arcs, etc.

Second, protection of maintenance personnel against hazards of the operating conditions. This requires clearance with operating supervision before doing any mechanical work, coordination of operating activities with mechanical work, and use of permits where necessary to formalize this coordination. For example, a mechanic could step back from a pump repair job into an aisle in front of a moving fork-lift truck carrying a pallet of drums, unless operating personnel is familiar with his assignment, he has posted warning signs to protect his work location, and he has made himself familiar with the movements of the operating personnel in their work.

Third, protection of maintenance personnel against hazards of their own work. Methods of doing work should be standardized where possible and written procedures prepared covering steps and key points. In this way we can avoid overlooking the lessons learned from previous mistakes and injuries. Too often we say, "every maintenance job is different, we cannot freeze them into a neat procedure." What we really mean is that we are too lazy to work out "agreed on" methods for repetitive jobs, and to put them down on paper.

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Shut Down and Start Up

Clear cut responsibility for each step is the key note of planning and execution of shut down and start up. Shut down of operating equipment should be the responsibility of operations, not maintenance or other service groups. Auxiliary service groups should handle their own specialties, such as a power group handling the outside steam, electric, air, gas, and other services to buildings. Close coordination is required. Notification of shut down to interested groups should be made as far in advance as possible.

Operating supervision must be held responsible for emptying, washing out, steaming out, purging with inert gas, and other steps to make equipment safe before turning it over to the maintenance group for working on it. Maintenance supervision has the responsibility to check as far as feasible to see that this has been accomplished before accepting the equipment. Key points are proper blanking off of pipelines connected to the equipment, proper ventilation, and testing for flammable vapors.

During actual shut down, and even more likely during start up, unusual thermal stress may be added to the normal mechanical stresses. Exposure of personnel to leaks and ruptures of equipment must be guarded against. No connections should be tightened during warm-up periods—we must wait until temperatures have leveled off. During shut downs and start ups special care must be taken to see that all "lock-out" procedures are followed closely for electrical work, for moving machinery, and valves.

Written procedures for emergency shut downs as well as for normal shut downs must be prepared, rehearsed, kept up to date, and kept available to people that have to use them.

Provision must be made for emptying safely all lines that are to be opened, for accounting for conditions in all equipment, and for knowing the condition of all vents and relieving devices.

Personnel must not be permitted to break into any pipeline without full protection against it being "loaded" regardless of draining and other procedures. Too often pipes have been plugged or partially plugged, trapping dangerous materials in them. Complete protection to the body means "acid-suit" protection or better against corrosive materials, and supplied air of breathing quality for respiratory protection against noxious fumes and gases.

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Entering Vessels and Confined Spaces

Entering vessels presents special problems because of the inability of the workmen to get out of the vessel without outside help in case of emergency and because of difficulty of communication. For these reasons, plus the possibility of emergency chemical exposures, rigidly enforced special precautions must be taken. These are required by statute or governmental regulation in many states. In general these include:

1. The vessel must be thoroughly cleaned by operations.
2. All connecting pipelines must be disconnected and blanked off.
3. All power driven devices (such as agitators) must be locked out at positive disconnect switches.
4. Air samples must be taken to prove absence of flammable vapors, and also in some cases, of toxic or noxious materials.
5. Air samples must be taken to prove presence of a normal amount of oxygen.
6. A tank entry permit must be signed by operating and maintenance supervision verifying that above steps have been satisfactorily complied with, and posted at the vessel site.
7. Men to enter vessel and watchman must be equipped with life belts and ropes. (Belts should be type fitting high under armpits for ease in lifting, not around waist. Handcuff types are preferred as alternates by some, opposed by others.)
8. In most cases, an air mask and fresh-air supply must be available for each man entering the tank and for the watcher. A chemical protective suit of impervious material completely enclosing the body, and provided with fresh breathing air and air conditioning for comfort not only serves that purpose but provides a safe comfortable working environment. It is equipped with an air-supply hose which also acts as a life line.
9. There must be one watcher at the vessel entrance who can keep in touch at all times with the man or men inside. In addition there must be at least one other man within call of the watcher to help in case of emergency. One man can do little by himself. Devices for signaling for additional help such as a "Freon" actuated horn are acceptable.
10. Rope or chain ladders with rigid rungs of wood or metal may be used for vessel entry where straight ladders cannot be used. How-

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ever, lowering of a man into a vessel without facilities for him to come out by himself should be avoided.

11. A man should not be allowed to go into a vessel through an opening which requires him to "squeeze through." He cannot be removed quickly enough in emergency conditions. A 22-in. manhole should be standard. Small men can enter as small an opening as 18 in. Anything less is extremely doubtful.

Similar principles should be followed when placing men in any confined space from which emergency exit may be hampered. Any pit or trench deeper than 5 ft, and any work on a roof or column where a man may be trapped in case of liberation of toxic fumes, requires special control procedures of similar principles.

Burning, Welding, and Other Flame-Producing Work

Because the chemical industry handles so many flammable and volatile materials, and because of the rapidly changing technology which in turn causes frequent changes in materials handled, control of ignition sources to prevent fires and explosions is of prime importance. Therefore, special procedures to reduce the hazard of fire from heat and flame producing work are essential. In general they cover these key points:

1. No welding or burning is permitted outside of designated welding shops and specified welding areas, without first obtaining permission of the operating supervision responsible through the use of a written, signed "burning permit" or "hot work permit." This should indicate the nature and location of the work, any particular restrictions required for safe performance, and the time during which the work is to be permitted. Since the issuance of a permit also entails the control of operations to prevent the creation of any hazardous conditions during the work period, it is important that the permit be made a responsibility of the operating-line organization, not a service or staff group such as the safety or fire-protection group. It may be necessary to assign additional personnel to act as fire watchers during the job, and they may be supplied by the safety or fire protection group, but the responsibility for authorizing the work in any given location should be put squarely on the supervision responsible for the operating conditions of that location.
2. Only qualified burners and welders should be given authority to perform this type of work, and mere mechanical skill is not enough.

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These men must be trained in the responsibility to properly analyze and protect surrounding flammable materials, to extinguish fires, and to handle emergencies. A permit system certifying qualified welders has been proved useful in many plants.

3. All burners and welders must have first-aid fire protection on the job with them. Water hoses are generally needed also. Cracks and flammable materials must be protected by incombustible covers or barriers. Overhead work must be analyzed to provide sufficient protection from sparks falling below. No flammable gas or oxygen cylinders should be permitted inside of operating, laboratory, or storage buildings, except under most unusual and carefully controlled circumstances.

Pressure Testing, Corrosion Inspection

While various instruments are now available to permit accurate measurement of thickness of vessel walls at selected areas, they do not guarantee that a weakness has not developed at some location not measured. Therefore, they do not take the place of periodic hydrostatic pressure testing to determine the ability of the vessel to withstand pressures in excess of those of normal operation. The generally accepted ratio for periodic testing during usage of a vessel is one and one-half times the normal working pressure; the frequency of hydrostatic test may be determined by analysis of the results on instrument studies of rate of thinning of the container walls, by measurement of container wall thickness by drilling or metallurgical study of plugs, and by experience. Once set, the hydrostatic testing schedule should be rigidly followed. Plans should be made in advance with operations so that production schedules can be arranged to fit.

Hydrostatic testing is normally done with water, but if water is incompatible with the use of the vessel, other nonhazardous inert liquids may be used—never air or other gas. The only time that gases may be used for pressure testing is when use of liquids is *not* feasible, and then only when the vessel is barricaded to protect personnel and property from missiles and blast force in case of rupture. The gas pressure in a vessel acts as an energy spring which will impel missiles at high velocities. Liquid pressure in a vessel drops instantly to zero on failure of the container.

There is no need to hydrostatically test pipe and certain equipment used for noncritical services, unless failure can expose personnel to injury. No hydrostatic testing program is better than its control. Adequate card files on each piece of equipment, adequate scheduling

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and communications with all parties concerned are needed to make it work.

Locking and Tagging for Safeguarding Personnel

While details vary from plant to plant, safe maintenance requires that no one may work on (or where exposed to) power-driven equipment without locking out or physically disconnecting the source of power beforehand.

This may be done either by (1) locking the electric switch on the power circuit (not the starting circuit) in the off position, (2) disconnecting the motor electrically or mechanically (3) by removing the belt drive or (4) locking feed valves to prime movers in the "off" position and blocking movement of pistons, crank arms, or fly-wheels. Any exceptions, such as adjusting glands and seals, must be approved by supervision.

Written procedures should be prepared and thorough training given in their use. In general these procedures will stress:

Operating supervision must first identify the equipment and equipment controls.

Operating supervision and each person who is to work on the equipment go to the controls and individually place their locks on the controls after they have been placed in the off position. Each person keeps the key to his own lock.

The equipment is rechecked then to be certain that it cannot be started. Work on it can then be commenced.

When the work is completed, the reverse procedure is completed before turning the equipment back to operating supervision.

When electric motors are disconnected, the switch box is still locked with the switch in the open position.

In large scale mechanical jobs where numerous men and crafts are concerned with the same equipment, most plants permit a "group lock-out" where only the mechanical foreman's lock is placed on the switch, and each mechanic places his individual tag on the lock. Only the mechanic can remove his own tag, and the foreman will not remove the lock until all tags are accounted for.

Whenever electricians work on electrical circuits or equipment, the same procedures can be followed unless testing or other work involving energizing the circuit is required. In these cases, after proper identification of the equipment and circuits by operating supervision, the

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circuits and equipment are turned over to the electrician, who affixes his "blocking out" tags to the control points. No one but this electrician can operate any controls after that until he removes his tags. As an additional safeguard, the electrician will lock the switch box during periods when his work will permit.

Similar principles should be followed in doing work on pipelines or piping systems, with the valves tagged and locked if possible. All lines should be disconnected and blanked if practicable.

Disposal of Chemically Contaminated Equipment

It is the responsibility of operating supervision to see that all equipment leaving the area is clean to a point where an employee, untrained in the hazards of corrosive, toxic, or flammable materials, can work on it safely. All equipment that is removed from service should be tagged immediately as to its state of chemical contamination, and the tag changed as conditions change. When it is clean it should be so tagged. Otherwise, there is always the danger someone may assume it is clean, and either move it or work on it. Obviously, it is impractical to decontaminate equipment before dismantling in many cases. In such cases cleaning and decontamination should be accomplished if possible before removal from the area. If it cannot be decontaminated at the area, it must be handled separately on a planned basis and taken to an adequate salvage area where it can be worked on. Each job may have to be individully studied and planned from a decontamination standpoint.

Among the details to remember is that it is important to give special attention to prevent pipe and valves from being discarded with materials trapped in them. They can become bombs. All valves should be cleaned, the bonnet should be loosened, and the gate opened before being discarded. Pipe may be heated at a burning ground. Flammable liquid wastes should not be allowed to reach drainage ditches or sewers. Glass should be handled separately from other waste materials. Other special problems will be apparent on detailed consideration. The important point is not to leave this phase of the maintenance work to chance.

Emergency Maintenance

Emergency maintenance should more properly be termed emergency repairs, since maintenance implies preventing emergency repairs. However, some emergencies do occur, and we must be prepared to meet

them. In general, day-to-day maintenance procedures will meet the situations arising, but some special problems require additional planning to meet. For example, what do we do if a pipe connection breaks off a chlorine tank? The time to plan to take care of it is in advance, not after it happens. Considering this case, special clamp fittings can be made in advance and kept in an emergency kit with supplementary equipment to meet just such an emergency. Suppose a sulfuric acid pipeline ruptures. Planning shut down, wash down, and repair activities in advance will make it possible to take such mishaps in stride with minimum exposures to personnel and property. The key point is to "brainstorm" such incidents, decide in advance who should do what, with what, and line it up so that it can be accomplished if it happens.

How about rupture of an underground pipeline? How are we going to handle the shut down? Who will be available to excavate? How will we flush out the broken pipe? How can it be plugged to keep it clean while the excavation is being pumped out? Are emergency sleeves suitable? Are they available? How about pipe stock?

What do we do when an electric line fails? Do we have alternate routes of supply? Where are the switching facilities? What effect does loss of power have on emergency shut down of operations? These are all typical problems of emergency maintenance for which solutions can and should be planned in advance.

There is one principle to adhere to in emergency maintenance. If it is not safe to do it a certain way under normal maintenance, then it is doubly unsafe to try that way under emergency conditions. A reasonably safe method can be found if we really try. If it is not safe to do electrical hot work under normal conditions, then it should be even more strongly forbidden during emergencies.

Equipment Inspection and Maintenance

Hand Tools. Several books could be written on ways in which hand tools can deteriorate into an unsafe condition; suffice to say the pipe wrench with dulled jaws has injured more mechanics than the most spectacular explosions. Mushroomed chisel heads, cracked or bent wrenches, faulty hammer and screw-driver handles, and poor chisel and screw-driver blade condition are all too common. We can meet these hazards only by special effort to educate our mechanics to keep their tools up to standard, and by making sufficient tool inspections to know that they are kept that way. Doing it after the injury helps, but periodic checking is better. A check list is desirable.

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Ropes, Slings, Chains, and Hoisting Equipment. Because the danger of failure presents unusually severe safety hazards, and because of the high wear factor, periodic inspection at a central point, with good record control, is a must for proper maintenance of ropes, slings, chains, and hoisting equipment. This includes life lines and life belts. Inspection for defects seems the best procedure in most cases. Overloading for test purposes in itself may cause failure later on the job. However, tests up to rated capacity may uncover hidden defects. Because of wide variation of deteriorating exposures, no rules can be given for frequency of inspection and test, but it pays to err on the conservative side. There is a wealth of material available from suppliers on safe use and maintenance of this equipment which can be used to advantage.

For example, synthetic fiber ropes may be much less subject to chemical attack and therefore give longer life with a greater margin of safety—but the user should allow for their being smoother and hence they provide him with less hand grip.

Ladders. Ladder failures during use usually result in falls and injuries—therefore they must be prevented. Standards for their purchase should be established. Use only the stronger industrial grade ladders, even if cheaper ones will pass American Standards Association standards. They give greater margin of safety against abuse and wear. The length of ladders permitted should be spelled out in standards. Ladders should be carefully inspected by trained personnel, including hammer testing, and the inspection dates as well as ownership should be marked on each ladder. Strays have a way of developing among ladders. Many plants inspect each ladder annually, others more often.

Supervision of Maintenance Personnel

Supervision of maintenance workers presents special problems of its own from a safety standpoint, but these problems are capable of solution. Because of the changing work locations and assignments, mechanics are usually "on their own" more than chemical operating or laboratory people. It requires more effort on the part of maintenance supervision than in the case of other groups to know how their men are performing, but it can and must be done. Sampling techniques applied to observation can be used because continuous observation is impractical. However, the setting of standards of performance in maintenance work and the training of men to achieve these standards is no more difficult than in other work groups. The same management

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principles apply. We have to know the capabilities and characteristics of each man, and give him guidance where he needs it so that he can reach his highest potential. Management tools of communication commonly effective are daily short "tail gate" or "tool box" meetings, scheduled individual contacts on safety subjects, scheduled inspection of work in various stages of completion to observe work techniques, condition of tools and equipment, and housekeeping.

In summary, good maintenance prevents accidents, by use of careful well-planned preventive maintenance, planning for emergencies, and day-to-day good techniques in management of men.

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28

Fire Extinguishing Agents and Their Applications

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28.1. INTRODUCTION

In recent years there have been increasingly rapid developments both in the field of fire extinguishing agents and fire extinguishing equipment. Simultaneously new and unusual fire hazards have also been increasing. These developments have made it difficult for persons concerned with fire protection in the chemical industry to make knowledgeable decisions as to what should be used to adequately provide needed fire protection. This chapter is intended to provide information that is not otherwise readily available to the director of industrial plant protection.

Where the word "approved" is used in this chapter, it refers to materials or devices listed as suitable after examination and test by the Underwriters' Laboratories, Inc., Underwriters' Laboratories of Canada, or the Factory Mutual Laboratories.

28.2. CLASSIFICATION OF FIRES

Fires are commonly divided into four basic classifications according to the nature of the combustible material.[16] However, there are different types of fires within each classification. For example, flam-

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mable liquids may be in depth, flowing (sometimes escaping under pressure), or in relatively thin layers, as in a spill fire. Metals can be in powder form, chips or turnings, ingots or castings.

Class A Fires

Normally Class A fires are defined as "fires in ordinary combustible materials such as wood, cloth, paper, etc.," all of which produce glowing embers as the result of the formation of carbonaceous material such as charcoal. Usually overlooked is the fact that charcoal itself is a Class A material which requires special consideration, because under certain circumstances neither water nor bicarbonate-base dry chemicals are effective extinguishing agents, as will be discussed later. Also, rubber, rubber-like materials, and certain plastics are in the early stages of combustion burning more like Class B materials, but in the latter stages are definitely Class A materials.

Class B Fires

Normally, Class B fires are defined as "fires in flammable petroleum products or other flammable liquids, greases, etc." However, there are certain solids, of which naphthalene is an excellent example, which melt while burning and exhibit all of the characteristics of a flammable liquid fire and have no embers. In recent years, metal alkyls have been found more frequently in the chemical industry, and these flammable liquids present special problems because of unusually low autoignition temperatures and, in some cases, violent reactivity with water.

Technically, at the present time flammable gases do not fall in any fire classification category, but practically they should be treated as Class B materials. For many years it has been common practice to recommend against extinguishing fires in escaping gas because it was felt that if the flames were extinguished the gas would continue to flow to form an explosive mixture which might become later ignited and cause greater damage than if the original fire had been allowed to burn. Practical experience, however, has shown that in some cases it is necessary to extinguish the flames in order to stop the escape of gas. Gases normally stored in liquid form, such as propane and vinyl chloride, present a more difficult fire when escaping in liquid state than when escaping in gaseous state.

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Class C Fires

Class C fires are defined as "fires involving energized electrical equipment where the electrical nonconductivity of the extinguishing media is of importance." Where the electrical equipment is de-energized, extinguishing equipment suitable for use on Class A fires may be used unless flammable liquids such as transil oil are involved. In the latter case extinguishers suitable for Class B fires should be employed. If a combination of Class A and Class B fire materials are involved, either water spray or multipurpose dry chemical should be used as the extinguishing agent.

Class D Fires

Class D fires are defined as fires in combustible metals. Low melting point metals such as sodium and potassium present problems in extinguishment because the fire soon involves only liquid metal which, being of low specific gravity, allows most extinguishing dry powders to sink through while the liquid metal is constantly exposed to the air. These metals also offer problems in that they spontaneously react with water, sometimes violently.

High melting point metals are found in a variety of forms: powder, chips and turnings, sheet, ingots, castings, and extrusions. An extinguishing agent that might be entirely suitable for use on fires in castings might be hazardous to use on powder, or chips and turnings. A very common combustible metal, magnesium, is unusual in that it falls between the extreme low melting point metals and the high melting point metals so that it is found in all of the solid forms listed but also melts quite readily while burning to form liquid magnesium.[22]

Although the fumes from any burning metal should not be inhaled, the fumes from burning radioactive metals present extremely serious health hazards to fire fighters. Otherwise, the problems of extinguishing fires in radioactive metals are similar to those encountered in the extinguishment of fires in nonradioactive metals.

When *dry* metal hydrides are burning, they should be considered equivalent to metal fires because both hydrogen and metal are burning. It is desirable to use dry powder metal fire extinguishing agents on such fires.

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28.3. EXTINGUISHING AGENTS AND METHODS OF APPLICATION

Water and Water-based Extinguishing Agents

PORTABLE FIRE EXTINGUISHERS

In this discussion soda and acid fire extinguishers and calcium chloride solution antifreeze fire extinguishers are considered as equivalent to those containing plain water because the chemicals do not increase the fire extinguishing effectiveness. Although loaded stream fire extinguishers are also antifreeze extinguishers, this type of extinguisher is discussed separately because of its greater extinguishing effectiveness on Class A fires and because it has a small degree of effectiveness on Class B fires.

Fire extinguishers containing water, calcium chloride antifreeze solutions, or soda and acid solutions are effective on Class A fires and on fires in wood soaked with oils or greases.

These extinguishers are approved in capacities from 1¼ gal to wheeled 33 gal sizes. The water or water solutions are expelled from the extinguishers by a manually operated pump (pump tanks), by carbon dioxide from the chemical reaction of sodium bicarbonate solution and sulfuric acid (soda-acid extinguishers), by carbon dioxide from cartridges (cartridge-operated extinguishers), or by air stored under pressure in the same chamber with the water or water solution (stored-pressure extinguishers). All of these extinguishers are equipped with a hose and a nozzle designed to throw a solid stream for distances ranging from 30 to 50 ft.

SODA AND ACID EXTINGUISHERS

All soda and acid extinguishers are put into operation by first inverting to allow the acid to mix with the sodium bicarbonate solution so as to react to form carbon dioxide. Because sodium bicarbonate in solution loses carbon dioxide as it slowly converts to sodium carbonate, these extinguishers should be recharged annually in order to insure that there will be a sufficient quantity of expellant gas produced when the solution is mixed with acid. Soda and acid extinguishers must be protected against freezing.

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WATER

Water cartridge-operated extinguishers are pressurized by inverting and bumping on a firm surface in order to puncture the seal of the cartridge and release the pressurizing carbon dioxide. Pump tanks and stored-pressure water extinguishers are operated while in the upright position. These extinguishers must be protected against freezing.

ANTIFREEZE EXTINGUISHERS

Calcium Chloride. Calcium chloride antifreeze solution cartridge-operated extinguishers are pressurized by inverting and bumping on a firm surface in order to puncture the seal of the cartridge and release the pressurizing carbon dioxide. Pump tanks and stored pressure extinguishers of this type are operated while in the upright position.

Because calcium chloride antifreeze solution is corrosive, approved extinguishers in which it is used are constructed of corrosion-resistant materials. Approved stainless steel extinguishers are not resistant to the corrosive effects of calcium chloride solution and it should never be used in these extinguishers. These extinguishers are suitable for use down to temperatures of −40°F.

Lithium Chloride. An antifreeze extinguisher using a solution of lithium chloride, and suitable for use to temperatures as low as −65°F, has been developed by the United States Department of Defense.[1]

Loaded Stream. The chemicals in water solution discussed so far have not increased the extinguishing effectiveness of the solutions. They served only to produce carbon dioxide as an expellant gas or to lower the freezing point. Other chemicals when added to water increase the extinguishing effectiveness and the best known of the extinguishers of this type is the "loaded stream extinguisher."

The extinguishing agent of a loaded stream extinguisher is a solution of potassium carbonate in water with other additives to reduce the freezing point to −40°F. These extinguishers are available in capacities from 1 to 33 gal. The older extinguishers of this type were operated by inverting which mixed acid with the potassium carbonate to form carbon dioxide expellant gas. Later models used carbon dioxide cartridges for the storage of carbon dioxide gas and were operated by inverting and bumping to puncture the cartridge seal and release the gas. More recent models have been of the stored

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pressure type in which air under pressure in the same chamber as the loaded stream solution expels the latter when a valve is opened with the extinguisher in the upright position.

In addition to depressing the freezing point to −40°F, the loaded stream solution improves the extinguishing effectiveness to the extent that 1¾ gal of loaded stream solution is given a 2-A rating by the Underwriters' Laboratories—which is obtained only by 2½ gal of plain water, soda and acid solution, or calcium chloride solution. A 2½ gal loaded stream extinguisher is given a 1-B rating by the Underwriters' Laboratories. On Class B fires, the loaded stream solution is most effective when applied in the form of spray. Rather specialized techniques are required to extinguish fires in volatile flammable liquids with loaded stream extinguishers.

Loaded stream solution should be used only in extinguishers in which its use has been approved. Other extinguishers may not be resistant to the corrosive effects of potassium carbonate, corrosion may impair the operating mechanism or weaken the shell and hazardous rupture of the extinguisher could result.

Ethylene Glycol. Some owners of water extinguishers have used ethylene glycol to reduce the freezing point because their extinguishers are not designed for the use of calcium chloride or loaded stream solutions. It requires 50% by volume of ethylene glycol with water to obtain a freezing point of −40°F. It has been observed that if such a solution completely controls a fire it is equal to water in extinguishing effectiveness. However, if complete control of the fire is not obtained prior to the exhaustion of the extinguisher, the water will be easily evaporated, and the fire will rekindle to become more intense because the ethylene glycol is a flammable liquid. It has also been stated that antifreeze agents of the ethylene glycol type may contribute to corrosion at the weld joints of stainless steel extinguishers. Such corrosion could result in either leaks or hazardous rupture of the extinguisher shell.

Wet Water. For certain purposes the extinguishing effectiveness of water may be improved by the addition of a wetting agent. A wetting agent is a compound which, when added to water in proper quantities, increases its penetrating and spreading abilities. Certain wetting agents in water solution will produce "wet water foam" when mixed with air by nozzles similar to those used in the production of mechanical foam. Wet water streams and wet water foam streams are both effective on Class A fires and wet water foam is effective on Class B

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fires of the hydrocarbon type, such as gasoline, but should not be used on fires in flammable liquids soluble in water, such as alcohol.

Depending upon the wetting agent, wet water streams sometimes can be used to emulsify certain flammable liquids thereby achieving extinguishment.

Experience has indicated that Class A fires can be extinguished by wet water in a shorter time and with less water than if plain water had been used. Wet water, because of its penetrating power, is particularly effective on fires such as those in baled cotton or stacked hay.

Not all materials that can be called "wetting agents" are suitable for fire protection purposes. Although NFPA No. 18 "Standard for Wetting Agents"[21] gives detailed information on wetting agent specifications and tests, the average person responsible for fire protection will find it best to use only those wetting agents listed by the Underwriters' Laboratories. Listed wetting agents are no more corrosive than plain water to steel, brass, bronze, or copper. Wet water should be used only in extinguishing equipment or storage tanks designed for such use since listed wetting agents, although noncorrosive, exhibit a tendency to accelerate corrosion because of the cleaning and penetrating action and will penetrate and loosen unbonded coatings. For continuous storage, even galvanized iron or lead coated iron are not suitable. Approved wheeled wetting agent extinguishers are available in capacities from 10 to 50 gal.

WATER SPRAY ("FOG")

The more effective use of water in the form of drops rather than a solid stream was first practically recognized in the installation of the perforated pipe extinguishing systems that preceded the automatic sprinkler systems (1864).[12] The value of spray nozzles on hose lines was recognized in the latter part of the nineteenth century, but it was only in the 1930's that hose-spray nozzles began to be used to an important extent by both public and industrial fire departments. It was also in the 1930's that special spray, or "fog," nozzles were developed for installation in systems. These spray nozzles produced directed streams of drops of water much smaller in size than those produced by the automatic sprinklers of that time. An automatic sprinkler improved in design to produce more finely divided drops of water in a better regulated pattern than the older automatic sprinklers was first used in 1952.[3]

In general, water spray may be used effectively for any one or any combination of the following purposes: extinguishment of fire,

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control of fire, exposure protection, or prevention of fire.[19] The short range of spray nozzles is not a factor where the nozzles are installed on a well-engineered system but the short range imposes a definite limitation on the effective use of spray nozzles on hose lines. The droplet size is related to the range of the streams from spray nozzles, the heavier drops traveling farther than the very fine drops. A considerable number of carefully controlled tests with portable spray nozzles have been run to determine the effect of nozzle pressure and droplet size on the control and extinguishment of both Class A and Class B fires.[15, 13, 25, 9] The conclusions drawn from the results of the tests may be summarized briefly as follows:

1. Increasing the nozzle pressure beyond 100 psi results in little or no increase in fire extinguishing effectiveness.
2. Very fine droplets tend to evaporate before reaching the seat of the fire and therefore control, but do not always extinguish the fire. On Class B fires, droplets having diameters of 100 to 150 microns are considerably more effective than droplets having diameters in the order of 300 microns, but the very fine droplet may evaporate before reaching the surface of the burning liquid which will therefore not be cooled.
3. Although coarse drops of spray do not evaporate as readily as very fine drops, the unevaporated portion of the coarse drops penetrates the flame zone to reach the seat of the fire and exert cooling action.

Where approach to the fire permits, portable water-spray nozzles are considerably more effective on Class A fires than straight streams because the water is applied with less run off. British tests showed that a spray gave more rapid control of a fire than a straight stream and that when straight streams were used more water was required to extinguish the test fires. Although very small gasoline fires can be extinguished under certain conditions by the use of water-spray nozzles, the latter are usually successful only in extinguishing flammable liquids having flash points of 150°F or higher.[3]

Electrical equipment involved in a fire should be de-energized as quickly as possible, but it is not always possible to do so. Even so, either fresh or salt water may be safely applied to energized electrical equipment if the following clearances between nozzles and electrical apparatus are observed or exceeded. (See Table 28.1.)

Spray nozzles, either on hose lines or in systems, are sometimes used only to control fires where extinguishment is not possible or extinguishment is not desired because the fire is in flammable gases or extremely volatile flammable liquids. Sometimes such fire control is combined

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TABLE 28.1. Table of Clearances[19]

Voltages	*Distances*
Up to 7,500	6 in.
7,500 to 15,000	12 in.
15,000 to 25,000	17 in.
25,000 to 37,000	24 in.
37,000 to 50,000	32 in.
50,000 to 73,000	44 in.
73,000 to 88,000	52 in.
88,000 to 110,000	64 in.
110,000 to 132,000	77 in.
132,000 to 154,000	89 in.
154,000 to 187,000	106 in.
187,000 to 220,000	124 in.

with the protection, by cooling, of exposed equipment, structures, or storage tanks.

Spray nozzle systems installed for extinguishment, control, or exposure protection may also sometimes be used for the prevention of fires if operated when hazardous materials have been accidentally released but before they have become ignited.

As a guide to the quantities and rates of application of water in spray form the following may be used:

(*a*) Extinguishment —0.2 to 0.75 gpm/sq ft
(*b*) Control —0.2 to 0.5 gpm/sq ft
(*c*) Exposure protection—0.2 to 0.25 gpm/sq ft

Water spray systems should be designed by experienced fire protection engineers to insure adequate protection for the hazard involved.

SOLID STREAMS OF WATER

When water-spray streams cannot practically be used because of lack of reach because of fire intensity or fire location, or where there are dangers from falling walls or possible explosions, solid streams must be used. Solid streams are, of course, used primarily in the extinguishment of Class A fires—structures, lumber storage, and so on. However, they are also used for the extinguishment of fires in high flash point Class B materials in thin layers or fires in flammable solids such as naphthalene. Solid streams are also used for the protection of exposed equipment, structures, and storage tanks when such protection

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is not afforded by spray-nozzle systems and are out of reach of water spray from hose lines.

Effective streams are the result of advance planning to insure adequate water supplies, of proper layout of water mains, and of training of the fire fighters to make best use of hydrants, hose, nozzles, and pumpers, if the latter are available. One of the best books for industrial and volunteer fire fighters, as well as large paid departments, is *Effective Streams for Fighting Fires* by Warren Y. Kimball, National Fire Protection Association. Other helpful information may be found in *Mobile Fire Equipment, Organization, Management,* National Fire Protection Codes, Volume VII, National Fire Protection Association. Information on water supplies and the layout of mains and hydrants may be found in *Fixed Extinguishing Equipment,* National Fire Code, Volume IV, and in the NFPA *Handbook of Fire Protection.*

Although no reports are yet available as to practical use, research is being carried on at Syracuse University for the United States Navy Bureau of Yards and Docks on *Additives to Improve the Fire-Fighting Characteristics of Water.* This research is aimed at evaluating the effectiveness of increasing the viscosity of water to decrease the rate of run-off and of increasing the opacity of water to transmission of infrared. It has been reported that the addition of opacifiers such as aluminum and bronze powders to water, increased in viscosity by certain chemical additives, has decreased the extinguishing time on certain standard fires to below that required for plain water.

Foam. There are two types of fire fighting foams: chemical foam in which the bubbles are filled with carbon dioxide, and mechanical foam in which the bubbles are filled with air. Chemical foam is produced by a chemical reaction which generates carbon dioxide bubbles in water solution containing a foaming ingredient. The reacting chemicals, usually sodium bicarbonate and aluminum sulfate, may be stored in separate water solutions, which are mixed when foam is wanted, or in powder form in separate containers and simultaneously mixed with water to form foam, or in powder form in a single container and mixed with water to form foam.

Portable chemical foam extinguishers all employ two solutions which are mixed when the extinguishers are inverted. Although chemical foam is used almost exclusively for the protection of Class B fire hazards, the Underwriters' Laboratories gives portable foam extinguishers Class A ratings equal to those given water extinguishers of the same volumetric capacity.

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Chemical foam solutions should not be exposed to temperatures lower than 40°F nor higher than 120°F. The sodium bicarbonate solution is especially sensitive to temperature conditions, the sodium bicarbonate crystallizing out of the water if the solution is frozen and decomposing to lose carbon dioxide when the solution is at temperatures exceeding 90°F. Annual recharge of portable foam extinguishers compensates for normal deterioration of the sodium bicarbonate solution.

However, chemical foam itself is also sensitive to the effect of temperature. At low temperatures the chemical reaction takes place more slowly and the foam has a lower expansion ratio as compared with the approximate ratio of eight found at normal ambient temperatures. At high temperatures the chemical reaction takes place rapidly, there is a high expansion ratio, and the foam breaks down more rapidly.

Approved hand portable chemical foam extinguishers are available in capacities of 1¼ to 5 gal, with the latter size intended primarily for use in industrial establishments where persons of ample strength will handle it. Approved wheeled extinguishers are available in capacities of 17 and 33 gal. The hose of these larger extinguishers are equipped with shut-off nozzles.

Stream ranges are in the order of 30 to 40 ft for hand portable extinguishers and up to 50 ft for wheeled extinguishers.

MECHANICAL (AIR) FOAM

Mechanical foam is produced by mixing air with a dilute solution of a liquid foaming agent in water. The air is mixed with the water solution by aspiration into a foam maker or by means of a specially designed pump. The liquid foaming agent is available in two concentrations: one intended for mixing in water to a 3% concentration and the other intended for use in 6% concentration.

Mechanical foams are classified by expansion ratios, that is, the gallons of foam produced per gallon of water-foaming agent solution mixed with air. The most common is low-expansion foam having an expansion ratio of 7 to 12. High-expansion foam has a ratio of 16 to 18.

A special, and less common, category of mechanical foams is the wetting agent type which is approved for use on Class A fires and, when having an expansion ratio of 8 to 10, is approved for Class B fires. There is also what might be called "super-high expansion" foam having an expansion ratio of 1000. This foam is produced by blowing

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air through a mesh kept wetted by a water solution of detergent with foam agent.

A foam agent introduced in 1964 contains a fluorochemical surfactant that creates a film over the surface of fuels similar to gasoline and thereby retards reignition even after the foam layer has broken down.[31] The foam is completely compatible with military specification potassium bicarbonate-base dry chemical. Tests with developmental equipment have indicated that the new agent, referred to as "light water," is approximately four times more effective than mechanical foams when used for the extinguishment of spill fires.

Ordinary mechanical foam concentrates should be stored at temperatures of 20°F or higher as specified by the concentrate manufacturer. Special "low-temperature" concentrates are available and these concentrates may be stored at temperatures as low as −20°F. Concentrates producing mechanical foam suitable for use on alcohols and ketones should be stored at 35°F or higher. However, no mechanical foam concentrate should be stored at temperatures higher than 120°F.

Although chemical foam is not affected, ordinary dry chemical causes mechanical foam to break down, the degree of breakdown depending to some extent on the formulation of the foam concentrate. However, there are special dry chemicals which have been examined and tested by the Underwriters' Laboratories and found suitable for use with mechanical foams which are designated by the Underwriters' Laboratories as "compatible for use with listed foam-compatible dry-chemical Extinguishers."[32] These compatible concentrates are generally 3 and 6% solutions of regular- and low-temperature concentrate. The foam concentrates for producing mechanical foam for use on alcohol and ketones are not compatible with foam-compatible dry chemical.

There are no approved portable extinguishers that produce mechanical foam although such extinguishers are used in Europe.

SYSTEMS

Hose Line Systems. Chemical-foam hose streams are almost invariably straight streams. The nozzle throat size is much larger than that commonly used with water. If the manufacturers recommend unavailable nozzle sizes, it is best to remove the tip from the play pipe and use the full 1¾ in. opening. Although it is possible to operate a chemical-foam generator with water pressure of 50 psi at the inlet, the inlet pressure should be between 75 and 125 psi. The back pressure at the discharge side of the generator should not exceed 40% of the

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generator inlet pressure. With a single powder generator it is best not to have more than 50 ft of hose between the generator outlet and the nozzle. With a dual hopper chemical foam generator using the separate powders, longer lines can be used between the generator and the nozzle as long as the back pressure is not in excess of 40% of the generator inlet pressure.

Mechanical foam hose streams are of two types: one in which the water and foam concentrate are mixed in the proper proportions before entering the hose line and air is aspirated to make the foam in the play pipe, and a second type in which the foam is made with a special pump and the foam itself moves through the hoseline. In the first case the length and size of hose are not important as long as the pressure at the nozzle is not less than 50 psi. However, when the foam is pumped through the hose the length and size of the hose becomes much more important and the manufacturers' recommendations should be closely followed. Mechanical-foam hose nozzles are available in a variety of types to produce straight streams or spray streams.

Fixed Nozzles Systems. Two-solution foam system equipment is in modern practice of limited capacity and intended primarily for the protection of small industrial hazards. Foam powders are generally used for extinguishing fires in large flammable liquid storage tanks. The dual powder system has the advantage of allowing longer runs of pipe between the point of introduction of the powders into the water streams and the protected tank because mixing of the two resulting solutions takes place at a foam-mixing chamber mounted on the tank. However, the dual powder system has the disadvantage of requiring more manpower than the single powder system.[3] Chemical foam is best made from solutions of water in the temperature range of 50° to 90°F.

Foam systems are used for the protection of specific Class B hazards where the quantity of water, the quantity of foam-producing agent, the rate of application, and the number of outlets can be predetermined. The type and the location of foam outlets for the protection of flammable liquids in depth are related to the rate of application of foam and the quantity of foam-producing material required because foam is more effectively applied if there is a minimum of submergence of the foam and a minimum of agitation of the surface of the flammable liquid.

On indoor hazards such as dip tanks foam is applied from fixed nozzles located along the edge of the tank or from pendant nozzles

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arranged overhead. On outdoor vertical storage tanks discharge outlets are sometimes supplemented with means for delivering foam onto the surface of the burning liquid without undue submergence or undue agitation of the surface of the liquid. This may be accomplished by a Moeller tube which is designed to unroll and fall to the flammable liquid level and which permits the foam to flow through the coarse mesh of the tube, or by a foam trough attached to the inside of the tank wall to form a descending spiral to within 4 ft of the bottom, or by a foam chute which is a delivery conduit within the tank with staggered openings so that the foam is delivered onto the surface of the flammable liquid from the opening just above the surface. When such methods of delivering foam are not provided, the amount of foam-producing agent required for extinguishment should be doubled.

Foam has been applied to vertical storage tanks to a limited extent by injecting the foam below the surface of the flammable liquid. This is called "subsurface application." A discussion of this method of application will be found in the April, 1946 *Quarterly of the National Fire Protection Association.*

Because foam is broken down by the heat of the fire and, to some extent, by the flammable liquids to which it is applied, the rate of application must be sufficiently high to offset the breakdown and to cover the flammable liquid surface to an adequate depth in a reasonable period of time.

Although the following discussion of rates of application and quantities required is based on water or water-foam agent solution, not foam, the intent of the recommendations is that a 6-in. blanket of foam be formed on localized inside hazards such as dip tanks and a 4-in. blanket of foam be formed on the surface of flammable liquids in outdoor storage tanks.

A foam system for a localized inside flammable liquid hazard should be designed to have an application rate of 0.16 gal/min/sq ft of flammable liquid surface and a sufficient quantity of foam-producing material to insure that foam is applied for not less than 3 min.

On outdoor storage tanks, the minimum rate of application should be 0.10 gal/min/sq ft of flammable liquid surface but should be considerably higher, even doubled, where very volatile materials (such as casing-head gasoline) or water soluble solvents are protected. If hose streams are used, the minimum recommended rate of application is 0.16 gal/min/sq ft of surface. The quantities of foam-producing material required for systems protecting outdoor storage tanks vary widely according to the flammable liquid and the method of applying

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the foam. For example for gasoline the system must be designed to apply foam for periods ranging from 30 min to as high as 65 min depending on the method of application.

Recommendations for the foam application rates and the quantities of materials required are given in considerable detail in NFPA No. 11, *Standard for Foam Extinguishing Systems.*[17]

Foam-Water Sprinkler Systems. Foam-water sprinkler systems are installed where it is desired to protect large areas where fires may be anticipated in thin layers of flammable liquid such as spills. The foam discharge is intended to cover the area regardless of intervening obstruction, and the system should be arranged to continue automatically as a deluge type water sprinkler system after foam injection is completed. The most complete specifications for foam-water sprinkler systems can be found in Chapter 16 of NFPA 409, *Standard on Aircraft Hangars.*[24] For hangars the recommended rate of application is 0.17 gal/min/sq ft with a supply of foam agent sufficient to allow foam to be supplied for 10 min.

Foam may also be used for the prevention of ignition of flammable liquid spills by laying down a blanket which allows less hazardous handling of the spill.

Even traces of certain wetting agents may prevent the formation of mechanical foam. This becomes important when a wetting agent has been used and later replaced by mechanical foam concentrate, or wetting agent foam is applied simultaneously with mechanical foam.

Dry Chemicals

A dry chemical extinguishing agent is a finely divided powdered material that has been specially treated to be water repellent and capable of being fluidized and free-flowing so that it may be discharged through hose lines or piping when under expellent gas pressure. The major components of three types of dry chemicals used in approved extinguishers are sodium bicarbonate, potassium bicarbonate, and ammonium phosphate (usually monoammonium phosphate).

TYPES OF DRY CHEMICALS

Sodium Bicarbonate-base. The use of sodium bicarbonate as the major component of a dry chemical extinguishing agent, expelled by gas pressure from an extinguisher, started in Germany in 1912. About 1926, the forerunner of the modern dry chemical extinguisher

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was first produced in the United States. The dry chemical extinguishing agent consisted of a fairly coarse sodium bicarbonate powder compounded with magnesium stearate to produce water repellency and free-flowing properties. In 1943 it was found that the extinguishing effectiveness of dry chemical could be greatly increased by using more finely divided sodium bicarbonate and later improvements in the method of applying the dry chemical stream to increase effectiveness even further, resulted in this type of fire extinguisher becoming of great importance as first-aid equipment for Class B fires.

In 1930 the effectiveness of dry chemical in quickly reducing the intensity of flames was recognized, even on Class A materials. It was also known that it would be advisable to follow up with the application of water to extinguish remaining smoldering embers. Improvements in agent and improvements in equipment resulted in recognition by the Factory Mutual Engineering Division in 1948, after a very thorough test program, that dry chemical extinguishers were preferable for use in cotton processing areas.[4] In 1952, extinguishers containing sodium bicarbonate-base dry chemical were submitted to the Underwriters' Laboratories for test on Class A fires. Although flames were more rapidly reduced in intensity when dry chemical was used, as compared with water, it was found that there was a greater tendency to reflash in a shorter period of time and the extinguishers were not approved.

Potassium Bicarbonate-base Dry Chemical. Recognition of the great effectiveness of dry chemical extinguishers resulted in increased research and development on powdered extinguishing agents other than those of sodium bicarbonate-base. The extinguishing effectiveness of potassium bicarbonate-base dry chemical on gasoline fires was first investigated by the Naval Research Laboratory and they reported in 1958 that this type of dry chemical was twice as effective as sodium bicarbonate-base dry chemical.[26] This work resulted in a military specification for the foam compatible potassium bicarbonate-base dry chemical which is now being used in Naval Air Stations in place of sodium bicarbonate-base foam compatible dry chemical.

Potassium bicarbonate-base dry chemical extinguishers were first approved in 1961 by the Underwriters' Laboratories. The results of their tests, as shown in Table 28.2, confirmed the high extinguishing effectiveness reported in 1958 by the Naval Research Laboratory.

Despite the greater effectiveness of potassium bicarbonate-base dry chemical on Class B fires, the chemical similarity between sodium

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TABLE 28.2. Comparative Effectiveness of Sodium Bicarbonate-Base and Potassium Bicarbonate-Base Dry Chemical Fire Extinguishers (Based on Underwriters' Laboratories Listings)[32]

	Ratings for Class B and C Fires	
Nominal Charge lb	*Potassium Bicarbonate-base*	*Sodium Bicarbonate-base*
2⅝	8B:C	6B:C
4¼	16B:C	—
4¾	—	10B:C
75	—	80B:C
125	160B:C	—
300	240B:C	—
350	—	160B:C

bicarbonate and potassium bicarbonate indicates that the latter would be basically similar in effectiveness on Class A fires.

Foam Compatible Dry Chemicals. The United States Air Force in 1950 evaluated sodium bicarbonate-base dry chemical as an extinguishing agent for aircraft crash fires. Although the agent was found suitable from an extinguishing standpoint the metal stearate treatment of dry chemical caused rapid breakdown of mechanical foam blankets. A good solution to the problem of foam compatibility of dry chemicals was not reached until water repellency and free-flow characteristics were obtained by coating the particles of dry chemical with a silicone polymer instead of a metal stearate.

Impetus to the solution of the problem of foam compatibility was given by the promulgation of a United States Coast Guard regulation that marine-type dry chemical fire extinguishers over 5 lb in capacity must contain foam compatible dry chemical if manufactured after January 1, 1962.[6]

The first standard for evaluating the foam compatibility of dry chemical agents was developed by the Naval Research Laboratory and incorporated in a military specification in 1956.[27] The Underwriters' Laboratories Incorporated developed a different procedure for the evaluation of foam compatible dry chemicals in 1961. The degree of foam compatibility required by the Underwriters' Laboratories Incorporated is greater than that required to meet the military specification. However, dry chemical meeting the military specification has been in use for several years and under practical fire fighting conditions has been found to be adequately foam compatible.

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Multipurpose Dry Chemical. The newest of dry chemical extinguishing agents is the so-called "multipurpose" dry chemical that is approved for use on Class A, B, and C fires.

In 1956 multipurpose dry chemical was being used in Germany but this material was of poor quality. It had limited effectiveness on both Class A and Class B fires and a pronounced tendency to cake. In 1960 the Underwriters' Laboratories Incorporated approved for the first time a multipurpose dry-chemical fire extinguisher which used an extinguishing agent based upon a patented German formula. By the end of 1961 a number of other multipurpose dry chemical extinguishers had been approved, including wheeled extinguishers. The majority of approved multipurpose dry chemical fire extinguishers are very effective on both Class A and Class B fires and also are listed as suitable for use on Class C fires. Table 28.3 shows the effectiveness of the highest rated multipurpose dry chemical extinguishers as compared with water on Class A fires and as compared with sodium bicarbonate-base dry chemical on Class B fires.

TABLE 28.3. The Effectiveness of Multipurpose Dry Chemical Extinguishers as Compared with the Effectiveness of Water and Sodium-Bicarbonate-Base Dry Chemical Extinguishers
(Based on Underwriters' Laboratories Listings)[32]

Nominal Charge		*Underwriters' Laboratories Ratings*			
		Class A		*Class B*	
Pounds	*Gallons*	*Water*	*Multi-purpose Dry Chemical*	*Sodium bicarbonate-base Dry Chemical*	*Multi-purpose Dry Chemical*
7.5	—	—	1-A	—	16-B
10	—	—	2-A	20-B	20-B
10.4	1¼	1-A	—	—	—
17	—	—	3-A	—	20-B
20	—	—	4-A	20-B	20-B
20.8	2½	2-A	—	—	—
41.6	5	4-A	—	—	—
125	—	—	20-A	—	80-B
150	—	—	—	80-B	—
275	33	20-A	—	—	—
300	—	—	40-A	—	160-B
350	—	—	—	160-B	—
558	67	40-A	—	—	—

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It is obvious that when considered on a pound-for-pound basis multipurpose dry chemical is approximately twice as effective as water on Class A fires and slightly more effective than sodium bicarbonate-base dry chemical on Class B fires.

Multipurpose dry-chemical extinguishers have certain obvious advantages where Class A fire hazards are to be protected:

1. For equivalent protection, they are lighter in weight which is advantageous where it is anticipated that women may use first-aid fire extinguishing equipment.
2. Where mixed Class A, B, and C fire hazards are involved, only one type of extinguisher is needed, and there is no chance of the wrong type of extinguisher being used on a fire.
3. Special models are approved for use as low as −65°F.
4. Where water damage is highly undesirable, such as in libraries, art museums, or other locations where there are articles or materials of high value that would be irreparably damaged by water, the multipurpose dry chemical extinguisher may furnish the best fire protection.

PORTABLE FIRE EXTINGUISHERS

Portable fire extinguishers using all three types of dry chemicals are of two general types, one in which the fluidizing and expellant gas is stored in a separate container under high pressure and released into the dry chemical container when it is wished to put the extinguisher into operation, and the other in which the expellant gas is stored in the same container with the dry chemical. Hand portable fire extinguishers of the first type have the expellant gas, usually carbon dioxide, contained in a small compressed gas cylinder commonly called a "cartridge." The expellant gas in the case of extinguishers approved for use at −65°F is nitrogen. In almost all approved extinguishers of the cartridge type, the expellant gas is released into the dry chemical container by puncturing a metal sealing disk. Some of the cartridge-operated hand portable extinguishers have the nozzle integral with the extinguisher. However, the majority are equipped with both hose and a controlling nozzle. Hand portable cartridge-type extinguishers range in capacity from 4 to 30 lb.

Wheeled extinguishers in which the gas is stored separately from the dry chemical chamber use nitrogen as the expellant gas, controlling the pressure within the dry chemical container by means of a regulator. This type of design permits the expellant gas to continue to flow

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during discharge of the extinguisher thereby maintaining a fairly constant pressure. As a result there is little change in the flow characteristics throughout the entire discharge. Wheeled extinguishers of the foregoing type range in capacity from 75 to 350 lb.

Extinguishers in which the expellant gas is stored in the same container with the dry chemical extinguishing agent are called "stored pressure" extinguishers. Although most stored pressure extinguishers are equipped with pressure gages there is one special type of approved stored pressure extinguisher that is not required to have a pressure gage. Inspection of this extinguisher requires weighing to detect possible loss of gas by leakage. This type of extinguisher is sometimes called a "sealed pressure" extinguisher because the dry chemical container must be factory filled and sealed, and is nonrefillable. Therefore it is sometimes called a "disposable shell" extinguisher.

Portable stored pressure extinguishers range in capacity from 1 to 250 lb. The smaller sizes have the nozzle integral with the control valve, but the larger sizes of hand portable extinguishers are equipped with hose, in most cases controlling the flow by means of the valve on the extinguisher, but in other cases the nozzle at the end of the hose is also to control the flow. All wheeled stored pressure extinguishers control the flow with the nozzle at the end of the hose.

Stream ranges of dry chemical extinguishers vary widely since even a single manufacturer may provide nozzles of two ranges for extinguishers otherwise identical in size and capacity. Hand portable extinguishers have stream ranges of 5 to 25 ft. Wheeled extinguishers have stream ranges of 10 to 45 ft.

HAND HOSE-LINE SYSTEMS

Dry chemical systems of the hand hose-line type range in capacity from 150 to 2000 lb. Most use nitrogen in separate cylinders for fluidizing and expelling the dry chemical, controlling the flow with regulators. Stored pressure hand hose-line systems are approved in capacities from 150 to 250 lb. It is possible to supply as many as eight hose stations from large systems but such arrangements should be engineered by the manufacturer of the equipment.

Dry chemical hand hose-line systems are generally located where it is not necessary to have the extinguishing equipment mobile, as in the case of wheeled extinguishers. A typical fire hazard protected by such systems is a petroleum-products loading rack.

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FIXED-NOZZLE SYSTEMS

Dry-chemical systems with piping and fixed nozzles are approved for both automatic and manual operation. Approved systems range in capacity from 30 to 500 lb. These systems may be used for the protection of specific hazards by local application of the dry chemical or installed so as to flood an entire room or building. The design and installation of a dry-chemical piped system should be supervised by qualified fire-protection engineers having full knowledge of the special problems of piping dry chemical to obtain the correct rate of application and the proper distribution from the nozzles. Helpful information is given by NFPA No. 17, *Standard for Dry Chemical Extinguishing Systems.*[20]

Dry-chemical piped systems are used for the protection of electrical equipment such as generators, circuit breakers, transformers, and for many other hazards where flammable liquids are involved. They have been notably successful in installations protecting asphalt impregnating equipment in the manufacture of roofing and siding. Because air dilution is not such an important factor with dry chemical, piped-system protection of duct work is quite common, and there is an increasing use of dry-chemical systems for the protection of cotton gins.

Because dry chemical is nonconductive, care should be taken in the use of dry-chemical extinguishers in locations where there are many delicate low-voltage electrical contacts, such as in telephone relay rooms.

SPECIAL DRY CHEMICAL AGENTS

Because of the flexibility allowable in composition of dry-chemical extinguishing agents, it is possible to compound free-flowing powdered materials for the control and extinguishment of fires in unusually hazardous chemicals. A typical example is an extinguishing agent for use on metal alkyl fires in which the agent is a mixture of sodium bicarbonate-base or potassium bicarbonate-base dry chemical and an activated adsorbent such as silica gel. The pyrophoric characteristics of short-chain metal alkyls such as triethylaluminum (which reacts violently in contact with water) allow extinguishment of the flames only during application of dry chemical. If application is discontinued, immediate reflash occurs. The special compound containing adsorbent

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material extinguishes the flames and at the same time the spilled metal alkyl is being adsorbed, resulting in extinguishment of the fire and allowing disposal of the now safe pyrophoric material.[33] Because of the necessity of adsorbing spilled material while controlling the fire, considerable quantities of the special agent are required. As a guide, from 8 to 10 lb of the special extinguishing agent are required for each pound of metal alkyl involved in the fire.

An alternative method of controlling metal alkyl fires is to apply an ordinary dry-chemical extinguishing agent on the flames simultaneously with the application of an activated adsorbent from a separate extinguisher. This requires that the adsorbing agent by itself possess good flow characteristics.

Other hazardous chemicals such as fluorine and chlorine trifluoride offer unusual problems when spilled, and special dry chemical agents have been used. A good reference manual is *The Handling and Storage of Liquid Propellents* issued by the Office of the Director of Defense Research and Engineering, Washington, D. C.

Approved dry-chemical extinguishing agents are not classified as toxic. Personnel of manufacturers and approval agencies have been exposed over a period of years to these dry chemicals and there have never been any ill effects reported. Persons inhaling dry chemical in high concentrations will experience discomfort because of the mechanical action of the dry material on moist mucous membranes.

Carbon Dioxide

Although the possibility of using carbon dioxide as an extinguishing agent was recognized as early as 1882[28] it was not until the 1920's that liquefied carbon dioxide came into general use for this purpose. The most important single factor in the successful development of portable carbon dioxide extinguishers was the use of an entrainment shield, or "horn," to limit the amount of air entrained by the carbon dioxide at the point of discharge.

PORTABLE EXTINGUISHERS

Approved hand portable carbon-dioxide extinguishers are available in capacities of 2 to 25 lb. The smaller sizes, 2 to 5 lb, usually have the discharge horn attached directly to the valve through a swivel connection and a metal tube. The larger extinguishers are equipped with both hose and horn. Most carbon dioxide wheeled extinguishers

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are 50, 75, or 100 lb in capacity but there is one low pressure (refrigerated) wheeled unit of ⅜ths ton capacity.

With the single exception of the ⅜ths ton unit, portable carbon-dioxide extinguishers consist basically of ICC 3A or 3AA cylinders for the storage of the liquid carbon dioxide (under a pressure of 850 psi at 70°F), a valve for controlling the flow, a horn, and either metal tubing or flexible hose connecting the horn to the valve. The extinguishers are always operated in the upright position and are provided with siphon tubes extending to close to the bottom of the cylinder so that liquid carbon dioxide is discharged from the orifice. As the liquid discharges from the orifice, within the horn, the carbon dioxide evaporates to form a mixture of gas and particles of solid carbon dioxide which forms an effective extinguishing stream as discharged from the horn.

HAND HOSE-LINE SYSTEMS

There are two types of liquid carbon-dioxide storage used for both hand hose-line systems and fixed-nozzle systems. In one type of storage the liquid carbon dioxide is in ICC cylinders, either single cylinders or manifolded, under a pressure of 850 psi at 70°F. These are called high-pressure systems. In the second type of storage, the liquid carbon dioxide is in insulated tanks under a pressure of 300 psi at 0°F with the reduced temperature maintained by refrigeration units. This type of system is called a low-pressure system, and it is used only where the quantity of carbon dioxide in storage is ⅜ths ton or greater.

Hand hose-line systems consist of a supply of carbon dioxide, either under high pressure or low pressure, connected through piping to one or more hose lines on reels or racks. Like all hand hose-line systems, carbon-dioxide hand hose lines are used for the protection of specific hazards or supplementary to a fixed-nozzle system.

FIXED-NOZZLE SYSTEMS

Fixed-nozzle systems are designed for the protection of specific hazards by local application or for the protection of rooms or buildings by flooding. Although normally considered as an extinguishing agent for Class B hazards, carbon dioxide in the proper concentration will extinguish fires in Class A materials in spaces that are tight enough to prevent leakage of carbon dioxide or entrance of air after the space has been flooded. For this reason carbon-dioxide flooding

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systems are used for the protection of record vaults, fur-storage vaults, and similar occupancies where the use of water would result in excessive damage to the contents. However, precautions must be taken to insure that the doors to such storage spaces are not opened until the contents have cooled to a point where reignition will not occur when air is admitted.

Carbon-dioxide extinguishing systems should be designed by, and the installation supervised by, qualified fire protection engineers on the basis of NFPA No. 12, *Standard for Carbon Dioxide Extinguishing Systems.*[18]

Spaces protected by fixed-nozzle carbon-dioxide systems should be provided with an adequate audible warning system with discharge of carbon dioxide delayed to allow personnel to leave safely. There is a considerable record of fatalities where personnel have been asphyxiated in protected spaces where no audible signal was provided.

Carbon dioxide, being a gas, leaves no residue when it is used on a fire, and it is not decomposed by the flames to produce corrosive chemicals. Being a nonconductor of electricity, it is therefore an excellent extinguishing agent for use where there are delicate low-voltage relays, as in a telephone exchange, or where electronic equipment is involved in a fire.

EFFECT BY TEMPERATURE

Normally the liquid carbon dioxide is expelled from its container by its own gas pressure. Portable extinguishers charged with the specified amount of carbon dioxide are approved for use from −40° to +120°F. However, the flow rate is reduced at the lower temperatures, and the fire extinguishing effectiveness is also reduced. The Underwriters' Laboratories recommends that the extinguisher be charged with only 90% of the normal amount for use at temperatures over 120°F and up to 130°F. When the extinguishers are to be used where the temperatures will be very low, normal practice is to charge with carbon dioxide to 90% of the standard charge and supercharge with nitrogen. The same procedures may be followed with hand hose-line systems of the high-pressure type. Where low pressure systems are used at extremely low temperatures, it may be necessary to provide heating systems as well as refrigerating systems with thermostatic control to maintain the temperature of the liquid carbon dioxide in the vicinity of 0°F.

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Fixed-nozzle systems are designed to deliver carbon dioxide at specific rates of application, and where there may be considerable ranges of temperature, high-pressure storage systems should be so located that they may be heated should the temperature fall below 32°F. At temperatures of over 120°F, the carbon dioxide may be delivered from local application nozzles at too high a velocity and may splash flammable liquids as the result.

Halon 1301

Bromotrifluoromethane, commonly called Halon 1301, is a liquefied compressed gas-extinguishing agent developed in the 1950's. Although it has been used for several years as an extinguishing agent for fires in aircraft engines while in flight, it has only recently become available to civilian users in the form of an approved 2½ lb hand portable extinguisher.

Although Halon 1301 is a halogenated hydrocarbon, tests have shown that the undecomposed vapors of this agent are less toxic than carbon dioxide. However, whereas carbon dioxide is not changed in toxicity by exposure to flame, Halon 1301 is decomposed to form vapors which are toxic, even though far less toxic than the products of decomposition of carbon tetrachloride.[11]

Vaporizing Liquids

TYPES

Vaporizing liquid extinguishing agents have as their major component carbon tetrachloride or chlorobromomethane. Both have additives to depress the freezing point to −50°F. Carbon tetrachloride has a boiling point of 171°F and chlorobromomethane has a boiling point of 219°F, and these agents are called "vaporizing liquids" because, although applied to a fire in the form of a liquid, they readily vaporize to form heavy gases that assist the extinguishing action by smothering the flames. Carbon tetrachloride-base extinguishers were first approved in 1912 and were the first to be approved for use on electrical fires and fires in flammable liquids. Chlorobromomethane was developed as an extinguishing agent by the Germans during World War II and approved extinguishers using chlorobromomethane-base extinguishing agent first appeared in the United States in the latter part of the 1940's.

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PORTABLE EXTINGUISHERS

Approved vaporizing liquid extinguishers are available in sizes from 1 quart to 3½ gal and the liquid is expelled either by pumping or by gas pressure from the stored pressure type using air, nitrogen, or carbon dioxide as expellant gases. Air and nitrogen are for all practical purposes insoluble in vaporizing liquids, but carbon dioxide readily dissolves in the liquids and the stream from a stored pressure extinguisher using carbon dioxide as the expellant gas is more of a spray than a straight stream because the carbon dioxide coming out of solution breaks up the stream into droplets. The Underwriters' Laboratories Incorporated lists vaporizing liquid extinguishers as suitable for use only on Class B and Class C fires. The Factory Mutual Laboratories, on the other hand, lists certain vaporizing liquid extinguishers as suitable for use on incipient Class A fires and on fires in electrical apparatus. "Specially designed" chlorobromomethane extinguishers are in addition approved for use on small flammable liquid fires.

The stream range of 1 to 2½ quart extinguishers is 16 to 28 ft and the range of large extinguishers is 30 to 35 ft. The larger stored pressure extinguishers are equipped with nozzles permitting the use of either a straight stream or a spray stream, the latter being more effective than the straight stream for use on fires in flammable liquids.

The smaller extinguishers of this type are used primarily for protection of electrical equipment, industrial trucks, and over-the-highway trucks. The larger extinguishers are used primarily for the protection of electrical equipment. Vaporizing liquids have only a small fraction of the cooling effectiveness of water and therefore are not as effective on Class A fires as a similar quantity of water, and they are not as effective as multipurpose dry-chemical extinguishers of similar weight capacity.

When vaporizing liquids are used on fires, corrosive fumes are liberated as the result of decomposition of the halogenated compounds. Accordingly, this type of extinguisher is not recommended where delicate electrical contacts may be involved or where fine tools or precision metal parts would be effected by corrosion.

The practical effect of the vapors released or produced when vaporizing liquids are applied to a fire has long been a matter of controversy. However, both the *Fire Protection Equipment List* of the Underwriters' Laboratories, Inc. and NFPA No. 10, *Portable Fire*

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Extinguishers, warn against the use of extinguishers of this type in confined spaces and recommend that operators and others should take precautions to avoid effects which may be caused by breathing the vapors or gases liberated or produced. Considerable discussion and data on the toxicity of vapors of various fire extinguishing agents may be found in NFPA Q 48-8 *The Halogenated Extinguishing Agents.* Using data presented in this booklet, Table 28.4 presents the comparative toxicities of agents that form gases or vapors. Carbon dioxide was assigned a value of 1 in this comparison because it is normally considered to be nontoxic and does not decompose when used on a fire.

TABLE 28.4. Toxicity of Vaporizing Liquids Compared with Carbon Dioxide and Halon 1301[11] (Ratio basis: Carbon Dioxide = 1)

Agent	*Natural Vapor*	*Decomposed Vapor*
Carbon Dioxide	1.0	1.0
Halon 1301	0.8	47.0
Chlorobromomethane	10.1	164.5
Carbon Tetrachloride	23.5	2195

The use of vaporizing liquid extinguishers may be prohibited in some states and municipalities. In addition, United States Coast Guard regulations have required that "Vaporizing-Liquid Type fire extinguishers, such as those containing carbon tetrachloride or chlorobromomethane, shall be removed from all vessels on or before January 1, 1962."[6]

SPRINKLER UNITS

There are two vaporizing liquid automatically operated sprinkler units, one containing 2 quarts of carbon tetrachloride and 1 pint of ammonium hydroxide (the latter to provide the expellant pressure and to counteract corrosion) and the other containing 1 gal of chlorobromomethane and pressurized with carbon dioxide. These units are intended primarily for protection where Class B fires may be expected and are limited in the volume of space that can be protected. Because of the limitations on installation recommended for these units by the Underwriters' Laboratories, Inc., reference should be made to the Fire Protection Equipment List published by the approval agency.

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Dry Powders for Fires in Combustible Metals

APPROVED AGENTS

The first approved agent specially compounded for extinguishing fires in combustible metals was made available in 1940 as the result of the increasing use of magnesium in aircraft construction. This first approved dry powder is composed of a commercial grade of graphite to which an organic phosphate has been added. The graphite absorbs heat from the fire, and the organic material breaks down to a gas that penetrates the spaces between the graphite particles, excluding air. Because the powder cannot be discharged through pipe or hose, it is applied to a fire by means of a scoop or shovel.

A second dry powder for use on fires in combustible metals was approved in 1958. The major component of this dry powder is sodium chloride with a noncombustible thermoplastic material added to bind the particles of sodium chloride together when exposed to the heat of a fire. The dry powder contains other ingredients to produce good flow characteristics, and it is treated with metal stearates to produce moisture repellency. This agent cannot only be applied with scoop and shovel but it can also be discharged from fire-extinguishing equipment. Portable fire extinguishers ranging in size from 30- to 350-lb capacity, charged with this agent, are approved for use on fires in combustible metals.[22]

Although the two dry powders are approved for use only on magnesium, powdered aluminum, sodium, potassium, and sodium-potassium alloy (NaK), in practice they have been used successfully on fires in other combustible metals such as titanium, zirconium, and uranium. The sodium chloride-base dry powder, because of its good flow characteristics, can be applied through systems of piping and fixed nozzles and a number of such installations have been made. Such installations are used to protect liquid metal pumping, storage, and filtering systems where the liquid metal is used as a heat transfer medium in connection with atomic power reactors. Under these conditions, fire fighting with manual equipment is impractical, and the extinguishing agent for the combustible metal must be applied through piping. A system typical of this type is designed to discharge 8000 lb of the sodium chloride-base dry powder from four 2000 pound units. There has been a very limited amount of fire experience with such systems.

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UNAPPROVED AGENTS

There are several nonapproved dry powders that have been specially compounded for the extinguishment of fires in combustible metals. One is primarily composed of a hard graphitic material that can be discharged from fire extinguishing equipment. Although this agent was originally compounded primarily for the extinguishment of fires in lithium, which are very difficult to extinguish because of the very low specific gravity of the liquid metal, it has been used successfully on many other combustible metals.

There are two other dry powders specially compounded for use on fires in combustible metals and intended for application by scoop or shovel. The first is a shale-like material mixed with tar or pitch and ammonium chloride. The second originated with the United Kingdom Atomic Energy Authority and is a patented mixture of sodium chloride, potassium chloride, and either barium chloride or lithium chloride, in such proportions as to form a eutectic mixture having a melting point between 900° and 1100°F.[2]

Many materials have been used on metal fires with varying degrees of success. Some materials readily absorb moisture and must be kept in tightly sealed containers. Others are successful in extinguishing small fires where large masses of material may be applied but may react with the burning metal if the fire is of considerable size. The following materials have been used on a variety of metal fires: foundry flux, lithium chloride, sodium chloride, zirconium silicate, Dolomite, soda ash, asbestos powder, talc, graphite, sand, and cast-iron borings.

Multipurpose dry chemical is not suitable for use on fires in combustible metals. Although under certain circumstances small magnesium fires may be extinguished, under other circumstances there may be a reaction between the burning magnesium and multipurpose dry chemical. The latter also reacts violently with burning lithium.

There are three liquid agents that are prepared especially for the extinguishment of fires in combustible metals. None is approved. One is a petroleum derivative applied from 2-quart and 2½-gal stored pressure extinguishers. The liquid acts as a cooling and smothering agent and under certain conditions, it is flammable. However, the application of additional liquid, if available, is said to cool the burning material below the fire point. It is suggested for use on only small magnesium fires. A second liquid agent is composed primarily of peanut oil which is discharged from an extinguisher pressurized

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with carbon dioxide. The extinguisher has a capacity of 2½ gal of oil and 1½ lb of carbon dioxide, the latter being in a separate container within the body of the extinguisher. A three-way valve allows first the discharge of the oil to act as a cooling and smothering agent with a final discharge of carbon dioxide to extinguish any fire which may result in the peanut oil. This agent also is suggested for use only on small magnesium fires.

The best known liquid extinguishing agent for fires in combustible metals is trimethoxyboroxine (TMB). TMB is applied from a 2½-gal stored pressure extinguisher which has a nozzle permitting use of either a spray or a straight stream. TMB is a flammable liquid organo-metallic compound similar in flammability characteristics to methyl alcohol. It burns with a green flame, liberating large volumes of dense white fumes. A glassy boric oxide coating remains on the metal. This coating will pick up moisture very rapidly from a humid atmosphere. The use of TMB as a fire extinguishing agent for combustible metals is patented.

The Naval Research Laboratory developed the TMB extinguisher for use on magnesium castings and structural shapes under aircraft crash fire conditions. Under these conditions of application, fast extinguishment results which can be quickly followed up by foam or water. TMB extinguishers are used primarily by the United States Navy Bureau of Weapons on crash fire and rescue trucks.

Although the flammability and heavy fuming characteristics of TMB may be undesirable under conditions of industrial fire fighting indoors, TMB is a good extinguishing agent for fires in oily or dry magnesium chips, turnings, or castings. It is also suitable for control and, in most cases, extinguishment of fires in titanium chips, turnings, sponge, and powder. TMB will control, and in some cases, will completely extinguish fires in zirconium chips or turnings.

TMB is *not* recommended for fires in sodium, potassium, sodium-potassium alloy (NaK) or lithium. TMB reacts violently with lithium and NaK.

Where combustible metals may ignite in enclosed equipment such as heat-treating furnaces, gaseous extinguishing agents may be used. Boron trifluoride and boron trichloride will control and sometimes extinguish magnesium fires in heat-treating furnaces. Boron trifluoride is considerably more effective than the boron trichloride. The gases may only control large fires which may require the application of suitable dry powders for extinguishment. The fumes of these gaseous agents are toxic and irritating, and suitable gas masks should be available.

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Argon, helium, and, sometimes, nitrogen can also be used to extinguish fires in combustible metals in enclosed spaces. Caution should be exercised in the use of nitrogen however, because this gas reacts readily with certain burning metals. If there is uncertainty as to whether a metal will burn in a nitrogen atmosphere, the application of a small amount of water to the residue of the metal burned in air will result in an odor of ammonia if the metal reacts with nitrogen. Argon and helium, of course, will not react.

Steam

Steam is the oldest of the smothering agents although it is seldom used in modern practice, having been replaced by carbon dioxide and other inert gases. It is most effective when used for the protection of relatively small spaces such as ovens at temperatures of 225°F and higher. The visible cloud of condensed vapor has little smothering action and will act mainly through cooling. Large volumes of steam are usually necessary because of the rapid condensation that takes place unless the walls of the enclosure are above the boiling point of water.

Steam should not be used for protection against fires in cotton, paper, wood pulp, and similar carbonaceous materials, because the charcoal produced by the fire will reignite by spontaneous heating very quickly after the steam has been shut off and air is introduced. The best information on steam smothering systems is in NFPA No. 86 *Standards on Class A Ovens and Furnaces.*[23]

Steam hose lines are sometimes used for extinguishing small fires in flammable liquids such as those that may occur from a leak in a pipe line.

28.4. MECHANISM OF EXTINGUISHMENT

Flames exist when there is a fuel, a substance which readily reacts with the fuel, and sufficient heat to speed the reaction to a point where visible and infrared radiation takes place. A familiar, and oversimplified, version of extinguishment states that it is accomplished by removal of the fuel (by blanketing with foam or interposing a layer of inert gas between the fuel and the flames), by removal of oxygen (by dilution with inert gases or vapors), or by removal of heat (by cooling with water or other extinguishing agents). All of the foregoing explanations of extinguishing action are correct but are insufficient in themselves to explain why loaded stream extinguishers are more

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effective than plain water extinguishers, why Halon 1301 is more effective than carbon tetrachloride, or why potassium bicarbonate-base dry chemical is more effective than sodium bicarbonate-base dry chemical.

It can be said with considerable confidence that water, whether in the form of a straight stream or a spray, with or without wetting agent, acts for all practical purposes entirely as a cooling agent for the removal of heat. Wood and similar Class A materials burn only when heated to the point where destructive distillation results in the evolution of combustible vapors. The cooling action of water stops the evolution of combustible vapors and the fire is extinguished.

Water spray and "fog" are practically effective only on flammable liquids having flash points in excess of 150°F. It is therefore obvious that even on Class B fires the cooling action of the water is of greatest importance.

The cooling action of water sometimes allows extinguishment of fires by application at very high rates of flow where low rates of flow would only increase the intensity of the fire because of chemical reaction between water and the burning material. One familiar example is the extinguishment of a fire in charcoal. If water is applied at too low a rate of flow, the well-known water-gas reaction takes place:

$$H_2O + C \rightarrow H_2 + CO$$

At high rates of application, the cooling effect of the water reduces the temperature to a point where the foregoing reaction will not proceed.

Another good example is the extinguishment of fires in magnesium castings. Applied at too low a rate, the water reacts with the burning magnesium:

$$H_2O + Mg \rightarrow H_2 + MgO$$

Applied at high rates of flow, the water cools the castings to the point where combustion no longer is sustained.

Loaded stream extinguishers containing a solution of potassium carbonate are more effective than extinguishers containing plain water not only on Class A fires but on Class B fires also. There are only theories as to why the addition of potassium carbonate to water increases the extinguishing effectiveness.[30] However, in addition to the cooling action of water it is possible that the heat of the fire evaporates the solution to leave solid particles of potassium carbonate that act in the same way as dry chemical to interrupt and suppress the chain reaction of the flame.[8]

Carbon dioxide can be considered for all practical purposes to act

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as a diluent to both fuel vapors and oxygen. When sufficient carbon dioxide is introduced into the fire area, the reacting materials are diluted to the point where the reaction cannot proceed with sufficient rapidity for the flames to exist. Where carbonaceous material is involved in a fire, however, reignition takes place unless it is possible to maintain a sufficient concentration of carbon dioxide until the previously burning material has cooled.

Although the action of halogenated extinguishing agents, such as Halon 1301, chlorobromomethane, and carbon tetrachloride, was once thought to be entirely because of cooling action and smothering because of the dilution of fuel vapors and air, it is now believed that the major extinguishing mechanism results from pyrolysis of the halogenated hydrocarbons and reaction of the resulting radicals with the active radicals present within the flame zone. Generally speaking, a halogenated hydrocarbon containing bromine is a more effective extinguishing agent than a halogenated hydrocarbon containing only chlorine, but the effectiveness does not depend only upon the percent of bromine in the molecule. Published data do not satisfactorily explain why Halon 1301 (bromotrifluoromethane) has such high extinguishing effectiveness as compared with other halogenated hydrocarbons.

The extinguishing action of foam is obvious in that it forms a barrier that prevents contact between fuel vapors and air.

The extinguishing action of dry chemicals has been given a great deal of study in recent years, but no one theory as to the mechanism involved has gained complete acceptance. Originally, it was thought that sodium bicarbonate decomposed upon striking flame to give off carbon dioxide and water vapor and extinguish the fire by simultaneously cooling and smothering. It is now known that, although this may occur, it is not an important factor because equally finely divided sodium chloride treated to flow and discharge properly is an effective dry-chemical extinguishing agent. One modern theory of the extinguishing action of dry chemical is that the fine particles capture sufficient of the free radicals in the flame zone to interrupt the chain reaction and suppress the flame practically instantaneously.[8] Opponents of this theory have pointed out that the mathematics involved, which relate to the diffusion of free radicals from the flame zone to the surface of the dry-chemical particles, can equally well support a theory that the dry-chemical extinguishing action is because of transfer of heat from the flame to the particles.

The relation between particle size and surface area of dry chemicals and the extinguishing effectiveness has been reported by several

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sources.[8,10] Experimental and theoretical studies have showed that the extinguishing effectiveness increases as particle size decreases and surface area increases. The most recent theory on the extinguishing mechanism of dry chemicals is that evaporation takes place and that the evaporated material acts as a flame inhibitor.[29] Using this theory also, the smaller the particle size, the more rapidly the particles will be heated to a temperature at which evaporation can proceed. The theory also takes into account "metal availability" in the salt which is inconsistent with the experimental evidence that ammonium phosphate-base dry chemical is more effective as an extinguishing agent on Class B fires than sodium bicarbonate-base dry chemical.

In summary, presently there is no completely satisfactory explanation as to how powdered solids extinguish fires or completely satisfactory explanation for the greater extinguishing effectiveness of ammonium phosphate and potassium bicarbonate.

The effectiveness of monoammonium phosphate-base multipurpose dry chemicals on fires in Class A materials is probably because of a dual extinguishing action. The flames are extinguished by an unknown mechanism as discussed in the foregoing paragraphs. The monoammonium phosphate is decomposed by the heat and leaves a residue of phosphoric acid or phosphoric anhydride on the material which had been burning. This residue prevents afterglow which would lead to renewed flaming.

The use of monoammonium phosphate-base dry chemical on a wood fire results in a fire retardant coating that is very effective in preventing reignition. This was discovered in trying to dispose of the charred 2 x 4's remaining from large Class A fire tests in which 18,000 board feet of lumber was used. The 2 x 4's on which water had been used were easily disposed of by burning, but a pile of charred 2 x 4's on which multipurpose dry chemical had been used resisted reignition to such an extent that it was necessary to haul them to the public dump.

28.5. COMPARATIVE EXTINGUISHING EFFECTIVENESS OF AGENTS

Evaluation of the effectiveness of extinguishing agents can be accomplished by several methods, but the final criterion is the effectiveness in actual use. Data gathered on the laboratory bench are of value only for the preliminary screening of agents for special applications. For example, data obtained by the peak flammability explosion buret method[14] do not correlate with fire extinguishing effectiveness data obtained with fixed nozzles and a 3 ft diameter gasoline fire.[8]

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The data obtained in tests with fixed nozzles may be used to predict the effectiveness to be expected in practice with fixed-nozzle local application systems.

In the use of manually operated fire-extinguishing equipment, the evaluation is really that of a combination of agent and equipment, and many variables can effect the results. For example, a fire fighter skilled in the use of one agent may not be adequately skilled in the use of other agents. Fire tests made with flammable liquids in depths of over 1½ in. are much more severe than fire tests that simulate spill fires. Also, an agent that may be excellent for extinguishing fires in flammable liquids in tanks or on spill fires, may be valueless when the flammable liquid is escaping under pressure or even just flowing. The extinguishment of flammable liquid fires indoors is more difficult for the less experienced operator than if the same size fire is attacked out-of-doors. The Underwriters' Laboratories uses wood panel fires and wood crib fires for determining the Class A rating of fire extinguishers, and observation of many tests shows that water extinguishers are more effective on the panel fires than on the crib fires whereas multipurpose dry-chemical extinguishers are more effective on the crib fires.

Two fire extinguishers containing exactly the same amount of the same agent may have widely different degrees of fire extinguishing effectiveness. Two important factors that determine effectiveness are the type of stream expelled from the nozzle and the rate of application of the agent.

The rate of application of an extinguishing agent is of critical importance. If the rate is too low, the fire may not be extinguished, and if the rate is too high the supply of agent may be exhausted before the fire is extinguished.[7,8] Where unlimited water supplies are available, it is obvious that the higher the rate of application, the sooner the fire will be extinguished. However, the statements regarding rates of application are also applicable to portable fire-extinguishing equipment, to hose-line systems using special extinguishing agents, and even to systems employing fixed nozzles.

The Underwriters' Laboratories in its test and examination of equipment submitted for listing evaluates the extinguishing effectiveness of agent and equipment as an integral unit. For example, in order to obtain a Class A rating the submitted equipment must be able to extinguish standard wood crib, wood panel, and excelsior fires. The extinguishment of these fires is a function of the rate of discharge, the amount of extinguishing agent, and the type of discharge stream.

Until recently the Underwriters' Laboratories Inc. had no standard

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TABLE 28.5. Maximum Effectiveness on Class A Fires of Underwriters' Laboratories Approved Extinguishers[32] (Weights and volumes denote nominal extinguisher charge)

Underwriters' Laboratories Class A Rating	*Multipurpose Dry Chemical**	*Water, Soda and Acid, Foam*		*Wet Water*		*Loaded Stream*		*Calcium Chloride Solution*	
	lb	*lb*	*(gal)*	*lb*	*(gal)*	*lb*	*(gal)*	*lb*	*(gal)*
1-A	7.5	10.4	(1¼)	—		11.5	(1)	13.2	(1¼)
2-A	10	20.8	(2½)	—		20.1	(1¾)	26.3	(2½)
3-A	17	33.3	(4)	—		—		42.1	(4)
4-A	25	41.7	(5)	—		—		52.6	(5)
6-A	—	—		83.3	(10)	—		—	
10-A	—	142	(17)	167	(20)	196	(17)	—	
20-A	125	275	(33)	—		380	(33)	347	(33)
25-A	—	—		375	(45)	—		—	
30-A	—	—		417	(50)	—		—	
40-A	300	—		—		—		—	

* Also listed as suitable for use on Class B and Class C fires.

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fire tests for ratings in excess of 4-A and water extinguishers were assigned ratings based on 75% of that which would be obtained by using proportionate values given to Class A extinguishers of lower capacity. However, when wheeled multipurpose dry-chemical extinguishers were submitted for examination and test, the Laboratories developed evaluation procedures using large wooden cribs made up of 2 x 4's. Tests with these large standard Class A fires verified the ratings previously given to large water extinguishers.

A fire extinguisher having a capacity of 1¼ gal of water and otherwise meeting the requirements of the Underwriters' Laboratories will, when used by an expert operator, consistently extinguish a standard 1-A test fire. Table 28.5 shows the maximum effectiveness on Class A fires of Underwriters' Laboratories listed extinguishers where only the highest ratings for each size of extinguisher are used.

The Underwriters' Laboratories procedures for assigning Class B ratings are considerably more involved than the procedures used for assigning Class A ratings. The fire tests are run using square steel pans with white gasoline as the fuel. Ordinary motor gasoline is not used because of the variation in volatility in winter and summer. The fuel is in 2 in. depth with 6 in. of tankside above the surface of the fuel. The fire is allowed to burn for one minute before being attacked. The test pans used by the Laboratories in the Class B fire tests are, in area, 2½, 5, 10, 15, 20, 25, 30, 40, 50, 100, 200, 300, 400, 500, and 600 sq ft.

The Underwriters' Laboratories uses expert operators to determine the maximum area extinguished consistently by one extinguisher. To obtain the Class B rating, the maximum area as determined by test is multiplied by 0.40 to give the rating. The latter is intended to represent the flammable liquid area that might be expected to be extinguished by inexperienced operators. Fire tests with hand portable extinguishers are run indoors in a test house having a 40 by 60 ft floor area with the ceiling height in excess of 20 ft, and always with large roof vents opened. The largest indoor fire is 50 sq ft which imposes a limit of 20-B as the highest rating presently obtainable with hand portable fire extinguishers. Extinguishing equipment larger than hand portable in size is tested on outdoor fires but only when the wind velocity is less than 10 miles per hour. The maximum effectiveness of Underwriters' Laboratories listed extinguishers on Class B fires is shown by Table 28.6.

It will be noted that 20-B ratings are obtained with potassium bicarbonate-base dry chemical extinguishers of only 9 lb capacity. The same rating is given to extinguishers of this type containing 18

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TABLE 28.6. Maximum Effectiveness on Class B Fires of Underwriters' Laboratories Approved Extinguishers[32]
(Weights and volumes denote nominal extinguisher charge)

Underwriters' Laboratories Class B Ratings	*Dry Chemicals*			*Halon 1301**	*Carbon Dioxide**	*Chlorobromomethane**		*Carbon Tetrachloride**		*Foam***		*Loaded Stream***	
	*$KHCO_3$ Base**	*Multi-Purpose**	*$NaHCO_3$ Base**										
	lb	*lb*	*lb*	*lb*	*lb*	*lb*	*(gal)*	*lb*	*(gal)*	*lb*	*(gal)*	*lb*	*(gal)*
1-B	—	—	1	—	—	—		3.0	(¼)	—		28.7	(2½)
2-B	—	—	1½	—	2	3.2	(¼)	6.1	(½)	10.4	(1¼)	—	
4-B	—	—	2½	2½	5	6.4	(½)	—		—		—	
6-B	—	—	2⅝	—	—	—		12.2	(1)	20.8	(2½)	—	
8-B	2½	2½	—	—	10	12.7	(1)	—		—		—	
10-B	—	4	—	—	12	—		—		—		—	
12-B	—	—	4½	—	15	19.1	(1½)	—		142	(17)	—	
16-B	4¼	7½**	—	—	—	—		—		—		—	
20-B	9	10**	10	—	50	—		—		—		—	
40-B	—	—	—	—	100	—		—		275	(33)	—	
80-B	—	125**	75	—	—	—		—		—		—	
160-B	125	300**	350	—	—	—		—		—		—	
240-B	300	—	—	—	—	—		—		—		—	

* Also listed as suitable for use on Class C fires.
** Also listed as suitable for use on Class A fires.

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and 27 lb of dry chemical although it is obvious that they must have considerably greater extinguishing affectiveness.

Using the data of Table 28.7 and taking into account the variations because of size, the extinguishers may be assigned *approximate* values to indicate relative effectiveness as shown below.

TABLE 28.7. Relative Extinguishing Effectiveness of Underwriters' Laboratories Listed Extinguishers on Class B Fires

Basis: Comparative weights of extinguishing agents for equal class B rating

Agent	*Relative Effectiveness*
Potassium bicarbonate-base dry chemical	100
Multipurpose dry chemical	71
Sodium bicarbonate-base dry chemical	67
Halon 1301	46
Carbon dioxide	19
Chlorobromethane	18
Carbon tetrachloride	14
Foam	5
Loaded stream	1

The Underwriters' Laboratories assigns Class C ratings to extinguishers having Class B ratings where the extinguishing agent is not a conductor of electricity.

In the past, extinguishers rated for use on both Class A and Class B fires were not rated for use on Class C fires because the extinguishing agents were electrically conductive. Also, extinguishers rated for use on both Class B and Class C fires were not sufficiently effective on Class A fires to obtain Class A ratings. Multipurpose dry chemical, being electrically nonconductive and also effective on Class A fires as well as Class B fires, has permitted the listing of extinguishers for all three classes of fires. Because there are many locations where protection must be furnished for more than one class of fire, Table 28.8 lists extinguishers approved as suitable for use on both Class A and Class B fires.

There are two agents approved for use on fires in combustible metals. Because of the complexities of determining comparative extinguishing effectiveness, no numerical ratings are assigned. Reference must be made to the respective lists of approved equipment for information as to the combustible metals for which the extinguishing agents are considered suitable and for guidance as to the quantities of agents required on various metal fires.[5, 32]

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TABLE 28.8. Maximum Effectiveness of Extinguishers Approved by the Underwriters' Laboratories as suitable for use on both Class A and Class B Fires[32]

(Weights and volumes denote nominal extinguisher charge)

Underwriters' Laboratories Class A:B Rating	*Multipurpose Dry Chemical** *lb*	*Foam*		*Loaded Stream*	
		Pounds	*(Gallons)*	*Pounds*	*(Gallons)*
1-A: 2-B	—	10.4	(1¼)	—	
1-A: 16-B	7½	—		—	
2-A: 1-B	—	—		28.7	(2½)
2-A: 6-B	—	20.8	(2½)	—	
2-A: 20-B	10	—		—	
3-A: 20-B	17	—		—	
4-A: 6-B	—	41.7	(5)	—	
4-A: 20-B	20	—		—	
10-A: 12-B	—	142	(17)	—	
20-A: 40-B	—	275	(33)	—	
20-A: 80-B	125	—		—	
40-A:160-B	300	—		—	

* Also listed as suitable for use on Class C fires.

The coordination of fire-protection systems in a chemical operation is beyond the scope of this chapter, but the reader is referred to his insurance carrier, to the N.F.P.A. and to the cited reference.[34]

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29

Action Stations and Disaster Planning

Alan L. Kling

It is not uncommon in a metropolitan area to see streets partially blocked with barricades, flashing lights, and signs which read, "Dig we must—for a growing New York." This is a way one of our large, progressive utility companies offers apology for any traffic inconvenience which it might be causing. At the same time, the message is a rather subtle reminder to the public, their customers, that they have a long-range plan in operation and are getting ready today for the demands of tomorrow.

This is precisely what we do in industry when we take preparatory action for possible future emergencies, and we might well paraphrase the electric company's slogan so that for our use it would read, "Plan we must—for greater security and better control of losses."

Sometimes there is ample warning of an impending emergency, such as when a hurricane or flood is headed our way, but more often, major trouble comes with the awful suddenness of an explosion or fast-spreading fire. There are, of course, other types of abnormal conditions, such as riot, civil commotion, wildcat walkouts, or unfavorable changes in the international situation. These are difficult to predict and hard to handle, but they too have "panic-button" characteristics which demand immediate attention. Regardless of how these conditions might develop, every prudent plant manager knows that a time could come when he would have to acknowledge that a catastrophe had overtaken him, and he was knee-deep in disaster. Like Artemus Ward, one of

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America's earliest commentators, he would have to say, "The Fack can't be no longer disgised that a Krysis is onto us."

How well the chief executive officer, whether he is called president, operating head, or plant manager, fulfills his responsibility for the safety of personnel and the protection of property will depend, in large part, on the plans which he has formulated and put into practice. The response of a company to a catastrophe will be reflected in the actions of every employee. If there has been preparation and training, control measures will be initiated automatically. Injury and physical damage will be kept at a minimum and recovery will be prompt and positive. Without forethought and planning, minor emergencies can become major disasters, and what might have been merely a delaying incident can very quickly become the final scene in a costly and unhappy tragedy.

Emergency preparation has been a frequent topic for discussion. There have been American Management Association conferences, government briefing sessions, and instructive meetings and field trips such as those sponsored by the National Institute for Disaster Mobilization. Many articles have been written which help outline procedures and summarize experience of both large and small companies. There is an immense quantity of reference material available, and information on any phase of emergency planning can be obtained without much difficulty. Competent personnel can also be found who will provide excellent consulting service.

Many companies appear reluctant to plan for a total emergency. We have lived near war for such a seemingly long period of time that complacency comes easy, and in time of peace or even cold war, national security does not have quite the priority over the immediate problems which must be handled in the office and shop on a daily routine basis. Actually no management is fulfilling its responsibility if it does not prepare plans which are broad enough to include its own security and future continuity. These are many compelling reasons why a comprehensive approach is important, and if the need is properly evaluated, sufficient time and talent can be found in every organization.

The task of preparing a program will look less formidable if responsibility centers are established for specific emergency functions. These action stations, when properly coordinated, will provide an adequate and effective over-all plan for total emergency.

What are some of the specific functions which must be considered? There are not too many, and each has been covered in considerable detail in previous conferences and publications. However, the follow-

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ing brief check list, with annotations, will serve as a reminder for those who are either developing a new plan or evaluating one which already exists.

CHECK LIST FOR TOTAL EMERGENCY PLANNING

1. *Policy.* Top management must state its philosophy indicating the importance it places on emergency planning and the extent to which it expects action.
2. *Organization.* Size and type of operation will dictate whether a full-time security officer should be appointed. A committee, in spite of frequent cynical comments about the ineffectiveness of such a group, can be productive if it has qualified leadership. For most companies the most practical plan appears to be assignment of specific functions to various department heads and coordination by one individual who regularly prepares status reports for top management. Regardless of the manner organized, there must be definite assignment of responsibility, coordination of activities, and periodic review of results.
3. *Continuity of Management.* The strength of a company depends not only on the ability of its officers but also upon their availability. Corporate by-laws must permit legal transaction of necessary business under emergency conditions with only a minimum number of directors. A chain of command should also be established so that there is no doubt or confusion as to who has the authority for making or approving all decisions. The managers of plants which are distant from a central corporate office and which could become isolated should have their scope of responsibility so broadened that under emergency conditions they can, at least on a temporary basis, take whatever action is necessary.
4. *Alternate Headquarters.* Under some conditions an office with minimum supplies and records might be desirable, but the most practical approach for most companies is the designation of a rendezvous point where officers and designated staff and line personnel can meet to assess the situation, initiate recovery or receive instructions from the government if the occurrence involves national welfare.
5. *Vital Records.* Good management safeguards its legal documents, accounting records, and operating data as a matter of course, and planned protection is imperative even for normal conditions.
6. *Money and Banking.* In multiplant companies each separate location must be certain it has access to temporary operating funds.

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7. *Process Data and Manpower Inventory.* Information should be available as to raw materials sources, product specifications, operating data, and the administrative and operating skills available within a company.
8. *Communications.* The problem of making contact with widely separated locations is primarily one for multiplant companies, but even a single unit operation must be able to communicate with suppliers, customers, and under conditions of national emergency, with the government itself.
9. *Government Contact.* The federal government and many of the states have made extensive plans for handling emergencies which are national in scope. Some industries, or plants within those industries, have been designated as key facilities. Every company should determine what its function will be under total emergency conditions, and how it will establish communication with designated government officials.
10. *Plant Emergency Programs.* The smooth, normal operation of a production unit can find itself in the middle of a crisis without much prior notice. Because modern plants are so highly integrated, all facilities will be effected. Detailed emergency plans will assign responsibility, outline a desired course of action, and establish means of coordination.
11. *Post-Attack Planning.* Thought must be given to recovery so that company assets, not totally destroyed, can be salvaged and production re-established, at least on a partial basis, as quickly as possible.

All of the items included in this check list envision preparation for a major emergency, one that is national in scope and of catastrophic proportion. Whether such a situation will ever develop is one of the perplexing questions which only future events can answer. There are few persons, if any, who would consider themselves qualified to assess the *probability* of a nuclear attack on this country. On the other hand, it would be hard to find a normal individual who would not readily admit the *possibility* of an all-out war involving all nations, even before the end of this century. So, *plan we must* for our own security. Those who do will have all of the survival odds in their favor.

29.1. IN-PLANT EMERGENCY PLANNING

We must also plan for better loss control on a day-to-day basis, because if the future is in any way similar to the past, we can expect

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fires, explosions, and other unscheduled, unplanned, unwanted, costly, abnormal occurrences which if not properly handled will adversely affect a company's position in the highly competitive market place, and actually challenges its economic survival.

Defensive planning consists of *establishing and co-ordinating* action stations within a plant so that strong control measures can be brought to bear quickly and effectively on any of the many emergency situations which can occur.

Action stations are really responsibility centers from which response is automatically initiated in time of need. Management specifies their location, the personnel who will serve, and the scope of their duties. It specifically defines an "emergency condition," grants authority for making emergency decisions, and provides means for declaring that an emergency situation exists.

Because organization and facilities vary from one company to another, what are crises for some locations may be minor inconveniences for others. In a plant that has no automatic sprinklers, no trained fire brigade, and is dependent on a volunteer or distant municipal fire department, even a small blaze constitutes a first-order emergency. Usually, however, an emergency can be defined as:

1. An accident causing fatal or severe injuries.
2. A fire or explosion in which damage exceeds a specified amount determined by management.
3. Actual or impending severe storm or flood conditions.
4. Any incident which could affect community relations, such as accidental discharge of toxic or noxious materials into the atmosphere or local waterways.

The management statement of emergency policy will clearly designate the line of authority and will make certain that persons who can make decisions are on hand and available at all times. There must be someone in responsible charge empowered to activate the emergency plan in full and complete detail.

A method of communication is needed so that all action stations can be notified. This can be a siren, bell, horn, public address system, or the telephone, but whatever system used, it must be dependable.

Management may also want to designate a coordinator. In some companies, a full-time security officer may be required, but generally, where responsibility for specific functions is delegated to personnel in many departments, the main job is one of careful integration. This can, and often is, a part-time job.

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CONTROL CENTER

An emergency of any size or duration must have a command post or control center. It is the focal point for communications, both within the plant and for incoming and outgoing calls. The individual in charge should make this his headquarters so that he can be reached easily. Time is one of the most essential elements in an emergency program, and many decisions simply will not wait until someone in charge can be found. Alternate locations should also be designated to provide flexibility. Often the guard headquarters at the main gate is an ideal place for the control center, but the plant manager's office, the purchasing department (because of generally easy access for outside visitors), production center or the insurance manager's office are possibilities.

CONTROL FACILITIES

Several plant groups are needed at the scene of an emergency to properly handle injured personnel and to initiate control measures. Most large companies have well-trained *fire brigades* on every shift with maintenance men, such as electricians, pipe fitters, and riggers, as well as members of the yard crew with their trucks, responding to all fire calls. If no brigade exists, selected employees should be trained in fire-fighting techniques; actually it is a worthwhile practice to teach all personnel the proper use of portable extinguishers.

MEDICAL SERVICES

Within a plant there may be a full-time physician, one or more nurses, or only a first-aid squad. In addition to their availability in time of emergency, they must also have quick access to stretchers, resuscitators, and various medical supplies. Sometimes these are carried on the fire truck, ambulance, or special vehicle equipped for the purpose. The *plant protection* groups, guards and watchmen, control the gates, handle traffic, safeguard property and often are key men in the communication system. *Technical personnel,* chemists and engineers, are often needed at the site of a disaster to give advice and suggestions to firemen and others regarding toxicity and flammability of materials involved.

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PERSONNEL PROTECTION

The safety director frequently has a wide-ranging assignment for both prevention of injury and conservation of property. If he has not permitted himself to become desk bound, but gets out into the plant regularly, he will be intimately familiar with the people, equipment, and products. This makes him well qualified to either direct the control facilities or advise those in charge of each of the individual functions.

INDUSTRIAL RELATIONS

Some of the most unpleasant and frustrating jobs fall into the lot of the industrial relations manager and his staff; most of them require an extra measure of patience, compassion, tact, and understanding. Notification to the family or next of kin when there has been a fatality or hospitalization because of serious accident is never easy. Sympathy is needed, but even more important is a keen appreciation for some of the simple but vital necessities, such things as grocery money, transportation to hospital or funeral parlor, baby sitters, and even guidance in legal and insurance matters. There is a very fine line separating the private and personal life of an employee and his dependents, and the proper area or extent of a company's assistance. Much depends on the type of plant: large or small, urban or rural, new or old, and the general climate of employee and labor relations. In any case, prompt action is an obligation when there is personal injury. Another important assignment of the industrial relations group, unless there is a separate public relations department, is handling news representatives. Though we would perhaps prefer to say nothing about the difficulties that we create or befall us, an accident of any magnitude becomes public property the minute it occurs, and as news it is the proper province of radio, television, and the press. Under these conditions a company has only two choices: to provide reporters with as much correct information as possible within their deadline demands, or accept the generally less favorable publicity resulting from news stories based on hearsay.

It has been the experience of most companies that if they cooperate with the news media, they will receive fair treatment. Other duties of the industrial relations action station include the issuance of passes to key personnel so that they can get through road blocks or police

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lines, the calling of off-duty employees for special assignment, obtaining food or clothing changes for those who cannot be relieved and in general performing all those functions which pertain to the welfare of persons involved in the emergency.

INSURANCE DEPARTMENT

The functions of the insurance manager are usually not well defined in most emergency procedures, and this is unfortunate for they have several important assignments. First, a contact man is needed for insurance company representatives. There will be many of these, as well as men from rating bureaus and fire marshal's office who converge on the scene of a large-scale accident and their activities need careful coordination. Second, even though the accounting department will have an established procedure for issuing job-order numbers and collecting loss data, the insurance manager should make certain that the method is satisfactory. Third, the claims of plant personnel and third parties will need careful handling to assure continuation of good employee and public relations. And fourth, in salvage work and the expediting of equipment delivery, the insurance companies can often be most helpful if their services are carefully coordinated by the insurance manager.

PRODUCTION, ENGINEERING, AND MAINTENANCE DEPARTMENTS

Each operating unit within a plant should have a detailed shutdown or hold-safe procedure. It should know the exact length of time it takes to discontinue safely any production unit and each of the hazards which must be safeguarded. Equally important, there will be understanding as to the effect on all other plant units of an accident in their own operation. Engineering and maintenance personnel will have special assignments depending upon the type and the seriousness of the emergency, but their services are an integral part of every loss control program.

OUTSIDE AGENCIES

Some of the most valuable and important action stations will be located outside the plant. If there is a mutual-aid organization, the task of developing and obtaining many needed services becomes infinitely easier. No plant is an island; it needs the support and help of many units, some public, some private, but all are useful at

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one time or another in managing an emergency. They include as follows:

(*a*) *Fire Departments.* Both municipal or those belonging to adjacent industrial plants.

(*b*) *Police and Highway Patrol.* It is essential that roads be kept open so that help can reach a plant.

(*c*) *Industrial Plants.* In addition to auxiliary fire departments, a certain amount of other vital equipment such as ambulances, cranes, and portable radios, is often available.

(*d*) *Red Cross and Salvation Army.* Their services are well known.

(*e*) *Civil Defense.* Wherever there is a CD unit that is well organized and not hampered by politics, a plant should include their facilities in the emergency program.

(*f*) *Ministerial Association.* A minister, rabbi, or priest can be especially helpful when there is serious injury.

(*g*) *Medical.* Local doctors, nurses, hospital facilities, and ambulance service must be carefully listed in the emergency procedure and arrangements made for their responding on call.

(*h*) *Public Utilities.* Contacts should be established with water, telephone, and power and light companies. Each has special contributions it can make. The telephone companies seem to have done an especially good job in developing emergency service.

(*i*) *Insurance Engineers.* Their experience can be helpful in many ways. They may have been closely associated with a similar emergency and know effective control measures; they may be familiar with the location of special equipment that is needed; or they can assist in the investigation after the emergency is over.

Each emergency program must be tailor-made to fit specific needs. There could be other outside services which could be useful to a local plant, and of course the number of action stations will depend upon normal organization, personnel available, and kind of operation. In summary, seven positive steps are suggested to keep direct and intangible losses to a minimum in case of disaster.

1. *Be Pessimistic—Expect the Worst.* The accident which we think will not happen, often does. A good approach to emergency planning was defined by Victor Hugo over a hundred years ago when he wrote, "Nothing is more imminent than the impossible and what we must always foresee is the unforeseen."
2. *Think Big.* A super-sized screen is needed to view all of the loss-producing possibilities. Identify hazards or combination of hazards

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which could cause large losses and visualize their potential. Employ the techniques of "brain-storming" or "imagineering" to get out of mental ruts and narrow thought channels.

3. *Develop a Plan.* Determine in advance the best procedure to be followed for all abnormal conditions.
4. *Assign Responsibility.* Every person has a job.
5. *Provide Backup.* An emergency plan is like a chain, and failure at any point can compound the disaster. Someone must be in responsible charge at all times and be empowered to take whatever decisive action is necessary.
6. *Practice Regularly.* A plan may be very impressive on paper, but when an emergency occurs, there is not time enough to read the instructions. Familiarity with responsibilities and procedures must be thorough so that response can be automatic and in accordance with the over-all plan.
7. *Review Procedures and Evaluate Performance.* Careful evaluation of practice drills will reveal shortcomings and inadequacies. Procedures should be frequently reviewed to reflect any changes in personnel, relocation of operations, or introduction of new processes. A plan is dependable only if it is accurate.

Certainly one of the characteristics of the average American is an optimistic outlook on life, a sanguine and confident attitude, and so it is difficult to spend much time contemplating possible catastrophes. However, major disasters do occur and we are being unrealistic and imprudent if we do not consider carefully the unpleasant and costly emergency situations which might confront us tomorrow.

Planning for the future is a basic responsibility of management and a matter of vital concern for all members of the management team. We may not have a knight like Don Quixote on our payroll, but we can appreciate what Cervantes had him say before charging into one of his many adventures, "Forewarned, forearmed; to be prepared is half the victory."

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Measuring Safety Effectiveness

John V. Grimaldi

Probably the most important factor in any organized effort is the system of measuring its effectiveness. In the absence of a credible measure, a program moves haltingly at best. Its administrator's efforts will not be recognized satisfactorily, and neither will the degree of contribution from those who implement the program's course.

When a measure that is not credible is tried, its value in motivating performance and signaling shifts in strength diminishes rapidly. In the final analysis, any system whose success depends on a current understanding of the vigor and direction of its components relies on measures of optimizing its effectiveness and determining the degree of recognition to be accorded its contributors.[1]

30.1. CRITERIA FOR EFFECTIVE MEASURES

The principal requirements for an acceptable measure are that it be *reliable* and *valid*. "Reliability" requires that the values reported by the measure will be reproducible by any qualified investigator, with much the same accuracy, within reasonable limits. "Validity" means that the measure truly appraises what it purports to measure.

Standard Measures

In the United States the standard means for appraising safety progress is the *American Standard Method of Recording and Measur-*

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ing Work Injury Experience, Z 16.1, R. 1959, published by the American Standards Association. This has been the accepted approach since 1937 for computing and measuring work-injury experience. It reflects the opinions and practical experience of those interested in or affected by the application of the measure. Each interested group (such as employers, employees, government, insurance companies, the National Safety Council, the American Society of Safety Engineers, and so on) named a representative and alternate to a committee, which was balanced with respect to opposite and allied interests, according to the procedures of the American Standards Association. This working group, representing a cross section of those interested in the standard, is known as a sectional committee. From time to time the standard is reviewed by the committee, and it is either re-affirmed or revised as necessary, according to the experience of its users.[2]

The accepted standard measures of work-injury experience are *frequency* and *severity*. The first term refers to the frequency of occurrence of disabling injuries as defined by the American Standard. The second term refers to the total days lost plus time charges for deaths and permanent disabilities resulting from the disabling injuries.

USES OF MEASURES

Detecting Changes in Effectiveness. A measure, as an indicator, facilitates taking necessary corrective action promptly. It has the equally important value of enabling the quick capitalizing on a notably successful development in the program.

Appraising the Efforts of Contributors. The principal developers of a program and those who are expected to support it cannot be appropriately rewarded or disciplined for the degree of their effort without referring to performance measures.

Motivating Accelerated Performance. A common application of safety measures (among other managerial measuring aids) is to employ them in a contest to stimulate employee effectiveness. Safety measures, therefore, often are used to compare the injury experience of one unit of a company with another. A difficulty occurs in such comparisons, however. Usually there are differences in exposure (one plant may have more hazardous operations or may be working under more trying circumstances) and as a consequence, the comparisons often are not equal and are criticized by the participants in the contest. Rarely do they operate on a completely fair level. In some cases they may not take into account all injuries of similar classifications.

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It will be seen in the following discussion of the American Standard that it is possible for a plant with many types of jobs and an alert, effective industrial medical center, to return to employment, without loss of time, an injured employee who has suffered no permanent disability, but who may not have been able to return to the job he had when injured. If the plant has a regularly established job to offer him, which will not aggravate his injury, it is common practice to place him in such an assignment. The standard does not count such a case if there is no lost time and no permanent injury. The large plant, then, obviously has an advantage over the smaller in being able to reduce the number of chargeable injury cases. The plant that cannot take advantage of this feature of the standard, but experiencing the same type of injury as its more fortunate associate, would have a case to report. The difference in its record would not necessarily imply that it is less effective in maintaining its safety program.

There are sound employee relations reasons for encouraging injured employees to return to work as promptly as their injuries will allow. On the other hand there is criticism of this action when it affects safety-record comparisons. In such cases, the swift return of an employee through the cooperation of the medical center and employee relations officer, and, because of the opportunity to provide a suitable temporary assignment, would be considered more appropriate to *injury control* than safety effectiveness. Injury control is a proper element of the safety-effectiveness effort, but not necessarily deserving of being measured by the standard approach to appraising safety effectiveness.

THE AMERICAN STANDARD METHOD

The Z 16.1 Standard represents a sincere attempt to establish a precise basis for computing work-injury frequency and severity rates. "Work injury" is defined as "any injury suffered by a person which arises out of and in the course of his employment." "Injury" is considered to include occupational disease and work-connected disability.

"Occupational disease" is defined by the standard as "a disease caused by environmental factors, the exposure to which is peculiar to a particular process, trade, or occupation, and to which an employee is not ordinarily subjected or exposed outside of or away from such employment."

Only disabling injuries are referred to in these rates. Sometimes they are referred to as "lost-time injuries," but the former term is more appropriate.

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Disabling (lost-time) injuries have been grouped into four categories of cases:

1. *Fatalities.* When death occurs from a work injury, it makes no difference how long after the injury the death took place for the purpose of classifying the injury.
2. *Permanent Total Disabilities.* These are injuries which are permanent and likely to reduce the possibility that the worker can perform his job again as effectively as before he was injured. Thus, the loss of or loss of use of both eyes, both hands, arms, legs, feet, or any combination of these would be considered permanently disabling. As a matter of fact the use of prosthetic appliances, rehabilitation programs, and the employers' increasing acceptance of disabled workers, with the help of second-injury fund laws in the states, have made it possible for people who have severe permanent injuries to return to gainful occupations. The appropriateness of this classification is questionable, therefore, but it does have statistical value.
3. *Permanent Partial Disabilities.* These injuries include the loss of or permanent impairment in the use of any part of the body unless a combination of several injuries incurred at the same time puts the case into the class described above (such as "Permanent Total Disabilities"). Some permanent injuries, apt to be suffered by a worker, are not included in this classification. For example, loss of teeth and disfigurement would not be calculated in this category. Neither would an inguinal hernia when repaired, nor loss of the tip of the finger without bone involvement be in this category.
4. *Temporary Total Disabilities.* This category includes all the injuries not resulting in death or permanent disability, but which render "the injured person unable to perform a regularly established job — which is open and available to him, during the entire time interval corresponding to the hours of his regular shift on any one or more days (including Sundays, days off, or plant shutdown) subsequent to the date of injury." The decision as to whether the injured worker is able to perform a regularly established job is made by the employer's physician. A job arranged only for therapy purposes or which ordinarily is not a regularly established job in the plant is not considered to fall within the requirements of the standard, when determining whether an injured but not permanently disabled worker has returned to work. It will be apparent that most of the work-disabling injuries will fall into this temporary total-disability classification.

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Other classifications of injuries, referred to in the American Standard, but not included in the calculation of the frequency and severity rates, are *medical-treatment* cases which may be further classified into *doctor's* cases and *first-aid* cases. The latter are those not qualifying for a doctor's attention while the former includes cases where the injuries are severe enough to be treated by a physician, but do not result in lost time or permanent disability.

Some industrial safety-program directors attempt to measure their progress by using the first-aid injury totals and/or the doctor's cases. The rationale for such a measure is that the greater number of cases gives a better picture of what is taking place accident-wise in the plant. However, there are sound reasons for using only the permanently disabling or temporary disability case. First, the records for these injuries are likely to be much more accurate than those for the doctor's or first-aid cases—particularly in smaller plants.

In many plants, it is difficult to say precisely how many first-aid injuries occur. For example, the workers may be lax in reporting to the dispensary, or supervision may discourage the employee from going to the dispensary, except for cases where it is obvious treatment is necessary. In some instances the dispensary may keep an incorrect record. On other occasions the dispensary may be too busy to record all the cases all of the time. And in some instances the dispensary counts every visit, including those for headache pills and cold tablets, as an indication of the extent of the services offered. Obviously this makes it much more difficult to make useful safety effectiveness comparisons from information based on dispensary records.

Another complication, in the use of doctor's and first-aid cases for evaluation comparisons of various components' work-injury experience occurs, where the plant's doctor sees all cases with little regard to their significance. Thus, the first-aid case and the more distinctive doctor's case would be grouped together.

The disabling-injury case, on the other hand, is more definitive, and it is almost certain to be recorded. Usually a record must be kept and filed promptly with the Workmen's Compensation Authority whenever an injury occurs which may be eligible for workmen's compensation indemnification. (There usually is no correlation between the incidence of workmen's compensation cases and the frequency rate calculated according to the American Standard. The criteria for determining the eligibility of an injury for workmen's compensation differ from the definitions of a disabling injury according to the American Standard.)

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Another reason for selecting the disabling-injury case as the basis for calculating frequency and severity rates is that the focus on this category eliminates the possibility that the relatively minor first-aid case may be discouraged by supervision from visiting the dispensary in order to improve the accident record. In minor cases it is very important that appropriate treatment be received promptly to reduce the possibility that an injury will become more severe.

Some safety directors become so absorbed in attempting to develop an extraordinary record of accomplishment that they encourage the employment office to "create" jobs for injured workers who have no permanently disabling injury, but who would be "lost-time" cases according to the standard measure. The failure to count such cases is contrary to the intent of the American Standard, and in such cases the computed work-injury experience would not be properly representative of the plant's accident record as defined by the standard. The practice, although reprehensible because it improperly shades the work-injury record, is not criticizable with respect to the worker, unless, of course, he is placed in an assignment where his injury may be aggravated or where his temporary incapacity would make him more vulnerable to another accident. Many times make-work type assignments are of genuine benefit to the injured worker's morale. Although they should be encouraged where possible it would be better if such moves were not made to favorably affect the work-injury record.

"Work activity or the environment of employment" are terms used by the American Standard to identify those disabling injuries on which the standard is based. The American Standard explains that employment means:

1. All work or activity performed in carrying out an assignment or request of the employer including incidental and related activities not specifically covered by the assignment or request.
2. Any voluntary work or activity undertaken while on duty with the intent of benefiting the employer.
3. Any activities undertaken while on duty with the consent or approval of the employer.

Injuries that occur in normal travel to and from work are not considered to "arise out of employment" unless they occur on the premises of the employer, but not in a parking lot provided by the employer unless the injured worker was carrying out duties in the parking lot for his employer at the time. On the other hand, work injuries do

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include those that happen while traveling in the interests of the employer.

When computing frequency and severity rates for the entire company, injuries from all departments (office, sales, as well as production) should be included along with the man-hour exposures for these operations. Also most companies compute the work-injury experience for the individual components of the company so that each unit can observe its progress.

FREQUENCY RATE

The frequency rate is defined as the number of disabling injuries per million man-hours worked. The formula is expressed as follows:

$$\text{Frequency} = \frac{\text{Number of disabling injuries} \times 1{,}000{,}000}{\text{Number of man-hours worked}}$$

Example: A chemical plant employing an average of 200 workers during 1963 had eight disabling-injury accidents during the year. Calculating on the basis of a 40-hr week for about 50 working weeks each man put in about 2000 hr during the year. Therefore:

$$\text{Frequency} = \frac{8 \times 1{,}000{,}000}{400{,}000} = 20$$

Saying that a production unit has a frequency rate of 20 means that the ratio between disabling injuries and million man-hours worked is 20:1. This frequently disturbs some when they recall, as in the case of our example, that only eight disabling injuries occurred and that in fact the plant would have to work approximately 2½ yr before 1,000,000 hr were accumulated. The 20, therefore, may appear to be unrealistic.

One of the difficulties in applying the standard measure occurs because of its attempt to include practically all disabling-injury accident cases which arise out of and in the course of employment. Sometimes it is not clear whether the injury should be charged as a responsibility of the employer, in the light of the circumstances associated with its cause. Questionable cases may be referred to the Committee on Interpretations of the American Standards Association.[3]

SEVERITY RATE

The severity rate is the number of days charged or lost per million man-hours worked. The lost-time charges include the total actual

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TABLE 30.1. The American Standard Schedule of Time Charges

Nature of Injury	*Time Charges as Number of Days Lost*
Death	6000
Permanent total disability	6000

Fingers, Thumb, and Hand

Amputation Involving All or Part of Bone	*Thumb*	*Fingers*			
		Index	*Middle*	*Ring*	*Little*
Distal phalange	300	100	75	60	50
Middle phalange	...	200	150	120	100
Proximal phalange	600	400	300	240	200
Metacarpal	900	600	500	450	400
Hand at wrist 3000					

Toe, Foot, and Ankle

Amputation Involving All or Part of Bone	*Great Toe*	*Each of Other Toes*
Distal phalange	150	35
Middle phalange		75
Proximal phalange	300	150
Metatarsal	600	350
Foot at ankle 2400		

Arm

Any point above elbow, including shoulder joint	4500
Any point above wrist and at or below elbow	3600

Leg

Any point above knee	4500
Any point above ankle and at or below knee	3000

Impairment of Function

One eye (loss of sight), whether or not there is sight in the other eye	1800
Both eyes (loss of sight), in one accident	6000
One ear (complete industrial loss of hearing), whether or not there is hearing in the other ear	600
Both ears (complete industrial loss of hearing), in one accident	3000
Unrepaired hernia	50

Note: If hernia is repaired, it is not counted as a permanent disability but rather a temporary total disability.
Finger tips: Loss of a finger tip without surgical bone involvement is counted as a temporary total disability.

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calendar days (including holidays, weekends, and plant shutdowns) when the injured person was unable to work (temporarily totally disabled) because of his accident. However, the day of the injury and the day the injured worker returns to work are not counted in the total lost-time charges.

The days-lost charges for permanent disability cases are taken from a schedule (see Table 30.1) provided in the American Standard and applicable for all deaths, permanent total, and permanent partial disability cases. In these cases the actual time lost from work when the accident results in death or permanent disability is not counted. The standard time charges alone are applied. They are considered sufficiently penalizing so that additional time charges are not appropriate. The time charge for a death is arbitrarily set at 6000 days. This is the estimated working life for the average worker. Injuries involving more than one part of the body are calculated from Table 30.1, so as to total the charges for each part except that the total may never exceed 6000 days. When a part of the body is permanently disabled the charge that is greatest for that part in Table 30.1 is used in the calculation, *not that charge plus the smaller charges* for the other lesser sections of the part lost (disabled). Where a person suffers a temporary total disability and a permanent partial disability in the accident the higher of the two injury charges is used.

When an injury results in partial, rather than complete, loss of use of a part of the body the percent loss of use is determined by the employer's physician. The time charge applied in such cases is equivalent to the percent of the loss of use of the member multiplied by the scheduled time charge for the complete loss of use of the member.

Example: A 20% loss of use of the thumb at the proximal joint would be charged as 20% of 600 or 120 days.

The severity formula is: Severity = standard time charges for deaths and permanent disabilities, plus actual days lost for temporary total disabilities, for all of the injuries that have occurred during the period covered by the rate, divided by the number of millions of man-hours worked.

This is more succinctly stated as:

$$\text{Severity} = \frac{\text{Total days lost and charged} \times 1{,}000{,}000}{\text{Number of man-hours worked}}$$

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Example: The chemical plant in the example used for calculating the frequency rate had the following lost-time and permanent disability injury cases during 1963:

Cases			
	Temporary total disabilities:		
3	Three cases resulting in a total of 18 days lost	18 days lost	
	Permanent partial disabilities:		
1	One thumb—10% loss of use at metacarpal joint		90 days charged
1	One eye—50% loss of sight		900 days charged
1	One index finger—amputated at middle phalange (joint)		200 days charged
1	One toe—amputated at distal joint		35 days charged
	Permanent total disabilities:		
1	Hand and foot amputation		6000 days charged
8		18 days lost	7225 days charged

The total time lost and charged for the eight cases in the example is: 7243 days. Therefore:

$$\text{Severity} = \frac{7{,}243 \times 1{,}000{,}000}{400{,}000} = 18{,}107 \text{ days lost and charged per million hours}$$

The frequency and severity rates calculated in the example are atypical for the chemical industry. In actual practice work-injury rates for chemical plants customarily are much lower than the national industrial average. (See page 7.)

Significance of the Standard Rates

Most safety specialists believe that of the two standard rates, frequency and severity, the frequency rate is the better measure of safety performance. This point of view is conditioned in part by the safety program's objective which simply is to eliminate accidents. Certainly when no accidents have occurred the frequency and severity rates are zero, and severity as a measure would have no significance. Although many plants successfully reach the objective, as a practical matter sustained long-term zero work-injury experiences are not likely. There always is the possibility that a momentary lapse will cause an accidental disabling injury, and the perfect zero (frequency = 0) will be interrupted. Then the severity rate assumes importance since it indicates the degree to which effective hazard controls were maintained. Inasmuch as it must be recognized that accidents may happen occasionally a second objective must be to control hazards to a

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degree where severe consequences are not apt to follow an accidental occurrence. The severity rate is a measure of meeting this objective when an accident occurs.

When the number of man-hours worked is small (for example only a few hundred thousand hours) every disabling injury case will cause the plant's frequency rate to rise markedly. In smaller plants, therefore, the work-injury frequency rate may vary widely from year to year and often because relatively mild accidents have taken place.

The frequency rate alone does not give a good indication of the degree to which the plant's hazards are being controlled so as to limit the possibility of any accidents having severe results. The severity rate, therefore, is an important complement of the frequency rate in the standard measure although it does not receive such recognition from many practicing safety specialists. The reason for its disfavor is that often an accident's severity is due largely to chance. For example, the difference between whether a worker mashes a toe, crushes an instep, or misses his foot entirely, when he accidentally drops a heavy section of pipe, is only a matter of inches.

It must be remembered, however, that the frequency rate also is subject to chance. Whether an employee is involved in an accident that results in no injury, a minor injury, or a severe disabling injury that would be included in the frequency rate, may be just a matter of proximity at the moment. Perhaps the principal objection that safety specialists have to the severity rate is that it swings widely, largely because of the penalty charges imposed when a permanent disability occurs. Thus, it becomes difficult for the safety director to identify a generally smooth performance trend and appraise the progress of his efforts. Nevertheless, the severity rate, as a weighted frequency rate, has value in its capacity to reflect the plant's success in controlling its severest hazards.

In general it should be recognized that both the frequency and severity rates are important for appraising safety performance. Certainly a plant with a low frequency but high severity rate would mislead itself if it ignored its severity experience and recorded only its seemingly favorable frequency. In the final analysis it must be remembered that while the practicing safety specialist's long-term objective is to eliminate hazards to the point where accidents no longer will happen, his short range goal must be the identification and control of those hazards which can cause severe loss to the plant and injury to employees. Progress toward both aims deserves continuous appraisal with the best measures available.

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AVERAGE SEVERITY

There is a valuable interrelationship between the frequency and severity rates which often is overlooked. When the severity rate is divided by the frequency, a ratio, the average days lost per disabling injury, results. This in itself often is a useful measurement statistic. It indicates the average severity of the disabling-injury accidents which have occurred during the period being measured.

When the average severity, frequency rate, and severity rate are compared as trends over a number of years, for example 10 yr, a three-dimensional type of measure becomes available.

It is sometimes assumed that a reduction in the frequency of disabling injury occurrence is followed automatically by a proportional improvement in the severity rate. Rarely is this so, however, for a number of reasons. Often the safety program concentrates on improving the frequency rate without applying sufficient emphasis on the steps to take to control the severest exposure. While the latter may not cause accidents frequently (probably because their implicit danger stimulates a greater safety awareness automatically), the time charges when an accident does occur are great enough to cause the severity rate to increase significantly. If, on the other hand, a safety program is successful in eliminating or controlling the plant's severe hazards, the severity rate will improve sharply, if it has been high, and will remain at a low figure once the controls are effective. The average severity trend tends to relate the relative effectiveness in controlling both the frequency of occurrence and severity of results in a plant's disabling-injury pattern.

Figure 30.1 is a "three-dimensional" comparison of the 10-yr frequency, severity, and average severity trends for one company. It will be noticed that both the frequency and severity rates were improving notably, but the average severity trend rose sharply. If the safety program had been uniformly successful in its efforts to reduce the number of disabling injury accidents, the severity rate would have improved proportionately, and the frequency and the average severity trend line would have been flat. A few years later the results of the same company's effective drive on the control of severe accidents is indicated in the pattern in Fig. 30.2. When using this three-dimensional application of the standard measures, it is important to remember that it should be applied in conjunction with the established safety program goals: elimination of accident-producing hazards (frequency

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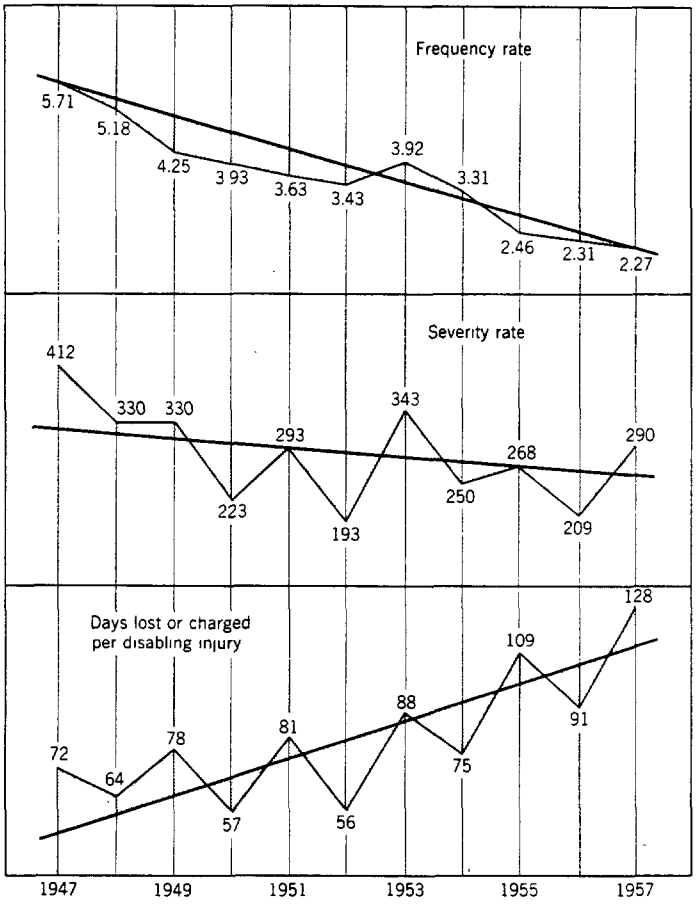

FIG. 30.1. Disabling injuries ten-year trends.

rate reducing to zero) and control of severe hazards to diminish the consequences of any accident that may occur (severity rate reducing to the level of the frequency rate).

Auxiliary Measures of Safety Effectiveness

The foregoing discussions will have indicated that the frequency and severity rates cannot assay fully the quality of a plant's safety

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effort. In the first place a zero frequency rate does not necessarily imply that all is being done perfectly with respect to safety. On the other hand, a high frequency rate does not necessarily mean that an extraordinarily poor safety program exists. In the latter case the type of industry and the operations it employs may limit for the moment the opportunity to develop safety successes common to other more easily controlled businesses. Other methods, therefore, must be

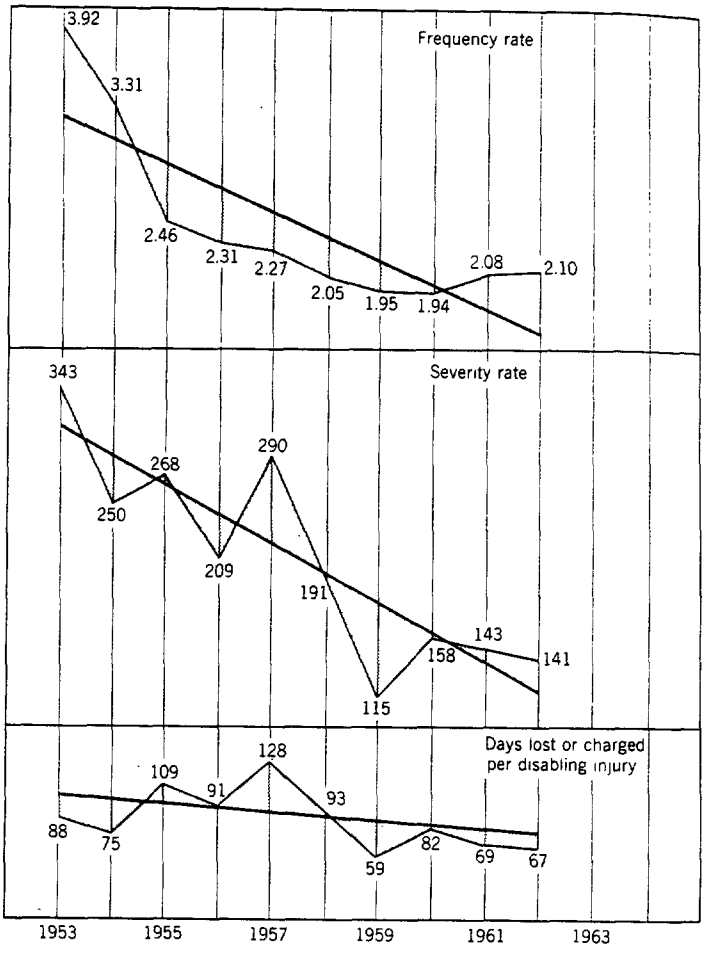

FIG. 30.2. Disabling injuries ten-year trends.

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used to determine whether a satisfactory effort is being exerted to achieve safety effectiveness.[4]

AUDITS

One means of appraising the quality of the plant safety effort is to employ an in-depth examination of the facilities and the attitude, plans, and work of those responsible for the plant. The audit probes the hazard-control effort of the operation and usually is conducted in behalf of the plant's principal manager. A carefully drawn report of the auditor's observation provides an authoritative basis for deciding whether a plant truly deserves the frequency rate it reports.

COMPARISONS

Another means for evaluating the quality of a plant's safety experience is to compare its experience to that of the industry it represents. It is well known that some industries, because of the inherent hazards in their operations, will consistently have higher frequency or severity rates than some others. The question then is whether the plant is doing better than its counterparts and over how long a span has it been improving or sliding.

Other Measures

Safety specialists have been searching vigorously for more descriptive and reliable methods for appraising safety effectiveness. The frequency and severity rates are bitterly condemned, at one time or another, by most safety specialists. However, the efforts of those who have experimented with other measuring methods have not become popular as yet. Among the measuring procedures which have been recommended or described by others are:

1. *The Modern Standard Method.*[1] Several years ago Simonds described a realistic method for relating a plant's accident experience to its costs. The research was conducted under a grant from the National Safety Council specifically to develop a simplified means for expressing the insurance cost plus the other expenses for the disabling-injury cases, doctor's cases, first-aid cases, and no-injury accidents. This method of computing the plant's accident experience has the advantage of being able to report a figure in dollars —a term that is readily recognizable. Frequency and severity, on

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the other hand, may be unintelligible to some. The "modern standard method" intends to overcome that difficulty by expressing itself in terms of the total accident cost experience, rather than only disabling injuries.

2. *Work Sampling Methods.* One means for determining the safety effectiveness of an operation is to sample the plant's work techniques periodically. This practice is becoming a common industrial engineering approach for identifying characteristics in an operation. With respect to safety, for example, a random sampling of unsafe practices and conditions could be obtained by looking for such deviations every 15 min for a brief period (5 min) through several hours of a shift at critical locations. The observations noted would be reported in an analysis that appraises the noted quality of the plant's safety effort. Appropriate recommendations usually conclude the report.
3. *Disabling Injury Index.*[2] Although not a part of the American Standard this measure is included in its appendix as an aid to combining the frequency and severity experience. The measure is:

$$\text{Disabling injury index} = \frac{\text{disabling injury frequency rate} \times \text{disabling injury severity rate}}{1000}$$

This is used primarily for ranking one plant or component against another. If it is to be used to indicate degree of improvement or to compare the degree of difference between plants, the square root of the index must be taken to make a mathematically correct comparison.

4. *Contingency Cost Measures.*[3] This approach relies on a relationship between costs that are a function of managerial performance and the plant's measured effectiveness in controlling severe hazards. The relationship was identified first in an intensive operations research study, and a measure was then constructed. Subsequent studies indicate that the measure should be tailored specifically for each type of industry to obtain the most accurate results. Variations occur in the measured "management variables" (direct labor costs, rework costs, scrap, building maintenance, equipment maintenance, complaint costs, shop costs, and net sales billed) probably because of business factors which are distinctive to the particular industry. However, there is good evidence that the measure generally appraises management's effectiveness in maintaining tight control of its operations, and that the degree of control is related to the plant's ability to control its severe hazards as meas-

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ured by the severity rate. The contingency cost measure in fact appears to have a capacity for forecasting the occurrence of severe accidents by approximately 9 months after the measure shows an established trend of diminishing managerial control.

While it is tempting to use cost figures to express degrees of progress in controlling a plant's work-injury experience, some caution is advised when applying such measures. Certainly costs are effective attention getters, and they are becoming increasingly important to the businessman as he struggles to survive in the market place. However, in many companies the accident experience has been improved to such a degree that its total cost appears almost insignificant compared to the other major sources of operating expense. It is difficult to make a strong case for accident costs, specifically in such an instance, although the management certainly is aware that without its safety programs its costs would be higher.

An overstressing of accident costs may in fact distract from the principal objectives of the safety program, namely, to eliminate or control hazards so that accidents are prevented or will not have severe consequences. Using accidental injuries and costs together as elements of the information-gathering process related to unsafe acts and conditions, and the significance of their influence on the plant's ability to reach its business objectives, would appear to be a most effective means of reporting safety progress.

Measures of safety effectiveness, like any measure, are of value only when they assist administrators to make correct decisions on how to proceed in meeting their responsibilities. The application of the American Standard measure of work-injury experience or any of the experimental indicators of safety effectiveness should be tempered with the knowledge that their principal service is their ability to indicate where weaknesses exist that must be buttressed and where strengths appear that may contain some special knowledge which will assist in moving the total effort forward another giant step.

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3. Committee on Intepretations of the American Standards Association, 10 East 40th St., New York, New York.
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The Future of Chemical Safety

Arthur H. Christian

With the future of chemistry itself almost beyond prediction, how can we predict what the future, even the next decade, will bring to chemical safety? We cannot exactly, but we can try to foretell reasonably the temper of the times ahead. Possibly many of our reflective predictions will not come to pass within the next decade or even the next century. Without question, however, it will be the era of the activist, and it is bound to be full of challenging change for all, particularly those working at chemical safety.

Everything seems to be growing exponentially: total population and new nations; new chemicals and different names for them; new problems and different variations of old problems.

Most important, the pyramid of knowledge is growing exponentially —truly exhibiting a "snowball" effect. With chemistry and chemicals involved with so very many of the "things" and the "action," who can doubt that chemical safety problems will increase proportionately —in numbers, in degrees, in uniqueness, in cost, both to solve and as a penalty for failure to solve, and in difficulty to detect and safeguard.

Some claim there are many existing chemical safety problems of the so-called "unsolvable type." This had better not be true if progress is to continue at the predicted rate. Moreover new techniques and new approaches will have to be found for curing some of our chemical-safety headaches, for undoubtedly soon there will be many tougher ones to solve than hardly could be conjured up in our wildest nightmares. It would be most pessimistic and quite unrealistic to think for a moment that awesome new fields will not be discovered with

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unique hazards not imagined now. These will necessitate unorthodox approaches for safety, just as the field of atomic energy did. All of the accident-prevention problems must be solved in a practical fashion for us to remain competitive as individuals, as companies, as industries, and, yes, even as nations and possibly even as a planet.

Many new fields with unimaginable accident-prevention problems may be opened up by the obvious expendiency of solving more of nature's age-old riddles. Everyone admits that mother nature really has something—for example, an aeronautical engineer knows that theoretically a bumblebee cannot possibly fly, yet the bee takes off anyway.

Imagine the chemical process industry that might evolve when all the chemical mysteries of the human body alone are completely elucidated—for example the exact mechanisms of seeing and hearing, so that light energy and sound energy, through transmutation, could be converted into another more desirable product. Moreover, very complex chemical procedures could be vastly simplified if they could be accomplished in the wonderfully direct manner of life processes.

Undoubtedly, too, the space age will result in chemical-producing plants on space platforms or on far planets. This may result in transportation back to earth of newly discovered elements or chemicals with absolutely unexpected hazards, but with end use of such value as to merit solution of any chemical-accident prevention problems.

Both the "big-science" effort to get man routinely away from earth and the new knowledge found "out there" should yield totally new disciplines in chemistry or involving chemistry. It would seem to be anyone's guess as to what they might be. For example, chemistry on our planet generally is water-oriented for quite obvious reasons. Imagine the personal-protection problems, to say nothing of the technical problems to be solved, if chemistry on a newly settled planet logically should be ammonia-oriented for equally obvious reasons.

What of hazards? There probably will be more acute versions of those presently known. Consider chemical processes—not merely for the foreseeable future but long range. There will be a plenitude of extremes. As a logical avenue of refinement and as a part of evolutionary development, research activities and production will involve more extreme conditions: both higher and lower temperatures; greater vacuums and higher pressures; greater reactivity in all mediums; more insidious toxicity with more unexpected chronic and acute physiological manifestations as a result of unexpected adverse synergistic effects; larger and smaller scale reactions; routes for molecular rearrangement not now known.

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Fundamentally, however, much of chemical accident prevention will remain the same. Any chemical can be handled safely provided full knowledge of all hazards is deliberately obtained and wisely used. Every chemical reaction should be researched in breadth and depth for safety parameters equally as thoroughly as usually is done to maximize quality, productivity, cost, and other production, sale, and use factors. This will be an urgent necessity for the more advanced, complicated, and unknown reactions, and it is most advisable for older processes.

In recent years a number of chemical plant disasters have resulted from unexpected phenomena where a certain set of conditions or sequence of events occurred for the first time, even though the process had been in use successfully and safely for many years. Engineering studies should include evaluation of stability and hazardous characteristics of reactants, the reaction mechanism itself, and the nature of intermediates. Other factors that should be studied include effects of error in the quantity or order of adding chemicals; problems arising from loss of cooling water, interruption of agitation, and malfunction of instrumentation. These may be coupled with excessive heat, pressure, and holding time.

Although actual laboratory or field investigations are invaluable in establishing widely expanded and detailed parameters for safe operation, the whole endeavor of necessity will be greatly simplified. Through use of a vastly improved compilation of data from fundamental research and record keeping, together with more high-speed and thorough methods of data retrieval and association, much more complete overall safety evaluations will be possible. With the growth in numbers of chemicals, the necessity for improved data systems becomes increasingly important, both economically and from a safety viewpoint.

New materials of construction, more knowledgeable and creative engineering design, and new operating techniques will eliminate many of the present-day chemical safety headaches.

For example, contact between people and chemical processes, even maintenance people, largely will be eliminated, as the equipment will be fail-safe, check itself out, and even automatically replace faulty miniaturized and unitized components.

As new materials for fabrication of equipment are discovered, devised, or formulated, many difficult problems will be solved. Corrosion will be eliminated. Standardization of reactor size and type will permit molded systems of complex piping so that an entire system can be replaced by remote control. Reactors themselves will

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play the role of catalyst. In similar fashion walls and other building parts will serve to filter and react any chemical contamination, converting it to a harmless or acceptable compound. We will come ever closer to perfection in many thought-provoking areas—the universal solvent with no toxicity, flammability, or other undesirable side effects; the perfect inert material for construction of everything from buildings and process equipment to packages and consumer products; recovery systems to reprocess practically everything as so-called raw materials will become more scarce and will be re-used more and more.

The problem of the aging and marginal chemical-producing or consuming plant will not be solved easily. While many of these no doubt will be in good use for many decades to come, again, to be competitive, they must be ever alert to improve their accident-prevention features, techniques, and safeguards. As for replacement, the population explosion probably will help in that urban redevelopment will overtake it.

With the continued growth and evolutionary maturing of chemical industry, the necessary location of both expansion phases and sophisticated new fields must be carefully considered. Air and water pollution alone will be tough problems to solve, as we know now. Add to this exposure hazards of types not yet encountered, such as sound, light, or other phenomena emotionally or physiologically harmful, and it would seem indicated that one logical course might be for these plants to be completely segregated from normal living areas using common services. This would be essentially a further refinement of the "industrial parks." Again, to be competitive and to control gross hazards, it may be necessary to use vast and complex disposal plants, with entire manufacturing areas "atmosphere conditioned" to preclude release of harmful materials. One advantage might be sharing maintenance and other service personnel.

Revolutionary new approaches might also be indicated, such as locating plants deep underground where they would be more immune to enemy assault, closer to raw materials, and utilize energy from deep within our earth.

Other plants might be located deep under the ocean or at least as an artificial island—again close to raw material, using solar or sea energy —remotely controlled and practically uninhabited.

Automation and computer control will team up to cause awesome changes in technology and operations. Not only will major strides continue in the present areas of controlling chemical processes by automatically measuring and correcting variables from predetermined

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"programs," but other refinements will benefit accident prevention. For example, by combining all applicable "instant literature" and knowledge from vast research, these machines will greatly outperform humans in sensing or predicting when an accident, such as an explosion, is about to take place, and avert it. This technique even will be brought to bear in prevention of "garden variety" injuries such as cut fingers.

Transportation of chemicals will become an increasingly significant safety consideration. Most trends obviously will not make problems simpler: volume increases; hazards and variety become greater; traffic will be more congested on highways; residential areas and onlookers much more prevalent to complicate matters in case there is trouble; consumers will be more widespread.

While there may be no revolutionary new modes of transporting chemicals, there unquestionably will be impressive evolutionary refinements. Emphasis will be on efficiency and savings—dehydration where possible, standardized sizes and unit packs, automated handling —in fact, separation of chemicals from humans both for handling and during transit. Use of pipelines, with greater variety of chemicals through the same system, solids as well as liquids and gases will increase. So will barges, ships, and underwater plastic tanks. Automated high-speed trains or driverless vehicles on special commercial superways or tunnels will further isolate chemical freight problems from the population.

Possibly our advances in accident prevention generally have actually lulled far too many of us into a false sense of security. In spite of headline accidents every now and then, who hesitates nowadays to step into a high-speed elevator, climb aboard a jet airliner, take a pill, or use a new oven cleaner? Few indeed!

The use of chemicals will be increasingly wider, and thus exposure will be greater. The education of vastly larger numbers of consumers in the safe use of many new chemicals is going to be a challenging problem in itself. It will not be restricted to large and small chemical *industries* themselves, but essentially will cut across all human activities. Chemicals in toy or educational chemistry sets will become more hazardous as will laboratory courses at school. Do-it-yourself kits and materials available for home use will become similarly more sophisticated with severe potential hazards. Certainly the manufacturing chemical industry has both a responsibility and a vested interest to insure that the safest products possible are formulated and marketed, and that the consuming public is well educated in safe

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practices and precautions. Hopefully such education will start early in school life.

Legislation to prevent marketing of possibly hazardous chemicals, or to require full labeling to show contents, hazards, and precautions may be steps in the right direction but cannot be the full answer. In fact, legislative fiat may not contribute to improved safety—only to confused mediocrity.

Disposal of waste is a problem that seems to increase in direct proportion to the advance of civilzation. Regarding chemicals, the rate may be more acute, both for manufacturer and consumer. As quantities increase, hazards become more complex, legislation becomes tighter on methods and exposure allowed, and as costs go higher, disposal will become a greater factor. Certainly existing processes well may have to be modified and initial research efforts on new products or processes will have to carefully appraise impact of disposal problems.

With all this, though, what may be some of the avenues to safe and practical disposal? Conversion to useful products, however elaborate may be the route, may be the most attractive goal. Others may include orbiting, but we shudder at contemplating space becoming a dumping ground.

Rapid advances in hazard control will be a must. New approaches, solid achievements in furthering fundamentals, and diligent application of specifics—all adding up to hard, hard work at controlling chemical hazards—will be necessary to allow continued great achievements and advancement in the chemical industry. Many rewards will come from interdisciplinary research in the form of startling refinements of existing knowledge and practices. More important, we should anticipate amazing breakthroughs in accident prevention, and these well may come from completely outside the field that will benefit the most. For example, Madame Curie was not a physician, but her discovery of radium benefited the practice of medicine profoundly. Hopefully chemical safety will be made easier and more positive from such blessings.

Much progress no doubt will ensue simply from application and refinement of currently recognized fundamentals. Competition among equipment manufacturers will be so keen that key among designers will be safety engineers. Possibility of product liability must be eliminated on the drawing board. Safety features will be prime sales lures. Mechanical guards and intricate electronic interlocks to avoid any exposure to physical injury will be automatically part of minimum

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or stripped models! Electrical shock will be a thing of the past, because of self-contained power sources. Falls will be unheard of. Each industrial worker will wear a tiny gyro stabilizer, controlling him nicely in preset planes. Scaffolding will be unnecessary, as workmen will simply use a by-then perfected degravitizer belt.

Even hand injuries will be an almost unremembered misadventure. In addition to greater inherent safety in "things" being handled, such as truly unbreakable bench-scale "glassware" equipment, the ultimate in hand-protection gear will be available. Through chemistry, indestructible, impenetrable, comfortable, and practical gloves will be commonplace.

Highly developed complex continuous monitoring devices will safeguard the entire working environment to protect people, property, process, and material absolutely against *all* potentially harmful chemicals or hazards, either in the process or in maintenance material. A speedy analysis on the spot of the total work area automatically will be fed into a computer for proper readout and corrective action. No longer can the process be safe, and a disaster wander in with repair kits. *Positive control will have arrived.*

Regardless of the wondrous advances in the field of chemistry and in other related fields of endeavor, all will have one common denominator—people. Only people can make things happen, and, of course, most regrettable things happen to people. While much detailed effort invested in preventing a chemically involved disaster probably will yield as in the past very gratifying results, efforts to control or change people and their action probably will be slow, frustrating, and disappointing. Mores will change for the better very slowly. It is extremely unlikely that a strain of workers might be bred that would have greater resistance to effects of toxic chemicals or be more accident proof. The so-called "personal factor" will continue to be a significant part of the cause of chemical accidents and loss, and a target worthy of much effort to control.

Hopefully, chemicals and other advanced techniques may open completely new fields to help people conquer safety problems as they have helped to cure mental illness. If electric shock and drugs can help eliminate or re-orient undesirable mental patterns, why cannot a safety vaccine be developed? Why cannot new employees receive the maximum in safety orientation and job training by the simple expedient of receiving a shot during the employment physical, followed by several sessions of wearing an electronic headpiece? An electronic headpiece well might serve a useful purpose also to program a person's activities during an entire working shift, probably shortened to a few

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hours. Precise actions to be followed would already have been programmed taking into consideration his abilities and limitations, both physical and mental. These then would be somewhat like old-time horse blinders. They would be a space-age version that would eliminate the personal factor in accidents by eliminating extraneous thoughts during the work period, and would keep the worker's attention fully concentrated on doing the job in exactly the safest and best manner.

Undoubtedly such a procedure will get stout resistance from many defenders of individual rights, as they will be appalled at the thought of such regimentation, and tinkering with the mind and its wondrous body. Few will stop to contemplate that this really would be only a question of degree—tinkering of this sort has been going on for ages, but not in such specifically tailored fashion.

In such an advanced age of enlightenment, safety education will be included truly at the "grass roots," beginning in very early school years. By the time the highly trained chemically oriented specialist is graduated, he will be highly proficient in the knowledge and practice of chemical safety. This single advance alone should go far to improve safety practices in the profession—from research through production to ultimate consumption and disposal.

In spite of all the probable progress in prevention, it would be unrealistic to postulate that every activity always would be under positive control, and the possibility of an unexpected event out of the question.

Protection of people as a secondary line of defense still will be most prudent but vastly more sophisticated. First, through great strides in medical science, pre-employment physicals will be a great deal more revealing, both as to exact status of applicant's health, in addition to his possible susceptibility to future occupational exposures. Much of this knowledge will come from actual complex analysis and diagnosis by instruments of the future, but with the final decisions by people.

When workers are exposed to possibly harmful chemicals, personal protection by complete encapsulation will be commonplace.

Cost of work injuries may have risen to prohibitive levels, and as much from defense to stay competitive as from interest in the workers' welfare, chemical companies will maintain completely integrated safety programs. Personnel will be monitored continuously on the job for certain factors, and quite thoroughly at the end of the work period. Various bodily functions of each worker, depending on exposure, will be followed by advanced techniques—pulse, respiration,

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temperature, and possibly as yet undiscovered "indicators." Physiological response would conclusively prove whether or not an injury occurred on the job; if so, when, and to what degree. The rapid but thorough complete physicals at end of shift could show if any exposure with possible delayed response had occurred.

Happily, if in spite of all this accident-prevention effort a serious injury does happen, severity will be greatly lessened by heroic medical measures. Complete rehabilitation and replacement of body organs and limbs will be commonplace, and chemical science will have made remarkable contributions to these advances in successful technique.

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Appendix I

Sources of Information on Chemical Safety

1. Agricultural Ammonia Institute, 703 DuPont Building, 22 South Second St., Memphis, Tenn. 38103 (telephone 901-5250811), is the educational trade association for the anhydrous ammonia industry. Zenas H. Beers is executive vice-president.

2. Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh 13, Pa. (telephone MAyflower 1-1100), is a nonprofit membership organization composed of industries with air pollution problems; manufacturers of air pollution-abatement equipment; control officials, and research, education, and consulting personnel. The Association's Technical Council works toward international adoption of reasonable engineering performance standards. APCA through its Council seeks to establish definitions, methods, procedures, and recommended practical limits of air-pollution emission for the guidance of the membership and others who are interested. The association publishes bimonthly the *Journal of Air Pollution Control Association* and a monthly *Abstract*. It is the only technical association which has as its only objective the control of atmospheric pollution.

3. Air Traffic Conference of America is a division of the Air Transport Association of America, 1000 Connecticut Ave., N.W., Washington 6, D. C. (telephone 296-5800). This group obtains information on chemicals and other items which may be offered for transport by air or carried on commercial airlines, and issues bulletins outlining the proper handling or prohibiting their transport. These bulletins are sent to subscribers of tariff 6-C. In view of the current interest in the role of cargo or baggage in air safety, restrictions and rules of this group are observed by commercial airlines. H. G. Gatlin, operations division of operation and engineering dept., handles technical problems.

4. American Association of Industrial Nurses, 170 East 61st St., New York 21, N. Y. (telephone TE 8-7625), is the professional organization of the industrial nursing specialty. Members are professional nurses employed by industrial, commercial, and business concerns in the United States and Canada. The monthly publication, *American Association of Industrial Nurses Journal,* contains frequent articles in the field of industrial health. Mrs. Helen C. Rush, R.N. is executive director.

5. American Chemical Society, 1155 Sixteenth St., Washington, D. C. (telephone RE 7-3337), is the professional society representing most

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chemists in the United States. Through the Committee on Chemical Safety, organized in 1963, the A. C. S. is engaged on a broad effort to increase safety awareness at all levels, from high school chemistry through industrial research. Chairman of the Committee is Dr. H. K. Livingston, Professor of Chemistry, Wayne State University, Detroit, Michigan; staff contact is Mr. David Roethel at the A.C.S. Washington headquarters.

6. American Conference of Governmental Industrial Hygienists, 1014 Broadway, Cincinnati 2, Ohio (telephone DU 1-2200, ext. 2654), is concerned with coordination of standards for safe use of chemicals insofar as governmental control is possible. Most widely known annual activity of this group is preparation of a revised threshold limit value for several hundred different gases, vapors, dusts, fumes, and mists. These values are based on experience or information which attempts to estimate the concentration level at which it is believed injury will not occur during normal work exposures. Further information about the listing and other work and publications of this group should be referred to Mr. A. Hosey, secretary.

7. American Industrial Hygiene Association, 14125 Prevost, Detroit, Michigan 48227 (telephone VE 6-0058), is concerned with the practice and science of industrial hygiene. Publications of the Association include the *Journal of the A.I.H.A.*, *Hygienic Guides* for over 100 chemicals and other substances, and manuals on air pollution, industrial noise, and respiratory protective devices. In preparation are manuals on engineering and on analytical guides. George D. Clayton is executive secretary.

8. American Institute of Chemical Engineers, 345 East 47th St., New York 17, New York (telephone PL 2-6800), has two groups concerned with safety. The program committee has a safety subgroup, which considers air and ammonia, refining and natural gas, and chemical safety. Six manuals on safety in air and ammonia plants are in print. Two surveys on safety in air and ammonia plants are available. The chairman of the safety subgroup is W. L. Bulkley, American Oil Co., P. O. Box 431, Whiting, Indiana.

The Equipment Committee of the A.I.Ch.E. formulates and promulgates recommended procedures for the testing of chemical engineering equipment. Stafford L. Ruhlen, E. I. DuPont de Nemours & Co., Inc., Beaumont, Texas, is chairman of the equipment testing committee. Ten equipment testing procedures manuals are available.

The Institute also publishes frequent articles on safety in its several publications, and it arranges safety symposia in design and operations at national meetings.

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9. American Medical Association, Department of Occupational Health, 535 N. Dearborn St., Chicago, Illinois (telephone 5271500) serves primarily member physicians. It does not act as an information center for inquiries by laymen.

One of the A.M.A. specialty journals is the *A.M.A. Archives of Environmental Health*. This monthly publication contains numerous articles on health, safety, and toxicology of chemicals, as well as on other factors in industrial hygiene control. Subscriptions are available from the American Medical Association. J. T. Siedlecki is assistant director.

10. American Nurses' Association, 10 Columbus Circle, New York 19, New York (telephone JU 2-7230) is the national professional organization of registered nurses. Mrs. Judith G. Whitaker, R.N., is executive director of the association.

Chemical Safety is the concern of the occupational health nurses section. Miss J. A. Cipolla, R.N., is the association director for this section. Objectives for the section include: improving nursing practice on the part of the practitioner, continuing the education of the occupational health nurse, and safeguarding the economic security of section members. The focus of occupational health nursing programs is going beyond the emergency care concept to placing more emphasis on the prevention of disease and promotion of health.

11. American Petroleum Institute, 1271 Avenue of the Americas, New York 20, New York (telephone JUdson 6-4200), is concerned with technical aspects of the petroleum and related industries. Various committees develop information and reports for sale at a nominal price on chemicals and other substances derived from or related to petroleum. Many of the petroleum practices and procedures apply in large measure to chemical operations, such as storage tanks, piping, cleaning of tanks, and tank cars, static prevention, fire protection, industrial hygiene practices, air pollution, and waste disposal.

A booklet entitled *List of Publications and Materials, American Petroleum Institute* is available from publications section of the A.P.I. J. F. McKenna is safety coordinator.

12. American Society of Mechanical Engineers, 345 East 47th St., New York (telephone PL 2-6800), is a technical society with phases which reach into chemical safety, such as corrosion, pressure vessels, pressure piping, and related subjects. The Committee on Air Pollution Controls of the A.S.M.E. publishes a semi-monthly newsletter titled "Smog News," a clipping service for articles in the public press on air pollution and related topics, and is available for $6 per year (24 issues). Technical papers on air pollution and other subjects are

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published as part of the Transactions of the A.S.M.E. Series A, in *Journal of Engineering for Power.*

13. American Standards Association, Inc., 10 East 40th St., New York 16, New York (telephone MU 3-3058), is the United States member of the International Organization for Standardization. The source of information on toxic dusts and gases, classed as Z37, is from a technical committee charged with responsibility for developing standards. These standards are sold at a nominal cost and include several on exposures to chemicals. A list of available American Safety Standards will be furnished on request. Henry G. Lamb is safety engineer for the A.S.A.

14. Association of Casualty and Surety Companies, Accident Prevention Department, 110 William St., New York 38, New York (telephone BE 3-0700), obtains information on accident prevention from varied sources and makes it available to casualty insurance companies which constitute its membership. Chemical information is published in a *Chemical Hazards Information Series,* which has been indexed covering 1949–1959, in March 1960. Another group of reports which includes some chemicals is the *Special Hazard Bulletin* series, an index for which covering 1948–1959 has also been issued under March 1960 date.

Copies of reports may be obtained from a member company or agent. James C. Roumas is director of technical research.

15. Bureau of Explosives, Association of American Railroads, 63 Vesey St., New York, New York (telephone CO 7-6788) formulates shipping regulations for dangerous substances. Mr. T. C. George, agent, published in the fall of 1963 I.C.C. Regulations No. 15 on the transportation of explosives and other dangerous articles. The U. S. Coast Guard Regulations are published as I.C.C. No. 16. B. E. Pamphlet No. 7 contains general information relating to explosives and other dangerous articles. Annual reports are published covering the various activities of the Bureau, and include a compilation of reported accidents that have occurred in transportation in which explosives or other dangerous articles were involved, the most recent of which is B. E. Report No. 57 for 1963. For further information and prices on publications, contact the Bureau. Mrs. N. Kelly is supervisor of tariffs and publications.

16. Chemical Specialties Manufacturers Association, Inc., 50 East 41st St., New York, New York (telephone MU 5-8722), is a trade association composed of 500 companies whose members manufacture and distribute chemical products for household and industry. The Association acts as a clearing house for scientific developments in the

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industries of its membership. In addition to publishing and distributing, free to members, copies of the proceedings of the annual and midyear meetings, CSMA publishes folders on labeling, caring for industrial floors, and testing products of industries it represents. The Association works with governmental agencies for uniformity in legislation in matters affecting the industry. It has also published compilations of economic poison laws, brake fluid and anti-freeze laws, labeling laws and regulations for hazardous substances, and an aerosol guide. Detailed information about the association or its activities may be obtained from the secretary, A. A. Milliken.

A 102-page booklet, *C.S.M.A. Vendors to the Trade*, is a guide to the material supplies offered by the membership, classifies products by makers, and lists the makers by their products.

17. Chlorine Institute, Inc., 342 Madison Ave., New York, New York (telephone MU 2-4324), is a nonprofit association which provides chlorine producers, users, and firms with related interests to deal constructively with common industry problems in the areas of safety, transportation, regulations, legislation, and community relations. Safety and related experiences and problems are shared through committees, principally the technical committee on container specifications and safety and the committee on transportation. The results of committee deliberations are distributed on a worldwide basis to chlorine producers and other interested persons in the *Chlorine Manual* (a 32-page booklet, the third edition was published in 1959) and some 60 engineering and design recommendations, and drawings. A copy of the Institute's current publication list will be sent on request to the secretary, Robert L. Mitchell, Jr.

18. Compressed Gas Association, Inc., 500 Fifth Avenue, New York, New York (telephone LA 4-4796), is a nonprofit membership organization which coordinates activity in the safe handling and use of various compressed and liquefied gases. These include the large tonnage gases, such as oxygen, nitrogen, carbon dioxide, fluorocarbons, hydrogen, acetylene, ammonia, and medical gases. Standards are available on valves, cylinder testing, and related subjects. A list of pamphlets is available on request. Frank Fetherston is secretary-treasurer.

19. Factory Mutuals Engineering Division, 1151 Boston-Providence Turnpike, Norwood, Massachusetts (telephone Norwood 762-4300) is the inspector and engineering service for several mutual fire insurance companies which write industrial fire insurance. Most of the data on chemicals and other industrial fire sources is available in *Handbook of Industrial Loss Prevention*, published by McGraw-Hill Book Co., New York, 1959. A monthly newsletter, "Factory Mutual Record,"

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is available by subscription, and frequently contains articles on the fire-safety aspects of chemicals and other industrial hazards. H. E. Magnuson is director of publications.

20. Industrial Hygiene Foundation of America, Inc., 4400 Fifth Avenue, Pittsburgh, Pennsylvania (telephone MA 1-1100), is an association of industries and groups interested in industrial health. Sources of information are current literature and reports of the research studies conducted in the foundation's laboratories. These are primarily toxicological, biochemical, and histopathological investigations. The Industrial Digest is a monthly abstract service of the current literature, which is published primarily for members. Dr. R. T. P. de-Treville is managing director.

21. Institute of Makers of Explosives, Room 2449, 420 Lexington Ave., New York, New York (telephone MU 3-4229) obtains information and experience reports on explosives and related substances and makes summary reports for its members only. Explosives consumption reports are sent to the U. S. Bureau of Mines for inclusion in the annual report. An index of the publications issued by the Institute on specific subjects, such as the American Table of Distances, and Safety in the Handling of Explosives, is available without charge.

22. Manufacturing Chemists' Association, Inc., 1825 Connecticut Ave., N.W., Washington, D. C. (telephone HU 3-6126), is the trade association representing many of the major producers and users of chemicals. Long aware of the importance of proper instructions for safe handling and proper use of chemicals, various M.C.A. committees have developed a large volume of authoritative information on specific substances, as well as on general topics, such as air pollution, waste disposal, tank cars, and laboratory safety. For example, nearly a hundred Chemical Safety Data Sheets have been issued, each on specific large volume chemical. A series of chemical safety guides covers miscellaneous aspects of safety in the chemical industry. *Guide for Safety in the Chemical Laboratory*, 234 pages, was published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, New York in 1954 after preparation by the General Safety Committee of M.C.A., and a revised edition is in preparation.

The M.C.A. offers a free information service dealing with any aspect of chemical safety. It also furnishes a free list of the various publications which are sold at nominal charge. F. Gordon Stephenson is staff secretary of the general safety and fire protection committee.

23. National Board of Fire Underwriters, 85 John St., New York, New York (telephone BE 3-1400), is an organization of capital stock fire insurance companies, maintained for the purpose of conserving

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life and property from fire, explosion and associated effects, by providing engineering, statistical, and educational services to the public. It maintains a staff of technically trained experts and research engineers to evaluate fire and explosion hazards and make recommendations for their alleviation. The engineering department is composed of three divisions: municipal surveys, codes and standards, and technical research. Standards and recommended practices for a large number of topics which include chemicals in various forms are available. A series of research and technical survey reports and special interest bulletins have been issued, including reports on the hazards of salt baths, chlorine dioxide, organic peroxides, and nitroparaffins. Further details on available information may be obtained by writing or calling the N.B.F.U. Dr. M. M. Braidech is director of research.

24. National Clearinghouse for Poison Control Centers, Division of Accident Prevention, Poison Control Branch, U. S. Public Health Service, Department of Health, Education and Welfare, Washington, D. C. (telephone WO 3-7513). This group obtains from many sources information on the various chemical constituents of household products and their toxicity. It welcomes submitted data on composition and emergency treatment of any substance that may be accidentally eaten, breathed, or otherwise find its way into a human body. The information is disseminated to over 500 member poison-control centers in the United States and Canada on 5 x 8 index file cards. These cards are available to operating poison-control centers, usually designated by state health departments. A periodic newsletter is available to anyone working in the area of poisoning, other accidents, or clinical medicine. Mr. Henry Verhulst is director of the national clearinghouse.

The various poison control centers in large cities keep their files open 24 hours a day for emergency consultation by physicians who are called to treat a poisoning case. In addition, an active program of public education on prevention of poisonings from chemicals is underway.

25. National Fire Protection Association, International, 60 Batterymarch St., Boston, Massachusetts (telephone HU 2-1630), is a nonprofit technical and educational organization with a total membership of 17,000. Its sole objective is the reduction of loss of life and property by fires and explosions. In addition to the regular publications issued (including the quarterly, which is the technical journal of fire protection), the N.F.P.A. has many active technical committees which develop standards of good practice and other recommendations to safeguard life and property. The N.F.P.A. committee on chem-

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icals and explosives, for example, has underway several projects involving the safe handling and use of chemicals and related substances. Among these projects are a revision of the table of common hazardous chemicals, a code on explosives and blasting agents, a manual of hazardous chemical reactions, and a standard for storage and handling ammonium nitrate. C. I. Babcock, Jr., is staff chemist and also manager of the fire records department.

26. National Plant Food Institute, 1700 Kay St., N.W., Suite 1004, Washington, D. C. (telephone 296-3225), is the national trade association which promotes the interests of the entire fertilizer industry. Its membership is composed of manufacturers, importers, and brokers of fertilizer and fertilizer materials. The Institute is primarily concerned with information of value in the storage, handling, and use of all plant foods, but is not concerned with economic poisons. The Institute strongly supports the program of the Fertilizer Section of the National Safety Council, and conducts a series of accident prevention schools. Numerous publications issued by the Institute include: *Plant Food Review* (a quarterly magazine available on subscription), a catalogue of films and other visual aids on plant foods and other services of the Institute. Paul T. Truitt is president, and Louis H. Wilson, vice-president of information.

27. National Safety Council, 425 N. Michigan Ave., Chicago, Ill. (telephone 527-4800), is a nonprofit organization chartered by the Congress of the United States to work for the prevention of injuries and deaths on the highway, in the home, and on the job. The monthly *National Safety News* frequently contains articles on chemical safety.

The Chemical Section of the Council, which is one of the largest sections of the Industrial Division, coordinates information for use by persons using chemicals and allied substances. The *Chemical Section Monthly Safety Newsletter* is devoted exclusively to chemical safety. Grant Shibley is staff representative, and Julian Olishifski is industrial hygienist.

The Occupational Health Nursing Committee, Mrs. A. Kloiber, R.N. chairman, and Mrs. D. Glover, R.N. staff representative, coordinates occupational health work of various other sections of the Council, and develops its own publications including a monthly newsletter.

A directory of N.S.C. services is available on request.

28. Society of the Plastics Industry, Inc., 250 Park Ave., New York, New York (telephone MU 7-2675) is a trade association which coordinates information for the plastics industry. The major technical data are presented in the *Plastics Engineering Handbook*, 3rd edition, 565 pages, published 1960 by Reinhold Publishing Corp., New York 22,

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N. Y. *The Plastics Safety Handbook,* 208 pages, contains essential information on a safety program for the plastics industry and related operations, and was jointly developed by the Society of the Plastics Industry with the National Safety Council in 1959. The S.P.I. Committee on Fire Prevention has developed a series of leaflets on various aspects of fire protection in the plastics industry. Information on various publications with their charges is available by writing the Society in care of William T. Cruse, executive vice-president.

29. U. S. Department of Agriculture, Agriculture Research Service, Pesticides Regulation Division, Independence Ave., between 12th and 14th St., S.W., Washington, D. C. (telephone RE 7-4142), is the group charged with insuring that commercial products comply with the Federal Insecticide, Fungicide, and Rodenticide Acts of 1947 as amended. Although much of the information is of confidential nature, the group will refer inquiries to the prime manufacturer of the chemical in question.

30. U. S. Army, Headquarters, Materiel Command, Building T7, Washington, D. C. (telephone OX 5-9595), is to perform assigned material functions of the Department of Army comprising research, development, engineering, testing and evaluation, procurement, and production. All army material is developed, produced, supplied, and maintained by the Army Materiel Command. Director of safety is Fred M. Bishoff.

31. U. S. Department of The Interior, Bureau of Mines, Washington, D. C. (telephone EX 3-6400), is the central administrative group for all activities of the bureau. The Explosives Research Laboratory is part of the Central Experiment Station of the bureau and is located at 4800 Forbes Ave., Pittsburgh, Pa. (telephone MA 1-4500). Information and reports on chemicals result from the laboratory investigation, and publications appear as Information Circulars, as Reports of Investigations, or in the outside literature. Robert W. Van Dolah is chief, Explosives Research Laboratory.

The Health and Safety Activity of the Bureau of Mines also has laboratory facilities at the Central Experiment Station in Pittsburgh. This group tests and publishes approval lists of respiratory protective equipment ranging from dust respirators to self-contained breathing apparatus. Selden J. Pearce is chief, Branch of Health Research.

All publications of the Bureau of Mines are listed in *New Publications, Bureau of Mines,* which is issued monthly.

32. U. S. Department of Health, Education and Welfare, Public Health Service, Communicable Disease Center, Technical Development Laboratories, P. O. Box 769, Savannah, Ga. (telephone 912-

8972741) is concerned with the toxicology of pesticides and other economic poisons. A list of publications of the Technical Development Laboratories, listing 289 references published between 1945 and 1959, is available on request as Reprint Number 294, "Pesticides in Relation to Public Health," by Wayland J. Hayes, Jr., reprinted from the *Annual Review of Entomology*, 5, 379–404, 1960.

Clinical Memoranda on Economic Poisons prepared by this group is a 78-page report (Public Health Service Pub. No. 476) on the fundamental aspects of toxicology of common poisons. Dr. Wayland J. Hayes, Jr., is a medical director and chief of the toxicology section, Toxicology Branch, Communicable Disease Center, U. S. Public Health Service, Atlanta, Ga. (telephone 912, 6345131).

U. S. Public Health Service, Occupational Health Branch, 1014 Broadway, Cincinnati, Ohio (telephone DU 1-2200, ext. 681), is a consulting organization which gathers, digests, abstracts, and re-issues information on occupational health problems including toxicity and safe handling of chemicals. No charge is made for information and publications supplied by this section. Any individual or organization, private or governmental, is privileged to request information and consultation services on matters of occupational health. Within reasonable limits of utilization of staff and facilities, every effort is made to supply requested information. Discretion is exercised with regard to the information but assurance of confidentiality can be granted only for specific cases. An Occupational Health Information Exchange has been established recently by the collection and exchange of information on all aspects of occupational health. Questions, contributions, and cooperation are welcomed. Dohrman H. Byers, scientist director, is in charge of the Occupational Health Information Exchange.

33. U. S. Department of Labor, Bureau of Labor Standards, Division of Safety, Washington, D. C. (telephone EX 3-2420), concerns itself with standards for federal education and regulations of labor. It prepared bulletins, pamphlets, charts, and other educational material for public distribution. Six wall charts on hazards and safe handling of various chemicals, and seven folders on hazards of other chemicals are included with other publications on labor legislation and administration, and child labor and youth employment. A booklet, *Selected Publications of the Bureau of Labor Standards*, 1962, is available on request. Robert D. Gidel is Director of the Office of Occupational Safety. Dr. F. A. Van Atta is Deputy Director, Office of Occupational Safety.

34. Underwriters' Laboratories, Inc., 207 East Ohio St., Chicago, Ill. (telephone MI 2-6969), is a nonprofit organization to establish.

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maintain, and operate laboratories for the examination and testing of devices, systems, and materials. Sponsored by the National Board of Fire Underwriters, it is operated for service, not for profit. Examination and tests of submitted products are conducted by a staff of technically trained and experienced engineers in the following departments: electrical, fire protection, gases and oils, chemicals, casualty and automotive, burglary protection, and inspection control. Chemicals of a proprietary type (trade-name labeled) are investigated for fire hazard, and the results are published in the Gas and Oil Equipment List, issued periodically. Lists with bimonthly supplements, are available free of charge to persons requesting them. Mr. Jack Bono is managing engineer of the Fire Protection Department of U. L.

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Appendix II

Threshold Limit Values for 1964

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The threshold limit values refer to air-borne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. Because of wide variation in individual susceptibility, exposure of an occasional individual at or even below the threshold limit may not prevent discomfort, aggravation of a pre-existing condition, or occupational illness.

Threshold limits should be used as guides in the control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. Exceptions are the substances given in Appendix A and certain of the substances given a "C" listing. The values not given a "C" listing refer to time-weighted average concentrations for a normal workday. The amount by which these concentrations may be exceeded for short periods without injury to health depends upon a number of factors such as the nature of the contaminant, whether very high concentrations even for short periods produce acute poisoning, whether the effects are cumulative, the frequency with which high concentrations occur, and the duration of such periods. All must be taken into consideration in arriving at a decision as to whether a hazardous situation exists. Enlightened industrial hygiene practice inclines toward controlling exposures below the limit rather than maintenance at the limit.

Threshold limits are based on the best available information from industrial experience, from experimental human and animal studies, and when possible, from a combination of the three. The basis on which the values are established may differ from substance to substance; protection against impairment of health

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may be the guiding factor for some, whereas reasonable freedom from irritation, narcosis, nuisance of other forms of stress may dominate the basis for others. The Committee holds to the opinion that limits based on physical irritation should be considered no less binding than those based on physical impairment; growing bodies of evidence indicate that physical irritation may promote and accelerate physical impairment. On what basis a limit is developed is given separately for each listed substance in "Documentation of Threshold Limit Values," a publication of the Threshold Limits Committee of the ACGIH.

Ceiling vs Time-Weighted Average Limits. Although the time-weighted average concentration provides the most satisfactory, practical way of monitoring air-borne agents for compliance with the limits, there are certain substances for which it is inappropriate. In the latter group are substances which are predominantly fast acting and whose threshold limit is more appropiately based on this particular response. Substances with this type of response are best controlled by a ceiling "C" limit that should not be exceeded. It is implicit in these definitions that the manner of sampling to determine compliance with the limits for each group must differ; a single grab sample, that is applicable to a "C" limit, is not appropriate to the time-weighted limit; here, a sufficient number of samples are needed to permit a time-weighted average concentration throughout a a complete cycle of operations or throughout the work shift.

Whereas the ceiling limit places a definite boundary which concentrations should not be permitted to exceed, the time-weighted average limit requires an explicit limit to the excursions that are permissible above the listed value. The magnitude of these excursions may be pegged to the magnitude of the threshold limit by an appropriate factor shown in Appendix C. It should be noted that the same factors are used by the Committee in making a judgment whether to include or exclude a substance for a "C" listing.

"Skin" Notation. Listed substances followed by the designation "Skin" refer to the potential con-

tribution to the over-all exposure by the cutaneous route including mucous membranes and eye. This attention-calling designation is intended to suggest appropriate measures for the prevention of cutaneous absorption so that the threshold limit is not invalidated.

Mixtures. Special consideration should be given also to the application of these values in assessing the health hazards which may be associated with exposure to mixtures of two or more substances. A brief discussion of basic considerations involved in developing threshold limit values for mixtures, and methods for their development, amplified by specific examples are given in Appendix B.

"Inert" or Nuisance Particulates. A number of dusts or particulates that occur in the working environment ordinarily produce no specific effects upon prolonged inhalation. Some insoluble substances are classed as inert (e.g. iron and steel dusts, cement, bentonite, silicon carbide, titanium dioxide, cellulose); others may be soluble (starch, soluble oils, calcium carbonate) but are of such a low order of activity that in concentrations ordinarily encountered do not cause physiologic impairment; still others may be rapidly eliminated or destroyed by the body (vegetable oils, glycerine, sucrose). In the case of the insoluble substances, there may be some accumulation in the respiratory passages. In the case of the soluble substances, this accumulation will ordinarily be temporary but may interfere to some extent with respiratory processes. Hence, it is desirable to control the concentrations of such particulates in the air breathed by any individual, in keeping with good industrial hygiene practice.

A threshold limit of 15mg/m^3, or 50 mppcf, whichever is less, is recommended for substances in these categories and for which no specific threshold limits have been assigned.

This limit, for a normal work day, does not apply to brief exposures at higher concentrations. Neither does it apply to those substances which may cause physiologic impairment at lower concentrations but for which a threshold limit has not yet been adopted.

Physical Factors. It is recognized that such physical factors as heat, ultraviolet and ionizing radia-

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tion, humidity, abnormal pressure and the like may place added stress on the body so that the effects from exposure at a threshold limit may be altered. Most of these stresses act adversely to increase the the toxic response of a substance. Although most threshold limits have built-in safety factors to guard against adverse effects of moderate deviations from normal environments, the safety factors of most substances are not of such a magnitude as to take care of gross deviations. For example, continuous work at temperatures above 90°F or over-time, extending the work-week more than 50%, might be considered gross deviations. In such instances judgment must be exercised in the proper adjustments of the threshold limit values.

These limits are intended for use in the field of industrial hygiene and should be interpreted and applied only by persons trained in this field. They are not intended for use, or for modification for use, (1) as a relative index of toxicity, by making a ratio of two limits, (2) in the evaluation or control of community air pollution or air pollution nuisances, (3) in estimating the toxic potential of continuous uninterrupted exposures, (4) as proof or disproof of an existing disease of physical condition, or (5) for carte blanche adoption by foreign countries.

These values are reviewed annually by the Committee on Threshold Limits for revisions or additions, as further information becomes available.

"Notice of Intent." At the beginning of each year, proposed actions of the Committee for the forthcoming year are issued in the form of a "Notice of Intent." This Notice provides not only an opportunity for comment, but solicits suggestions of substances to be added to the list. The suggestions should be accompanied by substantiating evidence.

Legislative Action The Conference does not consider the Threshold Limit Values appropriate matter for adoption in legislative codes and regulations, and recommends against such use.

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RECOMMENDED VALUES

(In Alphabetical Order)

	Substance	ppm*	Mg/M³**
	Acetaldehyde	200	360
	Acetic acid	10	25
	Acetic anhydride	5	20
	Acetone	1,000	2,400
	Acetonitrile	40	70
	Acetylene tetrabromide	1	14
	Acrolein	0.1	0.25
	Acrylonitrile - Skin	20	45
	Aldrin (1, 2, 3, 4, 10, 10-hexachloro-1, 4, 4a, 5, 8, 8 a-hexahydro-1, 4, 5, 8-dimethano-naphthalene) Skin	–	0.25
	Allyl alcohol - Skin	2	5
	Allyl chloride	1	3
C	Allyl glycidyl ether (AGE)	10	45
	Allyl propyl disulfide	2	12
	Ammonia	50	35
	Ammonium sulfamate (Ammate)	–	15
	Amyl acetate	100	525
	Amyl alcohol (isoamyl alcohol)	100	360
	Aniline - Skin	5	19
	Antimony & compounds (as Sb)	–	0.5
	ANTU (alpha naphthyl thiourea)	–	0.3
	Arsenic & Compounds (as As)	–	0.5
	Arsine	0.05	0.2
	Barium (soluble compounds)	–	0.5
C	Benzene (benzol) - Skin	25	80
	Benzidine	–	A1
	Benzyl chloride	1	5
	Beryllium	–	0.002
	Boron oxide	–	15

* Parts of vapor or gas per million parts of air by volume at 25°C and 760 mm. Hg pressure.
** Approximate milligrams of particulate per cubic meter of air.
A Numbers, See Appendix A

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Substance	ppm*	Mg/M³**
C Boron trifluoride	1	3
Bromine	0.1	0.7
Butadiene (1, 3-butadiene)	1,000	2,200
2-Butanone (methyl ethyl ketone)	200	590
2-Butoxy ethanol (Butyl Cellosolve) - Skin	50	240
Butyl acetate (n-butyl acetate)	200	950
Butyl alcohol	100	300
tert. Butyl alcohol	100	300
C Butylamine	5	15
C tert. Butyl chromate (as CrO_3) - Skin	–	0.1
n-Butyl glycidyl ether (BGE)	50	270
Butyl mercaptan	10	35
p-tert. Butyltoluene	10	60
Cadmium oxide fume	–	0.1
Calcium arsenate	–	1
Camphor	–	2
Carbon dioxide	5,000	9,000
Carbon disulfide - Skin	20	60
Carbon monoxide	100	110
Carbon tetrachloride - Skin	10	65
Chlordane (1, 2, 4, 5, 6, 7, 8, 8-octachloro-3a, 4, 7, 7a. tetrahydro-4, 7-methanoindane)	–	0.5
Chlorinated camphene, 60%	–	0.5
Chlorinated diphenyl oxide	–	0.5
Chlorine	1	3
Chlorine dioxide	0.1	0.3
C Chlorine trifluoride	0.1	0.4
C Chloroacetaldehyde	1	3
Chlorobenzene (monochlorobenzene)	75	350
Chlorobromomethane	200	1,050
Chlorodiphenyl (42% chlorine) - Skin	–	1
Chlorodiphenyl (54% chlorine) - Skin	–	0.5
C Chloroform (trichloromethane)	50	240
1-Chloro-1-nitropropane	20	100
Chloropicrin	0.1	0.7
Chloroprene (2-chloro-1, 3-butadiene)	25	90

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	Substance	ppm*	Mg./M³*
	Chromic acid and chromates (as CrO_3)	–	0.1
	Cobalt	–	0.5
	Crag (R) herbicide [sodium 2-(2, 4-dichlorophenoxy) ethanol hydrogen sulfate]	–	15
	Cresol (all isomers) - Skin	5	22
	Cyanide (as CN) - Skin	–	5
	Cyclohexane	400	1,400
	Cyclohexanol	50	200
	Cyclohexanone	50	200
	Cyclohexene	400	1,350
	2, 4-D (2, 4-dichlorophenoxy -acetic acid)	–	10
	DDT [2, 2-bis (p-chlorophenyl) - 1, 1, 1-trichloroethane] - Skin	–	1
	DDVP (O, O-Dimethyl-2, 2-dichloro-vinyl phosphate)	–	1
	Decaborane - Skin	0.05	0.3
	Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)	50	240
	Diborane	0.1	0.1
	1, 2-Dibromoethane (ethylene dibromide)	25	190
+ C	o-Dichlorobenzene	50	300
	p-Dichlorobenzene	75	450
	Dichlorodifluoromethane	1,000	4,950
	1, 1-Dichloroethane	100	400
	1, 2-Dichloroethane (ethylene dichloride)	50	200
	1, 2-Dichloroethylene	200	790
C	Dichloroethyl ether	15	90
	Dichloromonofluoromethane	1,000	4,200
C	1, 1-Dichloro-1-nitroethane	10	60
	Dichlorotetrafluoroethane	1,000	7,000
	Dieldrin (1, 2, 3, 4, 10, 10-hexachloro -6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4, 5, 8-dimethano-naphthalene) - Skin	–	0.25
	Diethylamine	25	75

+1964 Addition or deletion of "C"
†1964 Revision - see Tentative Values

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	Substance	ppm*	Mg/M³**
	Difluorodibromomethane	100	860
C	Diglycidyl ether (DGE)	0.5	2.8
	Diisobutyl ketone	50	290
	Dimethyl acetamide - Skin	10	35
	Dimethylaniline (N-dimethyl-aniline) - Skin	5	25
†	Dimethylformamide - Skin	—	—
	1,1-Dimethylhydrazine - Skin	0.5	1
	Dimethylsulfate - Skin	1	5
	Dinitrobenzene - Skin	—	1
	Dinitrotoluene - Skin	—	1.5
	Dinitro-o-cresol - Skin	—	0.2
	Dioxane (diethylene dioxide)	100	360
	Dipropylene glycol methyl ether - Skin	100	600
	Endrin (1,2,3,4,10,10- hexa-chloro-6, 7-epoxy-1,4,4a,5,6,7,8 8a-octahydro 1,4-endo-5, 8-dimethanonaphthalene) - Skin	—	0.1
	EPN (O-ethyl O-p-nitrophenyl thionobenzenephosphonate) Skin	—	0.5
	Ethyl acetate	400	1,400
	Ethyl acrylate - Skin	25	100
	Ethyl alcohol (ethanol)	1,000	1,900
	Ethylamine	25	45
C	Ethylbenzene	200	870
	Ethyl bromide	200	890
	Ethyl chloride	1,000	2,600
	Ethyl ether	400	1,200
	Ethyl formate	100	300
C	Ethyl mercaptan	20	52
	Ethyl silicate	100	850
	Ethylene chlorohydrin - Skin	5	16
	Ethylenediamine	10	30
+ C	Ethylene glycol dinitrate - Skin	0.2	1.2
	Ethylene imine - Skin	5	9
	Ethylene oxide	50	90
	2-Ethoxyethanol (Cellosolve) - Skin	200	740
	2-Ethoxyethanol (Cellosolve) - Skin	200	740
	2-Ethoxyethylacetate (Cellosolve acetate) - Skin	100	540

	Substance	ppm*	Mg/M³**
	Ferbam (ferric dimethyl dithiocarbamate)	–	15
	Ferrovanadium dust	–	1
	Fluoride (as F)	–	2.5
	Fluorine	0.1	0.2
	Fluorotrichloromethane	1,000	5,600
C	Formaldehyde	5	6
	Furfural	5	20
	Furfuryl alcohol	50	200
	Gasoline	500	2,000
	Glycidol (2, 3-Epoxy-1-propanol)	50	150
	Heptachlor (1, 4, 5, 6, 7, 8, 8a-heptachloro-3a, 4, 7, 7a-tetrahydro-4, 7-methanoindane	–	0.5
	Heptane (n-heptane)	500	2,000
	Hexane (n-hexane)	500	1,800
	Hexanone (methyl butyl ketone)	100	410
	sec-Hexyl acetate	50	295
	Hexone (methyl isobutyl ketone)	100	410
+	Hydrazine - Skin	1	1.3
	Hydrogen bromide	3	10
C	Hydrogen chloride	5	7
	Hydrogen cyanide - Skin	10	11
	Hydrogen fluoride	3	2
	Hydrogen peroxide, 90%	1	1.4
	Hydrogen selenide	0.05	0.2
†	Hydrogen sulfide	–	–
	Hydroquinone	–	2
C	Iodine	0.1	1
	Iron oxide fume	–	15
	Isophorone	25	140
	Isopropylamine	5	12
	Isopropyl glycidyl ether (IGE)	50	240
	Ketene	0.5	0.9
	Lead	–	0.2
	Lead arsenate	–	0.15
	Lindane (hexachlorcyclohexane, gamma isomer)	–	0.5
	Lithium hydride	–	0.025

+1964 Addition or deletion of "C"
†1964 Revision - see Tentative Values

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Substance	ppm*	Mg/M³**
Magnesium oxide fume	–	15
Malathion (O, O-dimethyl dithiophosphate of diethyl mercaptosuccinate) - Skin	–	15
C Manganese	–	5
Mercury - Skin	–	0.1
Mercury (organic compounds) - Skin	–	0.01
Mesityl oxide	25	100
Methoxychlor (2, 2-di-p-methoxy-phenyl-1, 1, 1-trichloroethane)	–	15
Methyl acetate	200	610
Methyl acetylene	1,000	1,650
Methyl acrylate - Skin	10	35
Methylal (dimethoxymethane)	1,000	3,100
Methyl alcohol (methanol)	200	260
C Methyl bromide - Skin	20	80
Methyl cellosolve (2-methoxy-ethanol) - Skin	25	80
Methyl cellosolve acetate (ethylene glycol monomethyl ether acetate) - Skin	25	120
C Methyl chloride	100	210
Methyl chloroform (1, 1, 1-trichloroethane)	350	1,900
Methylcyclohexane	500	2,000
Methylcyclohexanol	100	470
Methylcyclohexanone	100	460
Methyl formate	100	250
Methyl isobutyl carbinol (methyl amyl alcohol)	25	100
† Methyl mercaptan	–	–
+ C α Methyl styrene	100	480
Methylene chloride (dichloromethane)	500	1,750
Monomethyl aniline – Skin	2	9
Molybdenum (soluble compounds)	–	5
(insoluble compounds)	–	15

+1964 Addition or deletion of "C"
†1964 Revision - see Tentative Values

ETC 03612

Substance	ppm*	Mg/M³**
Naphtha (coal tar)	200	800
Naphtha (petroleum)	500	2,000
β - Naphthylamine	–	A2
Nickel carbonyl	0.001	0.007
Nicotine - Skin	–	0.5
† Nitric acid	–	–
p - Nitroaniline - Skin	1	6
Nitrobenzene - Skin	1	5
Nitroethane	100	310
C Nitrogen dioxide	5	9
C Nitroglycerin - + EGDN - Skin	0.2	2
Nitromethane	100	250
1 - Nitropropane	25	90
2 - Nitropropane	25	90
N - Nitrosodimethylamine (Dimethylnitrosamine) - Skin	A3	–
Nitrotoluene - Skin	5	30
Octane	500	2,350
Oil mist (mineral)	–	5
Osmium tetroxide	–	0.002
Ozone	0.1	0.2
Parathion (O, O - diethyl O - p - nitrophenyl thiophosphate) - Skin	–	0.1
Pentaborane	0.005	0.01
Pentachloronaphthalene - Skin	–	0.5
Pentachlorophenol - Skin	–	0.5
Pentane	1,000	2,950
Pentanone (methyl propyl ketone)	200	700
Perchloroethylene (tetrachloroethylene)	100	670
Perchloromethyl mercaptan	0.1	0.8
Perchloryl fluoride	3	13.5
Phenol - Skin	5	19
Phenyl glycidyl ether (PGE)	50	310
Phenylhydrazine - Skin	5	22
Phosdrin (2 - carbomethoxy - 1 - methyl vinyl dimethyl phosphate)	–	0.1

+1964 Addition or deletion of "C"
†1964 Revision - see Tentative Values

ETC 03613

	Substance	ppm*	Mg/M³**
†	Phosgene (carbonyl chloride)	–	–
	Phosphine	0.3	0.4
	Phosphoric acid	–	1
	Phosphorus (yellow)	–	0.1
	Phosphorus pentachloride	–	1
	Phosphorus pentasulfide	–	1
	Phosphorus trichloride	0.5	3
	Picric acid - Skin	–	0.1
	Platinum (Soluble Salts)	–	0.002
	Propyl acetate	200	840
	Propyl alcohol (isopropyl alcohol)	400	980
	Propyl ether (isopropyl ether)	500	2,100
	n-Propyl nitrate	25	110
	Propylene dichloride (1, 2-dichloropropane)	75	350
	Propylene imine - Skin	25	60
	Propylene oxide	100	240
	Pyrethrum	–	5
	Pyridine	5	15
	Quinone	0.1	0.4
	Rotenone (commercial)	–	5
†	Selenium compounds (as Se)	–	–
	Sodium fluoroacetate (1080) - Skin	–	0.05
	Sodium hydroxide	–	2
	Stibine	0.1	0.5
	Stoddard solvent	500	2,900
	Strychnine	–	0.15
+ C	Styrene monomer (phenylethylene)	100	420
	Sulfur dioxide	5	13
	Sulfur hexafluoride	1,000	6,000
	Sulfuric acid	–	1
	Sulfur monochloride	1	6
	Sulfur pentafluoride	0.025	0.25
	Sulfuryl fluoride	5	20
	2, 4, 5T (2, 4, 5 trichlorophenoxyacetic acid)	–	10
	TEDP (tetraethyl dithionopyrophosphate) - Skin	–	0.2

+1964 Addition or deletion of "C"
†1964 Revision - see Tentative Values

ETC 03614

	Substance	ppm*	Mg/M³**
	Teflon (R) decomposition products	–	A4
	TEPP (tetraethyl pyrophosphate) - Skin	–	0.05
	Tellurium	–	0.1
	1, 1, 2, 2 - Tetrachloroethane - Skin	5	35
	Tetrahydrofuran	200	590
	Tetranitromethane	1	8
	Tetryl (2, 4, 6 - trinitrophenyl - methylnitramine) - Skin	–	1.5
	Thallium (soluble compounds) - Skin	–	0.1
	Thiram (tetramethyl thiuram disulfide)	–	5
	Titanium dioxide	–	15
+	Toluene (toluol)	200	750
	o - Toluidine - Skin	5	22
C	Tolylene - 2, 4 - diisocyanate	0.02	0.14
	Trichloroethylene	100	520
	Trichloronaphthalene - Skin	–	5
	1, 2, 3 - Trichloropropane	50	300
	1, 1, 2 - Trichloro 1, 2, 2 - trifluoroethane	1,000	7,600
	Triethylamine	25	100
	Trifluoromonobromomethane	1,000	6,100
	Trinitrotoluene - Skin	–	1.5
	Triorthocresyl phosphate	–	0.1
	Triphenyl phosphate	–	3
	Turpentine	100	560
	Uranium (soluble compounds)	–	0.05
	(insoluble compounds)	–	0.25
C	Vanadium (V_2O_5 dust)	–	0.5
	(V_2O_5 fume)	–	0.1
C	Vinyl chloride (chloroethylene)	500	1,300
	Vinyl toluene	100	480
	Warfarin (3 - [α acetonylbenzyl] - 4 - hydroxycoumarin)	–	0.1
C	Xylene (xylol)	200	870
	Xylidine - Skin	5	25

+1964 Addition or deletion of "C"
†1964 Revision - see Tentative Values

ETC 03615

Substance	ppm*	Mg/M³**
† Yttrium	–	–
Zinc oxide fume	–	5
Zirconium compounds (as Zr)	–	5

Radioactivity: For permissible concentrations of radio-isotopes in air, see U S Department of Commerce, National Bureau of Standards, Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," June 5, 1959 Also, see U S. Department of Commerce National Bureau of Standards, Handbook 59, "Permissible Dose from External Sources of Ionizing Radiation," September 24, 1954, and addendum of April 15, 1958.

* Parts of vapor or gas per million parts of air by volume at 25°C and 760 mm. Hg pressure

** Approximate milligrams of particulate per cubic meter of air.

A Numbers, See Appendix A

†1964 Revision - see Tentative Values

MINERAL DUSTS

Substance	m.p.p.c.f.*
SILICA	
Crystalline	
Quartz, Threshold Limit calculated from the formula	$\frac{250\ **}{\%SiO_2 + 5}$
Cristobalite " " "	
Amorphous, including natural diatomaceous earth	20
SILICATES (less than 1% crystalline silica)	
Asbestos	5
Mica	20
Soapstone	20
Talc	20
Portland Cement	50
"Inert" or Nuisance Particulates	50 (or 15 mg/m³ whichever is the smaller)

Conversion factors

mppcf x 35.3 = million particles per cubic meter
= particles per c.c.

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* Millions of particles per cubic foot of air, based on impinger samples counted by light-field technics.

** The percentage of crystalline silica in the formula is the amount determined from air-borne samples, except in those instances in which other methods have been shown to be applicable.

[redacted]

TENTATIVE VALUES

Substance	ppm*	Mg/M³**
++Anisidine (o, p-isomers)		0.5
++Benzoyl peroxide		5
Calcium oxide		5
++Carbaryl (Sevin) (R)		5
Copper Fume		0.1
Dusts & Mists		1.0
++Cotton Dust (raw)		1
++Cyclopentadiene	75	200
Demeton (Systox) (R)		0.1
++1, 3-Dichloro-5, 5-dimethyl hydantoin		0.2
++Dimethyl 1, 2-dibromo-2, 2-dichloroethyl phosphate, (Dibrom) (R)		3
++Dimethylamine	10	18
+ Dimethylformamide - Skin	10	30
++Di sec. octyl phthalate (Di-2-ethylhexyl-phthalate)	–	5
Epichlorhydrin	5	19
Ethanolamine	3	6
Graphite	–	15mppcf
Hafnium	–	0.5
+Hexachloroethane - Skin	1	9.7
+Hydrogen Sulfide	10	15
++L. P. G. (Low pressure gas) (Liquid petroleum gas)	1,000	–
++Maleic anhydride	–	8
++Methane	1,000	–
++Methyl acetylene-propadiene mixture, (MAPP)	1,000	–
Methylamine	25	31
+ Methyl mercaptan	10	20
Methyl methacrylate	100	410
C Methylene bis phenylisocyanate	0.02	0.2
Mineral wool, fibrous glass	–	2
++Monomethyl hydrazine - Skin	0.2	0.35
++Morpholine - Skin	20	70

* Parts of vapor or gas per million parts of air by volume at 25°C and 760 mm. Hg pressure.
** Approximate milligrams of particulate per cubic meter of air
+1964 Revision.
++1964 Additions.

ETC 03617

	Substance	ppm*	Mg/M³**
	Naphthalene	10	50
++	Nickel, metal and soluble compounds	–	1
+	Nitric Acid	2	5
++	p-Nitrochlorobenzene	–	1
++	Nitrogen trifluoride	10	29
C ++	Oxygen difluoride	0.05	0.1
++	p-Phenylene diamine-Skin	–	0.1
+	Phosgene	0.1	0.4
++	Phthalic anhydride	2	12
++	Propane	1,000	1,800
	β Propiolactone	–	A5
+	Selenium compounds	–	0.2
+	Silver, metal and soluble compounds	–	0.01
	Tantalum	–	5
+	1, 1, 1, 2-Tetrachloro-2, 2-difluoroethane	500	4,170
	1, 1, 2, 2-Tetrachloro-1, 2-difluoroethane	500	4,170
	Tetraethyl lead-Skin	–	0.075
	Tin (inorganic compounds) (organic compounds as Sn) - Skin	–	2 0.1
+	Yttrium	–	1

* Parts of vapor or gas per million parts of air by volume at 25°C and 760 mm. Hg pressure.
** Approximate milligrams of particulate per cubic meter of air.
A numbers, See Appendix A
+1964 Revisions.
++1964 Additions.

Appendix A

A¹ Benzidine. Because of high incidence of bladder tumors in man, any exposure, including skin, is extremely hazardous.

A² β-Naphthylamine. Because of the extremely high incidence of bladder tumors in workers handling this compound, and the inability to control exposures, β-naphthylamine has been prohibited from manufacture, use and other activities that involve human contact by the State of Pennsylvania.

ETC 03618

A[3] N-Nitrosodimethylamine. Because of extremely high toxicity and presumed carcinogenic potential of this compound, contact by any route should not be permitted.

A[4] Teflon ® decomposition products. At least one identified component of Teflon decomposition products is extremely toxic, but in the absence of more complete toxicity information and suitable analytic methods, a definite Threshold Limit Value is not recommended at this time, but air concentrations should be minimal.

A[5] β-Propiolactone. Because of high acute toxicity and demonstrated skin tumor production in animals, contact by any route should be avoided.

Appendix B

B. 1 THRESHOLD LIMIT VALUES FOR MIXTURES

When two or more hazardous substances are present, their combined effect, rather than that of either individually, should be given primary consideration. **In the absence of information to the contrary, the effects of the different hazards should be considered as additive.** That is, if the sum of the following fractions,

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \cdots \frac{Cn}{Tn}$$

exceeds unity, then the threshold limit of the mixture should be considered as being exceeded. C_1 indicates the observed atmospheric concentration, and T_1 the corresponding threshold limit, (See Example 1A.a.).

Exceptions to the above rule may be made when there is good reason to believe that the chief effects of the different harmful substances are not in fact additive, but independent as when purely local effects on different organs of the body are produced by the various components of the mixture. In such cases the threshold limit ordinarily is exceeded only when at least one member of the series ($\frac{C_1}{T_1}$ or $\frac{C_2}{T_2}$ etc.) itself has a value exceeding unity, (See Example 1A.b.).

Antagonistic action or potentiation may occur with some combinations of atmospheric contaminants. Such cases at present must be determined individually. Potentiating or antagonistic agents are not necessarily harmful by themselves. Potentiating effects of exposure to such agents by routes other than that of inhalation is also possible, e.g. imbibed alcohol and inhaled narcotic (trichloroethylene) Potentiation is characteristically exhibited at high concentrations, less probably at low.

ETC 03619

When a given operation or process characteristically emits a number of harmful dusts fumes, vapors or gases, it will frequently be only feasible to attempt to evaluate the hazard by measurement of a single substance In such cases, the threshold limit used for this substance should be reduced by a **suitable** factor, the magnitude of which will depend on the number, toxicity and relative quantity of the other contaminants ordinarily present.

Examples of processes which are typically associated with two or more harmful atmospheric contaminants are welding, automobile repair, blasting, painting, lacquering, certain foundry operations, diesel exhausts, etc. (Example 2)

THRESHOLD LIMIT VALUES FOR MIXTURES

EXAMPLES

1A General case, where air is analyzed for each component.

a. **ADDITIVE EFFECTS**

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \frac{C_3}{T_3} + \ldots \frac{C_n}{T_n} = 1$$

Air contains 5 ppm of carbon tetrachloride (TLV, 10), 20 ppm of ethylene dichloride (TLV,50) and 10 ppm of ethylene dibromide, (TLV, 25).

$$\frac{5}{10} + \frac{20}{50} + \frac{10}{25} = \frac{65}{50} = 1.3$$

Threshold limit is exceeded.

b. **INDEPENDENT EFFECTS**

Air contains 0.15 mg/m³ of lead (TLV, 0.2) and 0.7 mg/m³ of sulfuric acid (TLV, 1).

$$\frac{0.15}{0.20} = 0.75; \frac{0.7}{1} = 0.7$$

Threshold limit is not exceeded.

1B. Special case when source of contaminant is a mixture and atmospheric composition is assumed similar to that of original material, i.e. vapor pressure of each component is the same at the observed temperature.

a **ADDITIVE EFFECTS**, approximate solution.

1. A mixture of equal parts (1) trichloroethylene (TLV, 100), and (2) methyl chloroform (TLV 350)

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$$\frac{C_1}{100} + \frac{C_2}{350} = \frac{C_m}{T_m}$$

Solution applicable to "spot" solvent mixture usage, where all or nearly all, solvent evaporates.

$$C_1 = C_2 = \frac{1}{2} C_m$$

$$\frac{C_1}{100} + \frac{C_1}{350} = \frac{2C_1}{T_m}$$

$$\frac{7C_1}{700} + \frac{2C_1}{700} = \frac{2C_1}{T_m}$$

$$T_m = 700 \times \frac{2}{9} = 155 \text{ ppm}$$

18 b General Exact Solution for Mixtures of N Components With Additive Effects and Different Vapor Pressures

(1) $\frac{C_1}{T_1} + \frac{C_2}{T_2} + \ldots + \frac{C_n}{T_n} = 1;$

(2) $C_1 + C_2 + \ldots + C_n = T;$

(2.1) $\frac{C_1}{T} + \frac{C_2}{T} + \ldots + \frac{C_n}{T} = 1.$

By the Law of Partial Pressures,

(3) $C_i = ap_i,$

And by Raoult's Law,

(4) $p_i = F_i\, p_i^\circ.$

Combine (3) and (4) to obtain

(5) $C_i = aF_ip_i^\circ.$

Combining (1), (2.1), and (5), we obtain

(6) $\frac{F_1p_1^\circ}{T} + \frac{F_2p_2^\circ}{T} + \ldots + \frac{F_np_n^\circ}{T} = \frac{F_1p_1^\circ}{T_1} + \frac{F_2p_2^\circ}{T_2} + \ldots + \frac{F_np_n^\circ}{T_n}$ and solving for T,

(6.1) $$T = \frac{F_1p_1^\circ + F_2p_2^\circ + \ldots + F_np_n^\circ}{\frac{F_1p_1^\circ}{T_1} + \frac{F_2p_2^\circ}{T_2} + \ldots + \frac{F_np_n^\circ}{T_n}}$$

or

(6.2) $$T = \frac{\sum_{i=1}^{i=n} F_ip_i^\circ}{\sum_{i=1}^{i=n} \frac{F_ip_i^\circ}{T_i}}$$

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T = Threshold Limit Value in ppm
C = Vapor concentration in ppm
p = Vapor pressure of component in solution.
p° = Vapor pressure of pure component.
F = Mol fraction of component in solution.
a = A constant of proportionality
Subscripts 1,2, . . n relate the above quantities to components 1,2, . . n, respectively.
Subscript i refers to an arbitrary component from 1 to n.
Absence of subscript relates the quantity to the mixture.

Solution to be applied when there is a reservoir of the solvent mixture whose composition does not change appreciably by evaporation

Exact Arithmetic Solution of Specific Mixture

	Mol. wt.	Density	T	p° at 25°C	Mol fraction in half-and half solution by volume
Trichloroethylene (1)	131.4	1.46 g/ml	100	73mm Hg	0.527
Methylchloroform (2)	133.42	1.33 g/ml	350	125mm Hg	0.473

$$F_1 p_1^\circ = (0.527)(73) = 38.2$$
$$F_2 p_2^\circ = (0.473)(125) = 59.2$$

$$T = \frac{38.2 + 59.2}{\frac{38.2}{100} + \frac{59.2}{350}} = \frac{(97.4)\quad(350)}{133.8 + 59.2} = \frac{(97.4)\quad(350)}{193.0} = 177$$

T = 177 ppm (Note difference in T.L.V. when account is taken of vapor pressure and mol fraction in comparison with above example where such account is not taken).

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2. A mixture of one part of (1) parathion (TLV, 0.1) and two parts of (2) EPN (TLV, 0.5)

$$\frac{C_1}{0.1} + \frac{C_2}{0.5} = \frac{C_m}{T_m} \quad C_2 = 2C_1$$

$$C_m = 3C_1$$

$$\frac{C_1}{0.1} + \frac{2C_1}{0.5} = \frac{3C_1}{T_m}$$

$$\frac{7C_1}{0.5} = \frac{3C_1}{T_m}$$

$$T_m = \frac{1.5}{7} = 0.21 \text{ mg/m}^3$$

1C. T. L. V. for Mixtures of Mineral Dusts.

For mixtures of biologically active mineral dusts the general formula for mixtures may be used. With the exception of asbestos, pure minerals are assigned TLV's of 2.5, 20 or 50.

For a mixture containing 80% talc and 20% quartz, the TLV for 100% of the mixture "C" is given by:

$$\frac{C}{TLV} = \frac{0.8}{20} + \frac{0.2}{2.5}$$

$$TLV = \frac{20}{2.4} = 8.4 \text{ mppcf}$$

Essentially the same result will be obtained if the limit of the more (most) toxic componet is used provided the effects are additive. In the above example the limit for 20% quartz is 10 mppcf.

For another mixture of 25% quartz 25% amorphous silica and 50% talc:

$$\frac{0.25}{2.5} + \frac{0.25}{20} + \frac{0.5}{20} = 7.3 \text{ mppcf}$$

The limit for 25% quartz approximates 8 mppcf.

ETC 03623

Appendix C

BASES FOR ASSIGNING LIMITING "C" VALUES

By definition in the Preface, a listed value bearing a "C" designation refers to 'ceiling' value that should not be exceeded; all values should fluctuate below the listed value. In general the bases for assigning or not assigning a "C" value rest on whether excursions of concentration above a proposed limit for periods up to 15 minutes may result in a) intolerable irritation, b) chronic, or irreversible tissue change, or c) narcosis of sufficient degree to increase accident proneness, impair self rescue or materially reduce work efficiency.

In order for the Committee to decide whether a substance is a candidate for a "C" listing, some guidelines must be formulated on the permissive fluctuation above the limit in terms of the seriousness of the response in the categories a, b, c, given above. For this the factors given in the table below have been used by the Committee. For both technical and practical reasons, the factors have been pegged to the concentration in an inverse manner. It will be noted that as the magnitude of the T. L. V. increases a correspondingly decreased range of fluctuation is permitted; not to decrease the factor for T. L. V.'s of increasing magnitude would permit exposures to large absolute quantities, an undesirable condition, a condition that is minimized at low T. L. V.'s. Moreover, larger factors at the lower T. L. V.'s are consistent with the difficulties in analyzing and controlling trace quantities.

T.L.V. RANGE ppm* or mg/m³	Test T.L.V. Factor	Examples
0 to 1	3	Toluene diisocyanate-T. L. V., 0.02 ppm, if permitted to rise above 0.06 ppm may result in sensitization in a single subsequent exposure. "C" listing recommended on category b.
1 + to 10	2	Maganese-T. L. V., 5mg·m³, contains little or no safety factor. All values should fluctuate below 5mg·m³. "C" listing recommended on category b.

T.L.V. RANGE ppm* or mg/m³	Test T.L.V. Factor	Examples
10 + to 100	1.5	Methyl styrene-T. L. V. 100 if encountered at levels of 150 ppm will prove intensely irritating, "C" listing recommended on category a.
100 + to 1000	1.25	Methyl chloroform-T. L. V. 350ppm, at 438 ppm for periods not exceeding 15 minutes is not expected to result in untoward effects relating to category c. No "C" listing recommended.

* Whichever unit is applicable

As stated in the preface, the same factors may be used as guides for reasonable excursions above the limit for substances to which the time-weighted average applies. The time-weighted average implies that each excursion above the limit is compensated by a comparable excursion below the limit.

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ETC 03625

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Appendix III

Chemical and Mineral Agents—Adverse Physiological Effects Upon Man

Agent	Industry
EYES	
Cresol	*Chemical Mfg., Oil Refining*
Quinone	*Chemical Mfg.*
Hydroquinone	*Synthetic Dye Industry*
Acetic Anhydride	*Textile Mfg.*
Acrolein	*Chemical Mfg.*
Benzyl Chloride	*Synthetic Dye Industry*
Butyl Alcohol	*Lacquer and Paint Industry*
UPPER RESPIRATORY-MUCOUS MEMBRANES	
Ozone	*Welding Operations*
Dimethylsulfate	*Chemical Mfg., Pharmaceutical Ind.*
Chromium	*Chromate Mfg., Chrome Plating*
Acetic Anhydride	*Textile Mfg.*
Acrolein	*Chemical Mfg.*
Hydrogen Sulfide	*Viscose Rayon Ind. Sewerage Treatment*
Butyl Alcohol	*Lacquer and Paint Mfg.*
Acetaldehyde	*Chemical Mfg., Paint Mfg.*
LUNGS	
Nickel	*Metallurgical Refining Processes*
Crystalline Silica	*Mining Ind., Foundry Ind.*
Asbestos	*Mining Ind., Weaving Ind.*
Beryllium	*Foundry Ind., Metallurgical Ind.*
Chromium	*Chromate Mfg.*
Hydrogen Sulfide	*Viscose Rayon Ind. Sewerage Treatment*
Allyl Chloride	*Plastic Mfg.*
Dichloroethyl Ether	*Insecticide Mfg., Oil Refining*
Mica	*Rubber Industry, Insulation Industry*
Talc	*Mining Industry*
Nitrogen Dioxide	*Chemical Mfg., Metal Pickling*
LIVER	
Cresol	*Chemical Mfg., Oil Refining*
Dimethylsulfate	*Chemical Mfg., Pharmaceutical Mfg.*
Chloroform	*Chemical Mfg., Plastic Mfg.*
Carbon Tetrachloride	*Chemical Mfg., Dry Cleaning Fire Extinguisher Service*
Trichloroethylene	*Chemical Mfg., Metal Degreasing*
Perchlorethylene	*Chemical Mfg., Dry Cleaning*
Toluene	*Rubber Ind., Paint Ind.*

Courtesy of Air Engineering. Figure of man above is by Andreas Vesalius (1514–64).

Agent	Industry
SKIN	
Butyl Alcohol	*Chemical Mfg. Lacquer and Paint Mfg.*
Nickel	*Metallurgical, Refining Processes*
Phenol	*Plastics Mfg.*
Trichloroethylene	*Chemical Mfg. Metal Degreasing*
BRAIN OR CENTRAL NERVOUS SYSTEM	
Benzene	*Rubber Industry, Chemical Mfg.*
Carbon Tetrachloride	*Solvent Mfg., Dry Cleaning*
Carbon Disulfide	*Viscose Rayon Mfg., Rubber Mfg.*
Butylamine	*Synthetic Dye Mfg. Pharmaceutical Mfg.*
Hydrogen Sulfide	*Viscose Rayon Mfg. Sewerage Treatment*
Tetra Ethyl Lead	*Chemical Mfg.*
Manganese	*Mining, Metallurgical Processing*
Mercury (80 different industries)	*Electrical Equipment Mfg., Lab Workers*
Lead	*Auto Mfg., Smelting, Battery Mfg.*
Dimethylaniline	*Chemical Mfg.*
Acetaldehyde	*Chemical Mfg.*
Nitrobenzene	*Synthetic Dye Ind., Shoe Polish Mfg.*
Thallium	*Pesticide Mfg., Fire Work Mfg.*
HEART	
Aniline	*Synthetic Dye Mfg., Paint Mfg. Rubber Industry*
KIDNEY	
Chloroform	*Chemical Mfg., Plastic Mfg.*
Mercury	*Electrical Equipment Mfg. Scientific Labs.*
Dimethylsulfate	*Chemical Mfg. Pharmaceutical Mfg.*
BLOOD	
Nitrobenzene	*Synthetic Dye Mfg. Shoe Polish Mfg.*
Aniline	*Paint Mfg., Rubber Ind.*
Arsenic (as Arsine)	*Metal Pickling*
Benzene	*Chemical Mfg., Rubber Ind.*
Carbon Monoxide	*Heat Treating Ind. Automobile Services*
Toluene	*Rubber Mfg.*

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Appendix IV

Identification of Contents

Proper and adequate designation of the contents of packages, bottles, carboys, drums, tank trucks, tank cars, tank ships, stationary tanks, and warehouses is important to the health and safety of the public as well as employees of manufacturing and transportation facilities.

Public Law 86-613,[1] Federal Hazardous Substances Labeling Act clearly specifies the information required on consumer packages. Several states and a few cities have similar ordinances intended to protect the public. Much preliminary work by committees of the Manufacturing Chemists' Association,[2] Association of British Chemical Manufacturers,[3] American Petroleum Institute,[4] and others contributed to the background of precautionary labeling. MCA manual L-1[2] is a particularly good source for proper wording of labels supplying the following information:

1. Name of the Product
2. Signal Word
3. Statement of Hazard
4. Precautions
5. First Aid and/or Emergency Action
6. Container Handling and Storage

The Interstate Commerce Commission[5] designates certain labels that must be affixed to packages and vehicles moving in interstate trade or by common carrier. Since their system is rather specific in exempting certain types of compounds and sizes of packages, the reader is referred to the reference manual for information. A familiar ICC requirement is that of labeling tank trucks to advise the public of the general nature of the hazard of its contents *flammable, corrosive,* etc. This information is quite general and does not specify the degree of hazard.

A recent activity of the Manufacturing Chemists' Association is the development of *Chem-Cards* to be given to truck drivers at the time of loading. Each card describes in simple language the hazards of one argo and instructs the driver and others in steps to be taken under mergency conditions.

Inside the industrial plant the identification problem is two-fold: to ninimize error in operations or maintenance and to safeguard the lives f personnel in time of fire or other emergency.

ASA Standard A13.1—1956, *Scheme for the Identification of Piping*

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TABLE III.1. Degrees of Severity

Identification of Health Hazard Color Code: BLUE		*Identification of Flammability Color Code: RED*		*Identification of Reactivity (Stability) Color Code: YELLOW*	
Type of Possible Injury		Susceptibility of Materials to Burning		Susceptibility to Release of Energy	
Signal		*Signal*		*Signal*	
4	Materials which on very short exposure could cause death or major residual injury even though prompt medical treatment were given.	4	Materials which will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or which are readily dispersed in air and which will burn readily.	4	Materials which are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.
3	Materials which on short exposure could cause serious temporary or residual injury even though prompt medical treatment were given.	3	Liquids and solids that can be ignited under almost all ambient temperature conditions.	3	Materials which are capable of detonation but require a strong initiating source and which must be heated under confinement before initiation.
2	Materials which on intense or continued exposure could cause temporary incapacitation or possible residual injury unless prompt medical treatment is given.	2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.	2	Materials which readily undergo violent chemical change.
1	Materials which on exposure would cause irritation but only minor residual injury even if no treatment is given.	1	Materials that must be pre-heated before ignition can occur.	1	Materials which are normally stable but which can become unstable in combination with other common materials or at elevated temperatures and pressures.
0	Materials which on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0	Materials that will not burn.	0	Materials which are normally stable.

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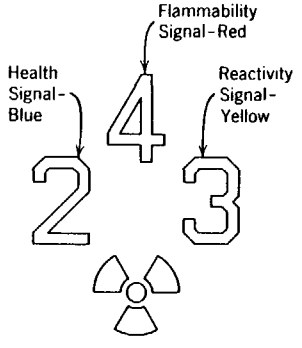
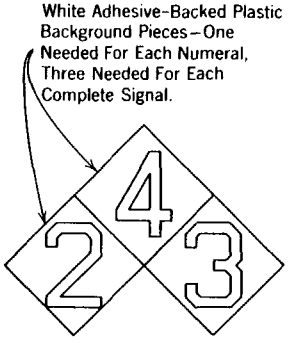
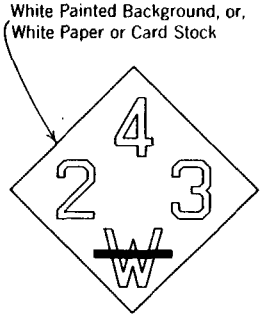


For Use Where White Background Is Not Necessary.



For Use Where White Background Is Used With Numerals Made From Adhesive-Backed Plastic.



For Use Where White Background Is Used With Painted Numerals, or, For Use When Signal is in the Form of Sign or Placard.

ARRANGEMENT AND ORDER OF SIGNALS —OPTIONAL FORM OF APPLICATION

Distance at Which Signals Must be Legible	Size of Signals Required
50 ft	1″
75 ft	2″
100 ft	3″
200 ft	4″
300 ft	6″

NOTE: This shows the correct arrangement and order of signals used for identification of materials by hazard.

FIG. III.1. Identification of materials by hazard signal arrangement.

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Systems,[6] describes a combination of name designations with color codes describing broad classes of contents:

Yellow. Hazardous
Green. Nonhazardous
Blue. Protective
Red. Fire Lines
Violet. High Value Materials

NFPA 704-M—1964, *Recommended System for the Identification of the Fire Hazards of Materials,*[7] is an outgrowth of work initiated about 1952 by the NFPA Flammable Liquids Committee incorporating an idea proposed by James J. Duggan.[8] He suggested a system for in-plant use to mark tanks, process vessels, storage areas, lines, etc. Hazards are identified in three categories, "health," "flammability," and "reactivity" (stability). Order of severity is expressed by numbers from "0" (no hazard) to "4" (severe hazard). Table III.1 outlines the degrees of severity within each category. Figure III.1 illustrates three alternate schemes for application of the diamond-shaped signals to plant tanks and other structures. The reader is referred to the most recent edition of NFPA 704-M for further details. NFPA 325, *Properties of Flammable Liquids* and NFPA 49M, *Hazardous Chemicals Data* will probably be revised to include the degrees corresponding to the three categories of 704-M.

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