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INDUSTRIAL TOXICOLOGY

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PREFACE

This book has been written in response to many requests for information concerning the toxicity of new, as well as old, substances of industrial importance. Its purpose is to serve as a bridge between the rapidly expanding field of toxicological investigation and the application of this knowledge of industrial poisons by the industrial hygienist.

Many of the substances described are not poisons in the usual sense. Indeed, some are not toxic at all. These represent materials newly used in industry, however, and concerning which some doubt has existed. The industrial hygienist is occasionally compelled to search through many periodicals and specialized books to acquaint himself with the current knowledge concerning these substances. All too frequently the toxic effects of a substance are presented in case reports, which are often confusing and detailed, and require careful study in order to define its toxicity. In the present manual this material has been surveyed and summarized with the object of relieving the industrial hygienist of much of this burden. Although this has required the examination of the available literature regarding each substance, only selected and pertinent bibliographical references are given, with such appraisal and interpretation as would serve to give the industrial hygienist an evaluation of toxicity without his having to digest a great mass of literature, or to seek out many obscure and difficultly obtainable publications. A short list of the more pertinent references is given at the end of each substance discussed. The references either relate directly to the subject matter, or are felt to be of general interest to the reader. No attempt whatsoever was made to append a complete bibliography—to do so would only expand the book without adding significantly to its value.

It will be apparent that whatever merit this book may possess is due to the vast fund of information which the many researchers in this field have contributed during the last two or three decades. The author's task has been to examine and compare these investigations and to assess them critically so that the gist of current thought is presented for the toxicological evaluation of a given substance.

The form in which the material is presented was arrived at after much consideration. It is largely based upon the needs of the industrial hygienist and is as brief as was felt consistent with his requirements. Some disparity of space will be found in that certain substances whose toxicity is well recognized are treated in more summary fashion, in comparison with those substances of obscure toxicity or substances which currently are of great importance, which are discussed in more detail.

The purpose in presenting the characteristics of the various substances

under consideration is related to more than mere identification. The physiological response to many substances depends to some extent upon their physical and chemical characteristics, such as volatility, solubility, solvent action, and stability. A knowledge of the outstanding characteristics of a substance is therefore often useful in defining a given occupational hazard. The chemical and physical constants are based upon the best information available for the pure substance and several may differ somewhat from those found in the usual tables. In all cases the most authentic values have been sought for these constants. They are of course particularly useful to the chemist in the examination of materials.

Under the section on industrial uses, an attempt has been made to gather from governmental and other sources such material as would indicate the extent of production and use. In many cases this will give a rough idea of the extent to which exposure may occur in industry.

Because of the diversity of the substances discussed, no attempt has been made to classify these substances in groups based upon either chemical resemblance or similarity of physiological response. Furthermore, it was felt that a simple alphabetical arrangement would facilitate reference. For further simplicity, the substances are broken down into two main groups—inorganic substances and the carbon compounds.

It has not been the author's intention to give detailed analytical instruction with reference to the various substances described in the following pages. Under the heading of analysis, reference is made to standard methods or to recently proposed methods. In a number of cases where no present method of analysis is available, the writer has suggested possible procedures.

The writer is most grateful for assistance from his colleagues in the Industrial Hygiene Division of the United States Public Health Service. However, he assumes full responsibility for the material as presented. Despite every good intention and every earnest and painstaking effort, imperfections and errors may occur; readers will confer a favor by reporting them so that they may be corrected in a future edition.

CONTENTS

Preface.....	v
Introduction.....	1

PART I

INORGANIC SUBSTANCES

Aluminum.....	15
Alundum.....	17
Ammonia.....	19
Antimony.....	21
Arsenic.....	25
Asbestos.....	29
Barium.....	32
Beryllium.....	34
Bismuth.....	38
Boron.....	40
Bromine.....	43
Cadmium.....	44
Cerium.....	49
Chlorine.....	51
Chromium.....	53
Cobalt.....	56
Columbium.....	60
Copper.....	61
Fluorine.....	64
Gallium.....	68
Germanium.....	70
Glass fiber and mineral wool.....	72
Hydrozoic acid.....	75
Hydrogen chloride.....	77
Hydrogen fluoride.....	79
Hydrogen nitrate.....	81
Hydrogen sulfate.....	82
Hydrogen sulfide.....	84
Indium.....	87
Iodine.....	89
Iron.....	91
Lanthanum.....	94
Lead.....	96
Magnesium.....	99
Manganese.....	102
Mercury.....	105
Mica.....	109
Molybdenum.....	111
Nickel.....	113
Nitrogen oxides.....	116
Osmium.....	120

Ozone	122
Palladium	125
Phosphine	127
Phosphorus	129
Platinum	132
Plutonium	134
Portland cement	137
Radioactive substances	140
Rubidium and cesium	142
Selenium	144
Silica	147
Silicones	151
Silver	153
Strontium	155
Sulfur	157
Sulfur chlorides	159
Sulfur dioxide	161
Sulfur hexafluoride	163
Talc	164
Tantalum	167
Tellurium	169
Thallium	171
Thorium	174
Tin	176
Titanium	179
Tungsten	181
Uranium	183
Vanadium	186
Zinc	189
Zirconium	191

PART II

CARBON COMPOUNDS

Acetaldehyde	197
Acetic acid	200
Acetic anhydride	202
Acetone	204
Acridine	206
Acrolein	208
Acrylonitrile	211
Allyl chloride and allyl bromide	213
Amyl acetate	215
Amyl alcohol	217
Aniline	220
Benzene	223
Benzene hexachloride	226
Benzoyl peroxide	229
Bromoform	231
1,3-Butadiene	232
2-Butanone	234

CONTENTS

ix

n-Butyl acetate.....	236
Butyl alcohols.....	238
n-Butyl methyl ketone.....	241
isoButyl methyl ketone.....	243
Carbon dioxide.....	244
Carbon disulfide.....	246
Carbon monoxide.....	248
Carbon tetrachloride.....	250
Carbonyl chloride (phosgene).....	253
Chlorinated diphenyls and chloronaphthalenes.....	255
Chlorinated mononitroparaffins.....	257
Chlorobenzene.....	259
2-Chloro-1,3-butadiene (chloroprene).....	261
Chloroform.....	263
Chloronitrobenzenes.....	265
Chloropicrin.....	267
Cresols—cresylic acid.....	270
Cyclohexane.....	272
Cyclohexanol.....	274
Cyclohexanone.....	276
Cyclohexene.....	278
Cyclopropane.....	280
Dibutyl phthalate.....	281
Dichlorobenzene.....	283
Dichlorodiphenyltrichloroethane (DDT).....	286
Dichloroethanes.....	288
Dichloroethylene.....	291
Dichloroethyl ether.....	293
Dichloromethane.....	295
2,4-Dichlorophenoxyacetic acid.....	297
1,2-Dichloropropane.....	299
Diethylene glycol monoethyl ether and related substances.....	301
Diethyl ether.....	303
Di(2-ethylhexyl)phthalate.....	305
Dimethylaniline.....	306
Dimethyl sulfate.....	308
Dinitrobenzene.....	310
1,4-Dioxane.....	311
Diphenyl.....	314
Ethyl acetate.....	316
Ethyl alcohol.....	318
Ethylbenzene.....	320
Ethyl bromide.....	322
Ethyl chloride.....	323
Ethylene chlorohydrin.....	325
Ethylene glycol.....	328
Ethylene glycol mono-n-butyl ether.....	331
Ethylene glycol monoethyl ether.....	332
Ethylene glycol monoethyl ether acetate.....	334
Ethylene glycol monomethyl ether.....	336

Ethylene glycol monomethyl ether acetate	338
Ethylene imine	340
Ethylene oxide	341
Ethyl formate	343
Ethyl silicate	345
Fluorocarbons	346
Formaldehyde	348
Formic acid	351
Furfural	353
Hydrocarbons, saturated—methane, ethane, propane, butane	355
Hydrocarbons, saturated—pentane, hexane, heptane, octane	357
Hydrocarbons, unsaturated—acetylene	359
Hydrocarbons, unsaturated—ethylene, propylene, butylene, amylene, hexylene ..	361
Hydrogen cyanide	363
Isophorone	366
Ketene	368
Mesityl oxide	369
Methanol	371
Methyl acetate	374
Methyl bromide	376
Methyl chloride	378
Methylcyclohexane	381
Methylcyclohexanol	382
Methylcyclohexanone	384
Methyl formate	385
Methyl iodide	387
Methyl methacrylate	388
Methyl <i>n</i> -propyl ketone (pentanone-2)	391
Metol	392
Naphtha	394
Naphthalene	395
Naphthylamine	397
Nitrobenzene	399
Nitro derivatives of aniline	401
Nitroethane	403
Nitroglycerin	405
Nitromethane	407
Nitropropane	409
Oxalic acid	411
Pentachloroethane	413
Pentachlorophenol	414
Phenol	416
Phenylenediamine	418
Phthalic anhydride	421
Picric acid	422
Propyl acetates	425
<i>n</i> -Propyl alcohol	427
<i>iso</i> Propyl alcohol	428
<i>iso</i> Propyl benzene	430
<i>iso</i> Propyl ether	431

CONTENTS

xi

Pyridine.....	433
Quinone and hydroquinone.....	435
Styrene monomer.....	437
Tetrachloroethane.....	439
Tetrachloroethylene (perchloroethylene).....	442
Tetranitromethane.....	444
Toluene.....	446
Toluidine.....	449
Trichloroethane.....	451
Trichloroethylene.....	453
Triorthocresyl phosphate.....	455
Triethanolamine.....	458
Trinitrotoluene (TNT).....	459
Turpentine.....	463
Vinyl chloride.....	465
Xylene.....	467
Xyldine.....	469
Index.....	473

INTRODUCTION

In an earlier period of our industrial development workmen were exposed to smoke, dust, fumes, and gases without regard to the possible injurious nature of many of these substances. Certain occupations, such as the mining of mercury, were formerly notorious in this respect. Furthermore, this condition was recognized in only very few instances and exposure to fumes or dusts of a deleterious type was generally recognized as a somewhat disagreeable and accepted condition of many occupations. The fact that some workers in mines, mills, or factories sickened, were forced to leave their occupation, and later died, did not always bring with it the realization that the nature of their work was a factor. In some occupations where industrial disease was prevalent there were often individuals who had been immersed in such an environment most of their working life and yet remained apparently strong and healthy. Such cases would be cited as indicating the general harmlessness of their occupation and those who sickened were regarded as weaklings. Many industrial diseases, such as phosphorus poisoning, were undetected for years, or, as in the case of manganese poisoning, were undetected for generations. The scrutiny of occupation as a factor in disease, although emphasized long ago by Ramazzini, is a comparatively modern development. Industrial physicians only a generation ago were largely concerned with the more external factors of employment—hernia, lumbago, cataracts in the case of glass workers, deafness in boilermakers—or in incidental disease, such as ankylostomiasis among miners or tuberculosis among cotton spinners. The latter were, of course, related to poor sanitation and poor nutrition, respectively, and were by no means peculiar to the occupation of the worker.

Knowledge, however, of the existence of occupational disease became more and more evident and, although locally confined at first, gradually spread. Thus, such terms as "grinder's rot", "phossy jaw", "painter's colic", "chrome itch", and "miner's phthisis" gradually appeared in industry and in the literature. Within the past generation industrial physicians have been alerted to the danger of much of the smoke, dust, or gases to which workers were exposed, scientists have actively investigated the effects of many of these aerial contaminants on animal life, and engineers have instituted control measures in industry to reduce the hazard of exposure.

Poisoning familiarly occurs as the result of ingestion of toxic substances and this doubtless influenced much of the earlier industrial hygiene thought. As a result, stringent sanitary measures were advocated and adopted in certain industrial processes in order to prevent possible entrance of indus-

trial poisons by mouth. These precautionary measures included such matters as a complete change of clothing on entering a shift, careful scrubbing of the hands and face before eating lunch, and a thorough washing and shower at the end of the work period. While excellent in themselves, these measures do not include the sanitation of breathing and instances of industrial poisoning have occurred where workers had observed strict cleanliness yet were exposed to dangerous concentrations of dust, fumes, or gases. Inhalation is now recognized as one of the most dangerous routes of entrance of industrial poisons.

GASES, FUMES, AND DUST

While the greater part of industrial smoke consists largely of carbon and is relatively harmless, it frequently contains gases which are dangerous if continuously breathed or if breathed in high concentration and, in addition, it may contain noxious fumes or toxic dusts from certain processes.

From the point of view of industrial hygiene a gas may be considered to be any aeriform or completely elastic fluid which does not become liquid or solid at ordinary temperatures. Fumes or vapors consist of material in the near-gaseous, or extremely fine particulate form which condense to liquids or solids at room temperature. Dusts, on the other hand, consist of larger particulate matter suspended in air. It must be realized that these definitions are not rigid and that they merely indicate somewhat roughly different stages of attenuation of matter. It is possible, for instance, to have mercury dust suspended in the air of a workroom, due to constant attrition of mercury spilled on the floor and carried into the air as extremely minute droplets following mechanical agitation. At the same time, mercury fume may be present as the result of heating this substance and finally the vapor tension of mercury is such that true, gaseous mercury may also be present to a slight extent. It is important for the industrial hygienist to keep these distinctions in mind. The detection and estimation of mercury gas in air by means of the photoelectric mercury detector depends upon the absorption of ultra violet light of a wave length of $2537 \text{ \AA}$ and the degree of absorption is a measure of the amount of *gaseous* mercury present. However, this instrument would not indicate the total mercury present in an atmosphere where particulate mercury or dust from any of its compounds was also present.

While dusts have been classified as particles or aggregates of particles of from 150 microns to one micron in diameter, fumes of from one micron to 0.2 micron in size, and smokes as particles less than 0.3 micron in diameter, size alone represents at best only a rough separation of these three classes. The mode of formation must also be considered. Thus, dusts ordinarily result from mechanical attrition and distribution, while fumes and smokes

are formed and carried into the air usually as the result of chemical reaction or the sudden dispersion of a chemically active substance by release of pressure or by explosion.

The disperse systems, or aerosols, in which the dispersion medium is a gas, differ from other disperse systems in the great disparity that exists between the density and structure of the disperse phase and the dispersion medium. The mere fact that two such disperse systems contain amicroscopic particles similar in magnitude does not necessarily mean that the properties of the two systems are identical, although they may have many points of similarity. In the case of dust, a great deal of work is required in order to reduce a solid to fine dust, i.e., to overcome the forces of cohesion that originally held the particles together in addition to the work required in distributing the particles throughout the dispersing medium. Even though a certain degree of uniformity finally is attained by settling or other means, dispersed dust of the finest order of magnitude is less uniform in structure than aerosols produced by the condensation of vapor. These factors have some weight in devising means of sampling and analysis of aerial contaminants.

The evaluation of aerial contaminants is very frequently a matter of importance to the industrial hygienist and a knowledge of the properties of such disperse systems as those indicated above, as well as the properties of gases and vapors in relatively low concentrations, is of particular value with reference to the analytical detection and determination of the constituent contaminants.

The composition of the aerial contaminant to which workmen in a given plant are exposed is of course of paramount importance to the industrial hygienist. This is usually known, or information may be obtainable from the management. In some cases, however, an unknown or unsuspected factor may be present and careful investigation may be necessary before the culprit is revealed. Cases have occurred, for example, where arsenic, cadmium, or selenium existing as unsuspected impurities in the material being fabricated have caused illness and death. An unrecognized by-product of manufacture may cause difficulty, or a change in the formula of basic material used in manufacture may bring about an unhygienic situation. The industrial hygienist is required not only to ferret out the occupational disease hazard but also—very necessarily—to know its characteristics, a proper method of sampling, and the most reliable method of analytical evaluation in terms of air content. His study includes the weighted or average exposure of employees at various stations and occupations. Furthermore, he is required to know something regarding the toxicity of the aerial contaminant in order to define the conditions under which employees are to be permitted to work in such an environment.

The toxic effects of many hazardous materials in industry are well known and it is comparatively easy to define safe working concentrations. There exist many substances in common use in industry, however, which are toxicologically not well defined. Unfortunately, toxicity cannot be evaluated with the ease with which a chemical constant, such as a boiling point, melting point, or index of refraction, may be determined. Even with arduous investigation extending over many months, the toxicologist can at best give only a very general answer regarding the poisonous nature of a given substance. It would be of inestimable benefit of course, if one could—knowing the composition and molecular structure of such a substance—predict its physiological properties.

CHEMICAL CONSTITUTION AND PHYSIOLOGICAL RESPONSE

The possibility of relating chemical constitution and physiological activity has long proved a fascinating field of speculation. The advantages of defining the toxicity of a substance from its constitution or structural formula are, as indicated above, obvious. Unfortunately, however, the matter is not simple. Certain relations exist, it is true, between structure and toxicity. For instance, ethyl and methyl alcohol, although differing in one important respect, are very similar in many of their other physiological properties, and propyl, butyl, and amyl alcohols might be assumed to act similarly. These latter alcohols do, in fact, resemble the lower members but with a progressive increase in toxicity. An analogous increasing toxicity might therefore be anticipated in the higher members of the alcohol series. This reasoning, however, is nullified by the changing physical properties of the higher members. In spite of a similar chemical structure, the higher alcohols become increasingly insoluble in body fluids and as a result there is an overall decreasing toxicity beyond a certain point. A similar increase in toxicity with an increasing number of carbon atoms is noted with sodium acetate, propionate, butyrate, and valerianate. Many other such relationships have been pointed out as more toxicological information has become available.

The replacement of a hydrogen atom with chlorine in the saturated hydrocarbons results in an immediate change in toxicity; the entrance of such a halogen group in the organic sulfur compounds greatly intensifies the toxicity of the resulting compound. When one chlorine group is introduced into ethyl sulfide, which is a weak poison, the resulting monochloroethyl sulfide, is found to be markedly toxic, while the introduction of a second chlorine atom results in dichlorodiethyl sulfide, or mustard gas, which is a very strong poison indeed. However, no such general rule can be applied in other cases. The successive replacement of hydrogens by chlorine in the methane molecule, which of itself is not toxic but merely

an asphyxiant, results in monochloromethane, CH_3Cl , dichloromethane, CH_2Cl_2 , trichloromethane, CHCl_3 , and tetrachloromethane, CCl_4 , respectively. These substances, however, do not follow a pattern of increasing toxicity. For instance, chloroform with its excellent narcotic properties, as well as the attendant possibilities of liver and heart damage, is less toxic in general than carbon tetrachloride on the one hand and much less toxic than methyl chloride on the other hand. Yet dichloromethane, which occupies an intermediate position, is far less toxic than any of the other members of this group. It does not follow therefore that there is any direct correlation between the number of chloro groups and the toxicity.

The relatively inert and inoffensive hydroxyl group when introduced into an organic molecule frequently results in an increase in toxicity. Thus, methanol, CH_3OH , has pronounced toxic properties compared with the parent substance and monohydroxybenzene, $\text{C}_6\text{H}_5\text{OH}$, or phenol, has marked poisonous properties over and above those of benzene. Increasing the number of hydroxyl groups may also increase the toxicity of the aromatics. For example, the introduction of a second hydroxyl group in the benzene ring yields resorcinol, $\text{C}_6\text{H}_4(\text{OH})_2$, which is more toxic than phenol, while the introduction of a third group yields phloroglycinol which is the most toxic of the three.

The entrance of an alkyl group into the molecule of a substance may also intensify its poisonous quality. Dimethyl resorcinol, $\text{C}_6\text{H}_4(\text{OCH}_3)_2$, is more toxic than resorcinol, $\text{C}_6\text{H}_4(\text{OH})_2$. On the other hand, an alkyl group may diminish the toxic effect in other substances. Dichloromethyl arsine, $\text{As}(\text{CH}_3)\text{Cl}_2$, is very toxic, while the introduction of a second methyl group, as in dimethyl chloroarsine, $\text{As}(\text{CH}_3)_2\text{Cl}$, yields a substance of weaker toxicity.

While the introduction of a chlorine group in aliphatic hydrocarbons increases the toxicity in general, this is not necessarily true in the case of the aromatic hydrocarbons. Thus, monochlorobenzene is less toxic than benzene itself and has been of no particular significance as an industrial poison.

It appears to be a general rule that *iso* compounds are somewhat less toxic than normal compounds. *iso*Propyl alcohol has a somewhat lower toxicity rating than normal propyl alcohol; *iso*butyl alcohol than normal butyl alcohol. A most interesting difference in toxicity has been found to exist in the benzene hexachlorides which have recently received attention as insecticides. In this case, the gamma derivative of 1,2,3,4,5,6 hexachlorocyclohexane, $\text{C}_6\text{H}_6\text{Cl}_6$, has been found to be especially lethal in action compared with the other four known isomers (1). Woodard and Hagan (2) found the gamma isomer to be as much as sixty times as toxic for certain warmblooded animals as other isomers of benzene hexachloride. In the

case of many other optically isomeric substances, great differences may also be found in toxicities. For instance, 1-hyoscyamine is twice as active physiologically as dl-hyoscyamine (atropine) and moreover the laevo compound is twelve to twenty times as active as the dextro compound (3). Usually, but not invariably, the laevo compounds are more active than dextro compounds. Thus, Cushny found 1-hyoscyne to be sixteen to eighteen times as active as d-hyoscyne and twice as active as dl-hyoscyne. Similarly 1-adrenaline was twelve to fifteen times as active as d-adrenaline in its vasoconstrictor action and twice as active as dl-adrenaline. On the basis of rather indirect evidence, it is possible that the difference in physiological behavior of such stereo-isomers is due to the ability of one or the other to combine with some protein or other constituent of the cell. However, sufficient quantitative data are not available to define clearly the mechanism of physiological activity and stereochemical configuration. The problem of relating chemical constitution and physiological action is even more confusing when it is recalled that substances of diverse chemical nature may produce similar physiological effects. The aliphatic narcotics, for example, include a large variety of structural type, such as hydrocarbons, alcohols, ethers, amines, and sulfones. According to Ing (4), these substances appear to achieve their effect by modifying the physico-chemical conditions of the cells due to certain physical properties shared by all classes of these compounds and not by the presence of certain pharmacodynamic groups.

It will be apparent therefore that while the temptation to rationalize regarding the prediction of toxicities may be great, the evaluation of toxicities of new substances is fraught with considerable uncertainty. Since no great rational scheme is available to aid, except rather sketchily, in deciding upon the toxicity of a given substance, it is inevitably necessary to carry out experimental work with animals.

EXPERIMENTAL TOXICOLOGY

Experimental industrial toxicology does not differ widely from that of experimental pharmacology, since they both use the resources of chemistry, physics, physiology, and pathology to achieve their purpose. However, the pharmacologist is primarily interested in therapy rather than toxicity. Furthermore, he is interested in the effects of administration of a substance by mouth, or by intravenous or subcutaneous injection and rarely in the effects of inhalation, except in the case of inhalation anesthetics. The refinements of approach to certain physiological reactions adopted by the pharmacologist, however, often yield data of fundamental importance within a relatively short space of time. The toxicologist on the other hand may be compelled to follow an intricate procedure which is arduous and

time consuming in order to define a given physiological response. Moreover, toxicological studies frequently depend upon pathological changes following the administration of small amounts of such toxic materials as gases, fumes, or dusts and these changes usually occur very slowly.

Toxicological investigations are in general based upon animal experimentation for human experimentation is, of course, indefensible. It is true that animal experiments provide only indirect evidence of the probable action of toxic substances on man, yet they are none-the-less of the greatest value. They not only afford information regarding upper toxic limits, but by long-continued study, reveal changes in lower concentrations which are of the greatest importance. In experimental work of this character, a considerable amount of interpolation is necessary and evaluation of the experimental results requires both acumen and careful judgment. Moreover, there are many poisons which produce completely different effects in different species of animals. Mice and guinea pigs, for example, are more sensitive to poisoning by trichloroethylene (acetylene trichloride) than cats, while rabbits are less sensitive than cats. On the other hand, cats are more sensitive to lead poisoning than dogs and the latter more so than rats. Although such qualitative and quantitative differences may exist, nevertheless there can be no doubt that animal experiments are of value since they give an indication of the type of toxic action, as well as the relative toxicity of the substance under investigation.

The great advantage of animal experimentation is, first of all, the control of dosage and, secondly, the degree to which poisoning can be carried. This yields most useful information in tracing similar effects in humans accidentally poisoned and in warning against human exposure beyond a certain degree.

Although the effects of exposure by inhalation are of paramount importance, animal studies also usually include other forms of administration, such as ingestion, intravenous injection, intraperitoneal injection, and subcutaneous injection. The latter form of administration is perhaps the least used as absorption is frequently slow and has less significance than the other forms. Intravenous injection provokes the most immediate response and is often useful in studying the immediate effects of substances upon the hemopoietic system. Intraperitoneal injection is one means of following the slow absorption of relatively insoluble substances, but is of particular value in studying the physiological response of various substances. For instance, when pure silica suspensions are intraperitoneally injected, a reaction occurs which is typical and fairly constant (5). Sayers and Miller found three types of reaction occurred with various dusts—absorptive, inert, and proliferative. The absorptive reaction occurs when fine dusts, such as calcite, limestone, gypsum, and cement, are injected. After suffi-

cient time, this material disappears from the peritoneal cavity without the formation of any scar tissue. In the case of the inert reaction, the dust remains distributed about the peritoneum by the action of phagocytes, sometimes forming flat nodules, which do not tend to progress or form fibrous scar tissue. Soapstone, carborundum, and coal dusts exhibit this inert reaction. In the proliferative reaction, nodules form which continue to increase in size with the formation of fibrous or scar tissue. Quartz, chert, and flint dust produce this reaction. These three types of reaction correspond very closely with the results obtained by the inhalation technique. While this method perhaps requires further exploration, it is useful in the approximate classification of dusts.

The inhalation technique with reference to dusts, fumes, and gases is by far the most useful method used in experimental toxicology. In the case of gases, the various concentrations to which animals are exposed may be regulated with accuracy. Hence, the exposure may be clearly and accurately defined. With fumes and dusts, the concentration of fume or dust in the air may be determined by exact chemical analysis. Whether or not the animals always breathe in the amount in the atmosphere may not be so accurately defined in many cases as small animals, such as guinea pigs, tend to huddle together and may be able to filter out some of the dust or fume to which they are exposed.

For the purpose of exposure, gas-tight or dust-tight exposure chambers of large size are usually used and animal cages may be placed directly in the exposure chamber. The gas may be introduced in known amounts and rapidly distributed throughout the exposure chamber by means of small fans. Substances which are sufficiently volatile, such as solvents, may be introduced in known amount into a constant current of air and the breathing concentration may be accurately calculated. In addition, of course, samples of the exposure atmosphere may be taken in most cases and analyzed chemically.

Fumes, such as metal fumes, may be generated by arcing between electrodes of the metal carrying 110 a.c. current and an appropriate resistance. In order to prevent the formation of metallic oxide fume, it is usually necessary to generate this fume in an atmosphere of inert gas, such as nitrogen or helium, and "bleed" it into an incoming air current. Oxide fumes are readily formed by arcing in air or in an atmosphere of oxygen. Fumes of many organic substances may be formed by heating the material to the volatilization temperature in the incoming air stream.

Dusts must be suspended in air in very finely divided form in order that they may remain in suspension as long as possible and so that the material is of sufficient degree of fineness to be carried deeply into the animals' lungs. An elutriating device is useful for this purpose (6), since it permits

constant flow of very finely divided dust of more or less uniform size. In the case of dust exposures, it is difficult to control the amount of dust in the atmosphere and hence it is necessary to draw small samples from time to time for analysis. Even though the dust concentration is accurately known, the amount carried into the animals' lungs is questionable as a variable amount is removed by the filtering action of the nose, part of the dust remaining in suspension is removed before the air enters deeply into the lungs. The ciliated epithelium found throughout the extent of the air-passages and their prolongations constantly sweeps out air-borne particles and only the very finest material penetrates to the lung alveoli.

Description of the means of evaluating the effects of various industrial poisons will be found given in detail in the various publications referred to in the succeeding text. It will be noted that a considerable latitude of experimentation is necessary in order to study the effects of a given industrial poison.

The degree of exposure (that is, the total amount of substance to which an animal has been exposed for a given length of time) is, of course, only preliminary to the evaluation of the toxicity of the substance. The behavior of the animal must be observed for this is an index of the manner in which the poison acts. Some substances may cause death immediately or within a few minutes—for example, hydrogen cyanide, hydrogen sulfide, or carbon monoxide. Other substances may act as irritants with symptoms of pain, salivation, vomiting, and purging. Ammonia gas, cadmium oxide fume, and chloropicrin, respectively, produce these effects. Other substances affect the central nervous system and produce characteristic symptoms, such as narcosis, convulsions, and paralysis.

The various symptoms, in general, serve at best only as a rough classification of toxic substances. The effects of poisons are often subtle and a variety of symptoms may be displayed. In chronic poisoning, or in the case of a cumulative poison, anatomical changes may be produced in certain organs or tissues which are characteristic for the poison. Blood changes may occur with an increase or decrease in hemoglobin, in red or white cells, and often with characteristic morphological changes in either or both the erythrocytes and leukocytes. All these and many other effects must be studied with care in the evaluation of the toxicity of a substance. It will be apparent therefore that the term *toxicity* does not refer to a fixed quantity, such as, say, a constant of nature. On the contrary, it is a descriptive term and is often more clearly understood when applied in relation to other analogous substances. When the toxicity of a substance is evaluated in the broad sense described above, however, the industrial toxicologist is able to advise somewhat definitely the limitation of possible exposure of human beings to industrial poisons.

It should be clearly indicated that, while such procedures as those briefly indicated above serve to establish useful limits with regard to industrial poisons, the more fundamental aspects of toxicology involve far more extensive and difficult physicochemical and physiological investigation. Various physical factors such as surface activity, solubility, dispersibility, polarity, partition coefficient, particle size, and electrophoretic properties may require study. The mechanism whereby many substances produce toxic effects in man is important and requires careful exploration. The fate of these substances in the body—the changes which organic compounds undergo and the metabolites formed—serves to indicate the means by which the body attempts to reduce their toxicity and thus protect itself against their poisonous effects. This is especially true of organic compounds completely foreign to the body. In their passage through the animal organism these substances interact with the normal biochemical systems which they encounter. The enzymic systems which carry out the oxidations, reductions, hydrolyses, and syntheses in the body may be variously affected. The metabolic processes involved reflect an attempt to reduce or abolish the toxic action or damage to the organism. However, it is not true that the product or products formed are invariably less toxic than the parent substance. For example, Channon and his associates (7) found that 2,4,6-trinitrotoluene (α -TNT) is partly converted in the animal organism to 2,6-dinitro-4-hydroxylaminotoluene which is excreted as such in the urine. Furthermore, the biological reduction product of picric acid is picramic acid. In both these cases the end-products are more toxic than the original substances. Nevertheless in the case of many other poisons the toxic substance is converted to harmless metabolites and eliminated. Fundamental investigation of the toxicity of a given substance therefore includes study of the course of the toxic agent through the body, its effects on various organs and tissues during its passage, and the changes produced in the substance by the detoxicating mechanism of the body as indicated by the metabolites formed.

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ASBESTOS

Characteristics

Asbestos, amianthus, earth flax, stone flax, mountain cork, is a characteristically silky, fibrous mineral, the composition of which varies with its source. The form known as chrysotile is derived from serpentine and is a hydrous magnesium silicate containing from 12.5 to 14 per cent water of crystallization. About 95 per cent of commercial asbestos is chrysotile. Chrysotile has the silkiest and strongest fiber and can be spun. The fibers may be as long as six inches in length. Asbestos derived from amphibole occurs as a variety of minerals consisting of iron, calcium, and magnesium with little water of constitution. The latter type of asbestos consists of short fibers and is usually inferior to that derived from serpentine. Amphibole asbestos (anthophyllite) while not so suitable for spinning is more stable chemically than chrysotile and more resistant to acids and heat.

Canada has been an important source for the chrysotile asbestos used largely in the United States. The Canadian asbestos industry is centered in the Thetford Mines area of the Province of Quebec. A new source for chrysotile type asbestos is a large quarry on the eastern shoulder of Belvidere Mountain in Vermont which was opened in the summer of 1944. This deposit is of importance because it represents the only large source of long-fibered chrysotile so far found in the United States. Deposits of amphibole asbestos are mined in Georgia and North Carolina.

Industrial Uses

Asbestos is an important substance in industry and consumption in the United States for 1945 amounted to 377,875 short tons (1). Due to its fibrous nature, flexibility and heat resistant properties, it is used extensively for valve packings, gaskets, boiler lagging, and pipe covering in industrial plants and as friction material in the automotive industry. A considerable market exists in the building industry for asbestos-cement products, heat insulation, and fire-proofing. The utilization of asbestos for fibers for spinning in the manufacture of asbestos clothing for fire fighting is an im-

portant use for asbestos. The largest single outlet for asbestos in manufactured products in 1944 was for clutch facings, and next in quantity of output were brake linings. Asbestos roofing consumed the third largest amount of asbestos in that year.

Industrial Injury

The inhalation of asbestos dust produces a condition known as asbestosis. While certain other minerals of minor importance have been shown to produce lung fibrosis, asbestos is the only important silicate apart from talc and mica which does not contain free silica and yet produces pulmonary lung fibrotic changes leading to disability and death. Asbestosis occurs chiefly in industrial plants where asbestos is fabricated. The spinning and weaving of asbestos in combination with other textiles results in exposure of workmen to asbestos dust. The long continued inhalation of asbestos dust results in a form of pneumoconiosis. The primary effect of inhalation of asbestos dust is an interstitial pulmonary fibrosis. On an X-ray film the shadows cast by this type of fibrosis resemble ground glass in appearance and usually extend over the lower portions of the lung fields, frequently being heavier on the right side (2). Unlike silicosis, nodular fibrosis has not been detected in asbestos workers (3). A progressive dyspnea, variable cough, substernal chest pains, decreased chest expansion, weakness, emaciation, clubbed finger tips, and curved fingernails are the chief symptoms of asbestosis, as in silicosis. A characteristic finding in asbestosis is that of asbestos bodies in the lungs and in the sputum (4). The so-called asbestos bodies are apparently formed only in the lungs and may be demonstrated microscopically on sectioning lung tissue or in the sputum. The core of the body is an asbestos fiber which is surrounded by protein deposits. Unstained specimens are golden yellow or golden brown. They are not stained with ordinary histological stains but may be demonstrated by the Prussian blue staining procedure. The reaction to the fibrous needle in the tissue which becomes manifest in exudate cell infiltration is accompanied by numerous giant cells containing foreign particles and an increase of diffuse interstitial connective tissue and fibrosis. While the essential reaction to asbestos particles is considered to be chemical by many investigators others consider the pathogenesis of the disease to be mechanical (5) in nature. When the lungs are examined by the naked eye after death, they are large and densely fibrotic. Often the lung is completely adherent to the chest wall and, in advanced cases, to the diaphragm with the formation of a thick and extremely dense layer of fibrous tissue. Four main complications and sequelae of pulmonary asbestosis are purulent bronchitis, bronchial pneumonia, pulmonary tuberculosis, and emphysema (6). Several cases of asbestosis have been reported which progressed to a fatal termina-

tion with heart failure and without evidence of infection or other complicating disease (7). Any appreciable decrease in the amount of asbestos dust will cause a decrease in the incidence and severity of asbestosis (8). It would appear that if the dust concentration in asbestos factories can be kept below five million particles per cubic foot, new cases of asbestosis would not arise (2).

Analysis

While the analysis of asbestos dust as an aerial contaminant is not of particular importance, its microscopy and above all the evaluation of the number of particles per cubic foot of air is of paramount importance. Air samples may be secured by the impinger method using 25-50 per cent alcohol as a collecting medium and dust counts made by the usual method. Microscopic examination of the dust reveals typical asbestos fibrous particles which may be accompanied also by cotton or other textile fibrous materials in samples taken from the air of weaving factories. The index of refraction being only slightly greater than that of Canada balsam, the relief is low. Other forms of asbestos than chrysotile have somewhat higher indices of refraction. Extinction is parallel except in the case of tremolite which has oblique extinction. The birefringence of chrysotile is moderate $n_x - n_z = 0.013$. The maximum interference color is bright yellow of the first order. The air sampling of asbestos dust both by the impinger method and by the electrostatic precipitator method is discussed in detail by Fehnel (9).

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SILICA

Silica (SiO_2) or silicon dioxide, is the most abundant of all the minerals and rocks that form the earth's crust. It is characterized by its hardness and chemical resistance to reagents. It is slightly soluble in alkalies but the finely particulate material is only very slightly soluble in water (1, 2).

Silica fractures into very minute angular particles. In the crystalline form it occurs as quartz but two other forms are also known which are tridymite and cristobalite and each of these exists in a number of modifications. Sand, flint, and agate are familiar forms of silica and diatomaceous earth, which is occasionally found in nature in large deposits, is composed of the silicious skeletons of diatoms. In view of what is known about the disease called "silicosis", it is important to distinguish between silica in the free state, as SiO_2 , and silica in the combined state, such as the various silicates. The silicates are still considered innocuous when inhaled as dust with the exception of talc, mica, and the fibrous silicates which are known as asbestos (3). The percentage of free silica in the various dusts which have been analyzed in connection with health studies of workers in dusty trades has been shown to range from 54 per cent to a trace (4). Silicosis is a chronic disease caused by the inhalation of particulate matter containing free or uncombined silica. It is characterized anatomically by generalized fibrotic changes with miliary nodulation in the lungs. Clinical signs are shortness of breath, a lowered vital capacity, a lowered capacity for work, increased susceptibility to tuberculosis, and a characteristic X-ray appearance of the lungs.

Silicosis is found to occur in such occupations as mining, the cutting of sandstone and granite, the coal industry, the smelting, refining, and grinding of metals, the manufacture of certain abrasives, the pottery industry, and the processing of the various forms of free silica. The number of workers exposed to dangerous amounts of silica dust has been estimated at more than one million (5).

Because of the disabling nature of silicosis (6), the extent to which exposure occurs in industry and the number of workers involved, many surveys have been made and these investigations have resulted in the setting up of efficient protective measures in working establishments. Dust control measures, taking into consideration the chemical composition of the dust and the size of the silica dust particles, as well as the concentration of the dust in the air, have been instituted. There is more or less general agreement that it is desirable to avoid concentrations of more than five million particles per cubic foot of air in working places where the dust contains a high percentage of free silica. Granite dust, which contains about 35 per cent free silica, when in concentrations of ten to twenty million particles per cubic foot has been found not to cause disabling silicosis in a working lifetime, while anthracite dust, containing less than 5 per cent free silica, has been found not to cause anthracosilicosis in concentrations of less than fifty million particles per cubic foot (3). Because air-borne dust may differ markedly from that of the source material from which it arises, it is common practice in appraising dust hazards to determine the

free silica content of samples. Furthermore, it has been indicated that toxicity increases sharply with silica dust below 3 microns in size (7). Since particles too large to be significant in silicosis production often contain a much higher percentage of free silica than fine particles of significant size, Holden and his associates (8) describe a procedure to eliminate the oversize particles before analysis.

The mechanism and pathology of silicosis have been very adequately described. It is well recognized that very fine particulate silica is carried to the air sac or alveolus which represents the terminal dilatation of the bronchioles in the lungs. The alveoli are in intimate contact with blood vessels through which the oxygen-carbon dioxide interchange phenomena of respiration occur and they are also in contact with lymphatics which are important for the removal of foreign or irritant material. This defense mechanism is motivated by the activity of phagocytic cells which carry off the minute silica particles to the lymph nodes. There an ineffective accumulation of this material occurs and fibrotic changes take place resulting in areas which constitute the silicotic lung marking revealed by the chest roentgenogram. Just why the phagocytic cell is affected by the silica—whether, in fact, silica has a direct toxic action, or whether it initiates other effects—is still in the realm of speculation.

Certain substances, such as aluminum, iron, and magnesium dusts, when used with quartz, as well as coal and cement dusts, have apparently been found to decrease the pulmonary changes associated with free silica alone. Outstanding in this respect is the work of Denny, Robson, and Irwin (9), who have shown that small quantities of metallic aluminum powder almost completely inhibit the solubility of silicious material. While this work represents an interesting and significant development in silicosis research, Heffernan (10) has recently pointed out that the surface activity of the silica particles is the important factor in the production of silicosis rather than solubility of the silicon dioxide. Recent investigation of the use of aluminum and alumina has been made by Policard (11), who confirms the view that the aluminum dust itself is innocuous and by King (12), who, in a critical discussion of the solubility of silica, reports that a mixture of one per cent of aluminum hydroxide with the quartz fractions lowered their solubility but did not prevent the formation of fibrosis in animals. The phase of silicosis therapy indicated above, however, is still in the stage of experimental investigation.

Since free silica or quartz is the important factor in causing silicosis, the identification of this substance and its quantitative evaluation as a dust constituent are of prime consideration. The microscopic examination of such dusts yields especially valuable information. Of the six distinct silica minerals, quartz, chalcedony, and opal are the more common. Tridy-

mite and cristobalite are more or less of volcanic origin and are also found as constituents of silica bricks, while lechatellierite is exceedingly rare. Quartz and chalcedony have refractive indices near that of Canada balsam and a birefringence of about 0.009. The other silica minerals have lower indices of refraction and weaker birefringence. The microscopic examination of such industrial dusts as are known to contain free silica can only be satisfactorily accomplished by the use of the petrographic microscope and a considerable amount of experience is necessary. Quantitative evaluation of the quartz content of a dust may be made microscopically by examining the dust and counting the dust particles in two different immersion media (13) having different indices of refraction. In one of these media all the particles are visible; in the other, having the same index of refraction as quartz, only the nonquartz particles are visible. The difference between these two estimations gives some approximation of the silica content of the dust. The method is not suitable for very fine particles and estimation based on particles of less than 10 microns in size is not good petrographic practice. Chemical methods for the estimation of free silica, such as the hydrofluosilicic acid method (14) and the fluoboric acid method (15), are tedious, time-consuming, and frequently yield information of no more quantitative value than less lengthy procedures. The X-ray diffraction method of dust analysis has become of increasing importance and is especially commendable from the point of view of speed, while it appears to yield results of as great accuracy as is obtainable by other methods of analysis.

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THE SILICONES

Characteristics

Silicon forms a large number of compounds which are analogous to those of carbon. The simplest of these is silane, SiH_4 , which corresponds to methane. While these compounds have been known for some time, they were, however, of academic interest only and received no practical application until about 1940 when the unique properties of the silicones caused them to assume considerable industrial importance. The silicones, R-SiO-R , correspond to the ketones but differ from the latter in most of their properties. The methyl silicones occur as oils, resins, and elastomers or rubber-like substances. The methyl silicone oils are soluble in benzene and the lighter hydrocarbons but are only partially soluble in alcohol. Many very complex alkyl and aryl silicones have been reported and studied within recent years. Some of these substances, such as methyl silicone oil, are characterized by their chemical inertness, low temperature coefficient of viscosity, wide liquid range, and low freezing point. Their high boiling points and heat stability are important properties for many industrial applications.

Industrial Uses

The uses of the silicones are as varied as their properties. Certain of the liquids are used as damping fluids for instruments and machinery. Other liquids find application as special lubricants for high temperature instruments, while others are used as high viscosity heat transfer liquids and as heavy diffusion pump oils. Minute amounts prevent foaming in fuel oils—an important problem in Diesel engines—and also the foaming of aqueous solutions. The relative insolubility of methyl silicone oil in petroleum oil may account for the success of this substance in suppressing foam. Silicone greases are used as hot valve lubricants, as insulating

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BENZENE

Characteristics

Benzene, benzol, C_6H_6 , boiling point $80.094^\circ C.$, melting point $5.51^\circ C.$, density $D_{4^2}^{20} 0.87895$, and index of refraction $n_D^{20} 1.50124$, is a colorless liquid with a characteristic odor. It is soluble in water only to the extent of 0.06 part per hundred at $20^\circ C.$, but is miscible with organic solvents. Its flash point is from $-12^\circ C.$ to $-10^\circ C.$ and ignition may be caused by open flames or sparks from electrical appliances. The "light oil" from the fractional distillation of coal tar consists principally of the hydrocarbons—benzene, toluene, xylene, and "solvent naphtha". On nitration, benzene yields both nitrobenzene with a boiling point of $209^\circ C.$ and *m*-dinitrobenzene with a melting point of $90^\circ C.$ On bromination, benzene yields bromobenzene, boiling point $157^\circ C.$ and *p*-dibromobenzene, melting point $89^\circ C.$ When heated with bromine plus iron catalyst, it yields mainly

p-dibromobenzene. It forms a picrate of colorless needles, melting point 83.9° C. With ClSO_3H , it yields benzenesulfonyl chloride, melting point 14° C., boiling point 251° C., and diphenyl sulfone with a melting point of 128° C. It is slowly sulfonated with boiling concentrated sulfuric acid.

Industrial Uses

Domestic production of benzene has more than tripled during the past decade, chiefly due to the increased demand for the manufacture of phenol and for a motor fuel additive. The production of benzene amounted to 36,555,643 gallons for all purposes except motor fuel in 1940. Nearly three times as much (101,140,079 gallons) was produced for use as motor benzene alone in that year (1). During the war, however, the use of benzene for chemical purposes increased considerably, while its use for motor fuel dropped correspondingly. Thus in 1945, the total production of benzene for motor fuel amounted to 32,151,532 gallons, while the production of benzene for all other purposes corresponded to 159,013,084 gallons (2). Apart from motor fuel, benzene is mostly used in manufacture of rubber, chemicals, dyestuffs and intermediates, explosives, aniline, phenol, resorcinol, benzidine, picric acid, and miscellaneous organic preparations. It is used as a solvent for oils, fats, waxes, gums, natural and synthetic resins, cellulose esters and ethers, and a large variety of varnishes, airplane dopes, as well as in paint and varnish removers.

Toxicity

On inhalation in high concentration, benzene is narcotic in action producing successively euphoria, hypermotility followed by sleepiness, and fatigue. The preliminary excitement is greater than with chloroform and as a general anesthetic, its action is more of a convulsive character. In concentrated form, it is especially toxic and may produce death. In dilute form, the vapors produce headache, vertigo, ataxia, twitchings, convulsions, and coma. Chronic poisoning in industry is characterized by leukopenia and aplastic anemia. Bowers has recently described a chronic case of benzene poisoning with fatal termination characterized by an intractable anemia, leukopenia, and thrombocytopenia following long continued exposure to benzene. In this case, the bone marrow was grossly hyperplastic with extensive areas of extramedullary hemopoiesis (3). It should be emphasized that blood changes alone cannot be accepted as evidence of benzene intoxication in the absence of estimations of benzene as an atmospheric contaminant (4). Benzene is absorbed through the skin but clinically detectable benzene poisoning has not been found from this source (5). However, absorption from the skin is of far less importance than absorption from inhalation. A test for detecting active absorption

of benzene may be made by determination of the ratio of the total urine sulfates to the inorganic sulfates (6). Since serious trouble may develop following exposure to benzene without any warning symptoms, the significance of neglected disorders is often apparent when too late. Lambin (7) has indicated a procedure for the detection of benzene poisoning applicable to large groups of individuals so exposed. The 1949 American Conference of Governmental Industrial Hygienists has accepted 35 parts of benzene in air as a maximum allowable concentration in workrooms.

Analysis

Methods for the determination of minute amounts of benzene are at best, methods of approximation only. The chemical methods are colorimetric in character and depend upon nitration and colorimetric evaluation of the reaction products. Various physical methods have been developed for the determination of benzene, such as the gas interferometer method and the combustible gas detector, and are useful when the air contaminant is solely benzene vapor. In contact with a nitrating mixture (equal parts of concentrated sulfuric acid and fuming nitric acid of d. 1.50) in the cold for 30 minutes, benzene is converted into a mixture of the *ortho*, *meta*, and *para* isomers of dinitrobenzene. The mixture contains about 95 per cent of the *meta* isomer. With aldehydes and ketones, the mixed dinitrobenzenes give a violet color in alkali solution. The *meta* isomer in particular gives a color with acetone. In low concentrations of benzene, the color develops within 30 minutes, is stable for three hours, and follows Beer's law. Schrenk and his associates (8) have adapted the nitration method to the determination of small amounts of benzene vapor as an air contaminant, using methyl ethyl ketone as reagent. A combined absorption nitration bubbler tube is used in which the benzene is converted to *m*-dinitrobenzene which is then estimated colorimetrically in saline solution with methyl ethyl ketone. Both Baernstein (9) and Dolin (10) have published methods for the determination of benzene in the presence of toluene and xylene, which depend upon oxidation of the nitro derivatives of the two latter substances. The oxidation products of the nitro derivatives of toluene and xylene are colorless under the conditions described and therefore do not interfere with the benzene determination.

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BENZENE HEXACHLORIDE

(Gamma Hexachlorocyclohexane)

Characteristics

Benzene hexachloride, hexachlorocyclohexane, $C_6H_6Cl_6$, one of the newer insecticides also known as "BHC" or "666", exists in five isomeric forms—the *alpha*, *beta*, *gamma*, *delta*, and *epsilon*. In the pure state, the isomers are well-defined colorless crystals, practically insoluble in water, soluble in organic solvents, and have a bitter taste and practically no odor. The melting points of the isomers are as follows: *alpha*, 157.5–158° C.; *beta*, 309° C.; *gamma*, 112.5° C.; *delta*, 138–139° C.; and *epsilon* (1), 218.5–219.3° C. At 40° C., the vapor pressure of these isomers are *alpha*, 0.06 millimeter of mercury; *beta*, 0.17 mm. Hg.; *gamma*, 0.15 mm. Hg.; and *delta*, 0.09 mm. Hg. The solubilities of the isomers of benzene hexachloride have been determined in each of forty-five organic solvents and the con-

INDEX

Detailed discussions shown by bold faced page numbers

- Abrasives, 18
 Acetaldehyde, 197, 288, 312, 318, 328
 Acetaldehyde phenylhydrazones, 197
 Acetamide, 368
 Acetanilide, 203, 222
 Acetic acid, 200, 243, 360
 Acetic acid, glacial, 200
 Acetic acid, synthetic, 200
 Acetic anhydride, 202, 368
 Acetic ether, 316
 Acetoacetic acid, 204
 Acetone, 204, 311, 350, 360, 368, 389, 428
 Acetone cyanohydrin, 364, 389
 Acetone oxime, 204
 Acetone phenylhydrazones, 204
 Aceto-p-toluidide, 203
 4-Acetylamino-1-isopropyl benzene, 430
 Acetyl chloride, 200
 Acetylene, 202, 205, 291, 316, 359
 Acetylene dichloride, 291
 Acetylene tetrachloride, 439
 Acetylene trichloride, 7
 Acetylides, 359
 Acetylsalicylic acid, 203, 369
 Acridine, 206
 Acridine complexes, 208
 Acridine Orange NO 207
 Acridine Yellow, 207
 Acriflavine, 207
 Acrolein, 208, 368, 378
 Acrylonitrile, 211, 364
 Adipic acid, 275, 277
 Adrenaline, 6
 Aerosols, 3
 Aerosol insecticide bomb, 64
 Agate, 148
 Alcohol, 360
 Alcohol, wood, 371
 Alizarin, 100, 175, 181, 193
 Alizarin red S, 17
 Alkyd resins, 404, 464
 Allanite, 49
 Allyl alcohol, 209
 Allyl bromide, 213
 Allyl chloride, 213
 A nico alloy, 57
 Aloxite, 17
 Alpha rays, 140
 Aluminum, 17
 A uminum, 15
 Aluminum bronze, 15
 Aluminum ethoxide, 316
 Aluminum phosphide, 128
 Alundum, 17
 Americ um, 134
 Am anthus, 29
 Aminobenzene, 220
 Am nodimethylaniline, 86
 Aminodimethylbenzene, 469
 o-(2)-Am nodiphenyl, 814
 p-Aminodiphenyl, 314
 1-Amino-4-hydroxyanthraquinone, 87
 para-Aminophenol, 392
 Ammonia, 9, 19
 Ammonia, synthetic, 20
 Ammonium chloroplatinate, 133
 Ammonium molybdate reagent, 28
 Ammonium paratungstate, 182
 Ammonium picrate, 423
 Amphetamine, 406
 Amphibole, 29
 Amyl acetate, 215
 Amyl alcohol, 217
 iso-Amyl alcohol, 218, 219, 220
 Amylene, 361
 Amyl hydroxide, 217
 Amyl nitrite, 365
 Anesthetics, 362
 Anglesite, 96
 Aniline, 203, 230, 306, 398, 422, 436
 Aniline dyes, 222, 376
 2-Anilinoethanol, 221
 Ankylostomiasis, 1
 Anode rays, 140
 Anodizing, 64
 Anthophyllite, 29
 Anthracene, 206
 Anthracosilicosis, 148
 Anti-fouling paints, 62
 Anti-freeze, 372
 Antimony, 21
 Apatite, 64, 129
 Arbutin, 436
 Argyria, 153
 Aristol, 89
 Armor-piercing shells, 423
 Arochlor, 255
 Arsenic, 3, 25
 Arsine, 360
 Asbestos, 29
 Asbestos bodies, 30
 Asbestos dust, microscopy of, 31
 sampling of, 31
 Asbestosis, 30
 Aspirin, 203
 Asthma, occupational, 420
 Atebrin, 207
 Atropine, 6
 Aurintricarboxylic acid, 17
 Automobile radiators, 412
 Aviation fuel, 430, 432, 468
 Azobenzene hydrochloride, 814

- Azo dyes, 470
 Azomide, 75
 Asophenol dyes, 418

Bacillus acetobutylicum, 204
Bacillus clostridium acetobutylicum, 236
Bacillus macerans, 204, 239
 Baddeleyite, 192
 Bakelite, 463
 BAL, 154, 170
 Barite, 32
 Barium, 32
 Barium carbonate, 32
 Barium chloride, 32
 Barium stearate, 32
 Barium sulfate, 32
 Barium sulfide, 33
 Bauxite, 18
 Belvidere Mountain, 29
 Benzal chloride, 448
 Benzaldehyde, 187, 204, 207, 384, 393, 460, 465
 Benzene, 223, 314, 417, 431, 468
 Benzene hexachloride, 5, 226
 Benzene monochloride, 259
 Benzenesulfonyl chloride, 224
 Bensidine, 51, 52, 84, 104, 173, 183, 199, 222, 365, 446, 457
 α -Benzil dioxime, 115
 Bensoflavine, 207
 Benzoic acid, 187, 320, 421, 430, 438
 Benzol, 223
 p-Benzquinone, 435
 Bensotrichloride, 307
 Benzoyl peroxide, 229, 291
 Benzyl aniline, 207
 Benzylpyridine, 433
 Beryllium, 34
 Beryllium alloys, 34, 62
 Beryllium nitrate, 174
 Beryllium oxide, 34
 Beryllium sulfate, 35
 Beryllium zinc silicate, 34
 Beta rays, 140
 BHC, 226
 Biotite, 109
 Bismark brown, 420
 Bismuth, 38
 Bismuth hepatitis, 39
 Bismuth hepta-dienecarboxylate, 39
 Bismuth nephritis, 39
 Bismuth trioxide, 38
 Bladder papillomata, 222
 Blasting gelatine, 405
 Blasting powder, 405
 Blood changes, 9
 Blood, vanadium in, 187
 Bone oil, 433
 Bone sarcoma, 135
 Borax, 41
 Boric acid, 40
 Boron, 40
 Boron carbide, 41
 Boron fluoride etherate, 65
 Boron phosphate catalyst, 202
 Boron trifluoride, 41
 Brass founder's ague, 190
 Bread, furfural in, 354
 Bromallylene, 214
 Bromine, 43
 Bromine burns, 44
 Bromobenzene, 223, 306
 Bromoethane, 323
 Bromoethylamine, 340
 Bromoform, 231
 3-Bromo-1-propene, 214
 Bromphenol blue, 44
 Buna N, 211, 212, 233, 235, 257, 289, 299
 Buna S, 211, 233, 433
 Bush sickness, 57
 Butadiene, 232, 354, 360
 Butadiene manufacture, 168
 Butane, 355
 Butanol-1, 238
 Butanol-2, 238
 2-Butanone, 234
 Butanone method for xylene, 469
 β -n-Butoxyethanol, 331
 n-Butyl acetate, 235, 243
 Butyl alcohol, 5, 238
 isoButyl alcohol, 5
 n-Butyl bromide, 240
 n-Butyl β -bromoethyl ether, 331
 Butylcarbinol, 218
 isoButylcarbinol, 218
 Butyl cellosolve, 331, 335
 n-Butyl β -chloroethyl ether, 331
 Butylene, 361
 isoButylene, 239
 2,3-Butylene glycol, 232
 n-Butyl β -hydroxyethyl ether, 331
 isoButyl methyl carbinol, 243
 isoButyl methyl ketone, 243
 n-Butyl methyl ketone, 241
 n-Butyraldehyde, 240
 isoButyric acid, 243

 Cable rash, 256
 Cacotheline, 178
 Cadion, 48
 Cadmium, 3, 44, 189
 Cadmium alloys, 45
 Cadmium hydroxide, 45
 Cadmium oxide, 9
 Calcium phosphide, 127
 Carbinol, 371
 Carbitol, 301, 335
 Carboic acid, 416
 Carbomethene, 368
 Carbon dichloride, 442
 Carbon dioxide, 244
 Carbon disulfide, 248
 Carbon monoxide, 9, 123, 248, 364, 371, 411, 453
 polycythemia from, 249
 Carbon tetrachloride, 250, 443, 467

- Carbonyl chloride, 253, 454
 Carbonyls, 248
 Carboxide, 342
 Carinoma, bladder, 398
 Carnallite, 142
 Casale process, 20
 Cataracts, 1, 285
 Catechol, 276
 Cathode rays, 140
 Celestite, 156
 Celliosolve, 332, 335
 Celliosolve acetate, 295, 334, 335, 363, 385, 404, 413, 440, 458
 Cellulose acetobutyrate, 404
 Cellulose acetopropionate, 404
 Cellulose formate, 369
 Cerite, 49, 94
 Cerium, 49
 Cerium nitrate, 174
 Cerium oxalate, 50
 Cerium oxide, 50
 Cerussite, 96
 Cesium, 142
 Chalcedony, 137
 Chemical constitution and physiological action, 4
 Chemical pneumonitis, beryllium, 35
 Chemical pneumonitis, delayed, 36
 Chemigum, 257
 Chlor acne, 256
 Chlorallylene, 213
 Chloramine, 53
 Chlorex, 293
 Chlorinated diphenyls, 255
 Chlorinated mononitroparaffins, 257
 Chlorine, 51
 Chloroanilines, 267
 Chlorobenzene, 221, 269
 2-Chloro-1,3-butadiene, 261
 1-Chloro-2-(beta-chlorethoxy)ethane, 293
 4-Chloro-1,2-dimercaptobenzene, 178
 1-Chloro-2,4-dinitrobenzene, 266
 Chloroethane, 323
 2-Chloro-ethanol, 325
 Chloroethyl alcohol, 325
 Chloroethylene, 465
 Chloroform, 205, 263, 373, 414, 443, 467
 Chloronaphthalenes, 255
 Chloronitrobenzene, 265
 1-Chloro-1-nitroethane, 258
 1-Chloro-1-nitropropane, 258
 2-Chloro-2-nitropropane, 258
 Chloropentane, 217
 Chloropicrin, 9, 253, 267, 376, 407
 Chloroprene, 261
 3-Chloropropene, 213
 Chrome holes, 54
 Chrome itch, 1
 Chromite, 53, 54
 Chromium, 53
 Chromium carbide, 60
 Chromium picrate, 423
 Chromium plating, 54
 Chromotropic acid, 298
 Chrysaniline, 207
 Chrysotile, 29
 birefringence of, 31
 Cinchonine hydrochloride, 183
 Citric acid, 349
 Claude process, 20
 Clay, 137
Clostridium acetobutylicum Weismann, 236, 239
 Coal tar naphtha, 394
 Cobalt, 56
 Cobalt, allotropic forms, 56
 Codeine sulfate, 146
 Codling moth, 26, 286
 Collidine, 434
 Colonial spirits, 371
 Columbian spirits, 371
 Columbium, 60
 Columbium carbide, 60
 Columbium fluoride, 168
 Columbium oxide, 168
 Columbium potassium fluoride, 61
 Contact acid, 82
 Contaminants, aerial, 8
 Copper, 61
 Copper acetylide, 289, 360
 Copper fever, 63
 Copper naphthenate, 62, 190
 Corn borer, 286
 Corundum, 17
 Cosmetic preparations, 301, 302, 312
 Cotton boll weevil, 227
 Crane fly, 284
 Cresol, 270, 382
 Cresylic acid, 270
 Cristobalite, 150
 Cryolite, 64, 79
 Cumene, 430, 431
 Cupric acetoarsenite, 26
 Cupric arsenite, 26
 Curcumin, 101
 Curium, 134
 Cyanide antidote, 365
 Cyanides, 376
 Cyanogen chloride, 363
 Cyclohexane, 272
 Cyclohexanol, 274, 279, 383
 Cyclohexanone, 276, 286, 384
 Cyclohexanone oxime, 277
 Cyclohexene, 278
 Cyclohexene 1,2-dithiocyanate, 279
 Cyclohexyl bromide, 279
 Cyclohexyl chloride, 275
 Cyclopropane, 260
 Cysteine, detoxicating action of, 58
 2, 4-D, 297
 DDT, 165, 227, 260, 386
 Decahydronaphthalene, 395
 Decalin, 395
 Dental caries, 65
 Dental erosion, 82, 83

- Dextro α -pinene, 464
 Diacetone, 205
 Diacetone alcohol, 370
 2,4-Di-(acetyl amino)-1-ethylbenzene, 320
p-Diaminobenzaldehyde, 220
 Diaminobenzene, 418
 Diaminophenol, 393
 Diamylphthalate, 230
 Diatomaceous earth, 148, 405
 Diatoms, 148, 387
 Dibenzalacetone, 204
 Dibenzoyl peroxide, 229
p-Dibromobenzene, 223
 1,2-Dibromocyclohexane, 279
 2,6-Dibromindophenol, 418
 Dibromomalonyl dibromide, 368
 Dibutyl phthalate, 230, 281, 286, 421
 Dibutyl sebacate, 282
 Dicarboxylic acid, 411
 Dichloroacetic acid, 201
 Dichloroacetyl chloride, 453
 8:3'-Dichloroarsoxybenzene, 267
 4:4'-Dichloroarsoxybenzene, 267
 Dichlorobenzene, 283
ortho-Dichlorobenzene, 260
para-Dichlorobenzene, 260
 Dichlorodiethyl sulfide, 4, 253
 Dichlorodifluoromethane, 64, 251, 346, 347
 Dichlorodiphenyltrichloroethane (DDT), 286
 Dichloroethanes, 288
 Dichloroethylene, 291, 359
 Dichloroethyl ether, 293
 β,β' -Dichloroethyl ether, 293
 Dichloroethyl sulfide, 4
 Dichloromethane, 5, 295, 378
 Dichloromethyl arsine, 5
 1,1-Dichloro-1-nitroethane, 258
 2,4-Dichlorophenoxyacetic acid, 297
 1,2-Dichloropropane, 299
 Dichlorotetrafluoroethane, 347
 Diethanolamine, 458
 Diethylamine, 247
 Diethylcarb' nol, 218
 Diethyldithiocarbamate, copper, 247
 1,4-Diethylene dioxide, 311
 1,4-Diethylene ether, 311
 Diethylene glycol, 328, 329, 335
 Diethylene glycol monoethyl ether, 301, 328
 Diethylene glycol monoethyl ether citrate, 301
 Diethylene glycol monoethyl ether laurate, 301
 Diethylene glycol monoethyl ether phthalate, 301
 Diethylene glycol monoethyl ether ricinoleate, 301
 Diethylene glycol monoethyl ether stearate, 301
 Diethyl ether, 303
 Di(2-ethylhexyl)phthalate, 282, 305, 422
 Diethyl oxide, 303
 Diethyl sulfate, 318
 2,2-Difluoropropane, 347
 1,4-Dihydroxyanthraquinone-2-sulfonic acid, 37
 1,4-Dihydroxybenzene, 436
 2,7-Dihydroxynaphthalene, 412
 1,8-Dihydroxynaphthalene 3,6-disulfonic acid, 298
 Dihydroxyoctachlorodiphenyl, 315
 Diiminoquinone, 420
 Diketene, 369
 2,3-Dimercaptopropanol (BAL), 154, 170
 Dimethylamine, 306
para-Dimethylaminobenzaldehyde, 254
p-Dimethylaminobenzalrhodanine, 154
p-Dimethylaminobenzylidene rhodanine, 126
p-Dimethylaminophenylazobenzenearsonic acid, 193
 Dimethylaniline, 269, 306, 388, 469
 Dimethylbenzene, 467
 Dimethylchloroarsine, 5
 Dimethylene imine, 340
 Dimethylethylcarbinol, 218
 Dimethyl gallium borohydride, 68
 Dimethylglyoxime, 115, 126, 162
 Dimethyl hexine diol, 389
 Dimethylketone, 204
 Dimethylphenylamine, 306
 Dimethyl-*p*-phenylenediamine, 52, 90
 Dimethyl phthalate, 286, 421
 1,1-Dimethyl-1-propanol, 218
 2,2-Dimethylpropanol, 218
 Dimethyl resorcinol, 5
 Dimethyl sulfate, 306, 332, 387
 4,6-Dinitro-2-aminophenol, 424
 Dinitrobenzene, 310, 400
m-Dinitrobenzene, 223, 225, 278
 3,5-Dinitrobenzoyl chloride, 304
 Dinitrohydroxylaminotoluene, 10
 Dinitrophenol, 395
 2,4-Dinitrophenylhydrazine, 206, 278, 355
 2,4-Dinitrotoluene, 447
 Dioctyl phthalate, 305
 Dioform, 291
 1,4-Dioxane, 311, 335
 Dioxane peroxide, 312
 Dipentene, 463
 Diphenyl, 314
 Diphenylamine, 207, 254
 Diphenylaminechloroarsine, 354
 Diphenylcarbazine, 55
 Diphenylcarbohydrazine, 255
 Diphenylchloroarsine, 253
 Diphenyloxide, 314
 Diphenylsulfone, 224
 Diphenylthiocarbazon, 39, 48, 63, 98, 107, 154
 Dipropylene glycol, 329
 Diisopropyl ether, 431
 α,α' -Dipyridyl, 93

- Disacryl, 209
 Dithione, 39, 48, 63, 98, 107, 154
 Dithymol di-iodide, 89
 Dolomite, 100, 165
 Dowicide G, 414
 Dow metal, 100
 Dowtherm A, 314
 Drehschmidt capillary, 119
 Dry cleaning industry, 409
 Dry ice, 245
 D-Stoff, 308
 Duprene, 261
 Duralumin, 15
 Dust, definition of, 2
 Dusts, experimental exposure to, 9
 reaction to, 7
 Dynamite, 405
- Earth flax, 29
 Electrical odor, 122
 Electron metal, 16
 Elon, 392
 Emery, 17
 Ensootic marasmus, 57
 Eosin, 44, 232
 Essence d'orient, 440
 Ethane, 355
 Ethane-diacid, 411
 Ethanoic acid, 300
 Ethano, 318
 Ethene, 361
 Ether, 303
 Ethide, 258
 Ethoxyacetaldehyde, 332
 2-Ethoxy-6,9-diaminoacridine, 207
 Ethyl acetate, 316, 386, 426
 Ethyl alcohol, 318, 362
 Ethylamine, 340
 Ethylbenzene, 330, 438
 Dow process of, 320
 p-Ethyl benzene sulfonamide, 321
 Ethyl bromide, 322
 Ethyl chloride, 323, 418, 467
 Ethylcyclohexane, 438
 Ethyl diethylene glycol, 301
 Ethyl-3,5-dinitrobenzoate, 304
 Ethylene, 326, 361, 466
 Ethylene acetal, 312
 Ethylene bromohydrin, 342
 Ethylene chloride, 324, 451
 Ethylene chlorohydrin, 325, 328, 458
 Ethylene cyanohydrin, 211
 Ethylene dichloride, 238, 466
 Ethylene glycol, 328, 332, 335, 349
 Ethylene glycol mono-n-butyl ether, 331
 Ethylene glycol monoethyl ether, 328, 332
 Ethylene glycol monoethyl ether acetate, 334
 Ethylene glycol monomethyl ether, 336
 Ethylene glycol monomethyl ether acetate, 338
 Ethylene imine, 340
- Ethylene oxide, 211, 332, 340, 341, 458
 Ethylene tetrachloride, 443
 Ethylene trichloride, 451, 453
 Ethyl ether, 303
 Ethyl formate, 343
 n-Ethyl-8-hydroxy-tetrahydroquinoline hydrochloride, 28
 Ethylidene chloride, 324
 Ethylidene diacetate, 202
 Ethyl iodide, 318, 403
 Ethyl polyglycol, 301
 1-Ethyl-1-propanol, 218
 Ethyl silicate, 345
 Ethyl sulfide, 4
 Ethyl sulfuric acid, 318
- Fatigue resistance, metal, 34, 187
 Fehling's solution, 197, 364, 436
 Ferrochrome, 54
 Ferron, 175
 Ferrophosphorus, 129
 Ferro-silicon, 127
 Ferrous phosphide, 127
 Fiberglass, 74
 Fire damp, 356
 Fire extinguishers, 376
 Fischer-Tropsch process, 57
 Flexol plasticizer DOP, 305
 Flint, 148
 Flour, bleaching of, 229, 230
 Flour mills, fumigation, 364
 Fluorescein, 124, 232, 283, 323, 422
 Fluorescein reaction, 306
 Fluorescent bead test, 185
 Fluorescent lamps, 36
 Fluorine, 64
 Fluorine burns, 65
 Fluorite, 64
 Fluorocarbons, 346
 Fluoroform, 347
 Formaldehyde, 343, 354, 372
 Formamide, 364
 Formic acid, 343, 351, 372
 Formic aldehyde, 343
 Formic ether, 343
 Formylic acid, 351
 Freon, 251, 286, 347
 Fruit, ripening of, 362
 Fuchsin, basic, 44, 210
 p-Fuchsin, 126
 Fuel tablets, 198
 Fulminate of mercury, 407
 Fume, definition of, 2
 generation of, 8
 Furfural, 216, 363, 427, 429, 465
 Furfural phenylhydrazones, 354
 Furfuraldehyde, 353
 α-Furil dioxime, 115
 Furoic acid, 354
 Furoil, 353
 Fused collars, 336
 Fusil oil, 215, 217, 427

- Galena, 96
 Gallic acid, 350
 Gallium, 68
 Gallium borohydrides of, 68
 Gallium hydroxide, 69
 Gallium thermometer, 68
 Gamma rays, 140
 Gammexane, 227
 Gases, definition of, 2
 Gas mantles, 174
 Gasolene, 394
 Gasolene, casing head, 217
 Gasolene, high octane, 79
 Gelatine dynamite, 405
 Gellignite, 405
 Germanium, 70
 excretion of, 71
 oxides of, 70
 Germanium hydride, 70
 Germanium sulfide, 72
 Germanium tetrachloride, 72
 Glass fiber, 73
 Glucuronic acid, 383, 385
 Glycerol, 209, 328
 Glycerol trichlorohydrin, 214
 Glyceryl trinitrate, 405
 Glycol, 312, 328
 Glyptal, 421, 463
 Golf greens, 284
 Grain alcohol, 318
 Grain oil, 217
 Granite dust, 148
 Griess reagent, 119
 Griess test, 406
 Grinder's rot, 1
 Gualacoldialdehyde test, 429
 Gun cotton, 405
 Gutzeit test, 27
 Gypsy moth, 26

 Haber process, 20
 Hafnium, 193
 Hafnium phosphate, 193
 Hair dye, 420
 Halowax, 255
 HCN disocids, 363
 Heavy naphtha, 394
 Hematite, 91
 Hematoxylin, 17
 Hemoglobinuria, 201, 331
 Heptane, 357
 Hexachlorobenzene, 227
 Hexachlorocyclohexane, 236
 Hexahydrobenzol, 373
 Hexahydrocresol, 383
 Hexahydromethylphenol, 383
 Hexahydrophenol, 374
 Hexahydrotoluene, 381
 Hexalin, 374
 Hexamethyl disiloxane, 152
 Hexamethylene, 373
 Hexamethylenetetramine, 170, 349
 Hexane, 357

 Hexanone-2, 241
 Hexone, 243
 Hexylene, 361
 Houseflies, 286
 Hycar O. R., 257
 Hydrazine chloride, 170
 Hydrazine hydrate, 75
 Hydrazoic acid, 75
 Hydrocarbons, saturated paraffins, 355, 357
 Hydrocarbons, unsaturated, acetylene, 359
 Hydrocarbons, unsaturated—olefins, 361
 Hydrochinone, 436
 Hydrochloric acid, 77
 Hydrochloric ether, 323
 Hydrocyanic acid, 363
 absorption of, 363
 preparation of, 363
 Hydroforming, 447
 Hydrogen aside, 75
 Hydrogen chloride, 77
 Hydrogen cyanide, 9, 363
 Hydrogen fluoride, 79
 Hydrogen nitrate, 81
 Hydrogen phosphide, 137
 Hydrogen selenide, 145, 146
 Hydrogen sulfate, 83
 Hydrogen sulfide, 9, 84, 360, 365
 Hydroquinone, 392, 417, 435
 Hydroxyacetic acid, 349
 Hydroxyanthraquinone, 42
p-Hydroxybenzaldehyde, 220
 Hydroxybenzene, 5, 416
p-Hydroxybiphenyl reagent, 199
β-Hydroxybutyric acid, 204
α-Hydroxy isobutyric acid, 339
 1-Hydroxy-2-chloroethane, 325
 Hydroxylamine, 162
 Hydroxylamine hydrochloride, 277
 4-Hydroxy-5-methoxyisophthalaldehyde test, 429
 8-Hydroxyquinoline, 17, 39, 61, 69, 88, 95, 101, 104, 175, 191
 Hydroxytoluene, 370
 Hyoscine, 6
 Hyoscyamine, 6
 Hypophosphorous acid, 129
 Hypovanadic oxide, 186
 Hypovanadous oxide, 186

 Igelite plastic, 466
 Ilmenite, 179
 Incendiary bombs, detection of, 145
 Indigo, 220, 372, 421
 Indium, 87
 Indulene dyes, 423
 Infra-red radiation, 142
 Inhalation, experimental, 8
 Insect repellent, 421
 Iodine, 89
 Iodine pentoxide method, 319
 Iodobenzene, 306

- p-Iodobenzohydrazide, 277
 Iodoform, 205, 318, 423
 7-Iodo-8-hydroxyquinoline-5-sulfonic acid (feron), 178
 Iodomethane, 337
 Iron, 91
 Iron, chilled, 189
 Iron picrate, 423
 Isoacetophorone, 368
 Isophorone, 368
 Isoprene rubber, 383

 Jamaica ginger, 456
 Jet propelled airplanes, 60

 Kelene, 323
 Ketene, 203, 368
 Ketoethylene, 368
 Keto-hexamethylene, 376
 β -Ketopropane, 204
 Kieselguhr, 406

 Laevo α -pinene, 464
 Lanthanum, 94
 Lanthanum hydride, 94
 Lead, 96
 Lead aside, 75
 Lead phthalate, 423
 Lead picrate, 423
 Lead poisoning, 97
 Lead tetraethyl, 98
 Lechatellierite, 150
 Lepidolite, 109
 Leptynol, 126
 Lighter flints, 50, 94
 Limonite, 91
 Lithopone, 33, 190
 Lucidol, 229
 Lucite, 389
 Luminous paint, 140
 Lutidine, 434

 Magnalium, 15
 Magnesium, 99
 Magnesium perchlorate, 252
 Magnesium phosphide, 127
 Magnesium silicate, 164
 Magnetite, 91
 Malachite green, 307
 Malarial control, 236
 Maleic anhydride, 233
 Malonic acid, 363
 Manganese, 102
 Manganese acetate, 197
 Marcasite, 91
 Marsh gas, 356
 Marsh test, 27
 Mercuric chloride paper, 131
 Mercuric sulfate, 197
 Mercury, 2, 105
 Mercury-cadmium iodide paper, 128
 Mercury detector, 2, 107
 Mesityl oxide, 369

 Mesothorium, 140, 174
 Metaldehyde, 197
 Metal fume fever, 190
 Meta-styrene, 438
 Methacrylate resins, 364
 Methacrylic acid, 358
 Methane, 355
 Methanoic acid, 351
 Methanol, 5, 364, 371, 374, 427
 Methanol, synthetic, 372
 Methemoglobinemia, 118, 221, 307, 402, 445
 Methemoglobinuria, 221, 398
 Methionine, 264
 Methoxyacetaldehyde, 336
 p-Methoxyphenyl-iso-thiocyanate, 398
 Methyl acetate, 371, 374, 386, 426
 Methyl alcohol, 371, 385
 Methylamine, 268
 p-Methylaminophenol sulfate, 392, 393
 Methylaniline, 308
 Methyl anone, 334
 Methyl benzene, 448
 Methyl benzoate, 371
 Methyl bromide, 376, 387
 2-Methyl-1-butanol, 218, 219
 3-Methyl-1-butanol, 218, 219
 2-Methylbutanol-3, 218
 2-Methyl-2-butanol, 218, 219
 Methyl iso-butenyl ketone, 369
 Methyl isobutyl ketone, 367
 1-Methyl-3-carbohydrazidopyridinium p-toluenesulfonate, 277
 Methyl cellosolve, 336
 Methyl cellosolve acetate, 338
 Methyl chloride, 378, 387
 Methyl chloroform, 451
 Methylcyclohexane, 381, 383
 Methylcyclohexanol, 382, 384
 Methylcyclohexanone, 383, 384
 4-Methyl-1,2-dimercaptobenzene, 178
 Methylene blue, 51
 Methylene chloride, 295
 Methylene di- β -naphthol, 349
 Methyl ethyl ketone, 334
 Methyl formate, 364, 386
 Methyl glycol acetate, 338
 1-Methyl-3-hydroxy-4-nitrosobenzene, 58
 Methyl iodide, 371, 387
 Methyl methacrylate, 230, 388
 Methyl nitrite, 447
 4-Methyl-3-pentenone-2, 369
 o-Methyl phenol, 270
 2-Methyl propanol-1, 238
 2-Methyl propanol-2, 238
 Methylpropylcarbinol, 218
 Methylisopropylcarbinol, 218
 Methyl n-propyl ketone, 311, 391
 Methyl silicones, 151
 Methyl sulfate, 393
 9-Methyl-2,3,7-trihydroxy-6-fluorone, 24
 Methyl violet, 268, 307
 Metol, 392

- Mica, 109
 Michler's ketone, 307
 Mineral wool, 73
 Miner's phthisis, 1
 Mischmetall, 50
 Molybdenum, 111
 Molybdenum chloride, 260
 Molybdenum trioxide, 112
 Monel metal, 64
 Monobromoethane, 323
 Monobromomethane, 376
 α -Monobromopropylene, 214
 Monochlorobenzene, 5, 259, 286, 417
 Monochloroethyl sulfide, 4
 Monochloromethane, 5, 373
 α -Monochloropropylene, 213
 Monoethanolamine, 458
 Monofluorinated hydrocarbons, 346
 Monofluorotrichloromethane, 347
 Monohydroxybenzene, 5
 Mononitrobenzene, 310
 Mononitroparaffins, chlorinated, 257
 Monosite, 50, 94, 174
 Moth balls, 395
 Moth proofing, 234
 Motor fuel, 224
 Mountain cork, 29
 Muriatic acid, 77
 Muscovite, 109, 166
 Mustard gas, 4, 362

 Naphtha, 394
 Naphtha, high flash, 394
 Naphtha, wood, 371
 Naphthalene, 157, 395, 397, 421
 Naphthalene cataracts, 396
 Naphthalene picrate, 395
 Naphthalene-4-sulfonic acid-1-*aso*-5-*ortho*-hydroxyquinoline, 126
 Naphthenic acid, 190
 α -Naphthol, 265, 397
 β -Naphthol, 265, 349, 397
 Naphthoquinoline, 48
 1,2-Naphthoquinone-4-sulfonic acid, 403
 Naphthylamine, 397
 α -Naphthylamine, 119, 406
 β -Naphthylamine, 222, 398
 1,8-Naphthylenediamine sulfate, 146
 Neoprene, 261, 273
 Neoprene cement, 273
 Neptunium, 134, 223, 258, 261
 Nessler's reagent, 21, 365
 Neutrons, 41, 135, 184
 Nickel, 113
 Nickel carbonyl, 114
 Nickel picrate, 423
 Nicotine, 165, 434
 Nicotinic acid, 434
 Nigrosine, 423
 Niobium, 60
 Nitric acid, 81
 Nitric acid pneumonia, 81
 Nitric oxide, 117
 Nitroaniline, 401
m-Nitroaniline, 310, 311, 401
o-Nitroaniline, 311, 401
p-Nitroaniline, 272, 401
p-Nitroaniline red, 402
o-Nitroanisole, 267
p-Nitroanisole, 267
o-Nitrobenzaldehyde, 278
 Nitrobenzene, 220, 223, 399
p-Nitrobenzene-*aso*-chromo-tropic acid, 42, 71
p-Nitrobenzene diazonium chloride, 21
 Nitrobruciquinone hydrate (cacotheline), 178
 Nitrocellulose, 216, 301, 316, 333, 367, 370, 374, 404, 458
 solutions of, 282, 425
 Nitrodiphenyl, 314
o-Nitrodiphenylamine, 311
 Nitroethane, 403, 407
 Nitroform, 267, 444
 Nitrogen dioxide, 117
 Nitrogen oxides, 116
 Nitroglycerin, 406
 5-Nitro-4-hydroxy-1,8-dimethyl benzene, 406
 Nitromethane, 407
 α -Nitronaphthalene, 397
p-Nitrophenylacetyl chloride, 427
 Nitropropane, 409
 1-Nitropropane, 407, 409
 2-Nitropropane, 407, 409
p-Nitrosodimethylaniline, 307
 Nitroso-2-hydroxynaphthalene-3,6-di-sulfonate of sodium, 58
 Nitroso- β -naphthol, 58
 α -Nitroso- β -naphthol, 58
 β -Nitroso- α -naphthol, 58
 Nitrosophenylhydroxylamine, 93
 Nitroso-R-salt, 58
 Nitrous oxide, 116
 Nitroxylene, 469
 Nordhausen acid, 82
 Novadelox, 230

 Octane, 357
 Oil of ants, 353
 Oil of bitter almonds, artificial, 399
 Oil of mirbane, 399
 Oleic acid, 354
 Oleum, 82
 Opal, 149
 Orcinol, 355
 Orthonitrosocresol, 58
 Osmium, 120
 Oxalic acid, 411
ortho-Oxytoluene, 270
 Ozone, 122

 Painter's colic, 1
 Paint remover, 295, 410
 Palladium, 125, 133
 Papillomatosis, bladder, 398

- Paraformaldehyde, 349
 Paraldehyde, 197
 Paris green, 26
 Parasite, 94
 Parvoline, 434
 Patronite, 187
 Peach tree borer, 284
 Pearls, artificial, 440
 Pellagra, 434
 Pentabromoresaniline, 377
 Pentabromotoluene, 381
 Pentachloroethane, 413, 442
 Pentachlorophenol, 414
 Pentaerythritol, 349
 Pentane, 357
 Pentanol, 218, 219
 Pentanone-2, 391
 Peracetic acid, 200
 Perbenzoic acid, 229
 Perchloroethylene, 443
 Peremesin, 50
 Petroleum, 361, 428, 430, 447
 Petroleum naphtha, 394
 Petroleum refining, 293, 378
 Phenol, 5, 416
 Phenoldisulfonic acid, 82, 119
 Phenol-formaldehyde industry, 417
 Phenolic resins, 271
 Phenolphthalein, 417
 Phenol red, 44
 Phenylamine, 220
 o-Phenylbenzamide, 314
 Phenylisocyanide, 222, 251, 264
 Phenylenediamine, 418
 m-Phenylenediamine, 199
 o-Phenylenediamine, 311
 p-Phenylenediamine, 402, 418
 Phenylethane, 320
 Phenylethylene, 437
 Phenylhydrazine, 209, 259, 354
 Phenylhydrazine hydrochloride, 350
 Phenylmethane, 446
 Phenylpyrazoline, 209
 Phlogopite, 109
 Phloroglucinol, 437
 Phosgene, 353, 307, 369, 453
 Phosphate rock, 129
 Phosphine, 127, 130, 360
 Phosphorous acid, 129
 Phosphorus, 129
 Phosphorus oxychloride, 131
 Phosphorus pentachloride, 130
 Phosphorus pentasulfide, 131
 Phosphorus, red, 130
 Phosphorus, tetra, trisulfide, 130
 Phosphorus trichloride, 130, 213
 Phosphorus tri-iodide, 387
 Phosphorus trisulfide, 130
 Phosphuretted hydrogen, 127
 Phossy jaw, 1
 Photoelectric cells, 142
 Phthalanil, 422
 Phthalic acid, 396, 421, 468
 isoPhthalic acid, 468
 Phthalic acid esters, 422
 Phthalic anhydride, 187, 383, 395, 417, 421
 Physiological response and chemical constitution, 4
 Piccoline, 434
 Pickling of metals, 27, 77
 Picramic acid, 10, 424
 Picric acid, 416, 423
 Picric acid in drinking water, 424
 Picrolonic acid, 175
 Picryl chloride, 424
 Pimelic acid, 276
 Pimelic ketone, 276
 Pinene, 463
 Piperidine, 460
 Platinum, 132
 Platinum black, 132
 Platinum sponge, 132, 133
 Plexiglas, 389
 Plutonium, 134
 Pneumoconiosis, 138, 177, 188
 Pneumonia, 139
 Pneumonia, lobar, susceptibility to, 139
 Pneumonitis, 145
 Polycythemia, 50, 57, 249
 Polystyrene plastics, 438
 Polytetrafluoroethylene, 65
 Polyvinyl chloride, 466
 Portland cement, 137
 Potassium beryllium sulfate, 35
 Potassium di-thio-oxalate, 115
 Potassium nitromethane, 407
 Potassium picrate, 423
 Potassium tantalum fluoride, 61
 Potato spirit, 217
 Potatone, 165
 Proflavine, 207
 Propane, 355
 Propanol-1, 437
 Propanol-2, 438
 2-Propanone, 304
 Propene nitrile, 211
 Propyl acetates, 426
 Propyl alcohol, secondary, 428
 iso-Propyl alcohol, 5, 204, 428
 n-Propyl alcohol, 5, 427
 iso-Propyl benzene, 430, 438
 Propyl bromide, 430
 iso-Propyl carbanilate, 429
 iso-Propyl chloride, 429
 iso-Propyl-3,5-dinitrobenzoate, 429
 Propylene, 280, 361, 428
 Propylene dichloride, 399
 Propylene glycol, 328, 329
 iso-Propyl ether, 431
 iso-Propylideneacetone, 369
 iso-Propyl iodide, 301
 n-Propyl iodide, 280
 iso-Propyl-p-nitrobenzyl phthalate, 429
 Prostigmine bromide, 406
 Prussian blue test, 365
 Prussic acid, 363

- Pyrethrin, 227
 Pyrethrum, 165, 286
 Pyridine, 170, 264, 331, 388, 414, 433
 Pyridine ethiodide, 435
 Pyridine methiodide, 435
 Pyridine picrate, 435
 Pyrite, 91
 Pyroacetic ether, 204
 Pyrocatechin, 417
 Pyrocatechol, 181
 Pyrogallol, 61
 Pyroligneous acid, 200
 Pyrolusite, 103
 Pyromucic aldehyde, 353
 Pyrophoric alloy, 50
 Pyrophyllite, 165, 166
 Pyrrol, 146
- Quartz, 137, 148
 Quinaacrine hydrochloride, 207
 Quinaldinic acid, 191
 Quinalizarin, 17, 42, 69, 71, 88, 95, 101
 Quinol, 436
 Quinone, 435
- Radioactive substances, 140
 Radioactivity, tolerance level, 136
 Radio antimony, 23
 Radio cobalt, 67
 Radio elements, 140
 Radium, 140
 Radon, 140
 Ramazzini, 1
 Rationite, 308
 Refrigerants, 466
 Resorcinol, 5, 61, 264, 268, 350, 422
 Resorufin, 52
 Rhodamine B, 24
 Rhodisonic acid, 33
 Rivanol, 207
 Rotenone, 165
 Rubber cement, 432
 Rubber, synthetic, 212, 370, 450, 452, 456
 Rubidium, 142
 distribution in tissues, 143
 Rubidium, silico-tungstate, 143
 Rutile, 179
- Safety glass, 316, 440, 466
 Saftfume briquets, 363
 Salicylic aldehyde, 220, 465
 Salt sickness, 57
 Sand, 148
 Saran, 291
 Sarcoma, osteogenic, 141
 Scheele's Green, 26
 Schiff's reagent, 44, 199, 373
 Seekay, 255
 Selenium, 3, 144
 Selenium, radioactive, 145
 Selenium sulfide, 107
 Serpentine, 29, 165
 Sesame oil, 286
- Shale, 137
 Shaver's disease, 18
 Ships, fumigation of, 363, 364
 Siderite, 91
 Silane, 151
 Silica, 147, 345
 Silicic acid, 345
 Silicone greases, 151
 Silicone resins, 152
 Silicone rubber, 152
 Silicones, 151
 Silicosis, 148
 Silver, 163
 Silver acetylde, 359
 Silver fulminate, 154
 Silver nitrate paper, 128, 131
 Silver permanganate, 128
 Soapstone, 164
 Sodamide, 75
 Sodium acetate, 201
 Sodium alizarin sulfonate, 67
 Sodium anilide, 220
 Sodium arsanilate, 51
 Sodium aside, 75, 158
 Sodium benzenesulfonate-p-diazonium chloride, 399
 Sodium chloride, electrolysis of, 52
 Sodium diethyldithiocarbamate, 63, 191
 Sodium diphenylamine sulfonate, 82
 Sodium fluoride, 64
 Sodium formate, 371
 Sodium formyl sulfonate, 269
 Sodium nitrite, 365
 Sodium nitromethane, 407
 Sodium nitroprusside, 86, 206
 Sodium pentachlorophenate, 415
 Sodium rhodizonate, 156
 Sodium tellurite, 170
 Sodium tetraborate, 40
 Sodium tungstate, 182, 183
 Soil disinfectants, 227, 293, 294
 Soil larvicide, 407
 Solaesthin, 295
 Solvay process, 245
 Solvent naphtha, 223, 394
 Sphalerite, 190
 Spine cells, 23
 Spirit, wood, 371
 Spotting fluids, 409
 Spray painting, 55
 Stannous phosphide, 127
 Steatite, 164
 Steel, stainless, 54, 114, 160, 179
 Stellite steels, 56
 Stibine, 22
 Stoddard Solvent, 394
 Stone flax, 29
 Strontianite, 155
 Strontium, 155
 Strontium, radioactive, 136, 156
 Strontium saccharate, 156
 Styrene, 320, 437
 Styrene dithiocyanate, 438

- Styrene monomer, 437
 Sugar cane grub, 284
 Sulfur, 157
 Sulfur dichloride, 159, 202
 Sulfur dioxide, 161
 Sulfur hexafluoride, 163
 Sulfuric acid, 82
 Sulfuric ether, 303
 Sulfur monochloride, 159
 Sulfur, pneumoconiosis from, 158
 Sulfur trioxide, 161
 Sulfur trioxide manufacture, 187
 Sulfuryl chloride, 159
 Sulfuryl oxychloride, 159
 Superphosphate, 129
 Sylvestrene, 463

 Talc, 164, 286
 Tannic acid, 51, 104, 183, 188
 Tantalum, 167
 Tantalum carbide, 168
 Tantalum fluoride, 168
 Tantalum oxide, 168
 Tar camphor, 395
 Teeth, mottled, 65
 Teflon, 65
 Tellurium, 169
 Tellurium dioxide, 169
 Tellurium hydride, 169
 Terephthalic acid, 468
 Tetrachloroethane, 439
 1,1,1,2-Tetrachloroethane, 439, 440, 441
 1,1,2,2-Tetrachloroethane, 439
 s-Tetrachloroethane, 291, 439, 453
 Tetrachloroethane collodion, 440
 Tetrachloroethylene, 413, 443
 Tetrachloromethane, 5, 378
 Tetraethylenepentamine, 63
 Tetraethyl lead, 77, 98, 470
 Tetraethylrhodamine, 24
 Tetraethyl *ortho*-silicate, 345
 Tetrahydrobenzene, 278
 Tetrahydronaphthalene, 395
 Tetrahydroxyquinone, 33
 Tetralin, 395
 Tetramethyldiaminobenzophenone, 307
 Tetramethyldiaminotriphenylmethane, 104
 Tetranitromethane, 444
 Tetranitromethanates, 445
 Tetryl, 307
 Thallium, 171
 Thallium cobaltinitrite, 173
 Thallium iodide, 173
 Thallium sulfate, 172
 Thermionic valves, 142
 Thermite incendiary bombs, 32
 Thermometry, high temperature, 68
 precision, 125
 Thetford mines, 29
 Thiocarbamid, 170
 Thiocyanate excretion, 212
 Thiodiethylamine, 340

 Thiokol, 289, 452
 Thionyl chloride, 159
 Thiourea, 122
 Thorite, 174
 Thorium, 174
 Thorium-alizarin lake method, 67
 Thorium dioxide, 174
 Thorium fluoride, 175
 Thorium nitrate, 67
 Thorium oxalate, 175
 Throium-x, 175
 Thoron, 140, 175, 176
 Thorotrast, 135, 174, 175
 Thylox process, 85
 Tin, 176
 Tinkal, 41
 Tin tetrachloride, 178
 Tin tetrahydride, 178
 Tin tetramethyl, 178
 Titanium, 179
 in human tissues, 180
 Titanium carbide, 179, 180
 Titanium dioxide, 179
 Titanium fluoride, 168
 Titanium pigments, 180
 Titanium tetrachloride, 180
 Titan Yellow, 101
 TNT, 459
 excretion of, 460, 461
 Tobacco reaction, 255
 Tobacco, thiocyanate excretion from, 212
ortho-Tolidine, 52, 90
 Tollen's reagent, 197, 353
 Toluene, 187, 431, 446, 468
 Toluene picrate, 447
 Toluidine, *ortho*, *meta*, and *para*, 449
 p-Toluidine, 203
 Toluidine blue, 450
 Toluol, 446
 m-Toluylenediamine, 207
 α -p-Tolyl-pyrrolidine, 433
 Topaz, 64
 Tourmaline, 64
 Toxicity, 9
 Tracer bullets, 32
 Transuranium elements, 134
 Tremolite, 165
 Tribromomethane, 231
 Tribromophenol, 417, 418
 Tributyl phosphate, 298
 Trichloroacetic acid, 201
 Trichlorobenzene, 229
 Trichloroethane, 451
 Trichloroethylene, 7, 265, 413, 453
 Trichloroethylene poisoning, 454
 Trichloromethane, 5, 363
 Trichloromonofluoromethane, 347
 Trichloronitromethane, 367
 Trichlorotrifluoroethane, 347
 Tricresol, 270
 Triorthocresyl phosphate, 74, 282, 455
 Tridymite, 149
 Triethanolamine, 458

- Triethylene glycol, 328, 329
 Triethylene glycol di(2-ethyl butyrate), 282
 Trifluoroethane, 346
 2,2',2''-Trihydroxytriethylamine, 458
 Trimethylamine hydrochloride, 378
 1,1,3-Trimethyl-cyclohexanone-5-sulfonic acid-3, 366
 3,5,5 - Trimethyl - 2 - cyclohexene - 1 - one, 366
 Trimethylene, 330
 Trimethylene bromide, 290
 Trimethylphenylammonium iodide, 388
 Trinitrobenzene, 395
 2,4,6-Trinitro-1-ethylbenzene, 321
 Trinitronaphthalene, 396
 2,4,6-Trinitrophenol, 416, 423
 Trinitrophenylmethylnitramine, 307
 Trinitrostilbene, 460
 Trinitrotoluene, 10, 395, 444, 459
 Trioxymethylene, 295, 349
 Tropaeol, 266
 Trypaflavine, 207
 Tryptophane, 210
 Tuberculosis, 1
 Tumors, bladder, 398
 Tungsten, 181
 Tungsten carbides, 182
 Turpentine, 463
 Turpentine oil, 463

 Uranium, 184, 183
 Uranium, hexafluoride, 65, 184
 Uranium isotopes, 184
 Uranium tetrafluoride, 184
 Uranyl salts, 184
 Urobilinuria, 216
 Ursol asthma, 420
 Ursol D, 419

 isoValeric acid, 243
 Vanadic oxide, 186, 188
 Vanadium, 186
 in blood, 187
 Vanadium pentoxide, 188, 421
 Vanadium sulfide, 188
 Vanillin, 307, 408, 465
 Vinegar, 200
 Vinegar naphtha, 316
 Vinyl acetals, 316
 Vinyl acetate, 466
 Vinyl acetylene, 261
 Vinylamine, 340
 Vinylbenzene, 437
 Vinyl chloride, 305, 451, 455
 Vinyl cyanide, 211
 Vinylidene chloride, 291
 Vinylidine, 305
 Vinylite, 466
 Vinyl resins, 367, 404, 466
 Vinyl resin solutions, 409
 Vinyl trichloride, 451
 Viscose, 211, 247
 Vomiting gas, 268

 Watch dial painting, 175
 Weed killer, 28, 297
 Welding rod coating, 179
 Welsbach mantle, 50
 Wire worms, 294
 Witherite, 32
 Wood alcohol, 371

 Xanthate reaction, 427
 Xanthogenate test, 241
 Xenylamine, 314
 X-rays, 140
 Xylene, 467
 isomers of, 468
 m-Xylenol, 406
 Xylidene, 469
 Xylol, 467

 Zapon lacquer, 219
 Zinc, 189
 Zinc blende, 190
 Zinc chloride fumes, 190
 Zinc chromate, 55
 Zinc diethyldithiocarbamate, 191
 Zinc hydroxide, 190
 Zinc naphthenate, 190
 Zinc nitroprusside, 163
 Zinc phosphide, 127
 Zinc sulfide, phosphorescent, 140
 Zircon, 192
 Zirconium, 191
 Zirconium-alizarin method for fluorides, 80
 Zirconium carbide, 192
 Zirconium dihydride, 193
 Zirconium dioxide, 192
 Zirconium phosphate, 193
 Zirconium silicate, 192
 Zirconium triethyl phosphate, 193
 Zyklon, 363

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