

PLAINTIFF'S
EXHIBIT

AL-40

TOXICITY

ARD 002702

Chapter II

TOXICITY AND THRESHOLD LIMITS

- I. Protective Mechanisms
- II. Degrees of Toxicity
- III. Human Variabilities
- IV. Routes of Entry
 - A. Inhalation
 - 1. Work vs Breathing Rate
 - 2. Altitude vs Breathing Rate
 - 3. CO₂ vs Breathing Rate
 - 4. Other Chemicals vs Breathing Rate
 - 5. Fate of Inhaled Materials
 - a. Gases and Vapors of High Solubility
 - b. Gases and Vapors of Low Solubility
 - c. Gases and Vapors of Intermediate Solubility
 - d. Aerosols
 - 6. Toxic Responses
 - 7. Interpretation of Atmospheric Analyses
 - a. Broad Line Between Safe and Harmful
 - b. Short Duration Exposures
 - c. Threshold Limit Values
 - B. Ingestion
 - C. Skin Absorption
- V. Dermatitis
 - A. Causes of Dermatitis
 - B. Symptoms of Dermatitis

Aluminum Company of America
INDUSTRIAL HYGIENE HANDBOOK

Chapter II

Toxicity and Threshold Limits

Bodily Protective Mechanisms

In his daily life man is subjected to a host of environmental stresses which would seriously threaten his existence were it not for the various protective mechanisms of his body. These protective mechanisms are quite effective; in fact man has much more natural protection against extraneous chemicals than have vegetation and materials of construction. In spite of this natural capacity for handling considerable stress, man's capacity to protect himself can be exceeded. When this happens the health of his body is impaired.

Degrees of Toxicity

Stresses may take the form of physical, chemical, biological or emotional insults. If the excessive insult is chemical, poisoning or intoxication results. The toxicity of a chemical, though, is a relative property. For example, sodium chloride is an essential requirement of the body. When deficient in this salt the body experiences a serious impairment of its functions. On the other hand, the ingestion of too much salt leads to intoxication. At certain levels, then, sodium chloride is toxic. It follows that the degree of toxicity of any material is judged by the dose required to exceed the capacity of the body defense mechanisms.

Human Variabilities

The biological variabilities characteristic of the human species have caused much confusion in those charged with the responsibility for determining the maximum concentration levels of potentially toxic chemicals that man can safely tolerate. But men, like all other living things, generally respond in a similar pattern to any given toxic material. These usual reactions are known as normal responses. When the response is outside of that normally expected, the affected individual is said to be either sensitive or resistant to the material in question. In industry, the factor of sensitivity is most commonly associated with the susceptibility of an individual to dermatitis and, somewhat less frequently, to irritation of the eyes and upper respiratory tract.

Inhalation

There are many routes of entry of chemicals into the body. Those of importance in industrial hygiene are inhalation, ingestion and skin absorption. Of these, inhalation is by far the most important. The primary function of the respiratory tract is to provide an exchange between the body organs and its gaseous environment. The structure of the respiratory organs is unique in that it provides a shield against environmental, biological and chemical stresses during this exchange. This is accomplished in part by the ciliary cells maintaining a fresh mucous lining in both the upper and lower respiratory tract. Inhaled foreign material is captured in the lining by impingement or dissolution. Displaced mucous containing the entrapped foreign material is swept into the throat through ciliary activity and then either expectorated or, as is more generally the case, swallowed. However, the capture of toxic material in the mucous lining can also have deleterious effects. Captured material may be absorbed directly or may cause irritation or may impair the ciliary activity, resulting in a predisposition to respiratory infection.

Work vs. Breathing Rate

Of all factors influencing the breathing rate of man, work is the most important. This is illustrated in Table 2.1. The table shows that as a man works harder, his breathing rate accelerates and his total air intake increases. It is easy to see that the greater the air intake, the greater will be the amounts of airborne contaminants taken into his system. In order to establish maximum safe limits of atmospheric concentrations (or threshold limits) for many of the contaminants to which a man is exposed, it is necessary to know his total requirement for air while on the job. During an eight-hour work day, the average employee breathes about ten cubic meters of air. This represents a work load comparable to walking at a rate of two to four miles per hour.

Table 2.1		
Oxygen Consumption and Volume of Breathing by Man		
	Oxygen consumed at 0° C. and 760 mm pressure, liters per minute	Air breathed at 20° C., liters per minute
Resting in bed	0.24	6
Sitting	0.30	7
Standing	0.36	8
Walking 2 m.p.h.	0.65	14
Walking 4 m.p.h.	1.20	26
Slow run	2.00	43
Maximum exertion	3.00-4.00	65-100

SOURCE: Henderson and Haggard Noxious Gases and the Principles of Respiration Influencing Their Action, Reinhold Pub. Corp. New York, N.Y., 1943

Altitude vs. Breathing Rate

At high altitudes, the body must compensate for the decreased oxygen content of air by more rapid breathing. At high altitudes a man will inhale more than the usual 10 m³ in 8 hours. Since the threshold limits are based on this volume of inspired air, it should be realized that a threshold limit in high altitude environments would necessarily be somewhat lower. This factor, however, is unimportant in the areas where Alcoa plants are located and may be ignored.

CO₂ vs. Breathing Rate

Since the carbon dioxide content of the blood is very influential in regulating the rate of breathing, it would appear then that the presence of carbon dioxide in air would also affect the breathing rate. However, stimulation of the breathing rate from a practical standpoint does not occur until the carbon dioxide content of the inhaled air exceeds about 2% (20,000 ppm). Such a high level is very unlikely under most conditions.

Other Chemicals vs. Breathing Rate

Some chemicals, notably carbon monoxide and certain nitroaromatic compounds, are able to combine with blood hemoglobin in such a way that the affected hemoglobin is unable to transport oxygen. The body attempts to compensate for this oxygen deficiency by an increase in the breathing rate. If atmospheric levels of these substances are held within the threshold limit (assuming the portal of entry to be inhalation), their effect on the rate of respiration is generally small.

Gases and Vapors of High Solubility

The fate of inhaled substances depends primarily on their physical characteristics, i.e., particle size, solubility and atmospheric concentration. Gases and vapors of high solubility such as hydrochloric, hydrofluoric and acetic acids, and the lower alcohols, aldehydes and ketones are largely removed by dissolving in the mucous of the upper respiratory tract. Some absorption may occur directly in the upper respiratory tract but, for the most part, the material is collected by the mucous and swallowed. Thus, to all intent and purpose, it has the same toxic action as if it were ingested. On the other hand, if the concentrations of non-irritating, soluble gases and vapors are sufficiently heavy, they may penetrate deeply. Heavy concentrations of irritants produce a throat spasm.

Gases and Vapors of Low Solubility

Gases and vapors of low solubility such as chlorinated and aliphatic hydrocarbons, the higher alcohols, hydrogen sulfide, oxides of nitrogen, ozone, mercury vapor, etc., readily reach the alveolar sacs of the lungs. They may be absorbed at this point and enter the blood stream or react with the tissue at the point of contact to produce an edema. The specific action of the inhaled material depends upon its toxic properties.

Gases and Vapors of Intermediate Solubility

Gases and vapors of intermediate solubility such as sulfur dioxide, chlorine and certain organic solvents, tend to be removed all along the respiratory tract. Thus, they may enter the body through the lungs and the digestive tract.

Aerosols

Aerosols (dusts, mists and fumes) above ten microns will be largely removed in the nasal passages and the back of the throat. A substantial part of the particulates between one and ten microns will also be removed in the upper respiratory tract but a significant portion will go beyond to be removed in the trachea and bronchial passages. Some, especially those in the low micron range, will gain access to the alveoli. In contrast, only a small portion of inhaled submicron particles will be removed in either the upper respiratory tract or the tracheal-bronchial area. Most of the submicron particles readily reach the alveolar sacs and of these, about 30% are retained in the alveoli. The remainder are exhaled with the expired air.

Toxic Responses

The toxicity of inhaled chemicals may be classified in many ways, i.e., in relation to the toxic mechanism involved, the response of the body, the dosage required to produce poisoning, the physical properties of the agents, etc. For industrial hygiene purposes, though, the most useful means of classification is according to the response of the body to toxic agents as described by Dr. H. F. Smyth, Jr. (1)

1. *Chronic Toxicity - The most dangerous effect of some substances is a progressive systemic injury, increasing in severity with continuing inhalation. Benzene, carbon disulphide, carbon*

tetrachloride and lead are the most familiar examples...Close medical supervision is required for the safe use of these substances. The standard for chronic toxic substances should refer to the time-weighted average concentration throughout a working day. Brief peaks of a few times a standard have no significance save as they increase the average.

- 2. Acute Toxicity - Some substances do not produce injury progressing with repeated inhalation. Such systemic injury as they may cause takes place as a result of one excessive inhalation or not at all. Familiar examples are carbon monoxide and hydrogen cyanide...*
- 3. Narcosis - The most dangerous effect of some substances is narcosis, which becomes anesthesia in its extreme stage. At a rather low concentration, they induce accidents by impairing judgment and delaying reaction time. Familiar examples are ethyl alcohol, ethyl ether and gasoline...*
- 4. Irritation - The most dangerous effect of some substances is irritation. Eye, nose and throat are irritated at a low concentration, the bronchi at a higher concentration, and fatal lung edema may be the result of inhaling an extreme concentration. The aldehydes, halogens and acids, are familiar examples. Highly odorous substances may also be considered in this category...*
- 5. Asphyxiation - Some substances are inert in the body and can injure only by asphyxias at extremely high concentrations, excluding the oxygen of the atmosphere. Familiar examples are the fluorochloro refrigerants...*
- 6. Fume Fever - The most important effect of some substances is a transient influenza-like condition known as fume fever. A familiar example is zinc oxide fume...*
- 7. Allergy - Some substances are known to sensitize an appreciable portion of exposed workmen. They may produce distressing and menacing asthma-like attacks when a sensitized person inhales a low concentration. Examples are ethylenediamine, and diisocyanates. At this time, there is no rational experimental basis for defining a concentration which will not sensitize a susceptible person, or one to which most previously sensitized workmen will respond...*

Interpretation of Analyses

Considerable care and study is required for the proper interpretation of the results of atmospheric tests for hazardous materials. Not only must the toxic nature of the material and the atmospheric levels found be taken into account but also the length of the employee's exposure to the toxic materials and the methods used to collect and analyze the air sample. The latter are particularly important in relation to respiratory irritants since most sampling techniques give an integrated average concentration over the sampling period. Thus, no information is furnished about the peak levels. In many instances, peak levels causing intense respiratory irritation may exist for short periods of time whereas the sample taken over a cycle of operation shows an average concentration well below the threshold limit. Obviously to interpret these results as proof of safe and satisfactory conditions is erroneous unless some method is devised to record the momentary peaks. In such instances more weight must be given to the degree of physiologic irritation experienced than to the concentration figure as determined by an integrated sample.

Broad Line Between Safe and Harmful

There is often the temptation to use threshold limit values to sharply differentiate between safe and unsafe atmospheric levels. Threshold limit values cannot be used for this purpose.

Although they represent those concentrations according to the best available information which are believed to be safe for repeated 8-hour daily exposures, they cannot provide a fine line between safe and dangerous levels. The normal biological variation in the response of individuals to toxic agents precludes this.

To illustrate how it is intended that the threshold limits be used, assume that the average exposure for a group of employees to lead fume is found to be 0.22 mg/m^3 . One would not ordinarily recommend costly local exhaust systems to reduce the exposure to 0.20 mg/m^3 , the threshold limit value for lead. Instead, a return visit should be made to the location, and if the results of the second study are essentially the same as before, recommendations should be made to observe these workmen clinically at four to six month intervals for evidence of lead absorption. If blood and urine values were above normal levels, then control measures would be indicated. On the other hand, if weighted exposures were above 0.50 mg/m^3 during the first study, control measures would have been recommended immediately and without hesitation. In other words, a few milligrams or parts per million below the threshold limit value does not necessarily mean the environment is safe nor would a dangerous situation exist with certainty if the threshold limit is exceeded slightly. A great deal of judgment is necessary in determining the exact cut-off point above which control measures should be instituted. It must be emphasized again that the threshold limits are designed to serve as guides only.

Short Duration Exposures

Another important aspect of the threshold limit values is that they refer to a weighted average concentration for an 8-hour work shift exposure rather than a maximum concentration that cannot be exceeded even momentarily. For example, the threshold limit for lead is 0.2 mg. per cubic meter of air for an 8-hour period. Accordingly, a level of 0.4 mg. per cubic meter would be permissible for four hours, 0.8 for two hours. There is obviously a limit, though, to which the weighted average exposure principle can be applied. The following general rules apply for brief exposures: concentrations of respiratory irritants should not substantially exceed the threshold value; concentrations of substances producing narcosis should seldom exceed three times the threshold value; concentrations of substances causing asphyxiation, fume fever or allergy should not substantially exceed the threshold limit value; and concentrations of substances causing acute and chronic poisoning should not exceed the threshold limit value by a factor of more than eight.

Threshold Limit Values

Tables 2.2-2.9 list most of the commonly used toxic chemicals. These tables show the threshold limit values for both long and short time exposures. The 8-hour weighted averages referred to in Tables 2.2-2.9 are calculated as mentioned above.

Ingestion

Although, in industry, ingestion is generally secondary to inhalation as a portal of entry for toxic material it is, nevertheless, important. In areas where highly toxic materials are involved, carelessness and poor hygienic practices can lead to the ingestion of significant quantities of the material and are to be avoided. The skin should always be kept clean of highly toxic materials to prevent the transfer of them from hand to mouth. Care should be taken to eliminate the possibility of contaminating lunches, tobacco, and chewing gum, etc. Storing and eating of lunches in areas where highly toxic materials are processed should be prohibited.

Threshold Limit Values of Airborne Contaminants AND INTENDED CHANGES Adopted By ACGIH For 1970



PREFACE THRESHOLD LIMIT VALUES FOR 1970

Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit, a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness.

Simple tests are now available (J. Occup. Med. 9, 537, 1967; Ann. N.Y. Acad. Sci., 151 Art. 2, p. 968, 1968) that may be used to detect those individuals hypersusceptible to a variety of industrial chemicals (respiratory irritants, hemolytic chemicals, organic isocyanates, carbon disulfide). These tests may be used to screen out by appropriate job placement the hyperreactive worker and thus in effect improve this "coverage" of the TLVs.

Threshold limit values refer to time-weighted concentrations for a 7 or 8-hour workday and 40-hour workweek. They should be used as guides in the control of health hazards and should not be used as fine lines between safe and dangerous concentrations. (Exceptions are the substances listed in Appendices A and E and those substances designated with a "C" or Ceiling value, Appendix C.)

Time-weighted averages permit excursions above the limit provided they are compensated by equivalent excursions below the limit during the workday. In some instances it may be permissible to calculate the average concentration for a workweek rather than for a workday. The degree of permissible excursion is related to the magnitude of the threshold limit value of a particular substance as given in Appendix C. The relationship between threshold limit and permissible excursion is a rule of thumb and in certain cases may not apply. The amount by which threshold limits may be exceeded for short periods without injury to health depends upon a number of factors such as the nature of the contaminant, whether very high concentrations - even for short periods - produce acute poisoning, whether the effects are cumulative, the frequency with which high concentrations occur, and the duration of such periods. All factors must be taken into consideration in arriving at decision as to whether a hazardous condition exists.

Threshold limits are based on the best available information from industrial experience, from experimental human and animal studies, and, when possible, from a combination of the three. The basis on which the values are established may differ from substance to substance; protection against impairment of health may be a guiding factor for some, whereas reasonable freedom from irritation, narcosis, nuisance or other forms of stress may form the basis for others.

The committee holds to the opinion that limits based on physical irritation should be considered no less binding than those based on physical impairment. There is increasing evidence that physical irritation may initiate, promote or accelerate physical impairment through interaction with other chemical or biologic agents.

In spite of the fact that serious injury is not believed likely as a result of exposure to the threshold limit concentrations, the best practice is to maintain concentrations of all atmospheric contaminants as low as is practical.

These limits are intended for use in the practice of industrial hygiene and should be interpreted and applied only by a person trained in this discipline. They are not intended for use, or for modification for use, (1) as a relative index of hazard or toxicity, (2) in the evaluation or control of community air pollution or air pollution nuisances, (3) in estimating the toxic potential of continuous uninterrupted exposures, (4) as proof or disproof of an existing disease or physical conditions, or (5) for adoption by countries whose working conditions differ from those in the United States of America and where substances and processes differ.

Ceiling vs Time-Weighted Average Limits. Although the time-weighted average concentration provides the most satisfactory, practical way of monitoring airborne agents for compliance with the limits, there are certain substances for which it is inappropriate. In the latter group are substances which are predominantly fast acting and whose threshold limit is more appropriately based on this particular response. Substances with this type of response are best controlled by a ceiling "C" limit that should not be exceeded. It is implicit in these definitions that the manner of sampling to determine compliance with the limits for each group must differ; a single brief sample, that is applicable to a "C" limit, is not appropriate to the time-weighted limit; here, a sufficient number of samples are needed to permit a time-weighted average concentration throughout a complete cycle of operations or throughout the work shift.

*Reprinted with permission from the American Conference of Governmental Industrial Hygienists.

Whereas the ceiling limit places a definite boundary which concentrations should not be permitted to exceed, the time-weighted average limit requires an explicit limit to the excursions that are permissible above the listed values. The magnitude of these excursions may be pegged to the magnitude of the threshold limit by an appropriate factor shown in Appendix C. It should be noted that the same factors are used by the Committee in making a judgment whether to include or exclude a substance for a "C" listing.

"Skin" Notation. Listed substances followed by the designation "Skin" refer to the potential contribution to the over-all exposure by the cutaneous route including mucous membranes and eye, either by airborne, or more particularly, by direct contact with the substance. Vehicles can alter skin absorption. This attention-calling designation is intended to suggest appropriate measures for the prevention of cutaneous absorption so that the threshold limit is not invalidated.

Mixtures. Special consideration should be given also to the application of the TLVs in assessing the health hazards which may be associated with exposure to mixtures of two or more substances. A brief discussion of basic considerations involved in developing threshold limit values for mixtures, and methods for their development, amplified by specific examples are given in Appendix B.

Nuisance Dusts. In contrast to fibrogenic dusts which cause scar tissue to be formed in lungs when inhaled in excessive amounts, so-called "nuisance" dusts have a long history of little adverse effect on lungs and do not produce significant organic disease or toxic effect when exposures are kept under reasonable control. The nuisance dusts have also been called (biologically) "inert" dusts, but the latter term is inappropriate to the extent that there is no dust which does not evoke some cellular response in the lung when inhaled in sufficient amount. However, the lung-tissue reaction caused by inhalation of nuisance dusts has the following characteristics: 1) The architecture of the air spaces remains intact. 2) Collagen (scar tissue) is not formed to a significant extent. 3) The tissue reaction is potentially reversible.

Excessive concentrations of nuisance dusts in the work-room air may seriously reduce visibility (iron oxide), may cause unpleasant deposits in the eyes, ears and nasal passages (Portland Cement dust), or cause injury to the skin or mucous membranes by chemical or mechanical action per se or by the rigorous skin cleansing procedures necessary for their removal.

A threshold limit of 10mg/M³, or 30 mppcf, of total dust < 1 μ SiO₂, whichever is less, is recommended for substances in these categories and for which no specific threshold limits have been assigned. This limit, for a normal workday, does not apply to brief exposures at higher concentrations. Neither does it apply to those substances which may cause physiologic impairment at lower concentrations but for which a threshold limit has not yet been adopted. Some "inert" particulates are given in Appendix D.

Simple Asphyxiants - "Inert" Gases or Vapors. A number of gases and vapors, when present in high concentrations in air, act primarily as simple asphyxiants without other significant physiologic effects. A TLV may not be recommended for each simple asphyxiant because the limiting factor is the available oxygen. The minimal oxygen content should be 18 percent by volume under normal atmospheric pressure (equivalent to a partial pressure, pO₂ of 135 mm Hg). Atmospheres deficient in O₂ do not provide adequate warning and most simple asphyxiants are odorless. Several simple asphyxiants present an explosion hazard. Account should be taken of this factor in limiting the concentration of the asphyxiant. Specific examples are listed in Appendix E.

Physical Factors. It is recognized that such physical factors as heat, ultraviolet and ionizing radiation, humidity, abnormal pressure (altitude) and the like may place added stress on the body so that the effects from exposure at a threshold limit may be altered. Most of these stresses act adversely to increase the toxic response of a substance. Although most threshold limits have built-in safety factors to guard against adverse effects to moderate deviations from normal environments, the safety factors of most substances are not of such a magnitude as to take care of gross deviations. For example, continuous work at temperatures above 90°F or over-time extending the workweek more than 25%, might be considered gross deviations. In such instances judgment must be exercised in the proper adjustments of the threshold limit values.

"Notice of Intent." At the beginning of each year, proposed actions of the Committee for the forthcoming year are issued in the form of a "Notice of Intent." This Notice provides not only an opportunity for comment, but solicits suggestions of substances to be added to the list. The suggestions should be accompanied by substantiating evidence. The list of Intended Changes follows the Adopted Values in the TLV booklet.

As Legislative Code. The Conference recognizes that the TLVs may be adopted in legislative codes and regulations. If so used, the intent of the concepts contained in the Preface

should be maintained and provisions should be made to keep the list current. These values are reviewed annually by the Committee on Threshold Limits for revision or additions, as further information becomes available.

Reprint Permission. This publication may be reprinted provided that written permission is obtained from the Secretary-Treasurer of the Conference and that it be published in its entirety.

ADOPTED VALUES
(In Alphabetical Order)

Substance	ppm ^{a)}	mg/M ³ b)
Abate	--	15
Acetaldehyde	200	380
Acetic acid	10	25
Acetic anhydride	5	20
Acetone	1,000	2,400
Acetonitrile	40	70
Acetylene	E	--
Acetylene dichloride, see 1, 2-Dichloroethylene	--	--
Acetylene tetrabromide	1	14
Acrolein	0.1	0.25
Acrylamide-Skin	--	0.3
Acrylonitrile-Skin	20	45
Aldrin-Skin	--	0.25
Allyl alcohol-Skin	2	5
Allyl chloride	1	3
**C Allyl glycidyl ether (AGE)	10	45
Allyl propyl disulfide	2	12
Alundum (Al ₂ O ₃)	--	D
2-Aminoethanol, see Ethanolamine	--	--
2-Aminopyridine	0.5	2
** Ammonia	50	35
Ammonium sulfate (Ammate)	--	15
n-Amyl acetate	100	525
sec-Amyl acetate	125	650
Aniline-Skin	5	19
Anilidine (o, p-isomers)-Skin	--	0.5
Antimony & compounds (as Sb)	--	0.5
ANTU (alpha naphthyl thiourea)	--	0.3
Argon	E	--
Arsenic & Compounds (as As)	--	0.5
Arsine	0.05	0.2
Azinphos-methyl-Skin	--	0.2
Barium (soluble compounds)	--	0.5
C Benzene (benzol)-Skin	25	80
Benzidine-Skin	--	A1
p-Benzoquinone, see Quinone	--	--
Benzoyl peroxide	--	5
Benzyl chloride	1	5
Beryllium	--	0.002
Diphenyl, see Diphenyl	--	--
Diaphenol A, see Diglycidyl ether	--	--
Boron oxide	--	15
Boron tribromide	1	10
C Boron trifluoride	1	3
Bromine	0.1	0.7
* Bromine pentafluoride	0.1	0.7
Bromoform-Skin	0.5	5
Butadiene (1, 3-butadiene)	1,000	2,200
Butanediol, see Butyl mercaptan	--	--
2-Butanone	200	590
2-Butoxy ethanol (Butyl Cellosolve)	--	--
- Skin	50	240
Butyl acetate (n-butyl acetate)	180	710

a) Parts of vapor or gas per million parts of contaminated air by volume at 25°C and 760 mm. Hg pressure.

b) Approximate milligrams of particulate per cubic meter of air.

** See Notice of Intended Change
Capital letters refer to Appendices.

Substance	ppm ^{a)}	mg/M ³ b)
sec-Butyl acetate	200	950
tert-Butyl acetate	200	950
Butyl alcohol	100	300
sec-Butyl alcohol	150	450
tert-Butyl alcohol	100	300
C Butylamine-Skin	5	15
C tert-Butyl chromate (as CrO ₃) - Skin	--	0.1
n-Butyl glycidyl ether (BGE)	50	270
* Butyl mercaptan	0.5	1.5
p-tert-Butyltoluene	10	60
Cadmium (Metal dust and soluble salts)	--	0.2
*C Cadmium oxide fume (as Cd)	--	0.1
Calcium carbonate	--	D
Calcium arsenate	--	1
Calcium oxide	--	5
** Camphor (Synthetic)	2	--
Carbaryl (Sevin ®)	--	5
Carbon black	--	3.5
Carbon dioxide	5,000	9,000
Carbon disulfide-Skin	20	60
Carbon monoxide	50	55
Carbon tetrachloride-Skin	10	65
Cellulose (paper fiber)	--	D
Chlordane-Skin	--	0.5
Chlorinated camphene-Skin	--	0.5
Chlorinated diphenyl oxide	--	0.5
* Chlorine	1	3
Chlorine dioxide	0.1	0.3
C Chlorine trifluoride	0.1	0.4
C Chloroacetaldehyde	1	3
*-Chloroacetophenone (phenacyl-chloride)	0.05	0.3
Chlorobenzene (monochlorobenzene)	75	350
o-Chlorobenzylidene malononitrile (OCBM)	0.05	0.4
Chlorobromomethane	200	1,050
2-Chloro-1, 3-butadiene, see Chloroprene	--	--
Chlorodiphenyl (42% Chlorine) - Skin	--	1
Chlorodiphenyl (54% Chlorine) - Skin	--	0.5
1-Chloro, 2, 3-epoxypropane, see Epichlorohydrin	--	--
Epichlorohydrin	--	--
2-Chloroethanol, see Ethylene chlorohydrin	--	--
Chloroethylene, see Vinyl chloride	--	--
C Chloroform (trichloromethane)	50	240
1-Chloro-1-nitropropane	20	100
Chloropicrin	0.1	0.7
Chloroprene (2-chloro-1, 3-butadiene)-Skin	25	90
Chromic acid and chromates (as CrO ₃)	--	0.1
Chromium, sol. chromic, chromous salts as Cr	--	0.5
Metal & insol. salts	--	1
Coal tar pitch volatiles (benzene soluble fraction) anthracene, BaP, phenanthrene, acridine, chrysene, pyrene	--	0.2

* 1970 Addition

** See Notice of Intended Change

Substance	ppm ^{a)}	mg/M ³ b)
Cobalt, metal fume & dust	--	0.1
Copper fume	--	0.1
Dusts and Mists	--	1
Corundum (Al ₂ O ₃)	--	D
Cotton dust (raw)	--	1
Crag® herbicide	--	15
Cresol (all isomers) - Skin	5	22
Crotonaldehyde	2	8
Cumene-Skin	50	245
Cyanide (as CN)-Skin	--	5
* Cyanogen	10	--
Cyclohexane	300	1,050
Cyclohexanol	50	200
Cyclohexanone	50	200
Cyclohexene	300	1,015
Cyclopentadiene	75	200
2, 4-D	--	10
DDT-Skin	--	1
DDVP, see Dichlorvos	--	--
Decaborane-Skin	0.05	0.3
Demeton™ -Skin	--	0.1
Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone)	50	240
1, 2-Diaminoethane, see Ethylene-diamine	--	--
Diazomethane	0.2	0.4
Diborane	0.1	0.1
C 1, 2-Dibromoethane (ethylene dibromide)-Skin	25	190
Dibutyl phosphate	1	5
Dibutylphthalate	--	5
*C Dichloroacetylene	0.1	0.4
C o-Dichlorobenzene	50	300
p-Dichlorobenzene	75	450
Dichlorodifluoromethane	1,000	4,950
1, 3-Dichloro-5, 5-dimethyl hydantoin	--	0.2
1, 1-Dichloroethane	100	400
1, 2-Dichloroethane	50	200
1, 2-Dichloroethylene	200	790
C Dichloroethyl ether-Skin	15	90
Dichloromethane, see Methylene-chloride	--	--
Dichloromonofluoromethane	1,000	4,200
C 1, 1-Dichloro-1-nitroethane	10	60
1, 2-Dichloropropane, see Propylenedichloride	--	--
Dichlorotetrafluoroethane	1,000	7,000
Dichlorvos (DDVP)-Skin	--	1
Dieldrin-Skin	--	0.25
Diethylamine	25	75
Diethylamino ethanol-Skin	10	50
**C Diethylene triamine-Skin	10	42
Diethylether, see Ethyl ether	--	--
Difluorodibromomethane	100	880
C Diglycidyl ether (DGE)	0.5	2.8
Dihydroxybenzene, see Hydroquinone	--	--
Disobutyl ketone	50	290
Diisopropylamine-Skin	5	20

* 1970 Addition

** See Notice of Intended Change

Substance	ppm ^{a)}	mg/M ³ b)
Dimethoxymethane, see Methylal	--	--
Dimethyl acetamide-Skin	10	35
Dimethylamine	10	18
Dimethylaminobenzene, see Xylidene	--	--
Dimethylaniline (N-dimethylaniline)-Skin	5	25
Dimethylbenzene, see Xylene	--	--
Dimethyl 1, 2-dibromo-2, 2-di-chloroethyl phosphate, (Dibrom)	--	3
Dimethylformamide-Skin	10	30
2, 6-Dimethylheptanone, see	--	--
Dilaobutyl ketone	--	--
1, 1-Dimethylhydrazine-Skin	0.5	1
Dimethylphthalate	--	5
Dimethylsulfate-Skin	1	5
Dinitrobenzene (all isomers)-Skin	--	1
Dinitro-o-cresol-Skin	--	0.2
Dinitrotoluene-Skin	--	1.5
Dioxane (Dichylene dioxide)-Skin	100	380
Diphenyl	0.2	1
Diphenyl amine	--	10
Diphenylmethane diisocyanate (see Methylene bisphenyl isocyanate (MDI))	--	--
Dipropylene glycol methyl ether-Skin	100	800
Di-sec, octyl phthalate (Di-2-ethylhexylphthalate)	--	5
Emery	--	D
Endosulfan (Thiodan ®)-Skin	--	0.1
Endrin-Skin	--	0.1
Epichlorohydrin-Skin	5	18
EPN-Skin	--	0.5
1, 2-Epoxypropane, see Propylene-oxide	--	--
2, 3-Epoxy-1-propanol, see Glycidol	--	--
Ethane	E	--
Ethanethiol, see Ethylmercaptan	--	--
Ethanolamine	3	6
2-Ethoxyethanol-Skin	200	740
2-Ethoxyethylacetate (Cellulosolve acetate)-Skin	100	540
Ethyl acetate	400	1,400
Ethyl acrylate-Skin	25	100
Ethyl alcohol (ethanol)	1,000	1,900
Ethylamine	10	18
Ethyl sec-amyl ketone (5-methyl-3-heptanone)	25	130
Ethyl benzene	100	435
Ethyl bromide	200	890
Ethyl butyl ketone (3-Heptanone)	50	230
Ethyl chloride	1,000	2,600
Ethyl ether	400	1,200
Ethyl formate	100	300
Ethyl mercaptan	0.5	1
Ethyl silicate	100	850
Ethylene	E	--
Ethylene chlorohydrin-Skin	5	18

Substance	ppm ^{a)}	mg/M ³ b)
Ethylenediamine	10	25
Ethylene dibromide, see 1, 2-Dibromoethane	--	--
Ethylene dichloride, see 1, 2-Dichloroethane	--	--
C Ethylene glycol dinitrate and/or Nitroglycerin-Skin	0.2 ^{d)}	--
Ethylene glycol monomethyl ether acetate, see Methyl cellosolve acetate	--	--
Ethyleneimine-Skin	0.5	1
Ethylene oxide	50	90
Ethylidene chloride, see 1, 1-Dichloroethane	--	--
N-Ethylmorpholine-Skin	20	94
Ferban	--	15
Ferrovandium dust	--	1
Fibrous glass	--	D
Fluoride (as F)	--	2.5
Fluorine	0.1	0.2
Fluorotrichloromethane	1,000	5,600
*C Formaldehyde	5	6
Formic acid	5	9
Furfural-Skin	5	20
Furfuryl alcohol	50	200
Gasoline	--	A ³
Glycerine mist	--	D
Glycidol (2, 3-Epoxy-1-propanol)	50	150
Glycol monoethyl ether, see 2-Ethoxyethanol	--	--
Graphite, (Synthetic)	--	D
Guthion, ® see Azinphosmethyl	--	--
Gypsum	--	D
Hafnium	--	0.5
Helium	E	--
Heptachlor-Skin	--	0.5
Heptane (n-heptane)	500	2,000
Hexachloroethane-Skin	1	10
Hexachloronaphthalene-Skin	--	0.2
Hexane (n-hexane)	500	1,800
2-Hexanone	100	410
Hexone (Methyl isobutyl ketone)	100	410
sec-Hexyl acetate	50	300
Hydrazine-Skin	1	1.3
Hydrogen	E	--
Hydrogen bromide	3	10
C Hydrogen chloride	5	7
Hydrogen cyanide-Skin	10	11
Hydrogen fluoride	3	2
Hydrogen peroxide	1	1.4
Hydrogen selenide	0.05	0.2
Hydrogen sulfide	10	15
Hydroquinone	--	2
* Indene	10	45

d) An atmospheric concentration of not more than 0.02 ppm, or personal protection may be necessary to avoid headaches.

Substance	ppm ^{a)}	mg/M ³ b)
Indium and compounds, as In	--	0.1
C Iodine	0.1	1
Iron oxide fume	--	10
Iron salts, soluble, as Fe	--	1
Isoamyl acetate	100	525
Isoamyl alcohol	100	380
Isobutyl acetate	150	700
Isobutyl alcohol	100	300
Isophorone	25	140
Isopropyl acetate	250	950
Isopropyl alcohol	400	980
Isopropylamine	5	12
Isopropylether	500	2,100
Isopropyl glycidyl ether (IGE)	50	240
Kaolin	--	D
Ketene	0.5	0.9
Lead	--	0.2
Lead arsenate	--	0.15
Limestone	--	D
Lindane-Skin	--	0.5
Lithium hydride	--	0.025
L. P. G. (Liquified petroleum gas)	1,000	1,800
Magnesite	--	D
Magnesium oxide fume	--	15
Malathion-Skin	--	15
Maleic anhydride	0.25	1
C Manganese and compounds, as Mn	--	D
Marble	--	0.1
* Mercury-Skin	--	0.01
* Mercury (organic compounds)-Skin	--	0.01
Mesityl oxide	25	100
Methane	E	--
Methanethiol, see Methyl mercaptan	--	--
Methoxychlor	--	15
2-Methoxyethanol, see Methyl cellosolve	--	--
Methyl acetate	200	810
Methyl acetylene (propyne)	1,000	1,850
Methyl acetylene-propadiene mixture (MAPP)	1,000	1,800
Methyl acrylate-Skin	10	35
Methylal (dimethoxymethane)	1,000	3,100
Methyl alcohol (methanol)	200	260
Methylamine	10	12
Methyl amyl alcohol, see Methyl isobutyl carbinol	--	--
* Methyl isoamyl ketone	100	475
Methyl (n-amyl) ketone (2-Heptanone)	100	485
C Methyl bromide-Skin	20	80
Methyl butyl ketone, see 2-Hexanone	--	--
Methyl cellosolve-Skin	25	80
Methyl cellosolve acetate-Skin	25	120
*C Methyl chloride	100	210
Methyl chloroform	350	1,900
Methylcyclohexane	500	2,000
Methylcyclohexanol	100	470

* 1970 Addition
** See Notice of Intended Changes

* 1970 Addition
** See Notice of Intended Changes

* 1970 Addition
** See Notice of Intended Changes

Substance	ppm ^{a)}	mg/N ^{3 b)}
o-Methylcyclohexanone-Skin	100	460
Methyl ethyl ketone (MEK), see 2-Butanone	--	--
Methyl formate	100	250
Methyl iodide - Skin	5	28
Methyl isobutyl carbinol-Skin	25	100
Methyl isobutyl ketone, see Hexone	--	--
Methyl isocyanate - Skin	0.02	0.05
Methyl mercaptan	0.5	1
Methyl methacrylate	100	410
Methyl propyl ketone, see 2-Pentanone	--	--
C Methyl silicate	5	30
C or Methyl styrene	100	480
C Methylene bisphenyl isocyanate (MDI)	0.02	0.2
Methylene chloride (dichloromethane)	500	1,740
Molybdenum (soluble compounds)	--	5
(insoluble compounds)	--	15
Monomethyl aniline-Skin	2	9
C Monomethyl hydrazine-Skin	0.2	0.35
Morpholine-Skin	20	70
Naphtha (coal tar)	100	400
Naphthalene	10	50
β-Naphthylamine	--	A ¹
Neon	E	--
Nickel carbonyl	0.001	0.007
Nickel, metal and soluble cmpds, as Ni	--	1
Nicotine-Skin	--	0.5
Nitric acid	2	5
Nitric oxide	25	30
p-Nitroaniline-Skin	1	6
Nitrobenzene-Skin	1	5
p-Nitrochlorobenzene-Skin	--	1
Nitroethane	100	310
Nitrogen	E	--
Nitrogen dioxide	5	9
Nitrogen trifluoride	10	29
Nitroglycerin-Skin	0.2	2
Nitromethane	100	250
1-Nitropropane	25	90
2-Nitropropane	25	90
N-Nitrosodimethylamine (dimethyl-nitrosoamine)-Skin	--	A ¹
Nitrotoluene-Skin	5	30
Nitrotrichloromethane, see Chloropicrin	--	--
Nitrous oxide	E	--
Octachloronaphthalene-Skin	--	0.1
Octane	400	1,900
Oil mist, particulate	--	5h
Oil mist, vapor	i) A ³	--
Osmium tetroxide	--	0.002
Oxalic acid	1	1
Oxygen difluoride	0.05	0.1
Ozone	0.1	0.2
Paraquat-Skin	--	0.5

h) As sampled by method that does not collect vapor.

i) According to analytically determined composition.

* 1970 Addition

** See Notice of Intended Changes

Substance	ppm ^{a)}	mg/N ^{3 b)}
Parathion-Skin	--	0.1
Pentaborane	0.005	0.01
Pentachloronaphthalene-Skin	--	0.5
Pentachlorophenol-Skin	--	0.5
Pentaerythritol	--	D
* Pentane	500	1,500
2-Pentanone	200	700
Perchloroethylene	100	670
Perchloromethyl mercaptan	0.1	0.8
Perchloryl fluoride	3	13.5
* Petroleum Distillates (naphtha)	i) A ³	--
Phenol-Skin	5	19
p-Phenylene diamine-Skin	--	0.1
Phenyl ether (vapor)	1	7
Phenyl ether-Diphenyl mixture (vapor)	1	7
Phenylethylene, see Styrene	--	--
Phenyl glycidyl ether (PGE)	10	60
Phenylhydrazine-Skin	5	22
Phosdrin (Mevinphos [®])-Skin	--	0.1
Phosgene (carbonyl chloride)	0.1	0.4
Phosphine	0.3	0.4
Phosphoric acid	--	1
Phosphorus (yellow)	--	0.1
Phosphorus pentachloride	--	1
Phosphorus pentasulfide	--	1
Phosphorus trichloride	0.5	3
Phthalic anhydride	2	12
Picric acid-Skin	--	0.1
Pival [®] (2-Pivalyl-1, 3-indandione)	--	0.1
Plaster of Paris	--	D
Platinum (Soluble Salts) as Pt	--	0.002
Polytetrafluoroethylene decomposition products	--	A ²
Propane	E	--
β-Propiolactone	--	A ¹
Propargyl alcohol-Skin	1	--
n-Propyl acetate	200	840
Propyl alcohol	200	500
n-Propyl nitrate	25	110
Propylene dichloride	75	350
Propylene imine-Skin	2	5
Propylene oxide	100	240
Propyne, see Methylacetylene	--	--
Pyrethrum	--	5
Pyridine	5	15
Quinone	0.1	0.4
RDX-Skin	--	1.5
Rhodium, Metal fume and dusts, as Rh	--	0.1
Soluble salts	--	0.001
Runnel	--	10
Rotenone (commercial)	1	5
Rouge	--	D
Selenium compounds (as Se)	--	0.2
Selenium hexafluoride	0.05	0.4
Silicon carbide	--	D

i) According to analytically determined composition.

Capital letters refer to Appendices.

* 1970 Addition

** See Notice of Intended Changes

Substance	ppm ^{a)}	mg/N ^{3 b)}
Silver, metal and soluble compounds	--	0.01
Sodium fluoroacetate (1080)-Skin	--	0.05
Sodium hydroxide	--	2
Stibine	0.1	0.5
Starch	--	D
* Stoddard solvent	200	1,150
Strychnine	--	0.15
**C Styrene monomer (phenylethylene)	100	420
Sucrose	--	D
Sulfur dioxide	5	13
Sulfur hexafluoride	1,000	6,000
Sulfuric acid	--	1
Sulfur monochloride	1	6
Sulfur pentafluoride	0.025	0.25
Sulfuryl fluoride	5	20
Systox, see Demeton [®]	--	--
2, 4, 5 T	--	10
Tantalum	--	5
TEPP-Skin	--	0.2
Tellon [®] decomposition products	--	A ²
Tellurium	--	0.1
Tellurium hexafluoride	0.02	0.2
TEPP-Skin	--	0.05
C Terphenyls	1	9
1, 1, 1, 2-Tetrachloro-2, 2-di-fluoroethane	500	4,170
1, 1, 2, 2-Tetrachloro-1, 2-di-fluoroethane	500	4,170
1, 1, 2, 2-Tetrachloroethane-Skin	5	35
Tetrachloroethylene, see Perchloroethylene	--	--
Tetrachloromethane, see Carbon tetrachloride	--	--
Tetrachloronaphthalene-Skin	--	2
Tetraethyl lead (as Pb)-Skin	--	0.100 i)
Tetrahydrofuran	200	590
Tetramethyl lead (as Pb)-Skin	--	0.150 i)
Tetramethyl succinonitrile-Skin	0.5	3
Tetramtormethane	1	8
Tetryl (2, 4, 6-trinitrophenyl-methyl)triamine-Skin	--	1.5
Thallium (soluble compounds)-Skin as Tl	--	0.1
Thiram	--	5
Tin (inorganic cmpds, except SnI ₄ and SnO ₂)	--	2
Tin (organic cmpds)	--	0.1
Tin oxide	--	D
Titanium dioxide	--	D
Toluene (toluol)	200	750
C Toluene-2, 4-diisocyanate	0.02	0.14
o-Toluidine-Skin	5	22
Toxaphene, see Chlorinated camphene	--	--
Tributyl phosphate	--	5
1, 1, 1-Trichloroethane, see Methyl chloroform	--	--
1, 1, 2-Trichloroethane-Skin	10	45

j) For control of general room air, biologic monitoring is essential for personnel control.

* 1970 Addition

** See Notice of Intended Changes

Substance	ppm ^{a)}	mg/M ³ b)
Trichloroethylene	100	535
Trichloromethane, see Chloroform	--	--
Trichloronaphthalene-Skin	--	5
1, 2, 3-Trichloropropane	50	300
1, 1, 2-Trichloro 1, 2, 2-tri- fluoroethane	1,000	7,600
Triethylamine	25	100
Trifluoromonomobromomethane	1,000	6,100
Trimethyl benzene	25	120
2, 4, 6-Trinitrophenol, see Picric acid	--	--
2, 4, 6-Trinitrophenylmethylnitramine, see Tetryl	--	--
Trinitrotoluene-Skin	--	1.5
Triorthocresyl phosphate	--	0.1
Triphenyl phosphate	--	3
Tungsten & compounds, as W	--	--
Soluble	--	1
Insoluble	--	5
Turpentine	100	560
Uranium (natural) sol. & insol. compounds as U	--	0.2
C Vanadium (V ₂ O ₅ dust)	--	0.5
(V ₂ O ₅ fume)	--	0.1
Vinyl benzene, see Styrene	--	--
**C Vinyl chloride	500	1,300
Vinylcyanide; see Acrylonitrile	--	--
Vinyl toluene	100	480
Warfarin	--	0.1
Xylene (xylol)	100	435
Xylidine-Skin	5	25
Yttrium	--	1
Zinc chloride fume	--	5
Zinc oxide fume	--	5
Zirconium compounds (as Zr)	--	5

Radioactivity: For permissible concentrations of radioisotopes in air, see U.S. Department of Commerce, National Bureau of Standards, Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," June 5, 1959. Also, see U.S. Department of Commerce National Bureau of Standards, Handbook 59, "Permissible Dose from External Sources of Ionizing Radiation," September 24, 1954, and addendum of April 15, 1958.

^a 1970 Addition
^{**} See Notice of Intended Changes

MINERAL DUSTS

Substance	m.p.p.c.f. ^{a)}
SILICA	
Crystalline	
** Quartz, Threshold Limit calculated from the formula	250 f) %SiO ₂ .5
** Cristoballite " " "	
Amorphous, including natural diatomaceous earth	20
SILICATES (less than 1% crystalline silica)	
** Asbestos, all types	5
Mica	20
Portland Cement	50
Soapstone	20
Talc (non-asbestiform)	20
Talc (fibrous), use asbestos limit	--
Tremolite, see asbestos	--
Graphite (natural)	15
** "Inert" or Nuisance Particulates	50 (or 15 mg/M ³ whichever is the smaller) of total dust < 1% SiO ₂
see Appendix D	
Conversion factors	
mppcf x 35.3 = million particles per cubic meter = particles per c.c.	

- e) Millions of particles per cubic foot of air, based on impinger samples counted by light-field technique.
- f) The percentage of crystalline silica in the formula, is the amount determined from airborne samples, except in those instances in which other methods have been shown to be applicable.

** See Notice of Intended Changes for Mineral Dusts.

NOTICE OF INTENDED CHANGES (for 1970)

These substances, with their corresponding values, comprise those for which either a limit has been proposed for the first time, or for which a change in the "Adopted" listing has been proposed. In both cases, the proposed limits should be considered trial limits that will remain in the listing for a period of at least two years. During this time, the previously Adopted Limit will remain in effect. If, after two years no evidence comes to light that questions the appropriateness of the values herein, the values will be placed in the "Adopted" list. Documentation is available for each of these substances.

Substance	ppm	mg/M ³
2-Acetylaminofluorene-Skin	--	A ¹
Allyl glycidyl ether	5	22
4-Aminodiphenyl-Skin	--	A ¹
Ammonia	25	18
Ammonium chloride fume	--	10
Asphalt (petroleum) fumes	--	5
Butyl lactate	1	5
Camphor (synthetic)	2	12
Diazon-Skin	--	0.1
2-N Dibutylamino ethanol-Skin	2	14
Dichlorobenzidine-Skin	--	A ¹
Diethylene triamine-Skin	1	4
4-Dimethylaminoazobenzene	--	A ¹
Fibrous glass	g)	D
* C Formaldehyde	2	3
Iron pentacarbonyl	0.01	0.08
* Mercury (Alkyl compounds) - Skin	--	0.01
* Methyl chloride	100	210
Methyl 2-cyanoacrylate	2	8
* Methylcyclopentadienyl manganese tricarbonyl (as Mn)	0.1	0.2
Methyl demeton-Skin	--	0.5
Methyl parathion-Skin	--	0.2
Phenothiazine-Skin	--	5
* Rosin Core Solder, pyrolysis products	--	0.1 (as alde- hyde)
Styrene	100	420
* C Subtilisin (Proteolytic enzymes)	--	0.0003 (as 100% pure crystal- line en- zyme)
* Vanadium (V ₂ O ₅ Fume) as V	--	0.05
Vinyl acetate	10	30
Vinyl chloride	200	770
* Wood dust (non allergenic)	--	5

* Mercury (All forms except alkyl). . . .0-05 mg/m³
^a 1970 Revision Addition
 Capital letters refer to Appendices
 g) < 5-7 μ Diameter. No TLV for coarse fibrous glass has yet been set.

NOTICE OF INTENDED CHANGES (Cont'd) MINERAL DUSTS

SUBSTANCE	TLV
Asbestos (All types)	5 fibers/ml > 5 μ in length ^k
Coal dust (bituminous)	2 mg/m ³ (respirable dust)(m)
Cristobalite	Use one-half the value calculated from the count or mass formulae for quartz.
'Inert' or Nuisance Particulates	10 mg/M ³ or 30 mppcf (whichever is the smaller) of total dust < 1% SiO ₂ ⁿ
Quartz	TLV in mppcf: $\frac{300}{\%SiO_2 \cdot 10}$ TLV for respirable dust in mg/m ³ $\frac{10 \text{ mg/M}^3 \text{p}}{\% \text{ Respirable quartz} \cdot 2}$ TLV for "total dust", respirable and nonrespirable: $\frac{30 \text{ mg/M}^3}{\% \text{ quartz} \cdot 3}$
Silica, fused Tridymite	Use quartz formulae Use one-half the value calculated from formulae for quartz.

* 1970 Revision or Addition

- As determined by the membrane filter method at 430 X magnification phase contrast illumination. Concentrations > 5 fibers/ml, but not to exceed 10, may be permitted for 15-minute periods each hour up to five times daily.
- "Respirable" dust as defined by the British Medical Research Council Criteria (1) and as sampled by a device producing equivalent results (2).
 - Hatch, T.E. and Gross, P., Pulmonary Deposition and Retention of Inhaled Aerosols, p. 149. Academic Press, New York, New York, 1964.
 - Interim Guide for Respirable Mass Sampling, ABHA Aerosol Technology Committee, ABHA J. 31, 2, 1970, p. 133.
- This automatically reduces all particulate substances in Adopted list with TLV of 15 mg/M³ to 10 mg/M³.
- Both concentration and per cent quartz for the application of this limit are to be determined from the fraction passing a size-selector with the following characteristics:

Aerodynamic Diameter (μ) (unit density sphere)	% passing selector
2.5	90
2.5	75
3.5	50
5.0	25
10	0

APPENDIX A

- A¹ Because of the high incidence of cancer, either in man or in animals, no exposure or contact by any route, respiratory, oral or skin should be permitted for the compounds:

2-Acetylaminofluorene	beta-Naphthylamine
4-Aminodiphenyl	4-Nitrodiphenyl
Benzidine & its salts	N-Nitrosodimethylamine
Dichlorobenzidine	beta-Propiolactone
4-Dimethylaminoazobenzene	

Because of the extremely high incidence of bladder tumors in workers handling beta-naphthylamine and the potential carcinogenic activity of the other compounds, the State of Pennsylvania prohibits the manufacture, use and other activities that involve human exposure without express approval by the Department of Health.

- A² Polytetrafluoroethylene* decomposition products. Thermal decomposition of the fluorocarbon chain in air leads to the formation of oxidized products containing carbon, fluorine and oxygen. Because these products decompose in part by hydrolysis in alkaline solution, they can be quantitatively determined in air as fluoride to provide an index of exposure. No TLV is recommended pending determination of the toxicity of the products, but air concentrations should be minimal.

- A³ Gasoline and/or Petroleum Distillates. The composition of these materials varies greatly and thus a single TLV for all types of these materials is no longer applicable. In general, the aromatic hydrocarbon content will determine what TLV applies. Consequently the content of benzene, other aromatics and additives should be determined to arrive at the appropriate TLV (Elkins, et al. A.I.H.A.J. 24, 99, 1963).

* Trade Names: Algonlon, Fluon, Halon, Teflon, Tetran

APPENDIX B

B.1 THRESHOLD LIMIT VALUES FOR MIXTURES

When two or more hazardous substances are present, their combined effect, rather than that of either individually, should be given primary consideration. In the absence of

information to the contrary, the effects of the different hazards should be considered as additive. That is, if the sum of the following fractions,

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \dots + \frac{C_n}{T_n}$$

exceeds unity, then the threshold limit of the mixture should be considered as being exceeded. C₁ indicates the observed atmospheric concentration, and T₁ the corresponding threshold limit, (See Example 1A.a.).

Exceptions to the above rule may be made when there is good reason to believe that the chief effects of the different harmful substances are not in fact additive, but independent as when purely local effects on different organs of the body are produced by the various components of the mixture. In such cases the threshold limit ordinarily is exceeded only when at least one member of the series ($\frac{C_1}{T_1}$ or $\frac{C_2}{T_2}$ etc.) itself has a value exceeding unity, (See Example 1A.b.).

Antagonistic action or potentiation may occur with some combinations of atmospheric contaminants. Such cases at present must be determined individually. Potentiating or antagonistic agents are not necessarily harmful by themselves. Potentiating effects of exposure to such agents by routes other than that of inhalation is also possible, e.g. imbibed alcohol and inhaled narcotic (trichloroethylene). Potentiation is characteristically exhibited at high concentrations, less probably at low.

When a given operation or process characteristically emits a number of harmful dusts, fumes, vapors or gases, it will frequently be only feasible to attempt to evaluate the hazard by measurement of a single substance. In such cases, the threshold limit used for this substance should be reduced by a suitable factor, the magnitude of which will depend on the number, toxicity and relative quantity of the other contaminants ordinarily present.

Examples of processes which are typically associated with two or more harmful atmospheric contaminants are welding, automobile repair, blasting, painting, lacquering, certain foundry operations, diesel exhausts, etc., (Example 2.)

APD 002715

THRESHOLD LIMIT VALUES FOR MIXTURES EXAMPLES

1A. General case, where air is analyzed for each component

- a. Additive effects. (note: It is essential that the atmosphere be analyzed both qualitatively and quantitatively for each component present, in order to evaluate compliance or noncompliance with this calculated TLV.)

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \frac{C_3}{T_3} + \dots = 1$$

Example No. 1: Air contains 5 ppm of carbon tetrachloride (TLV = 10 ppm) 20 ppm of ethylene dichloride (TLV = 50 ppm) and 10 ppm of ethylene dibromide (TLV = 25 ppm)

Atmospheric concentration of mixture =

$$5 + 20 + 10 = 35 \text{ ppm of mixture}$$

$$\frac{5}{10} + \frac{20}{50} + \frac{10}{25} = \frac{25 + 20 + 20}{50} = 1.3$$

Threshold Limit is exceeded. Furthermore, the TLV of this mixture may be calculated by reducing the total fraction to 1.0; i.e.

$$\text{TLV of mixture} = \frac{35}{1.3} = 27 \text{ ppm}$$

Example No. 2: Air contains 200 ppm of hexane (TLV = 500 ppm) 100 ppm of methylene chloride (TLV = 500 ppm) and 20 ppm of perchlorethylene (TLV = 100 ppm)

Atmospheric concentration of mixture =

$$200 + 100 + 20 = 320 \text{ ppm of mixture}$$

$$\frac{200}{500} + \frac{100}{500} + \frac{20}{100} = \frac{200 + 100 + 100}{500} = \frac{400}{500} = 0.8$$

Threshold Limit is not exceeded. The TLV of this mixture = $\frac{320}{0.8} = 400 \text{ ppm}$

1B. Special case when the source of contaminant is a liquid mixture and the atmospheric composition is assumed to be similar to that of the original material; e.g. on a time weighted average exposure basis, all of the liquid (solvent) mixture eventually evaporates.

a. Additive effects (approximate solution)

1. The percent composition (by weight) of the liquid mixture is known, the TLVs of the constituents must be listed in mg/M³.

(NOTE: In order to evaluate compliance with this TLV, field sampling instruments should be calibrated, in the laboratory, for response to this specific quantitative and qualitative air-vapor mixture, and also to fractional concentrations of this mixture; e.g., 1/2 the TLV; 1/10 the TLV; 2 X the TLV; 10 X the TLV; etc.)

$$\text{TLV of mixture} = \frac{1}{\frac{f_a}{\text{TLV}_a} + \frac{f_b}{\text{TLV}_b} + \frac{f_c}{\text{TLV}_c} + \dots + \frac{f_n}{\text{TLV}_n}}$$

Example No. 1: Liquid solvent contains (by weight) 50% heptane (TLV = 2000 mg/M³) 30% methylene chloride (TLV = 1740 mg/M³) 20% perchlorethylene (TLV = 670 mg/M³)

$$\text{TLV of mixture} = \frac{1}{\frac{0.5}{2000} + \frac{0.3}{1740} + \frac{0.2}{670}} = \frac{1}{.00025 + .00017 + .0003}$$

$$= \frac{1}{.00072} = 1390 \text{ mg/M}^3$$

Of this mixture: 50% or 695 mg/M³ is heptane, 30% or 417 mg/M³ is methylene chloride and 20% or 278 mg/M³ is perchlorethylene

These values can be converted to ppm as follows:

heptane: $\frac{2000 \text{ mg/M}^3}{1 \text{ mg/M}^3} = 500 \text{ ppm}$
 $\frac{695 \text{ mg/M}^3}{1 \text{ mg/M}^3} = 695 \text{ ppm}$

methylene chloride: $\frac{1740 \text{ mg/M}^3}{1 \text{ mg/M}^3} = 1740 \text{ ppm}$
 $\frac{417 \text{ mg/M}^3}{1 \text{ mg/M}^3} = 417 \text{ ppm}$

perchlorethylene: $\frac{670 \text{ mg/M}^3}{1 \text{ mg/M}^3} = 670 \text{ ppm}$
 $\frac{278 \text{ mg/M}^3}{1 \text{ mg/M}^3} = 278 \text{ ppm}$

The TLV of this mixture = 174 + 110 + 42 = 335 ppm.

1B.b. General Exact Solution for Mixtures of N Components With Additive Effects and Different Vapor Pressures.

$$(1) \frac{C_1}{T_1} + \frac{C_2}{T_2} + \dots + \frac{C_n}{T_n} = 1;$$

$$(2) C_1 + C_2 + \dots + C_n = T;$$

$$(2.1) \frac{C_1}{T} + \frac{C_2}{T} + \dots + \frac{C_n}{T} = 1.$$

By the Law of Partial Pressures,

$$(3) C_1 = a p_1,$$

and by Raoult's Law,

$$(4) p_1 = F_1 p_1^0.$$

Combine (3) and (4) to obtain

$$(5) C_1 = a F_1 p_1^0.$$

Combining (1), (2.1) and (5), we obtain

$$(6) \frac{F_1 p_1^0}{T} + \frac{F_2 p_2^0}{T} + \dots + \frac{F_n p_n^0}{T} = 1$$

$$\frac{F_1 p_1^0}{T_1} + \frac{F_2 p_2^0}{T_2} + \dots + \frac{F_n p_n^0}{T_n}$$

and solving for T,

$$(6.1) T = \frac{F_1 p_1^0 + F_2 p_2^0 + \dots + F_n p_n^0}{\frac{F_1 p_1^0}{T_1} + \frac{F_2 p_2^0}{T_2} + \dots + \frac{F_n p_n^0}{T_n}}$$

$$\text{or } \frac{1}{T} = \sum F_i p_i^0$$

$$(6.2) T = \frac{1}{\sum \frac{F_i}{T_i}} = \frac{1}{\sum \frac{F_i p_i^0}{T_i p_i^0}}$$

$$1 = \sum \frac{F_i p_i^0}{T_i}$$

T = Threshold Limit Value in ppm.
 C = Vapor concentration in ppm.
 p = Vapor pressure of component in solution.
 p⁰ = Vapor pressure of pure component.
 F = Mol fraction of component in solution.
 a = A constant of proportionality.

Subscripts 1, 2, . . . n relate the above quantities to components 1, 2, . . . n, respectively.

Subscript i refers to an arbitrary component from 1 to n.

Absence of subscript relates the quantity to the mixture.

- 1B.c. Solution to be applied when there is a reservoir of the solvent mixture whose composition does not change appreciably by evaporation.

Exact Arithmetic Solution of Specific Mixture

	Mol. wt.	Density	TLV	p ⁰ at 25°C	Mol fraction in half-and-half solution by volume
Trichloroethylene (1)	131.4	1.46g/ml	100	73mmHg	0.527
Methylchloroform (2)	133.42	1.33g/ml	350	125mmHg	0.473

$$F_1 p_1^0 = (0.527) (73) = 38.2$$

$$F_2 p_2^0 = (0.473) (125) = 59.2$$

$$TLV = \frac{38.2 + 59.2}{\frac{38.2}{100} + \frac{59.2}{350}} = \frac{(97.4) (350)}{133.8 + 59.2} = \frac{(97.4) (350)}{193.0} = 177$$

TLV = 177 ppm (Note difference in TLV when account is taken of vapor pressure and mol fraction in comparison with above sample where such account is not taken.)

2. A mixture of one part of (1) parathion (TLV, 0.1) and two parts of (2) EPN (TLV, 0.5).

$$\frac{C_1}{0.1} + \frac{C_2}{0.5} = \frac{C_m}{T_m} \quad C_2 = 2C_1$$

$$C_m = 3C_1$$

$$\frac{C_1}{0.1} + \frac{2C_1}{0.5} = \frac{3C_1}{T_m}$$

$$\frac{7C_1}{0.5} = \frac{3C_1}{T_m}$$

$$T_m = \frac{1.5}{7} = 0.21 \text{ mg/M}^3$$

1C. TLV for Mixtures of Mineral Dusts.

For mixtures of biologically active mineral dusts the general formula for mixtures may be used.

For a mixture containing 80% talc and 20% quartz, the TLV for 100% of the mixture is given by:

$$TLV = \frac{1}{\frac{0.8}{20} + \frac{0.2}{2.5}} = 8.4 \text{ mppcf}$$

Essentially the same result will be obtained if the limit of the more (most) toxic component is used provided the effects are additive. In the above example the limit for 20% quartz is 10 mppcf.

For another mixture of 25% quartz, 25% amorphous silica and 50% talc:

$$TLV = \frac{1}{\frac{0.25}{2.5} + \frac{0.25}{20} + \frac{0.5}{20}} = 7.3 \text{ mppcf}$$

The limit for 25% quartz approximates 8 mppcf.

APPENDIX C

PERMISSIBLE EXCURSIONS FOR TIME-WEIGHTED AVERAGE (TWA) LIMITS

The Excursion TLV Factor in the Table automatically defines the magnitude of the permissible excursion above the limit for those substances not given a "C" designation; i.e., the TWA limits. Examples in the Table show that nitrobenzene, the TLV for which is 1 ppm, should never be allowed to exceed 3 ppm. Similarly, carbon tetrachloride, TLV 10 ppm, should never be allowed to exceed 20 ppm. By contrast, those substances with a "C" designation are not subject to the excursion factor and must be kept below the TLV.

These limiting excursions are to be considered to provide a 'rule-of-thumb' guidance for listed substances generally, and may not provide the most appropriate excursion for a particular substance. Efforts are being made to develop such specific excursions, when indicated to be significantly different from that recommended by the present excursion factors.

Substance	TLV	Excursion Factor	Max. Conc. Permitted for short time
Nitrobenzene	1 ppm	3	3 ppm
Carbon tetrachloride	10 ppm	2	20 ppm
Carbon monoxide	50 ppm	1.5	75 ppm
Acetone	1000 ppm	1.25	1250 ppm
Boron trifluoride	C 1 ppm	-	1 ppm
Butylamine	C 5 ppm	-	5 ppm
Styrene monomer	C 100 ppm	-	100 ppm

For all substances:

TLV = 0 - 1 (ppm or mg/m ³), Excursion Factor	= 3
TLV = 1 - 10 "	" = 2
TLV = 10 - 100 "	" = 1.5
TLV = 100 - 1000 "	" = 1.25

BASIS FOR ASSIGNING LIMITING "C" VALUES

By definition in the Preface, a listed value bearing a "C" designation refers to a 'ceiling' value that should not be exceeded; all values should fluctuate below the listed value. Thus, in effect, makes the "C" designation a maximal allowable concentration (MAC). In general, the bases for assign-

ing or not assigning a "C" value rest on whether excursions of concentration above a proposed limit for periods up to 15 minutes may result in a) intolerable irritation, b) chronic, or irreversible tissue change, or c) narcosis of sufficient degree to increase accident proneness, impair self-rescue or materially reduce work efficiency.

APPENDIX D

Some "Inert" or Nuisance Particulates q)

Alundum (Al ₂ O ₃)	Kaolin
Calcium carbonate	Limestone
Cellulose (paper fiber)	Magnesite
Portland Cement	Marble
Corundum (Al ₂ O ₃)	Pentaerythritol
Emery	Plaster of Paris
Glycerine Mist	Rouge
Graphite (synthetic)	Silicon Carbide
Gypsum	Starch
Vegetable oil mists	Sucrose
(except castor, cashew	Tin Oxide
nut, or similar irritant	Titanium Dioxide
oils)	

q) When toxic impurities are not present, e.g. quartz <1%.

APPENDIX E

Some Simple Asphyxiants - "Inert" Gases and Vapors

Acetylene	Hydrogen
Argon	Methane
Ethane	Neon
Ethylene	Nitrogen
Helium	Nitrous Oxide
	Propane

1970 TLV COMMITTEE MEMBERS

Paul E. Caplan	Harold N. MacFarland, Ph. D.
Hervey B. Elkins, Ph. D.	Frederick T. McDermott
W. G. Fredrick, Sc. D.	E. Mastromatteo, M. D.
Bernard Grabis, P. E.	Col. Walter W. Melvin, Jr., M.D.
Paul Gross, M. D.	Ralph G. Smith, Ph. D.
Wayland J. Hayes, Jr., M. D.	Mitchell R. Zavon, M. D.
John W. Knauber	

Herbert E. Stokinger, Ph. D., Chairman
William D. Wagner, Recording Sec'y

Copyright 1970, by American Conference of Governmental Industrial Hygienists.

The American Conference of Governmental Industrial Hygienists will welcome requests for permission to republish or reprint these Threshold Limit Values. Requests for such permission should be directed to the Secretary-Treasurer, 1014 Broadway, Cincinnati, Ohio 45202.

Price Each

1 - 49 Copies	50¢
50 - 999 Copies	40¢
1000 - 4999 Copies	30¢
5000 or more Copies	15¢

Documentation of Threshold Limit Values. A separate companion piece to the TLVs is issued by ACGIH under this title. This publication gives the pertinent scientific information and data with reference to literature sources that were used to base each limit. Each documentation also contains a statement defining the type of response against which the limit is safeguarding the worker. For a better understanding of the TLVs it is essential that the Documentation be consulted when the TLVs are being used.

Information concerning the availability of copies of the Documentation of Threshold Limit Values should be directed to the Secretary-Treasurer.

Table 2.2 (continued)

Radioactivity: For permissible concentrations of radioisotopes in air, see "Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water," Handbook 52, U. S. Department of Commerce, National Bureau of Standards, March, 1953. In addition, see "Permissible Dose from External Sources of Ionizing Radiation," Handbook 59, U. S. Department of Commerce, National Bureau of Standards, Sept. 24, 1954.

U. S. Department of Commerce Handbook 52 has been superseded by Handbook 69, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure," subsequent to the presentation of this report.

Handbook 59, U. S. Department of Commerce, has been revised by addition of addendum, April 15, 1958.

§Milligrams of dust, fume, or mist per cubic meter of air.

Mineral Dusts

SUBSTANCE	MPPCF	SUBSTANCE	MPPCF
Aluminum oxide	50	Silica	
Asbestos	5	high (above 50% free SiO ₂)	5
Dust (nuisance, no free silica)	50	medium (5 to 50% free SiO ₂)	20
Mica (below 5% free silica)	20	low (below 5% free SiO ₂)	50
Portland cement	50	Silicon carbide	50
Talc	20	Soapstone (below 5% free SiO ₂)	20

||Millions of particles per cubic foot of air.

TENTATIVE VALUES

SUBSTANCE	PPM	Approx. Mg. per Cu. M.*	SUBSTANCE	PPM	Approx. Mg. per Cu. M.*
Allyl glycidyl ether (AGE)	10	45	Ethyl mercaptan	250	640
Boron trifluoride	1	3	Furfuryl alcohol	50	200
n-Butyl glycidyl ether (BGE)	50	270	Glycidol	50	150
Butyl mercaptan	10	35	sec-Hexyl acetate	100	590
Chlorine dioxide	0.1	0.3	Isopropyl glycidyl ether (IGE)	50	240
Chloroacetaldehyde	1	3	Lithium hydride		25 µg/m ³
Chlorobromomethane	400	2,100	Methyl mercaptan	50	100
Diglycidyl ether (DGE)	10	55	Perchloromethyl mercaptan	0.1	0.8
Dimethyl formamide	20	60	Phenyl glycidyl ether (PGE)	50	310
1,1-Dimethyl hydrazine	0.5	1	Phosphoric acid		1
Dipropylene-glycolmethyl- ether	100	600	n-Propyl nitrate	25	110
			1,2,3-Trichloropropane	50	300

Table 2.2 (continued)

SUBSTANCE	PPM	Approx. Mg. per Cu. M.*	SUBSTANCE	PPM	Approx. Mg. per Cu. M.*
Triorthocresyl phosphate		0.1	Teflon decomposition products	*	*
Yttrium & inorganic compounds		5	Pentaborane (B ₅ H ₉)	*	*

||Parts of vapor or gas per million parts of air by volume.

*Approximate milligrams per cubic meter of air.

*Until more data are forthcoming, it is important that atmospheric concentrations of these materials to which workers are exposed must be kept as near 0 as possible.

WILLIAM L. BALL	H. E. STOKINGER	HERVEY B. ELKINS	W. H. REINHART
W. CLARK COOPER	KEITH H. JACOBSON	ALLAN L. COLEMAN, Chairman	

Table 2.3

CHEMICALS CAUSING CHRONIC TOXICITY

For exposures of less than eight hours duration the eight-hour weighted average exposure should not exceed the Threshold Limit Value (refer to text, "Short Duration Exposures"). Brief exposures should not exceed eight times the Threshold Limit Value.

Aldrin (HHDN) - also skin absorption
 Aniline - also skin absorption
 Antimony
 Antu (Alphanaphthylthiourea)
 Arsenic
 Benzene
 Beryllium
 Butyl Cellosolve - also skin absorption
 Calcium arsenate
 Carbon disulfide
 Carbon tetrachloride
 Cellosolve
 Cellosolve acetate
 Chlordane - also skin absorption
 Chlorinated camphene - also skin absorption
 Chlorinated diphenyl oxide
 Chlorodiphenyl
 Chloroform
 Chloroprene - also skin absorption
 Crag (Butoxy polypropylene glycol) - also skin absorption
 Cresol
 2, 4-D (2, 4-Dichlorophenoxy acetic acid)
 DDT (Dichlorodiphenyl trichloroethane) also skin absorption
 O-Dichlorobenzene
 1, 1-Dichloroethane
 Dieldrin, skin absorption
 Difluorodibromomethane
 Dimethylaniline - also skin absorption
 Dinitrobenzene - also skin absorption
 Dinitrotoluene - also skin absorption
 Dioxane
 Dipropylene Glycol Methyl Ether
 Ethylene Dibromide
 Ethylene Dichloride
 Fluoride Dust
 Hydrogen Fluoride
 Lead
 Lead arsenate
 Lindane (Gamma-Benzene Hexachloride) also skin absorption
 Manganese
 Mercury
 Mercury Organic - also skin absorption
 Methoxychlor (methoxy DDT)
 Methylal (formal)
 Methyl Bromide

Table 2.3 (continued)

Methyl Cellosolve
 Methyl Cellosolve Acetate
 Methyl Chloride
 Methylene Chloride
 Molybdenum
 Monomethylaniline - also skin absorption
 Nicotine - also skin absorption
 P-Nitroaniline - also skin absorption
 Nitrobenzene - also skin absorption
 Nitrotoluene - also skin absorption
 Paradichlorobenzene
 Pentachloronaphthalene
 Phenol - also skin absorption
 Phenylhydrazine - also skin absorption
 Prosphine
 Phosphorus (yellow)
 Picric acid - also skin absorption
 Propylene dichloride
 Pyridine
 Selenium compounds
 Tellurium
 P-Tertiarybutyltoluene
 Tetrabromoethane (acetylenetetra bromide)
 Tetrachloroethane
 Tetryl - also skin absorption
 Thallium
 Thiran (tetramethylthiuram disulfide)
 O-Toluidine - also skin absorption
 Trichloronaphthalene
 Trinitrotoluene - also skin absorption
 Triorthocresyl phosphate - also skin absorption
 Uranium
 Warfarin (3-((alpha-acetonylbenzyl))-4-hydroxy coumarin)
 Yttrium and inorganic compounds
 Xylidine - also skin absorption

Table 2.4

CHEMICALS CAUSING ACUTE TOXICITY

For exposures of less than eight hours' duration the eight-hour weighted average exposure should not exceed the Threshold Limit Value (refer to text, "Short Duration Exposures"). Brief exposures should not exceed eight times the Threshold Limit Value.

Acrylonitrile - also skin absorption
 Arsine
 Barium
 Cadmium oxide
 Carbon monoxide
 Cyanide
 Decaborane
 Dimethylsulfate - also skin absorption
 Dinitroorthocresol - also skin absorption
 EPN (Ethyl parnitro phenylthionubenzene phosphonate)
 Ethylene chlorohydrin - also skin absorption
 Ethyleneimine - also skin absorption
 Ethyl silicate
 Fluoroacetates
 HETP
 Hydrogen cyanide
 Hydrogen selenide
 Malathion (0, 0-Dimethyldithiophosphate of diethyl mercapto succinate)
 Nitroethane
 Nitroglycerine - also skin absorption
 Nitromethane
 2-Nitropropane
 Parathion (0, 0-Diethyl parnitrophenylthiophosphate) - also skin absorption
 Pentaborane
 Pentachlorophenol - also skin absorption
 Propyleneimine - also skin absorption
 Stibine
 Strychnine
 TEDP (tetraethyldithionopyrophosphate)
 TEPP (tetraethylpyrophosphate)
 Tetranitromethane - also skin absorption

Table 2.5

CHEMICALS CAUSING NARCOSIS

Brief exposures should not exceed three (3) times
the Threshold Limit Value

Acetone	Mesityl oxide
Amyl Acetate	Methyl acetate
Amyl Alcohol	Methyl alcohol
Butadiene	Methyl chloroform
Butanone (methyl ethyl ketone)	Methyl cyclohexane
Butyl Acetate	Methyl cyclohexanol
Butyl Alcohol	Methyl cyclohexanone
Ter-Butyl Alcohol	Methyl formate
Chlorobenzene	Methylisobutylcarbinol
Chloro Bromo Methane	Methyl styrene
Cyclohexane	Naphtha (petroleum)
Cyclohexanol	Naphtha (coal tar)
Cyclohexanone	Octane
Cyclohexene	Pentane
Cyclopropane	Pentanone (methylpropylketone)
Diacetone alcohol	Perchloroethylene
1, 2-Dichloroethylene	Propyl acetate
Diisobutyl ketone	Propyl alcohol (isopropanol)
Ethyl acetate	Propyl ether
Ethyl alcohol	Stoddard solvent
Ethyl benzene	Styrene monomer
Ethyl chloride	Tetrahydrofuran
Ethyl ether	Toluene
Ethyl formate	Trichlorethylene
Furfuryl alcohol	Trichloropropane
Gasoline	Trifluoromonobromomethane
Heptane	Turpentine
Hexane	Vinyl chloride
Hexanone (methyl butyl ketone)	Vinyl toluene
Hexone (methyl isobutyl ketone)	Xylene
N-Hexyl acetate	

Table 2.6

CHEMICALS CAUSING IRRITATION

Brief exposures should not substantially exceed the
Threshold Limit Value

Acetaldehyde	Glycidol
Acetic acid	Hydrazine
Acetic acid anhydride	Hydrogen bromide
Acrolein	Hydrogen chloride
Allyl alcohol	Hydrogen fluoride
Allyl chloride	Hydrogen peroxide
Allyl glycidyl ether	Hydrogen selenide
Allyl propyl disulfide	Hydrogen sulfide
Ammage (sodium sulfamate)	Hydroquinone
Ammonia	Iodine
Benzyl chloride	Isophorone
Boron trifluoride	Isopropylglycidyl ether
Bromine	Isopropylamine
Butyl amine	Lithium hydride
n-Butyl glycidyl ether	Methyl acetylene
Butyl mercaptan	Methyl acrylate
Chlorine	Methyl mercaptan
Chlorine dioxide	Nickel carbonyl
Chlorine trifluoride	Nitric acid
Chloroacetyl aldehyde	Nitrogen dioxide
1-Chloro-1-nitro propane	Ozone
Chloropicrin	Pentaborane
Chromates	Perchloromethylmercaptan
Chromic acid	Phenylglycidyl ether
Diborane	Phosgene
Dichloroethyl ether - also skin absorption	Phosphoric acid
1, 1-Dichloro-1-nitroethane	Phosphorus pentachloride
Diethylamine	Phosphorus pentasulfide
Diglycidyl ether	Phosphorus pentasulfide
Dimethyl formamide	Phosphorus trichloride
1, 1-Dimethyl hydrazine	N-Propyl nitrate
Epichlorhydrin	Propylene oxide
Ethyl acrylate	Pyrethrum
Ethylamine	Quinone
Ethyl bromide	Rotenone
Ethyl mercaptan	Sodium hydroxide
Ethylene oxide	Sulfur dioxide
Ethyl mercaptan	Sulfuric acid
Ferbam (ferric dimethyldithio carbamate)	Sulfur monochloride
Ferro vanadium dust	Sulfur pentafluoride
Fluoride dust	Triethylamine
Fluorine	Turpentine
Formaldehyde	Vanadium
Furfural	Zirconium

Table 2.7

CHEMICALS CAUSING ASPHYXIATION

Brief exposures should not exceed the Threshold Limit Value

Carbon dioxide
Dichlorodifluoromethane
Dichloromonofluoromethane
Dichlorotetrafluoroethane
Fluorotrichloromethane
Sulfur hexafluoride

Table 2.8

CHEMICALS CAUSING FUME FEVER

Brief exposures should not substantially exceed the Threshold Limit Value

Iron oxide fume
Magnesium oxide fume
Teflon decomposition products
Zinc oxide

Table 2.9

CHEMICALS CAUSING ALLERGY

Brief exposures should not substantially exceed the Threshold Limit Value

Diisocyanotoluene
Ethylenediamine

Skin Absorption

The third order of importance by which toxic chemicals enter the body is skin absorption. As is usual, the body provides means which tend to prevent this type of intoxication. There are two defense mechanisms of the skin that protect the underlying tissue against the entry of foreign material. One is the keratinized epidermis and the other is the covering, or mantle, of waxes and fatty acids secreted by the sebaceous glands. While these layers are effective barriers against most water soluble irritants, they are subject to attack by strong acids, alkalis and organic solvents. The protective mantle is not continuous but is broken by skin openings of gland ducts and hair follicles. It can be seen then that these openings provide an avenue whereby certain chemicals, especially the water soluble type, can gain entrance. Likewise, any impairment to the health of the skin can lead to increased absorption of toxic materials.

Dermatitis

There are many ways whereby chemicals act to alter or remove components in the dermal protective mechanism. These chemicals have been classified according to their action on the skin by Schwartz, Tulipan and Birmingham. (2)

1. *Keratin Solvents, such as alkalis and soaps.*
2. *Fat Solvents, such as turpentine, petroleum distillates, and volatile hydrocarbon solvents and detergents.*
3. *Desiccators or Hygroscopic Agents, which take the water out of the skin, such as sulphuric acid, powerful alkalis, and calcium oxide.*
4. *Protein Precipitants, or denaturants such as heavy metal salts, which form albuminates in combining with the skin.*
5. *Oxidizers, which by their strong affinity for the hydrogen in water will liberate oxygen. Examples are chlorine gas, peroxide of hydrogen, chromic acid and its salts.*
6. *Hydrolizers. - Some substances tend to hydrolize when coming in contact with the moisture of the skin, and thus form irritating compounds. An example of this class is hexamethylenetetramine, which on hydrolizing first forms formaldehyde and later goes on to formic acid.*
7. *Keratogenic Agents. - Certain substances act as stimulants to the keratin-forming cells of the skin and are apt to cause acne-like lesions and new growths. Petroleum, coal tar, solid chlorinated hydrocarbons, and their products, are examples of this class.*
8. *Sensitizers. - There is still another group, to which the skin becomes sensitive after exposure for varying lengths of time. These substances may be called anaphylactoid in their action. The nitro and nitroso compounds and certain plants and fungi belong to this class.*
9. *Photosensitizers. - Certain chemicals and plants have a photosensitizing effect on the skin. Workers exposed to coal tar, petroleum, and many of their derivatives are exceedingly susceptible to dermatitis solaris and develop marked melanosis. Photosensitivity has been reported from many plants and also for some dyes, especially the fluorescent dyes.*

Causes of Dermatitis

There are many predisposing causes of dermatitis. Among the foremost are the race, age, sex and type of skin of the individual, also season of the year, preexisting skin diseases and cleanliness. Of all these, cleanliness is by far the most important single factor in preventing dermatitis. Skin cleanliness goes beyond the mere periodic washing of the hands. It includes the overall skin consideration, i.e., daily bathing, wearing clean work clothing, and using protective clothing. In fact, most dermatitis results from a combination of soiled clothing which provides a prolonged close skin contact with the dermatitis producing agent and a failure to thoroughly clean the skin at appropriate intervals. The cleansing agent itself may require special attention since many solvent cleaners and even harsh soaps are frequently responsible for dermatitis. Some of the more important chemicals that cause dermatitis either by direct contact or by sensitization have been listed by Schwartz, Tulipan and Birmingham (2) and are shown in Tables 2.10 and 2.11.

Table 2.10

PRINCIPAL PRIMARY IRRITANTS

INORGANIC:

1. Acids (including some of their salts)

Arsenious	Hydrobromic	Perchloric
Chloroplatinic	Hydrochloric	Phosphoric
Chlorosulfonic	Hydrofluoric	Sulphuric
Chromic	Hydrofluosilic	
Hydriodic	Nitric	

2. Alkalies

Alkaline sulphides
Sodium hydrate, carbonate, silicate and metasilicate
Potassium hydrate and carbonate
Ammonium hydrate and carbonate
Barium hydrate and carbonate
Calcium oxide, hydrate, carbonate and cyanamide
Trisodium phosphate

3. Irritant Elements and Salts

Antimony and salts
Arsenic and salts
Chromium and alkaline chromates
Copper sulfate, copper cyanide
Mercuric salts
Silver nitrate
Zinc chloride
Elements sodium, potassium and phosphorus burn the skin

Table 2.10 (continued)

ORGANIC:

1. Organic Acids and Anhydrides

Acetic, anhydride, chloracetic (mono, di, tri)	
Amino naphthol sulfonic acids (F.H.J. Koch's, Laurent's)	
Anisic	
Carbolic	Maleic
Cresylic	Metanilic
Formic	Oxalic
Lactic	Salicylic

2. Organic Alkalis

Ethanolamines
Methylamines

3. Organic Solvents

Petroleum solvents	Turpentine
Coal tar solvents	Terpenes
Chlorinated hydrocarbon solvents	Carbon bisulfide
Esters	Alcohols
Ketones	

4. Essential Oils

5. Acne Producers

Petroleum oils	Solid chloronaphthalenes
Cutting oils	Solid chlorobenzols
Pitch	Solid chlorodiphenyls
Tar	Chlordiphenyloxides
Paraffin (impure)	Solid chlorophenols

Table 2.11

SENSITIZERS

1. Dye Intermediates

Aniline and compounds	Naphthalene and compounds
Chlor compounds	Benzidine and compounds
Nitro compounds	Benzanthrone and compounds
Acridine and compounds	Naphthylamines

2. Dyes

Fur and Hair	- Paraphenylenediamine Aniline black Paramido phenol	
Leather	- Chrysoidine Bismark brown Nigrosine Amido-azo-toluene Amido-azo-benzene	
Fabric	- Crystal and methyl violet Malachite green Auramine Metanil yellow Brilliant indigo, 4 G Erio black	Hydron blue Indanthrene violet, R.R. Ionamine, A.S. Pyrogene violet brown Orange Y Safranine Sulphanthrene pink Rosaniline

3. Photo Developers

Metol	Pyrogallol
Paraphenylenediamine	Bichromates
Hydroquinone	Paraformaldehyde
Para-amido-phenol	

4. Rubber Accelerators and Anti-oxidants

Hexamethylene tetramine
 Guanidines
 Mercapto benzo thiazole
 Tetramethyl thiuram monosulphide and disulphide
 Para toluidine
 Ortho toluidine
 Tri-ethyl tri-methyl triamine
 Phenyl beta naphthylamine
 Monobenzyl ether of hydroquinone (causes leukoderma)

Table 2.11 (continued)

Soaps

Containing excess of free alkali
 Containing perfumes
 Containing antiseptics

6. Insecticides

Creosote	Mercury compounds)	
Nicotine	Phenol compounds)	
Tar	Petroleum distillates)	
Pyrethrum	Arsenic compounds)	Also P.I.
Rotenone	Fluorides)	
Thiocyanates	Lime)	
Organic Phosphates		

7. Cosmetics

Those containing irritant or photosensitizing dyes, essential oils, perfumes and resins

8. Oils

Cutting oils (the inhibitor or antiseptic they contain)
 Coning oils (cellosolves, eugenols)
 Sulphonated oils
 Linseed oil
 Mustard oil - also P.I.
 Coconut oil
 Cashew nut oil - also P.I.
 Tung oil
 Essential oils of plants and flowers

9. Resins

Natural	Pine rosin	Japanese lacquer	
	- Wood rosin	Dammar	
	Burgundy Pitch	Copal	
	Alkyd	Melamine formaldehyde	Chlorophenols
	Vinyl	Sulfonamide formaldehyde	Cumaron
Synthetic	- Acrylic acid resins	Chloro-naphthalenes	Epoxies
	Phenol formaldehyde	Chlorobenzols	Polyesters
	Urea formaldehyde	Chlorodiphenyls	

10. Coal Tar and Its Direct Derivatives

Acridine	Carbazole	Naphthalene
Anthracene	Pyridine	Phenol - also P.I.
Phenanthrene	Fluorene	Cresol - also P.I.

Table 2.11 (continued)

11. Explosives

Trinitrotoluol (TNT)	Lead styphnate
Trinitromethylnitramine (Tetryl)	Ammonium nitrate
Fulminate of mercury	Sodium nitrate
Hexanitrodiphenylamine	Potassium nitrate
Dinitrophenol	Picric acid and picrates
Dinitrotoluol	Sensol

12. Plasticizers

Propylene stearate	Methyl cellosolve oleate
Butyl cellosolve stearate	Methyl phthalylethylglycolate
Diamyl naphthalene	Phenylsalicylate
Dibutyl tin laurate	Stearic acid
Dioctylphthalate	Triglycol di (2, ethyl butyrate)

Symptoms of Dermatitis

The task of diagnosing occupational dermatoses lies within the responsibility of the industrial physician and the dermatologist. However, an acquaintance with the general symptoms of the dermatoses is important to the industrial hygienist not only in his responsibility for suggesting preventive measures but also in investigating cases of alleged occupational origin. The symptoms have been well described. (2)

These (symptoms) depend in large measure on the cause and the clinical type of the lesion. In cases caused by concentrated irritants or by hypersensitivity, where the onset is sudden, the patient first notices itching of the exposed parts. This is followed by an erythema, papules, vesicles, edema, oozing and crusting. The eruption is an acute moist eczema. The inflammation may be arrested at any of these stages, and if due to a chemical usually improves during the week end while away from work. A worker may not develop symptoms for a period of time varying from a few hours to a few days after contact with the offending substances, and in certain cases of hypersensitivity it may take years of contact to become sensitized. It is likely that in such a case an established immunity was broken down.

Some workers develop only a mild dermatitis, are able to continue working and finally become immune. In others, the dermatitis is so severe that they have to stop working. Workers who suffer a severe attack do not as often develop an immunity as those who suffer a mild attack. Immunity, if developed, generally lasts only a short time, from a week to a month, after discontinuing work, but in a few cases may last for many years. The worker who, after working without any trouble for many years, suddenly becomes sensitized to materials he formerly handled with impunity and reacts with a severe dermatitis never becomes immune. Some dermatologists say that such a worker may even become hypersensitive to many of the ordinary materials of daily life and as a result suffer from a chronic eczema even when he gives up his occupation. Fortunately, this rarely occurs and the author has not encountered it.

In cases of exposure to mold irritants over long periods of time the early symptoms are not annoying, but consist only of a mild irritation followed by thickening of the skin and loss of elasticity. This later results in cracks and fissures, and the open sores are irritated and kept inflamed by the entrance of more of the causative agents. Ulcers result and these heal only with difficulty while the patient is working. Such cases present the picture of a chronic fissured eczema. Dehydrating agents such as salt, sugar, and low concentrations of lime and formaldehyde may cause such lesions. Such cases are not due to allergy but to an exhaustion of the defense mechanism of the skin.

Substances like mineral oil, grease, paraffin, chlorinated synthetic waxes, and coal tar pitch can not only cause dermatitis but if allowed to stay in contact with the skin for long periods will block the pores, irritate the epithelium of the skin glands, and cause comedones, acnes and cysts, which may become infected and result in folliculitis and boils.

Petroleum, unrefined paraffin, grease, tar, and pitch cause epithelial proliferation which may result in keratoses, papillomata, and epithelioma of the exposed parts. Tar, pitch, soot and petroleum may also cause scrotal cancers. Exposure for long periods to certain aniline derivatives such as alphanaphthylamine, betanaphthylamine, and benzidine may cause papillomata and carcinomata of the bladder. Arsene produces keratosis of the palms and soles when taken internally but the author has never seen these lesions from occupational exposure to arsenic.

Occupational mycotic infections such as ringworm of barbers and mycoses of the hands and nails of vegetable and fruit canners are not infrequent, but their appearance does not differ from similar infections of non-industrial origin and it is often difficult to prove occupational origin.

Parasitic diseases induced by acari form only a small group among occupational skin affections. The symptoms do not vary from those found in non-occupational parasitic diseases in any way and they must be identified as occupational by means of other criteria.

Bibliography

1. Smyth, H.F., Jr., "Improved Communication - Hygiene Standard for Daily Inhalation," AIHA Quarterly 17, No. 2, 129-185 (June 1956)
2. Schwartz, L., Tulipan, L. and Birmingham, D.J. Occupational Diseases of the Skin, Lea and Febiger, Philadelphia, Pa., 3rd ed., 1957.