

ACCIDENT PREVENTION MANUAL

for Industrial Operations

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INDUSTRIAL HYGIENE

Free silica is uncombined silicon dioxide (SiO_2). Silicates contain silicon and oxygen combined with other elements in more complex molecules. The SiO_2 reported in chemical analyses for mineral and geological reports is the *total* of the silicon dioxide present, both the free silica (if present), and the silica combined in the mineral. Such analyses are not reliable indications of the silicosis potential of the material, because it is the uncombined or free silica that is most important in industrial dust exposure. So that an exposure can be properly evaluated, the percentage of uncombined silica must be determined by petrographic analysis using a polarizing microscope or, preferably, by X-ray diffraction analyses and special analytical chemical procedures.

There has been some experimental evidence that some dusts may tend to inhibit the action of silica on the body, but this inhibiting action is so slight and uncertain that it must be discounted in practice. In fact, there is also evidence that the nonsiliceous components of a dust mixture containing free silica may provoke a disabling condition more severe than that caused by the silica acting alone.

With the exception of asbestos and some talcs, the silicate dusts do not ordinarily cause a serious disabling lung condition such as is produced by free silica. Much higher levels of silicate dusts than of free silica dust can be tolerated. In many industries, men have worked with silicate dusts that contained no free silica without development of disability or of nodulation in the lungs. The X-ray may show shadows indicating dust deposits in the lungs, but the pneumoconiosis is essentially harmless. However, partially disabling pneumoconioses have been reported where men have worked for long periods of time in very high concentrations of certain silicate dusts. Disabling pneumoconioses from exposure to abnormally high concentrations of mica, tremolite talc, and kaolin dusts have been described in the literature. The clinical signs are not the same for these silicate dusts as for free silica, but the symptoms can be marked.

Asbestosis. Several minerals having a fibrous character are classed as "asbestos"—hydrated silicates of magnesium with variable amounts of iron, calcium, sodium, potassium, and aluminum present as impurities.

The fine airborne fibers of asbestos can pass through the upper respiratory tract to the lower parts of the lungs to cause irritation and to form "asbestos bodies" where the fibers are encapsulated. This diffuse fibrosis probably begins as a "collar" about the terminal bronchioles. There is evidence that other minerals having a fibrous character (except glass fiber) can produce a reaction similar to that of asbestos.

Following a study by the U.S. Public Health Service of the asbestos textile industry,* it was recommended that the dust concentration be kept at less than 5 mppcf to prevent asbestosis. Evaluation of an exposure to asbestos dust is based on the *total* amount of dust, since the concentration of injurious fibers will be kept within safe limits if the fine dust is kept below the suggested threshold limit.

Miscellaneous pneumoconioses. Even though a dust is classified as harmless, amounts above the TLV can lead to trouble by causing a pneumoconiosis, mechanically irritating the walls of the respiratory system, or interfering with ordinary lung processes. Mica dust and kaolin dust are two good examples of dusts that ordinarily are considered benign but amounts above the TLV can cause a troublesome pneumoconiosis. Mica pneumoconiosis has been observed in grinding operations where mica dust, but no free silica was present. There were marked changes in the X-ray pictures of the lungs and some disability. The cases occurred where the dust exposures were massive over many years.

Toxic dusts and fumes

Systemic reactions are caused by toxic dusts and fumes of various elements and their compounds and by certain organic compounds. All metallic fumes are irritating, especially when freshly generated. Industrially important metals and their compounds that can have a toxic effect when the dust or fumes are inhaled include arsenic, antimony, cadmium, chromium, lead, manganese, mercury, selenium, tellurium, thallium, uranium, and a few others.

*U.S. Public health Service, Washington, D.C. "A Study of Asbestosis in the Asbestos Textile Industry." Bulletin No. 241. 1938.



EYES
UPPER
RESPIRATORY
MUCOUS
MEMBRANES



LIVER



Agent	Industry
Cresol.....	Chemical Mfg., Oil Refining
Quinone.....	Chemical Mfg.
Hydroquinone.....	Synthetic Dye Industry
Acetic Anhydride.....	Textile Mfg.
Acrolein.....	Chemical Mfg.
Benzyl Chloride.....	Synthetic Dye Industry
Butyl Alcohol.....	Lacquer and Paint Industry
Ozone.....	Welding Operations
Dimethylsulfate.....	Chemical Mfg., Pharmaceutical Ind.
Chromium.....	Chromate Mfg., Chrome Plating
Acetic Anhydride.....	Textile Mfg.
Acrolein.....	Chemical Mfg.
Hydrogen Sulfide.....	Viscose Rayon Mfg., Sewerage Treatment
Butyl Alcohol.....	Lacquer and Paint Mfg.
Acetaldehyde.....	Chemical Mfg., Paint Mfg.
Nickel.....	Metallurgical Refining Processes
Crystalline Silica.....	Mining Ind., Foundry Ind.
Asbestos.....	Mining Ind., Weaving Ind.
Beryllium.....	Foundry Ind., Metallurgical Ind.
Chromium.....	Chromate Mfg.
Hydrogen Sulfide.....	Viscose Rayon Ind., Sewerage Treatment
Allyl Chloride.....	Plastic Mfg.
Dichloroethyl Ether.....	Insecticide Mfg., Oil Refining
Mica.....	Rubber Industry, Insulation Industry
Talc.....	Mining Industry
Nitrogen Dioxide.....	Chemical Mfg., Metal Pickling
Cresol.....	Chemical Mfg., Oil Refining
Dimethylsulfate.....	Chemical Mfg., Pharmaceutical Mfg.
Chloroform.....	Chemical Mfg., Plastic Mfg.
Carbon Tetrachloride.....	Chemical Mfg., Dry Cleaning, Fire Extinguisher Service
Trichloroethylene.....	Chemical Mfg., Metal Degreasing
Perchloroethylene.....	Chemical Mfg., Dry Cleaning
Toluene.....	Rubber Ind., Paint Ind.
Butyl Alcohol.....	Chemical Mfg., Lacquer and Paint Mfg.
Nickel.....	Metallurgical, Refining Processes
Phenol.....	Plastics Mfg.
Trichloroethylene.....	Chemical Mfg., Metal Degreasing



Agent	Industry
Benzene.....	Rubber Industry, Chemical Mfg.
Carbon Tetrachloride.....	Solvent Mfg., Dry Cleaning
Carbon Disulfide.....	Viscose Rayon Mfg., Rubber Mfg.
Butylamine.....	Synthetic Dye Mfg., Pharmaceutical Mfg.
Hydrogen Sulfide.....	Viscose Rayon Mfg., Sewerage Treatment
Tetra Ethyl Lead.....	Chemical Mfg.
Manganese.....	Mining, Metallurgical Processing
Mercury (80 different industries).....	Electrical Equipment Mfg., Lab Workers
Lead.....	Auto Mfg., Smelting, Battery Mfg.
Dimethylaniline.....	Chemical Mfg.
Acetaldehyde.....	Chemical Mfg.
Nitrobenzene.....	Synthetic Dye Ind., Shoe Polish Mfg.
Thallium.....	Pesticide Mfg., Fire Work Mfg.
Aniline.....	Synthetic Dye Mfg., Paint Mfg., Rubber Industry
Chloroform.....	Chemical Mfg., Plastic Mfg.
Mercury.....	Electrical Equipment Mfg., Scientific Labs.
Dimethylsulfate.....	Chemical Mfg., Pharmaceutical Mfg.
Nitrobenzene.....	Synthetic Dye Mfg., Shoe Polish Mfg.
Aniline.....	Paint Mfg., Rubber Ind.
Arsenic (as Arsenic).....	Metal Pickling
Benzene.....	Chemical Mfg., Rubber Ind.
Carbon Monoxide.....	Heat Treating Ind., Automobile Services
Toluene.....	Rubber Mfg., Paint Mfg.

BRAIN

OR
**CENTRAL
NERVOUS
SYSTEM**

HEART

KIDNEY

BLOOD

Figure of man above is by
Andreas Vesalius (1514-64),
modern father of anatomy.

Fig. 40-1. Industrial chemicals: their source and their effect upon the body.

Courtesy "Air Engineering" Magazine

TABLE 40-B. THRESHOLD LIMIT VALUES FOR 1963

Adopted at the 25th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, May 6-7, 1963.

These values should be used as guides in the control of health hazards and should not be regarded as fine lines between safe and dangerous concentrations. They represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. The values listed refer to time-weighted average concentrations for a normal workday. The amount by which these figures may be exceeded for short periods without injury to health depends upon a number of factors such as the nature of the contaminant, whether very high concentrations even for short periods produce acute poisoning, whether the effects are cumulative, the frequency with which high concentrations occur, and the duration of such periods. All must be taken into consideration in arriving at a decision as to whether a hazardous situation

exists. Because it has been recognized that the threshold limits of certain acutely acting substances may not provide a safety factor comparable to that of chronically acting substances for which a time-weighted average applies, a "C" designation or "ceiling" has been affixed to such values indicating that the Threshold Limit Value should not be exceeded. The bases for the "C" listing are given in appendix C.

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

Threshold limits are based on the best available information from industrial experience, from experimental studies, and, when possible, from a combination of the two. These values are based on various

criteria of toxic effects or on marked discomfort; thus, they should not be used as a common denominator of toxicity, nor should they be considered as the sole criterion in proving or disproving diagnosis of suspected occupational disease.

These limits are intended for use in the field of industrial hygiene and should be interpreted and applied only by persons trained in this field. They are not intended for use, or for modification for use, (1) as a relative index of toxicity, by making a ratio of two limits, or (2) in the evaluation or control of community air pollution or air pollution nuisances, or (3) in estimating the toxic potential of continuous uninterrupted exposures.

These values are reviewed annually by the Committee on Threshold Limits for revisions, or additions, as further information becomes available. The Committee welcomes the suggestion of substances to be added to the list and also comments, references, or reports of experience with these materials.

ELEMENTS OF INDUSTRIAL TOXICOLOGY

TABLE 40-B. THRESHOLD LIMIT VALUES FOR 1963 (Continued)

MINERAL DUSTS, TENTATIVE VALUES, AND APPENDIX A

Mineral Dusts

Tentative Values

Substance	mppcf
SILICA	
Crystalline	
Quartz, Threshold Limit calculated from the formula	250
	%SiO ₂ + 5
Cristobalite " " "	
Amorphous, including natural diatomaceous earth	20
SILICATES (less than 1% crystalline silica)	
Asbestos	5
Mica	20
Soapstone	20
Talc	20
Portland Cement	50

Miscellaneous (less than 1% crystalline silica)		50
Conversion factors		
mppcf X 35.3 = million particles per cubic meter		
= particles per c.c.		

Tentative Values

Substance	ppm*	mg/cu m**
C tert. Butyl chromate (as CrO₃)—Skin		
Calcium oxide	—	0.1
Camphor	—	5
Copper Fume	—	2
Dusts & Mists	—	0.1
DDVP (O,O-Dimethyl-2,2-dichlorovinyl phosphate)	—	1.0
	—	1

Substance	ppm*	mg/cu m**
Demeton (R) (Systox)	—	0.1
Endrin (1,2,3,4,10,10,-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octa-hydro 1,4-endo-5,8-dimethanonapthalene—Skin	—	0.1
Epichlorhydrin	5	19
Ethanolamine	3	6
Graphite	—	15 mppcf
Hafnium	—	0.5
Heptachlor (1,4,5,6,7,8,8a-heptachloro-3a, 4,7,7a-tetrahydro-4,7-methanoindene)	—	0.5
Methylamine	25	31
Methyl Methacrylate	100	410
C Methylene bis phenylisocyanate	0.02	0.2
Mineral Wool (Fiberglas)	—	2
Napthalene	10	50
Oil (mineral)	—	5
β-Propiolactone	—	A-5
Silver	—	0.05
Tantalum	—	5
1,1,1,2,-Tetrachloro-2,2,-difluoroethane	1000	8340
1,1,2,2-Tetrachloro-1,2,-difluoroethane	500	4170
Tetraethyl lead—Skin	—	0.075
Tin		
(inorganic compounds)	—	2
(organic compounds as Sn—Skin	—	0.1

NOTE: The word "Skin" following a substance indicates that the substance can penetrate the skin to contribute to the exposure and TLV should be reduced accordingly.

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

**Approximate mg of particulate per cu m of air.

§ Millions of particles per cu ft of air, based on impinger samples counted by light-field techniques.

‡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.

A numbers, see specific number in Appendix A.

C substances, see Appendix C.

Appendix A

A-1 Benzidine. Because of high incidence of bladder tumors in man, any exposure, including skin, is extremely hazardous.

A-2 β -Naphthylamine. Because of the extremely high incidence of bladder tumors in workers handling this compound, and the inability to control exposures, β -naphthylamine has been prohibited from manufacture, use and other activities that involve human contact by the State of Pennsylvania.

A-3 N-Nitrosodimethylamine. Because of extremely high toxicity and presumed carcinogenic potential of this compound,

contact by any route should not be permitted.

A-4 Teflon® decomposition products. At least one identified component of Teflon decomposition products is extremely toxic, but in the absence of more complete toxicity information and suitable analytic methods, a definite threshold limit value is not recommended at this time; but air concentrations should be minimal.

A-5 β -Propiolactone. Because of high acute toxicity and demonstrated skin tumor production in animals, contact by any route should be avoided.

TABLE 40-C. MAXIMAL ACCEPTABLE CONCENTRATIONS

Meaning*

It is generally recognized that there are levels of concentration of atmospheric contaminants to which a person may be exposed without known ill effects or discomfort. Since it is not practical to maintain completely uncontaminated air in most industrial situations, it is necessary to establish maximal acceptable concentrations of atmospheric contaminants encountered in industrial operations. These concentrations in themselves do not represent a scale of relative toxicity; they represent the concentrations of contaminants below which ill effects are unlikely to be experienced by any but hypersusceptible individuals.

These concentrations are usually based upon data obtained by one or more of the following procedures:

- (1) Laboratory tests on animals
- (2) Laboratory tests using human subjects
- (3) Environmental and medical investigations in plants.

A common feature of these procedures is that the experimental exposure shall correspond to the normal work pattern. This should be taken into consideration also in the application of maximal acceptable concentration values.

Three criteria have governed the establishment of these concentrations:

- (1) Organic or other tissue changes
- (2) Functional reactions that have no discernible untoward effects on health but cause impairments, such as in-coordinations and increased proneness to accidents
- (3) Discomfort or adverse sensory effects.

In those cases in which the concentrations have been established on the basis of organic changes, it is logical to assume that repeated exposure to concentrations significantly in excess of the acceptable concentration probably would produce injury. When the level has been established on the basis of a functional change or discomfort, it is logical to assume that exposure to concentrations not greatly exceeding the acceptable concentration would not produce materially injurious effects. Hence it is important to understand the criteria upon which any

such maximal acceptable concentration has been established.

Though the purpose of the acceptable concentration is to minimize health hazards, its immediate use is for guidance in establishing engineering procedures to prevent objectionable concentrations of toxic or noxious materials from being present in the air of work places. Comparison of the results of air analyses with maximal acceptable concentrations indicates acceptable conditions or otherwise the need, extent, and urgency of control measures. Sampling and analysis should be performed by competent personnel using an acceptable method that will provide a reliable measure of actual exposure.

Air analyses in conjunction with acceptable concentrations of such atmospheric contaminants as are encountered in industrial operations serve as a measure of exposure, but not as a means of diagnosis of occupational disease. Diagnosis should be based on a consideration of all factors, including results from clinical and physical examination, as well as from air analyses, from means of assessing amounts of materials in the body, and a knowledge of toxicological effects of the materials under consideration.

In the application of the standards, it should be kept in mind that:

- (1) The acceptable concentrations serve as standards for good industrial hygiene practice.
- (2) They serve as engineering guides. Design and operation should aim at maintaining all concentrations below the acceptable maximum.
- (3) They should be applied and interpreted by competent individuals with a full understanding of the basis and limitations of the information from which the standard has been developed.
- (4) It is advised that these standards are considered to be guides toward good industrial hygiene and are not intended as legal requirements.
- (5) The levels are applicable only for exposure to a single substance. In the case of exposure to mixtures, the effect may be increased or decreased, and controls should be based on the specific situation.

*From American Standard Z37.23-1962.

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in the handling of wet dross from a light metals plant, in the cleaning of tank cars which have held sulfuric and hydrochloric acids, in the cleaning of pipes with an acid contaminated with arsenic, in the precipitation of cadmium with metallic zinc, and in other operations.

Arsine rapidly destroys the red cells. After it has been inhaled, the first signs are those of lack of oxygen. After some time the body begins to excrete the damaged red cells, which appear as a dark or bloody urine. The kidneys may then become too clogged to operate at all. Arsine, in very small amounts, is also capable of producing a chronic type of poisoning, but it is more typically a source of acute episodes.

The possibility of arsine formation should always be considered when there is freshly formed hydrogen around ores of the heavy metals, since arsenic is widely distributed in small amounts and only a trace of it is required to produce enough arsine to be troublesome.

One of the more common sources of arsine incidents in recent years has been the handling of dross from the aluminum refining of metals. Probably the most significant observation about these cases, aside from the fact that the moisture in the atmosphere is enough to form arsine, is the fact that the people involved in them have not been aware of the garlic-like odor which is supposed to be a warning of the presence of arsine.

See Hygienic Guide.

Asbestos is a hydrated magnesium silicate found in the minerals chrysotile, amianthus, actinolite, and tremolite. Practically all the commercial asbestos is either chrysotile or amianthus, and about 90 per cent of that used in this country is chrysotile. It is used almost exclusively for heat insulation or for textiles which must resist high temperature, such as heat-resistant clothing and brake linings.

Inhalation of excessive quantities of asbestos fiber can produce a fibrosis in the lungs similar to that found in silicosis but somewhat milder and usually not so rapidly progressive. Like silicosis, the condition develops and advances slowly and is equally resistant to treatment. There is also good evidence that inhaled asbestos causes lung cancer.

See Hygienic Guide.

Barium, in the form of its soluble salts, is toxic on both ingestion and inhalation and highly caustic when applied to the skin. The carbonate and sulfide are sufficiently soluble to be toxic, although not very caustic. The sulfate, which is used as a contrast medium in X-ray work, is too insoluble to show any toxicity, and soluble sulfates are specific antidotes for ingested barium salts.

Since these salts produce violent stimulation of all muscle, upon ingestion they produce severe disturbances of the digestive system. After absorption, the barium salts increase blood pressure by constriction of the arterial muscle, slow down heart beat by an action similar to that of digitalis, and first excite and then paralyze the central nervous system. In spite of the high inherent toxicity, there are few cases of industrial poisoning with barium.

Barium is a heavy metal, and the dust of the insoluble salts will collect in the lungs and give rise to the condition known as baritosis. Its nodular appearance on X-ray film may be mistaken for that of silicosis. Men showing the sign of baritosis are apparently not disabled or inconvenienced in any way.

See Hygienic Guide.

Benzene (benzol) is a colorless, flammable, volatile liquid with a rather pleasant aromatic odor. Its fire hazard is between ethyl alcohol and ethyl ether. The greatest hazard is that of chronic poisoning by inhalation of comparatively small amounts over a long period of time. It is one of the two or three most dangerous organic solvents in commercial use, and acts primarily on the blood-forming organs, producing severe anemia, bleeding under the skin, and great reduction in the ability of the blood to clot.

The most convenient measurement of damage is given by a blood count. People who may be exposed to benzene vapor should have blood counts at regular intervals and significant changes in the count should be closely investigated.

Headaches, dizziness, fatigue, loss of appetite, irritability, nervousness, nosebleed, and other signs of abnormalities of the blood may or may not be present in chronic poisoning.

A single heavy exposure to benzene vapor may produce a serious acute effect, similar