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INDUSTRIAL HYGIENE AND TOXICOLOGY

Second Revised Edition

FRANK A. PATTY, *Editor*

VOLUME II

TOXICOLOGY

David W. Fassett and Don D. Irish, Editors

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Skin Irritation. Propylene dichloride on the open skin causes only mild irritation. Single short contacts will probably be without any effects. The intensity of the reaction is greatly increased when bandaged on the skin or when held close to the skin by clothing.

Eye Irritation. Propylene dichloride causes some pain and irritation when splashed into the eye. It would not be expected to cause serious or permanent injury. It should be washed out immediately with water.

4. Hygienic Standards of Permissible Exposure

The threshold limit of propylene dichloride was established by the American Conference of Governmental Industrial Hygienists, in April, 1959, at 75 p.p.m. (350 mg./cu. meter.)

5. Flammability

The flammable limits of propylene dichloride are 3.4 to 14.5 per cent in air. The ignition temperature is 557 to 570°C.

VINYL CHLORIDE, CH_2=CHCl (Monochloroethene)

1. Uses and Industrial Exposures

Vinyl chloride is used as a chemical intermediate primarily as a monomer in plastic manufacture. The fire and explosion hazard is by far the dominant problem in handling vinyl chloride.

2. Physical and Chemical Properties

Physical state: gas
Molecular weight: 62.5
Specific gravity: 0.9121 (20°/4°C.)
Melting point: —153.71°C.
Boiling point: —13.8°C.
Vapor density: 2.15 (air = 1)
Vapor pressure: 2580 mm. Hg (20°C.)
Solubility: slightly soluble in water; soluble in ethanol and ethyl ether
Flash point: —78°C. (open cup)
1 mg./liter ≏ 391 p.p.m. and 1 p.p.m. ≏ 2.56 mg./cu. meter at 25°C., 760 mm. Hg

3. Physiological Response

Vinyl chloride appears to be a material of relatively low toxicity. The principal response seems to be one of central nervous system depression, which may result in symptoms of dizziness and disorientation that are somewhat similar to the response from ethyl chloride exposure. There is the possibility of some lung irritation occurring from chronic exposure as some edema is observed in acute vapor

exposure. Most investigators did not observe kidney or liver damage. One group of authors indicated some hyperemia of the liver and kidneys from acute exposure. It is concluded that the material has essentially a narcotic effect, with some lung irritation and a possibility of organ injury. There has been quite extensive use of this material in the chemical industry but no clinical reports of injury.

Acute Vapor Exposure. Patty *et al.*[100] reported the response of guinea pigs to single exposures to varying concentrations. The maximum time-concentrations in air for a single exposure survived by guinea pigs were as follows: 5 to 7 per cent for 1 hour and $2^1/_2$ per cent for 8 hours. The maximum time-concentration in air for a single exposure without serious disturbance was $1^1/_2$ per cent for 1 hour and 0.5 per cent for 8 hours. It will be noted that it requires a high concentration to cause death.

The same authors report that a concentration of $2^1/_2$ per cent of vinyl chloride in the air for a period of 3 minutes will cause dizziness and disorientation in exposed men. They also observed a faintly pleasant odor at this concentration. Animals that died from acute exposures showed edema of the lungs and hyperemia of the kidneys and liver.

Men exposed to vinyl chloride detected a slight odor at 4100 p.p.m. This is the lowest concentration at which an odor was detected. At 6600 p.p.m. for 1/2 hour, they noticed dizziness, sleepiness, and distinct odor.

Vinyl chloride has been investigated as a possible material for anesthetic purposes by Peoples and Leake[101] and by Oster *et al.*[102] It was concluded that vinyl chloride was unsatisfactory for use as an anesthetic because of its circulatory and cardiac effects. These studies were at 10 to 20 vol. % and are hardly significant for industrial exposure.

Chronic Vapor Exposure. Essentially no investigations have been published on the response to chronic vapor exposure. Schaumann[85] exposed mice and rats and found that they tolerated a level sufficient for "light narcosis" for periods of hours daily for 5 to 8 consecutive days or for 1 hour daily for 4 weeks without showing kidney or liver injury.

Torkelson *et al.*[102a] (to be published) report repeated exposures of animals to 7 hours/day, 5 days/week. At 500 p.p.m., rats showed increased liver weight and micropathology. At 200 and 100 p.p.m., rats showed increased liver weight, but no changes could be observed in dogs or guinea pigs. All species tolerated 50 p.p.m. for 6 months. Repeated exposures for 1 hour/day at 200 or 100 p.p.m. were tolerated without observable effect.

[85] *Chemical Safety Data Sheet SD-56*. Manufacturing Chemists Assoc., Washington, D. C. 1954.

[100] F. A. Patty, W. P. Yant, and C. P. Waite, *Public Health Repts. U. S.*, Reprint No. 1405, 45, No. 34 (Aug., 1930).

[101] S. A. Peoples and C. D. Leake, *J. Pharmacol. Exptl. Therap.*, 48, 284 (1933).

[102] R. H. Oster, C. J. Carr, J. C. Krantz, and M. J. Sauerwald, *Anesthesiology*, 8, (1947).

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5. Flammability[85]

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6. Odor and Warning Properties

Vinyl chloride has a mild
property for excessive exposur

VINYLIDENE CHLORIDE,

1. Uses and Industrial Exposure

Vinylidene chloride is u
monomer in the production of

2. Physical and Chemical Prope

Physical state: clear col
Molecular weight: 96.9
Specific gravity: 1.218
Freezing point: —122.5
Boiling point: 31.7°C.
Vapor density: 3.34 (ai
Vapor pressure: 591 mn
Refractive index: 1.427
Per cent in "saturated" a
Density of "saturated" a
Solubility: insoluble in
Flash point: —15°C. (
1 mg./liter ≈ 252 p.p.n
Hg

T. R. Torkelson, F. Oyer

Skin. The boiling point of vinyl chloride is so low that if the liquid material were spilled on the skin, there is a possibility of severe cooling and possibly frost bite.

Absorption, Excretion, and Metabolism. Very little is known of the metabolism of this compound. It is apparently readily absorbed by the lungs and rapidly excreted by the lungs. The little information that is available would indicate that a large part is excreted by the lungs unchanged.

Hygienic Standards of Permissible Exposure

The threshold limit of vinyl chloride was established by the American Conference of Governmental Industrial Hygienists, in April, 1959, at 500 p.p.m. (1300 mg./cu. meter).

Torkelson *et al.*[102a] suggest 100 p.p.m.

Flammability[a]

The explosive limits of vinyl chloride are: lower, 4% and upper, 22% (by vol. in air). The autoignition temperature is 472.22°C.

Odor and Warning Properties

Vinyl chloride has a mild, sweetish odor. The odor is not an adequate warning property for excessive exposure.

VINYLIDENE CHLORIDE, $CH_2=CCl_2$ (1,1-Dichloroethylene)

Uses and Industrial Exposures

Vinylidene chloride is used as a chemical intermediate, particularly as a monomer in the production of plastics.

Physical and Chemical Properties

Physical state: clear colorless liquid
Molecular weight: 96.95
Specific gravity: 1.218 (20°/4°C.)
Freezing point: −122.5°C.
Boiling point: 31.7°C.
Vapor density: 3.34 (air = 1)
Vapor pressure: 591 mm. Hg (25°C.)
Refractive index: 1.427 (20°C.)
Per cent in "saturated" air: 78
Density of "saturated" air: 2.8 (air = 1)
Solubility: insoluble in water; soluble in organic solvents
Flash point: −15°C. (open cup)
1 mg./liter ≏ 252 p.p.m. and 1 p.p.m. ≏ 3.97 mg./cu. meter at 25°C., 760 mm. Hg

[a] T. R. Torkelson, F. Oyen, and V. K. Rowe, *Am. Ind. Hyg. Assoc. J.*, **22**, 354 (1961).

Cement and Concrete

Cement is made from cement rock or a mixture of finely ground limestone, or other form of calcium carbonate, with clay, shale, slate, or blast furnace slags, rarely sandstone, and certain accelerators or retarders. The mixed powders are heated in a kiln, usually rotary, to about 1300 to 1400°C. The kilns are heated by fuel jets of powdered coal, gas, or oil. The cement rock rarely contains more than 6 or 8 per cent quartz; the finished product usually less than 1 per cent, though occasionally it may contain up to 6.5 per cent. The dusts are ordinarily classed as nuisance dusts but their concentration may exceed the most liberal ideas of permissible limits.

There are several dust-producing operations and they are amenable to control measures. Some of these sources are: stone quarrying, crushing, grinding, the rotary kiln, screens, bagging operations, and the loading and unloading of cars. Dust clouds, if uncontrolled, not only are conducive to undesirable working conditions but also constitute an atmospheric pollution nuisance in the community. Electrostatic precipitation as well as centrifugal collectors have been used successfully to remove the dust from the effluent air from kilns and silos, and the amount recovered is said sometimes to exceed 5 per cent of total raw materials. A method that has been successfully applied to the rotary kiln elsewhere (see Sand Refining) is to exhaust the hot kiln gases through baffled water-spray chambers and conduct the water flowing from the sprays through a settling basin from which the sludge may be recovered. The important factors in evaluating exposures are the degree of dust control and the free silica content of dust particles less than 5 μ in diameter. Lung injury from exposure to cement dust, however, has not been demonstrated and the most frequent, harmful result of exposure is that of skin irritation from the alkaline action of cement. In the mixing and use of concrete, the irritant, alkaline action of the wet mixture is similar to that of the cement dust, and both warrant suitable control to prevent prolonged contact with the skin.

Chlorinated Waxes and Oils

Synthetic Chlorowaxes. The synthetic chlorowaxes comprise a number of chlorinated hydrocarbons that are derivatives of naphthalene or diphenyl. Halowax is the trade name of one manufacturer for the chlorowaxes.

The damage that may occur from inhalation, ingestion, and skin absorption of the chlorowaxes will vary with the degree of chlorine saturation of the compounds. The amount of dermatitis and poisoning increases rapidly as the amount of chlorine in the waxes increases. The commonly accepted maximum permissible limit for atmospheric contamination with trichloronaphthalene is 5 mg. per cubic meter of air. Pentachloronaphthalene, one of the chlorowaxes carrying a high percentage of chlorine is restricted to 0.5 mg. per cubic meter of air.

Systemic poisoning from the chlorowaxes is generally characterized by damage to the liver. Serious exposure may produce acute yellow atrophy. The

skin effects are commonly in the form of acne, which is more widely distributed on the body than common acne.

Among the recommendations for the prevention of chlorowax poisoning are: (*1*) vapors and dust should be controlled by exhaust ventilation to prevent exposure to amounts of the compounds in excess of the safe limits mentioned above; (*2*) foremen and workers should be told of the toxicity of the materials that they are handling and instructed to keep skin contacts with the material to a minimum; (*3*) preemployment and periodical physical examinations should be given with special attention to the skin and to the liver, liver function tests being performed periodically; and (*4*) the best hygienic conditions should prevail, including the provision of clean work clothing, protective gloves, and protective creams. Those manufacturers who have had the most favorable results in preventing chlorowax poisoning have provided double locker rooms, one for street clothes and one for work clothes, with a shower room in between. The workers should be required to take a shower every day before leaving the factory; it is well to provide supervision to make certain that this practice is complied with.

Air analysis for the chlorowaxes is most commonly performed by passing the air over heated platinum in an electrically heated quartz tube; the waxes decompose and the effluent gas is scrubbed in a column of glass beads moistened with sodium carbonate; the chlorine is converted to sodium chloride which is recovered by washing the beads, and is usually determined nephelometrically. The impinger, using amyl acetate as the collecting medium, has also been employed for collection of samples; afterward the samples are burned, products of combustion collected and chlorides determined.

Chlorinated Oils. There are two general types of oils falling within this class; the first contains additive substances such as carbon tetrachloride to improve cutting properties; the second has chlorine combined in complex organic structure.

The chlorine additive agents may be recovered by distillation and are released from the oils in accordance with vapor pressure laws. The use of oil plus chlorinated hydrocarbon may be hazardous unless exhaust ventilation is provided. Nausea and malaise are common complaints of workers handling the mixtures. The haphazard methods used in preparing the mixtures tend to increase the danger. Commonly the chlorine compound is added in unknown proportion as an antidote for cutting difficulties. In some instances the mixture has been found to contain as much as 40 per cent carbon tetrachloride.

The chlorine in the second type of oil is firmly bound at lower temperatures; upon heating, little decomposition occurs below 200°C.; near and above 250°C. hydrogen chloride is evolved. It is known that temperatures in excess of 300°C. are produced locally from heavy cutting operations. This type of oil probably can be used safely for light precision machining.

Animal experimentation has shown that chlorine compounds in oils may be absorbed through the intact skin to cause liver damage. Dermatitis from chlorinated oils also occurs.

Photographic Industry

Dermatitis and skin sensitization are the hazards of the photographic industry. Nasal and bronchial irritation and asthma are also reported from contact with developers and other photographic chemicals. The aminophenols are among the most common sources of skin disease from developers. Other irritating chemicals include caustics, iron salts, mercuric chloride, strong acids, bromides, iodides, pyrogallic acid, and silver nitrate. The last substance is reported to have caused argyria, a condition in which silver is deposited beneath the skin. It is difficult, if not impossible, to remove the deposits completely.

The prevention of dermatitis lies in reducing to a minimum the contact of the chemicals with the skin. Cleanliness, protective clothing, and protective creams are the triumvirate for controlling the hazard.

Plastics and Synthetic Resins

Synthetic resins that have undergone complete condensation cause little difficulty in the cold, but where heat is applied, or an imperfectly combined component is present, skin irritation and sensitization may result. The phenol-formaldehyde and urea–formaldehyde resins owe their irritant and sensitizing properties chiefly to formaldehyde,[35] but phenol and furfural (phenol-furfural resins) may also have some irritant effect. It is advisable to provide process ventilation for any dust-producing or vapor-producing process involving the manufacture, fabrication, or use of plastics whereby formaldehyde is released into the workroom atmosphere. Hexamethylenetetramine, which has a bad reputation as a sensitizer, is harmful because it releases formaldehyde.[36] Cashew nutshell liquid-formaldehyde resin is particularly offensive if any uncombined cashew nutshell liquid remains in the resin. "Oil stop," a waterproof resin made by mixing cashew nutshell liquid to a paste with powdered paraform (a polymer of formaldehyde) and allowing it to "set" or condense, is popular with electricians. Both of the constituents are irritants and sensitizers and there is a high incidence of dermatitis among users who carelessly contaminate their hands and clothing with the mixture.

Plastic glues for the manufacture of plywood, laminated asbestos, fiberboard, glass fabric, and similar products may be made of incompletely condensed resins containing formaldehyde along with acids, alkalies, peroxides, and other irritants and sensitizers. The screening, scaling, and mixing of such powdered glues are productive of dust and conducive to dermatitis.

Many plastics such as vinyl chloride, vinyl acetate, polyethylene, polystyrene, and methyl methacrylate have proved to be more or less inert physiologically. Antioxidants and stabilizers added to some plastics, however, may occasionally cause adverse physiological effects. The majority of the dermatitis

[35] A. G. Cranch, *Ind. Med.*, **15**, 168 (1946).
[36] L. Schwartz, *J. Invest. Dermatol.*, **6**, 239 (1945).

cases arising from prolonged contact with plastics of this nature are caused by plasticizers added to eliminate brittleness and to produce flexibility. Some of these plasticizers are susceptible to the effects of heat and moisture and may separate from plastics that are in prolonged contact with the skin and cause either primary irritation or, more likely, sensitization. This presents a use problem rather than a production problem. These plasticizers[36] include derivatives of glycol, glycolic acid, phthalic acid, phosphoric acid, ricinoleic acid, and sebacic acid.

In evaluating and controlling exposures arising from the manufacture, fabrication, or use of plastics, dermatitis is the primary consideration, but eye irritation and even the possibility of lung irritation should be considered. Dusts, especially those involving incompletely reacted materials, and curing agents, especially organic amine vapors, should be controlled by engineering methods; excessively warm and humid atmospheres also should be controlled; and direct skin contact with suspected irritants or sensitizers should be avoided. A supervised program of personal cleanliness and frequent changes of clothing are the best personal control measures wherever dermatitis is involved.

Occasionally persons do not respond to "hardening" and the standard preventive and protective measures. In such cases of unusual susceptibility it is necessary to transfer the workers to other work.

Pottery Industry

Silicosis and lead poisoning are the traditional occupational diseases to potters. Free silica is present as flint in the pottery slip in amounts that make dust control of a high order imperative. Respirable sizes of dust commonly show 40 to 50 per cent free silica in slip houses. The use of lead compounds in decorating ware also necessitates a high degree of dust elimination.

Most of the dangerous silica operations are concentrated in a few departments. The slip house normally has more than half of the total significantly exposed workers. Lead exposure is confined to sprays and dust from ware prior to its being fired.

Jiggering and batting out normally do not involve harmful exposures. Stampers should be provided with exhaust ventilation, however, as should finishers. Dish makers do not have significant dust exposures. This statement also applies to casting shops. Bisque and glost kiln placing and drawing are dust-free operations. Flatware brushing is one of the dustiest occupations outside of the slip house and it requires control. The transfer of raw materials from boxcars to storage bins may involve excessive dust exposures.

It is poor hygienic practice to draw hot air directly from the fire chambers of the kilns into the workrooms to heat them: a system of heat exchangers should be used.