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IARC MONOGRAPHS
ON THE
EVALUATION OF THE
CARCINOGENIC RISK
OF CHEMICALS TO HUMANS

Some Monomers, Plastics and
Synthetic Elastomers, and Acrolein

VOLUME 19

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This publication represents the views and expert opinions
of an IARC Working Group on the
Evaluation of the Carcinogenic Risk of Chemicals to Humans
which met in Lyon.
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INTERNATIONAL AGENCY FOR RESEARCH ON CANCER

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The following compounds were considered but no monograph was prepared because of lack of carcinogenicity data: adipic acid, hexamethylenediamine and nylon 6/6; dimethylterephthalate, terephthalic acid and polyethylene terephthalate; isoprene and polyisoprene; methacrylic acid; vinylidene fluoride and polyvinylidene fluoride.

¹Unable
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- (e) Refractive index: n_D^{20} 1.3700
- (f) Spectroscopy data: Infra-red, nuclear magnetic resonance and mass spectral data have been tabulated (Grasselli & Ritchey, 1975).
- (g) Solubility: Slightly soluble in water (0.11 g/100 g at 25°C) (Hardie, 1964); soluble in ethanol; very soluble in ether, carbon tetrachloride and benzene
- (h) Volatility: Vapour pressure is 2530 mm at 20°C (Hardie, 1964)
- (i) Stability: Flash-point, -78°C (closed cup) (Hardie, 1964); polymerizes in light or in the presence of a catalyst (Windholz, 1976); on combustion it degrades to hydrogen chloride, carbon monoxide, carbon dioxide and traces of phosgene (O'Mara *et al.*, 1971)
- (j) Reactivity: On treatment with strong alkalis at high temperatures it loses hydrogen chloride (Miller, 1969).
- (k) Conversion factor: 1 ppm in air = 2.6 mg/m³

1.4 Technical products and impurities

Vinyl chloride is generally supplied as a liquid under pressure. Usually no inhibitor is added when it is to be shipped within the US. A typical analysis of a commercial US grade is as follows: water, 50 mg/kg (ppm); nonvolatile residue, 5 mg/kg (ppm); acetaldehyde, <1 mg/kg (ppm); acetylene, <1 mg/kg (ppm); iron, 0.1 mg/kg (ppm); hydrogen chloride, <0.1 mg/kg (ppm); and hydrogen peroxide, 0.01 mg/kg (ppm).

In Japan, commercial vinyl chloride meets the following specifications: purity, 99.9% min; water, 200 mg/kg (ppm) max; hydrogen chloride, 1 mg/kg (ppm) max; iron, 1 mg/kg (ppm) max; and evaporation residue, 50 mg/kg (ppm) max. Chlorinated hydrocarbons may be present as impurities.

2. Production, Use, Occurrence and Analysis

2.1 Production and use

(a) Production

The first synthesis of vinyl chloride appears to have been made in 1835 (Regnault, 1835). Addition of hydrogen chloride to acetylene,

formerly the most halogenation of ethylene in the US and Japan. Ethylene is reacted with dichloride, which produces hydrogen chloride.

Vinyl chloride production (US Tariff production of 258 million kg in 1976 (US Department of Commerce, 1976) 150 million kg to Canada (8), Colombia (8), etc.

Total western production in the following: Republic of Germany (690), The Netherlands (430), and the UK (430).

In Japan, consumption in 1976, eighteen million kg; 115 million kg.

(b) Use

About 96% of vinyl chloride was for the production of PVC. The remainder was used in the production of vinylidene chloride.

The largest use is in plastic piping and in consumer goods. For detailed description of vinyl chloride-vinyl acetate copolymer.

Hardie (1964) reports that vinyl chloride is used as an extender in the production of chlorinated polyethylenes (CPEs); however, it is not being used for the production of CPEs.

Limited quantities of vinyl chloride are used as a propellant, but it is not used as a propellant in the US Environmental Protection Agency (EPA) tests.

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formerly the most important route of synthesis, has been displaced by the halogenation of ethylene; over 95% of the vinyl chloride monomer produced in the US and Japan in 1976 was made from ethylene. In this process, ethylene is reacted with hydrogen chloride and oxygen to give ethylene dichloride, which is subsequently cracked to produce vinyl chloride and hydrogen chloride.

Vinyl chloride has been produced commercially in the US for over fifty years (US Tariff Commission, 1928). In 1976, nine companies reported the production of 2580 million kg (US International Trade Commission, 1977). US imports have been negligible; exports amounted to 291 million kg in 1976 (US Department of Commerce, 1977), and in 1977, exports were about 150 million kg to the following countries (% of total): Brazil (28), Canada (8), Colombia (11), Mexico (14), Norway (12) and Yugoslavia (14).

Total western European production in 1976 amounted to 3925 million kg, in the following countries (millions of kg): Belgium (490), the Federal Republic of Germany (990), Finland (25), France (620), Greece (25), Italy (690), The Netherlands (340), Spain (190), Sweden (95), Switzerland (30) and the UK (430). Exports from western Europe in that year were 44 million kg.

In Japan, commercial production of vinyl chloride began prior to 1946. In 1976, eighteen companies produced a total of 1281 million kg vinyl chloride; 115 million kg were exported.

(b) Use

About 96% of the 2274 million kg vinyl chloride used in the US in 1976 was for the production of vinyl chloride homopolymer and copolymer resins. The remainder was used (essentially by one company internally) in the production of methyl chloroform and as a comonomer with vinylidene chloride in the production of resins. For a detailed description of the uses of vinylidene chloride-vinyl chloride copolymers, see p. 450.

The largest use for polyvinyl chloride resins is in the production of plastic piping and conduit. Other important uses are in floor coverings, in consumer goods, in electrical applications and in transport applications. For detailed descriptions of the uses of polyvinyl chloride and vinyl chloride-vinyl acetate copolymers, see pp. 406 and 414.

Hardie (1964) reported that vinyl chloride has been used as a refrigerant, as an extraction solvent for heat-sensitive materials and in the production of chloroacetaldehyde (an intermediate in the synthesis of sulphonamides); however no evidence was found that vinyl chloride is presently being used for these purposes.

Limited quantities of vinyl chloride were used in the US as an aerosol propellant, but in 1974 it was banned from use in pesticide aerosol products (US Environmental Protection Agency, 1974a), in self-pressurized household

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containers, and as an ingredient of drug and cosmetic products (US Consumer Product Safety Commission, 1974a,b).

Vinyl chloride was used in western Europe in 1977 in the production of polyvinyl chloride (95%) and for other uses, including the production of methyl chloroform (5%).

In Japan in 1976, vinyl chloride was used in the production of polyvinyl chloride (92-94%) and for other uses, such as in copolymers (6-8%).

The US Occupational Safety and Health Administration's health standards for exposure to air contaminants require that an employee's exposure to vinyl chloride not exceed an eight-hour time-weighted average of 2.6 mg/m³ (1 ppm) in the workplace air in any eight-hour work shift of a forty-hour work week. During any work shift an employee's exposure may not exceed a ceiling concentration limit of 13 mg/m³ (5 ppm), averaged over any period of 15 minutes or less (US Occupational Safety and Health Administration, 1974).

The work environment hygiene standards for exposure to vinyl chloride in various countries, in terms of time-weighted averages (8-hr) and ceiling concentrations (10- or 15-min), were as follows in 1977: Canada, 10 ppm (8-hr) and 25 ppm (15-min); Finland, 5 ppm (8-hr) and 10 ppm (10-min); Italy, 50 ppm (8-hr), although this is expected to change to 25 ppm (8-hr); Japan, expected to be 10 ppm; The Netherlands, 10 ppm (8-hr); Norway, 1 ppm (8-hr) and 5 ppm (15-min); Sweden, 1 ppm (8-hr) and 5 ppm (15-min); USSR, 12 ppm (Bertram, 1977). In France, the standards were reported to be 5 ppm for 1 week, with a ceiling concentration of 15 ppm, in already existing factories, and 1 ppm and 5 ppm, respectively, for new factories; in Spain, no limits; in Denmark, 1 ppm (8-hr); in Belgium, 5 ppm (1 week), ceiling 15 ppm; in the Federal Republic of Germany, the same as for France in existing factories, and 2 ppm (1 year) and ceiling 15 ppm (1-hr) for new factories; in the UK, 10 ppm (8-hr), ceiling 30 ppm max; and in Switzerland, 10 ppm (1 week, 8-hr day for 5 days) (Thomas, 1977).

In August 1977, the proposed European value was 3 ppm over one year for existing and future plants, with an 'alarm-value' of 15 ppm (Commission of the European Communities, 1977a).

The US Environmental Protection Agency has proposed new rules to reduce the national emission standard for vinyl chloride from 10 ppm to 5 ppm in order to reduce vinyl chloride emissions by one-half within 3 years of the actual rulemaking. This would result in hourly emissions (based on new average-sized plants) of 5.1 kg from an ethylene dichloride-vinyl chloride plant (instead of 10.3 kg); 9 kg from a dispersion process polyvinyl chloride plant (instead of 17.5 kg); and 13.5 kg from a suspension process polyvinyl chloride resin plant (instead of 16 kg) (US Environmental Protection Agency, 1977).

In the Federal Republic of Germany, exposure is limited to 3 kg/1000 m³ (0.3 mg/m³) (99% confidence limit).

The Commission of the European Communities has set a limit of 1 mg/kg (1 ppm) as a maximum for packaging and 0.05 mg/kg (0.05 ppm) for the level of 0.05 mg/l (0.05 ppm) in the Republic of Germany (Thomas, 1977).

2.2 Occurrence

Vinyl chloride

The occurrence of vinyl chloride in the environment (US Environmental Protection Agency, 1977).

(a) Occupational

The air concentration of vinyl chloride prior to ventilation and scraping procedure found during scrap hands during scrap. Between 1950 and 1970, it was found in one factory. Air concentrations of vinyl chloride-producing plants were 100-800 mg/m³ (40-300 ppm) (Filatova & Gronsbom, 1969); in 1976, in a Russian plant (Bol'shakov, 1969) 0.35 ppm (Murdoch, 1977) stated that 20 000 mg/m³ of vinyl chloride in manufacturing.

On a time-weighted average to which coagulation (50-250 ppm) (Barefoot, 1977) the US National Institute for Environmental Health Sciences found vinyl chloride ranges from 0.01-84.77 mg/m³ (0.01-84.77 ppm) in the vinyl chloride plants in the

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In the Federal Republic of Germany, the emission in the environment is limited to 3 kg/hr/source or 150 mg/m³/source, with a ground level of 0.3 mg/m³ (99% confidence) in inhabited areas (Thomas, 1977).

The Commission of the European Communities has adopted a level of 1 mg/kg (1 ppm) as the amount of vinyl chloride which can be present in packaging and 0.01 mg/kg (ppm) in foodstuffs packed in polyvinyl chloride (Commission of the European Communities, 1977b, 1978). A maximum migration level of 0.05 mg/kg has been adopted in Belgium, Denmark, the Federal Republic of Germany, France, Italy, The Netherlands, Spain and Sweden (Thomas, 1977).

2.2 Occurrence

Vinyl chloride is not known to occur as a natural product.

The occurrence of vinyl chloride in ambient air near vinyl chloride and polyvinyl chloride plants, in water, and in food has been reviewed (US Environmental Protection Agency, 1975a,b).

(a) Occupational exposure

The air concentration of vinyl chloride in a polymerization reactor prior to ventilation is of the order of 7800 mg/m³ (3000 ppm); during the scraping procedure, 130-260 mg/m³ (50-100 ppm); and that close to the hands during scraping, 1560-2600 mg/m³ (600-1000 ppm) (Cook *et al.*, 1971). Between 1950 and 1959, concentrations up to 10.4 g/m³ (4000 ppm) were found in one factory near the polymerization reactors (Ott *et al.*, 1975). Air concentrations of vinyl chloride in working places in polyvinyl chloride-producing factories have been reported variously to range from 100-800 mg/m³ (40-312 ppm), with peaks up to 87.3 g/m³ (33 500 ppm) (Filatova & Gronsberg, 1957); from 112-356 mg/m³ (43-214 ppm) (Angheliescu *et al.*, 1969); and >195 mg/m³ (>75 ppm) in a Yugoslav plant (Orusev *et al.*, 1976). In a Russian synthetic leather plant, <113.6 mg/m³ (44 ppm) (Bol'shakov, 1969) and in three UK cable factories, 0.4-0.9 mg/m³ (0.15-0.35 ppm) (Murdoch & Hammond, 1977) were detected. In 1974, it was estimated that 20 000 US workers, past and present, had been exposed to vinyl chloride in manufacturing plants (Heath *et al.*, 1975).

On a time-weighted average, the concentration of vinyl chloride monomer to which cogulator operators are exposed ranges from 130-650 mg/m³ (50-250 ppm) (Baretta *et al.*, 1969). However, in a more recent survey for the US National Institute for Occupational Safety and Health of three vinyl chloride plants it was reported that the time-weighted average exposure to vinyl chloride ranged from 0.2-70 mg/m³ (0.07-27 ppm) (Milby, 1977). Barnhart *et al.* (1975) found <0.03-15 mg/m³ (<0.01-5.89 ppm), 0.03-220 mg/m³ (0.01-84.77 ppm) and 0.03-57 mg/m³ (0.02-21.8 ppm) in 3 vinyl chloride plants in the US.

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In 1974, it was reported that polyvinyl chloride leaving certain manufacturing plants may have contained 200-400 mg/kg (ppm) vinyl chloride monomer; on delivery to the customer, this level was about 250 mg/kg (ppm); and after processing, levels of 0.5-20 mg/kg (ppm) were reached, depending on the method of fabrication (Anon., 1974). Wilkinson *et al.* (1964) found 100 mg/kg (ppm) residual vinyl chloride monomer in polyvinyl chloride dispersions. However, new processing methods leave as little as 1-2 mg/kg (ppm) residual vinyl chloride in vinyl chloride resins (US Food and Drug Administration, 1975). Residual vinyl chloride in commercial food grade resins has been reduced by processing and stripping techniques to 115 µg/kg (ppb) for resin, less than 0.048 µg/kg (ppb) for compound and less than 0.043 µg/kg (ppb) for sheet polyvinyl chloride (Saggese *et al.*, 1976). Industrial grade polyvinyl chloride-coated films used for food packaging were found to contain 5-71 µg/kg (ppb) of monomer (Gilbert *et al.*, 1975) and plastic bottles up to 7.9 mg/kg (ppm) (Breder *et al.*, 1975).

(b) Air

It has been estimated that prior to 1975 vinyl chloride emissions from US polyvinyl chloride plants amounted to 110 million kg/year (US Environmental Protection Agency, 1975b) and that the average concentration of vinyl chloride in air around these plants was 44 µg/m³ (17 ppb) (US Environmental Protection Agency, 1976). Vinyl chloride has been determined in the air in the Houston, Texas, area (where an estimated 40% of the US production capacity is located) in concentrations of 8 µg/m³ - 3.2 mg/m³ (3.1-1250 ppb) (Gordon & Meeks, 1977) and in the ambient air near two vinyl chloride plants in the Long Beach, California, area in concentrations of 0.26-8.8 mg/m³ (0.1-3.4 ppm) (National Field Investigations Center, 1974). It has also been detected in the air in Delaware City, Delaware, in maximum concentrations of 3.9 mg/m³ (1.5 ppm) with a mean of 2 mg/m³ (0.8 ppm) (Lillian *et al.*, 1975).

(c) Water

Vinyl chloride has been detected in effluent discharged by chemical and latex manufacturing plants and in raw water in the US (Shackelford & Keith, 1976). The highest concentration of vinyl chloride detected in finished drinking-water in the US was 10.0 µg/l (Safe Drinking Water Committee, 1977; US Environmental Protection Agency, 1975a).

In 1974, it was estimated that about 12.3 kg/day vinyl chloride were discharged in the waste-water effluent from 2 vinyl chloride plants in the Long Beach, California, area (National Field Investigations Center, 1974).

(d) Food

In May 1973, a branch of the US Treasury Department banned the use of polyvinyl chloride for the packaging of alcoholic beverages (Anon., 1973a), as a result of studies reported by the US Food and Drug Administration indicating that up to 20 mg/kg (ppm) vinyl chloride monomer were present in

alcoholic beverages. Vinyl chloride has been found in mg/kg (ppm) (Will levels of up to 9

It has been found (ppm) (Roesli *et al.* in butter and margarine (et al., 1975), which contains vinyl chloride

(e) Other

Vinyl chloride concentrations of another study (Go 16 new or used auto

Vinyl chloride and little cigars. Marijuana cigarette

2.3 Analysis

A comprehensive methods of sampling sphere, ambient air is available (Eggar vinyl chloride have 1975b). A review of water, and water f

A gas chromatograph National Institute of Standards and Technology chloride in the water 5-litre air sample 1977).

A gas chromatograph mission of the European Commission foodstuffs and in contact with

An official analysis of Germany for detection. It is based on the method by gas chromatography and has a limit of detection. Normen Ausschuss,

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alcoholic beverages packaged in this material (Anon., 1973b). Vinyl chloride has been found in a variety of alcoholic drinks at levels of 0-2.1 mg/kg (ppm) (Williams, 1976a,b; Williams & Miles, 1975) and in vinegars at levels of up to 9.4 mg/kg (ppm) (Williams & Miles, 1975).

It has been found in edible oils, in concentrations of 0.05-14.8 mg/kg (ppm) (Roesli *et al.*, 1975; Williams, 1976a; Williams & Miles, 1975), and in butter and margarine, in concentrations of 0.05 mg/kg (ppm) (Fuchs *et al.*, 1975), when these products were packaged and stored in polyvinyl chloride containers.

(e) Other

Vinyl chloride has been found in 2/7 new automobile interiors in concentrations of 1-3 mg/m³ (0.4-1.2 ppm) (Hedley *et al.*, 1976). In another study (Going, 1976), no concentrations above 10 ppb were found in 16 new or used automobiles or in 4 new or old mobile homes.

Vinyl chloride has been detected in domestic and foreign cigarettes and little cigars, in concentrations of 5.6-27 ng/cigarette, and in a marijuana cigarette at a level of 5.4 ng/cigarette (Hoffmann *et al.*, 1976).

2.3 Analysis

A comprehensive critical review, containing over 100 references, of methods of sampling and analysis of vinyl chloride in the workplace atmosphere, ambient air, water, food, cigarette smoke and polyvinyl chloride is available (Egan *et al.*, 1979). Methods of collection and analysis of vinyl chloride have also been reviewed (US Environmental Protection Agency, 1975b). A review of methods used to determine vinyl chloride in air, water, and water piping is available (Larany, 1977).

A gas chromatographic method of analysis has been accepted by the US National Institute for Occupational Safety and Health for determining vinyl chloride in the workplace atmosphere, in the range of 0.008-5.2 mg/m³ in a 5-litre air sample (National Institute for Occupational Safety and Health, 1977).

A gas chromatographic analytical method has been proposed by the Commission of the European Communities for determining vinyl chloride in foodstuffs and in vinyl chloride polymers and copolymers intended to come into contact with food (Commission of the European Communities, 1977b).

An official analytical method has been drafted in the Federal Republic of Germany for determining residual vinyl chloride in polyvinyl chloride. It is based on treatment of the polymer with N,N-dimethylacetamide, followed by gas chromatographic analysis of the solution with flame-ionization detection and has a limit of detection of 0.5 mg/kg (ppm) (Deutsche Industrie Normen Ausschuss, 1977).

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