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Vinyl chloride

Vinyl chloride is the [organochloride](#) with the formula $\text{CH}_2\text{:CHCl}$. It is also called vinyl chloride monomer, or VCM. This colourless compound is an important industrial chemical chiefly used to produce the [polymer polyvinyl chloride](#) (PVC). At ambient pressure and temperature, vinyl chloride is a gas with a sickly sweet odor. It is highly toxic, flammable and carcinogenic.

History

Vinyl chloride was first produced in 1835 by [Justus von Liebig](#) and his student [Henri Victor Regnault](#). They obtained it by treating [ethylene dichloride](#) with a solution of [potassium hydroxide](#) in [ethanol](#).

In 1912, Frans, a German chemist working for Griesheim-Elektron, patented a means to produce vinyl chloride from [acetylene](#) and [hydrogen chloride](#) using mercuric chloride as a catalyst. Whereas this method was widely used during the 1930s and 1940s, it has since been superseded by more economical processes based on ethylene, at least in the West.

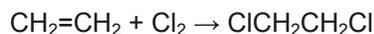
Production

Vinyl chloride is produced on a substantial scale - approximately 31.1 million tons were produced in 2000 ^[1]. Two methods are employed, the [hydrochlorination](#) of acetylene and the [dehydrochlorination](#) of ethylene dichloride (1,2-dichloroethane). ^[2]

Manufacturing details from ethylene dichloride

Direct chlorination

The production of vinyl chloride from 1,2-dichloroethane (DCA) consists of a series of well-defined steps. DCA is prepared by reacting [ethylene](#) and [chlorine](#). ^[3] In the presence of [iron\(III\) chloride](#) as a catalyst, these compounds [react](#) exothermically:



This process is very selective, resulting in high purity DCA and high yields. However any dissolved catalyst and moisture must be removed before DCA enters the VCM production process.

Thermal cracking

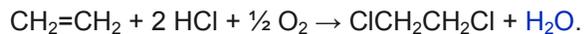
When heated to 500 °C at 15–30 atm (1.5 to 3 MPa) pressure, DCA vapor decomposes to produce vinyl chloride and anhydrous HCl.



The thermal cracking reaction is highly endothermic, and is generally carried out in a fired heater. Even though residence time and temperature are carefully controlled, it produces significant quantities of chlorinated hydrocarbon side products. In practice, DCA conversion is relatively low (50 to 60 percent). The furnace effluent is immediately quenched with cold DCA to stop undesirable side reactions. The resulting vapor-liquid mixture then goes to a purification system. Some processes use an absorber-stripper system to separate HCl from the chlorinated hydrocarbons, while other processes use a refrigerated [continuous distillation](#) system.

Oxychlorination

Modern VCM plants use recycled HCl is to produce more DCA via oxychlorination, which entails the reaction of ethylene, oxygen and hydrogen chloride over a [copper\(II\) chloride](#) catalyst to produce DCA:



The reaction is highly exothermic.

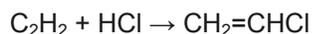
Due to the relatively low cost of ethylene, compared to acetylene, most vinyl chloride has been produced via this technique since the late 1950s. This is despite the lower yields, lower product purity and higher costs for waste treatment. By-products of the oxychlorination reaction, may be recovered, as feedstocks for chlorinated solvents production. One useful byproduct of the oxychlorination is [ethyl chloride](#), a topical anesthetic.

Waste treatment

For environmental reasons, the acidic aqueous wastestream is treated to remove organic compounds and neutralized before it can be sent to the plant's "outfall". An outfall is a monitored wastewater stream that must conform to the plant's standards. Some very hazardous wastes are generated in the recovery of the product vinyl chloride. These wastes require specialized procedures. These wastes are burned onsite in hazardous waste burners that again are subject to strict standards.

Production from acetylene

[Acetylene](#) reacts with anhydrous [hydrogen chloride](#) gas over a mercuric chloride catalyst to give vinyl chloride:



The reaction is exothermic and highly selective. Product purity and yields are generally very high.

This was the most common industrial route to VCM, before ethylene became widely distributed. When VCM producers shifted to using the thermal cracking of DCA described above, some used byproduct HCl in conjunction with a colocated acetylene-based unit. The hazards of storing and shipping acetylene meant that the VCM facility needed to be located very close to the acetylene generating facility.

Storage

Vinyl chloride is stored as a liquid. Often, the storage containers for the product VCM are high capacity spheres. The spheres have an inside sphere and an outside sphere. Several inches of empty space separate the inside sphere from the outside sphere. This void area between the spheres is purged with an inert gas such as nitrogen. As the nitrogen purge gas exits the void space it passes through an analyzer that is designed to detect if any vinyl chloride is leaking from the internal sphere. If vinyl chloride starts to leak from the internal sphere or if a fire is detected on the outside of the sphere then the contents of the sphere is automatically dumped into an emergency underground storage container.

Uses

Vinyl chloride is a chemical intermediate, not a final product. Due to the hazardous nature of vinyl chloride to human health there are no end products that use vinyl chloride in its monomer form. Polyvinyl chloride is very stable, storable, and less acutely hazardous than the monomer.

Vinyl chloride liquid is fed to polymerization reactors where it is converted from a monomer to a polymer [PVC](#). The final product of the polymerization process is PVC in either a flake or pellet form. Literally, tens of billions of pounds of PVC are sold on the global market each year. From its flake or pellet form PVC is sold to companies that heat and mold the PVC into end products such as [PVC](#) pipe and bottles.

Until 1974, vinyl chloride was used in [aerosol spray propellant](#). Prior to the removal of vinyl chloride from hair spray the accumulation of vinyl chloride vapor in hair salons may have exceeded the NOAEL (No Observable Adverse Effect Level) exposure guidelines.

Vinyl chloride was briefly used as an [inhalational anaesthetic](#), in a similar vein to [ethyl chloride](#), though its toxicity forced this practice to be abandoned.

Fire and explosion hazard

OSHA lists VCM as a Class IA Flammable Liquid, with an [National Fire Protection Association](#) Flammability Rating of 4. Because of its low boiling point, liquid VCM will undergo [flash evaporation](#) (i. e., autorefrigerate) upon its release to atmospheric pressure. The portion vaporized will form a dense cloud (more than twice as heavy as the surrounding air). The risk of subsequent explosion or fire is significant. According to OSHA, the flash point of VCM is -78 C (-108 F). Its flammable limits in air are: lower 3.6 volume % and upper 33.0 volume %. Fire may release toxic hydrogen chloride (HCl) and carbon monoxide (CO).^[4]

Health effects

Vinyl chloride monomer

Almost all vinyl chloride [monomer](#) (VCM) is used to create polymers, primarily PVC (polyvinyl chloride).^[5]

Historically, workers in PVC plants were often exposed to high levels of VCM. Due to the carcinogenicity of VCM; many of those workers have contracted and died from cancer. The hepatotoxicity of VCM has long been established since the 1930's when the PVC industry was just in its infant stages. In the very first study about the dangers of Vinyl Chloride (VC), published by Patty in 1930, it was disclosed that exposure of test animals to just a single short-term high dose of VC caused liver damage.^[6] In 1949, a Russian publication by Tribukh discussed the finding that VC caused liver injury among workers.^[7] In 1954, Dr. Rex Wilson, Medical Director, and William McCormick, Industrial Hygienist and Toxicologist, both of B.F. Goodrich Chemical, published an article that stated that it was known VC caused liver injury for short-term exposures; but almost nothing was known about its long-term effects. They also stated that long-term animal

toxicology studies should be performed to fill this void of information. It was noted in the study that if a chemical did not justify the cost of testing, and you knew what it could do to workers and the public, the chemical should not be made.^[8] Thereafter, in 1963, Lester and Greenberg published an article reporting their findings from research paid for in part by Allied Chemical. They too found liver damage in test animals from exposures below 500 parts per million (ppm).^[9]

Then, in 1963, a Romanian researcher, Suciu, published his findings of liver disease in VC workers.^[10] In 1968, Mutchler and Kramer, two Dow researchers, reported their finding that exposures as low as 300 ppm caused liver damage in VC workers thus confirming earlier animal data in humans.^[11] In a 1969 presentation given in Japan, Dr. P. L. Viola, a European researcher working for the European VC industry, indicated, "every monomer used in V.C. manufacture is hazardous....various changes were found in bone and liver. Particularly, much more attention should be drawn to liver changes. The findings in rats at the concentration of 4 to 10 ppm are shown in pictures." In light of the finding of liver damage in rats from just 4-10 ppm of VC exposure, Dr. Viola added that he "should like some precautions to be taken in the manufacturing plants polymerizing vinyl chloride, such as a reduction of the threshold limit value of monomer ..."^[12] In 1970, Dr. Viola, reported that test animals exposed to 30,000 ppm of VC developed cancerous tumors. It should be noted that Viola began his research looking for the cause of liver and bone injuries found in VC workers. Dr. Viola's findings in 1970 were a "red flag" to [B.F. Goodrich](#) and the industry.^[13] In 1972, Dr. Maltoni, another Italian researcher for the European VC industry, found liver tumors (including angiosarcoma) from VC exposures as low as 250 ppm for four hours a day.^[14]

In the late 1960's the cancers that all of these studies warned of finally manifested itself in workers. Dr. John Creech from [B.F. Goodrich](#) discovered [angiosarcoma](#) (a very rare cancer) in the liver of a worker at the B.F. Goodrich plant in Louisville, Kentucky. Then, finally, on January 23, 1974, [B.F. Goodrich](#) informed the government and issued a press release stating that it was "investigating whether the cancer deaths of three employees in the polyvinyl chloride operations at its Louisville, Ky. plant were related to occupational causes." By then there really was no doubt that vinyl chloride caused [angiosarcoma](#) of the liver; it had been shown in both animal studies and worker experience.

A 1997 U.S. Centers for Disease Control and Prevention (CDC) report concluded that the development and acceptance by the PVC industry of a closed loop polymerization process in the late 1970s "almost completely eliminated worker exposures" and that "new cases of hepatic angiosarcoma in vinyl chloride polymerization workers have been virtually eliminated."^[15]

According to the [United States Environmental Protection Agency](#) (EPA), "vinyl chloride emissions from polyvinyl chloride (PVC), ethylene dichloride (EDC), and vinyl chloride monomer (VCM)

plants cause or contribute to air pollution that may reasonably be anticipated to result in an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness. Vinyl chloride is a known human carcinogen that causes a rare cancer of the liver."^[16] EPA's 2001 updated Toxicological Profile and Summary Health Assessment for VCM in its Integrated Risk Information System (IRIS) database lowers EPA's previous risk factor estimate by a factor of 20 and concludes that "because of the consistent evidence for liver cancer in all the studies...and the weaker association for other sites, it is concluded that the liver is the most sensitive site, and protection against liver cancer will protect against possible cancer induction in other tissues."^[17]

A 1998 front-page series in the Houston Chronicle claimed the vinyl industry has manipulated vinyl chloride studies to avoid liability for worker exposure and to hide extensive and severe chemical spills into local communities.^[18] Retesting of community residents in 2001 by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR) found dioxin levels similar to those in a comparison community in Louisiana and to the U.S. population.^[19] Cancer rates in the community were similar to Louisiana and US averages.^[20]

Dioxins

The environmentalist group [Greenpeace](#) has advocated the global phase-out of PVC because they claim [dioxin](#) is produced as a byproduct of vinyl chloride manufacture and from incineration of waste PVC in domestic garbage. The European Industry, however, asserts that it has improved production processes to minimize dioxin emissions. Dioxins are a global health threat because they persist in the environment and can travel long distances. At very low levels, near those to which the general population is exposed, dioxins have been linked to immune system suppression, reproductive disorders, a variety of cancers, and endometriosis.^[21] According to a 1994 report by the British firm, ICI Chemicals & Polymers Ltd., "It has been known since the publication of a paper in 1989 that these oxychlorination reactions [used to make vinyl chloride and some chlorinated solvents] generate polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs). The reactions include all of the ingredients and conditions necessary to form PCDD/PCDFs.... It is difficult to see how any of these conditions could be modified so as to prevent PCDD/PCDF formation without seriously impairing the reaction for which the process is designed." In other words, dioxins are an undesirable byproduct of polymerizing PVC and eliminating the production of dioxins while maintaining the polymerization reaction may be difficult. Dioxins created by vinyl chloride production are released by on-site incinerators, flares, boilers, wastewater treatment systems and even in trace quantities in vinyl resins.^[22] The US EPA estimate of dioxin releases from the PVC industry was 13 grams TEQ in 1995, or less than 0.5% of the total dioxin emissions in the US; by 2002, PVC industry dioxin emissions had been further reduced by 23%.^[23]

The largest well-quantified source of dioxin in the US EPA inventory of dioxin sources is barrel burning of household waste.^[24] Studies of household waste burning indicate consistent increases in dioxin generation with increasing PVC concentrations.^[25] According to the EPA dioxin inventory, landfill fires are likely to represent an even larger source of dioxin to the environment. A survey of international studies consistently identifies high dioxin concentrations in areas affected by open waste burning and a study that looked at the homologue pattern found the sample with the highest dioxin concentration was "typical for the pyrolysis of PVC". Other EU studies indicate that PVC likely "accounts for the overwhelming majority of chlorine that is available for dioxin formation during landfill fires."^[26]

The next largest sources of dioxin in the EPA inventory are medical and municipal waste incinerators.^[27] Studies have shown a clear correlation between dioxin formation and chloride content and indicate that PVC is a significant contributor to the formation of both dioxin and PCB in incinerators.^[28]

In February 2007, the Technical and Scientific Advisory Committee of the US Green Building Council (USGBC) released its report on a PVC avoidance related materials credit for the LEED Green Building Rating system. The report concludes that "no single material shows up as the best across all the human health and environmental impact categories, nor as the worst" but that the "risk of dioxin emissions puts PVC consistently among the worst materials for human health impacts."^[29]

See also

[polyvinyl chloride](#)

[Vinyl](#)

External links

Information on the aerosol propellant controversy

ATSDR Toxicological Profile for chloroethene / vinyl chloride

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