15. H. E. Frey, *Chemical Economics Handbook Marketing Research Report on Vinyl Acetate, Polyvinyl Acetate, and Polyvinyl Alcohol*, Stanford Research Institute, Menlo Park, Calif., Nov. 1979.
16. J. E. Moreland, *Text. Chem. Color.* 12(4), 21 (Apr. 1980).
17. D. L. Nehrenberg, *AATCC RA73 Research Committee Warp Size Symposium, Atlanta, March 7, 1981*, Atlanta, Ga., published by DuPont Co., Wilmington, Del.
18. G. Davidowich and G. D. Miller, *Pulp Pap.* 50(8), 118 (July 1976).

General References

Ref. 8 is also a general reference.
J. G. Pritchard, *Poly(Vinyl Alcohol) Basic Properties and Uses*, Gordon and Breach, Science Publishers, Inc., New York, 1970.
R. L. Davidson, ed., *Handbook of Water-Soluble Gums and Resins*, McGraw-Hill Book Company, New York, 1980, Chapt. 20.
M. K. Lindemann in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. 14, John Wiley & Sons, Inc., New York, 1971, p. 149.

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VINYL CHLORIDE AND POLY(VINYL CHLORIDE)

Vinyl chloride. 865
Poly(vinyl chloride). 886

VINYL CHLORIDE

Vinyl chloride [*75-01-4*], CH_2=CHCl, by virtue of the wide range of applications for its polymers in both flexible and rigid forms, is one of the largest commodity chemicals in the United States and is an important item of international commerce. Growth in vinyl chloride production is directly related to demand for its polymers and, on an energy-equivalent basis, rigid poly(vinyl chloride) [*9002-86-2*] (PVC) is one of the most energy-efficient construction materials available (See Engineering plastics). Initial development of the vinyl chloride industry stemmed from the discovery that, with plasticizers, PVC can be readily processed and converted into a rubbery product (1). However, it was not until after World War II that vinyl chloride production grew rapidly as a result of the increased volume of PVC products for the consumer market.

Vinyl chloride was first prepared from the reaction of dichloroethane with alcoholic potash (2). On prolonged exposure to sunlight in a sealed tube, white flakes deposited from the vinyl chloride. This white solid was studied in 1872 and was described as *Kaperenchorid*, empirical formula $(C_2H_3Cl)_n$ (3). The reaction between hydrogen chloride and acetylene was studied and, in 1912, a patent was obtained for the use of mercuric chloride as a catalyst for this reaction and established an effective industrial

route to vinyl chloride (4). The acetylene-based process has been supplanted by a balanced process from ethylene and chlorine in which vinyl chloride is made by pyrolysis of ethylene dichloride (1,2-dichloroethane) (see also Chlorocarbons and chlorohydrocarbons).

Vinyl chloride, chloroethylene, is a colorless gas at normal temperature and pressure. Industrially, vinyl chloride is handled as the liquid (bp, −13.4°C). However, no human contact with the liquid is allowed. Vinyl chloride is an OSHA-regulated material.

Physical Properties

The physical properties of vinyl chloride are listed in Table 1. Vinyl chloride is slightly soluble in water, 0.11 g/100 g H_2O at 25°C. The solubility of water in vinyl chloride at −15°C is 0.03 g/100 g CH_2=CHCl. Vinyl chloride is soluble in hydrocarbons, oil, alcohol, chlorinated solvents, and most common organic liquids.

Table 1. Physical Properties of Vinyl Chloride

Property	Value	Refs.
molecular weight	62.499	5
melting point, °C	−153.8	5
boiling point, °C	−13.4	5
specific heat, J/(kg·K)[a]		
vapor at 20°C	858	6
liquid at 20°C	1352	6
critical temperature, °C	156.6	5
critical pressure, MPa[b]	5.60	5
critical volume, cm³/mol	169	5
compressibility factor	0.265	5
Pitzer's acentric factor	0.122	5
dipole moment, C·m[c]	5.0×10^{-30}	5
latent heat of fusion, J/g[a]	75.9	
latent heat of evaporation, J/g[a]	330	5
standard enthalpy of formation, kJ/mol[a]	35.18	5
standard Gibbs energy of formation, kJ/mol[a]	51.5	5
vapor pressure, kPa[b]		
−30°C	50.7	5, 7
−20°C	78.0	
−10°C	115	
0°C	164	
viscosity, mPa·s (= cP)		
−40°C	0.3388	5
−30°C	0.3028	
−20°C	0.2730	
−10°C	0.2481	
explosive limits in air, vol %	4–22	8
self-ignition temperature, °C	472	8
flash point (open-cup), °C	−77.75	8
liquid density (at −14.2°C), g/cm³	0.969	5

[a] To convert J to cal, divide by 4.184.
[b] To convert MPa to psi, multiply by 145.
[c] To convert C·m to D, divide by 3.336×10^{-30}.

Reactions

Polymerization. The most important reaction of vinyl chloride is its polymerization and copolymerization in the presence of a radical-generating catalyst (see below).

Substitution at the Carbon–Chlorine Bond. Vinyl chloride is generally considered to be inert to nucleophilic replacement compared to alkyl halides. However, recent work has shown that the chlorine can be exchanged rapidly under nucleophilic conditions in the presence of palladium and other transition metals (9–15). Vinyl acetates, alcoholates, vinyl esters, and vinyl ethers can be readily produced from these reactions. The mechanism for the reaction generally is thought to proceed through an addition–elimination path with initial formation of a π-complex (9,16).

Reaction of vinyl chloride and carbon monoxide with low valent transition metals yields acryloyl chloride (16). The mechanism for this reaction may proceed by oxidative addition of a low valent metal. Use of alcohol as a solvent for carbonylation with reduced Pd catalysts gives vinyl esters (17–18). Addition of radical scavengers to the reaction solutions does not inhibit the reactions, showing that the products do not form by a free-radical path during the oxidative-addition reaction.

Reaction of vinyl chloride with butyllithium and then with CO_2 in ether, at low temperatures, gives high yields of α,β-unsaturated carboxylic acids (19). When vinyl chloride reacts with borane in THF (tetrahydrofuran) solution, chlorine is replaced by hydrogen to yield ethylene (20).

Vinylmagnesium chloride (Grignard reagent) can be directly prepared from vinyl chloride (21). This compound can be used to add a vinyl anion to numerous organic functional groups in the normal Grignard reaction (qv) sequence. The vinylmagnesium compound can be coupled with cuprous chloride at −60°C to give butadiene (22). It also adds to α,β-unsaturated compounds giving γ,δ-unsaturated compounds (23). Vinyl ketones and alcohols can also be prepared by the addition of vinylmagnesium chloride to organic acids (24–25).

A useful vinyllithium compound can be formed directly from vinyl chloride by means of a lithium dispersion containing 2 wt % sodium at 0–10°C (26). The vinyllithium-compound is a reactive intermediate for the formation of vinyl alcohols from aldehydes, vinyl ketones from organic acids, vinyl sulfides from disulfides, and monosubstituted alkenes from organic halides (27–29). It can also be converted to a vinyl copper compound, which can be used to introduce a vinyl group stereoselectively into a variety of α,β-unsaturated systems (30). Vinyllithium reagents also can be converted to secondary alcohols with trialkylboranes (31) (see also Hydroboration).

Ethyl vinyl ether is produced from vinyl chloride and sodium ethoxide (32) (see Vinyl polymers, vinyl ether, monomers and polymers). A wide range of alcoholates can take part in this reaction. The reaction of vinyl chloride with hydrogen fluoride over a Cr_2O_3-on-Al_2O_3 catalyst at 380°C yields vinyl fluoride (33).

Oxidation. The oxidation of vinyl chloride by a chlorine-atom-sensitized reaction yields 74 vol % ClCHO and 25 vol % CO in the gas phase with 30–32% conversion (34). The reaction proceeds by a nonchain path at high oxygen–chlorine ratios. The reaction with triplet oxygen [O(3p)] atoms gives high yields of CO and chloroacetaldehyde, (CH_2ClCHO); the rate of this reaction with O(3p) atoms has been reported (35). Oxidation of vinyl chloride with oxygen in the gas phase above 250°C produces no C_2 carbonyl compounds; the main products are CO, HCl, HCO_2H, and ClCHO. This

Refs.
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oxidation reaction proceeds by a nonradical path which is unique to vinyl chloride among the chloroolefin compounds. The ozone reaction with vinyl chloride can be used to remove it from gas streams in a vinyl chloride production plant (36–37). Ozonolysis in liquid or gas phase gives formic acid and formyl chloride. At −15° to −20°C, vinyl chloride reacts with oxygen, with uv initiation, to give a peroxide $+OCH_2CHClO+_n$ (38). On heating to 35°C, this peroxide decomposes to formaldehyde, CO, and HCl. In aqueous solution at pH 10, it is possible to oxidize vinyl chloride to CO_2 with $KMnO_4$. This oxidation can be used for wastewater purification (39–40) (see Water, water reuse). The reaction of hypochlorous acid with vinyl chloride yields chloroacetaldehyde (41).

Addition. The chlorination of vinyl chloride can proceed by either an ionic or a radical path. In the liquid phase and in the dark, 1,1,2-trichloroethane forms by an ionic path when a metal catalyst ($FeCl_3$) is used. The same product forms in radical reactions at up to 250°C (42). The photochemically initiated chlorination also produces 1,1,2-trichloroethane by a radical path (43). Above 250°C, the chlorination of vinyl chloride gives unsaturated chloroethylenes produced by dehydrochlorination of 1,1,2-trichloroethane. The presence of small amounts of oxygen greatly accelerates the rate of the radical-chain chlorination reaction at above 250°C (44). Other halogens can be added to vinyl chloride to form similar 1,2-addition products but have not been thoroughly studied. Sulfuryl chloride, (SO_2Cl_2), in the presence of pyridine reacts with vinyl chloride to give 1,1,2-trichloroethane and 1,2-dichloroethanesulfonyl chloride. The addition reaction of hydrogen chloride and hydrogen iodide to vinyl chloride proceeds by an ionic mechanism (45–46). The addition of hydrogen bromide involves a chain reaction in which a bromine atom is the chain carrier. The product of the addition of hydrogen halides to vinyl chloride by either mechanism is the 1,1-adduct. Zinc chloride on Celite is an effective catalyst for the addition of HCl to vinyl chloride in the gas phase.

Various vinyl chloride adducts can be formed under acid-catalyzed Friedel-Crafts (qv) conditions. Vinyl chloride can be condensed with ethyl chloride to yield 1,1-dichloroethane and 1,1,3-trichlorobutane (47). The reaction of 2-chloropropane with vinyl chloride yields 1,1-dichloro-3-methylbutane (47). At 0–5°C, vinyl chloride reacts with benzene resulting in a mixture of 1-chloroethylbenzene and 1,1-diphenylethane (48–49). With aromatics, the initially formed product reacts faster with a second aromatic molecule to produce the 1,1-substituted products. The rapid reaction of the initially formed product with toluene leads to a 68% yield of 1,1-ditolylethane, whereas anisole (methoxybenzene) gives a 42% yield of 1,1-di-*p*-anisylethane (50–51). Phenol also reacts to give *p*-vinylphenol (52). Condensation of vinyl chloride with formaldehyde and hydrogen chloride (Prins reaction) yields 3,3-dichloro-1-propanol and 2,3-dichloro-1-propanol (53–54). In the presence of iron pentacarbonyl, bromoform ($CHBr_3$) adds to vinyl chloride (55). Vinyl chloride can be hydrogenated over a 0.5% Pt/Al_2O_3 catalyst to ethyl chloride and ethane (56). This reaction is zero order in olefin and first order in hydrogen.

Pyrolysis. Vinyl chloride is more stable than saturated chloroalkanes to thermal pyrolysis. Because of this, one of the principal reactions for its production is the thermal dehydrochlorination of 1,2-dichloroethane. When vinyl chloride is heated to 450°C, small amounts of acetylene form (57). Although little conversion of vinyl chloride occurs, even at 525–575°C, the main products are chloroprene and acetylene. The use of HCl during the pyrolysis of vinyl chloride lowers the amount of chloroprene formed.

The combustion of vinyl chloride in air at 510–795°C produces mainly carbon dioxide and hydrogen chloride along with carbon monoxide. A trace of phosgene also forms (58). When dry and in contact with metals, vinyl chloride does not decompose below 450°C. However, in the presence of water, vinyl chloride can corrode iron, steel, and aluminum because of the presence of trace amounts of hydrogen chloride. This hydrogen chloride may result from the hydrolysis of the peroxide formed between oxygen and vinyl chloride (38).

Manufacture

Vinyl chloride monomer was first produced commercially in the 1930s from the reaction of hydrogen chloride with acetylene (qv) derived from calcium carbide (see Acetylene-derived chemicals). As demand for vinyl chloride increased, more economical feedstocks were sought. After ethylene (qv) became plentiful in the early 1950s, commercial processes were developed to produce vinyl chloride from ethylene and chlorine. These processes included direct chlorination of ethylene to produce 1,2-dichloroethane (ethylene dichloride, EDC) and pyrolysis of EDC to produce vinyl chloride. However, since the EDC cracking process also produced HCl as a coproduct, the industry did not expand immediately except in conjunction with acetylene-based technology. The development of ethylene-oxychlorination technology in the late 1950s encouraged new growth in the vinyl chloride industry. In this process, ethylene reacts with HCl and oxygen to produce ethylene dichloride. Combining the component processes of direct chlorination, EDC pyrolysis, and oxychlorination provided the so-called balanced process for production of vinyl chloride from ethylene and chlorine with no net consumption or production of HCl.

Although a small fraction of the world's vinyl chloride capacity is still based on acetylene or mixed acetylene–ethylene feedstocks, most production is conducted by the balanced process based on ethylene and chlorine (59). The reactions for each of the component processes are shown in equations 1–3 and the overall reaction is given by equation 4:

Direct chlorination $$CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl \quad (1)$$

Oxychlorination $$CH_2{=}CH_2 + 2\,HCl + \tfrac{1}{2}\,O_2 \rightarrow ClCH_2CH_2Cl + H_2O \quad (2)$$

Ethylene dichloride pyrolysis $$2\,ClCH_2CH_2Cl \rightarrow 2\,CH_2{=}CHCl + 2\,HCl \quad (3)$$

Overall reaction $$2\,CH_2{=}CH_2 + Cl_2 + \tfrac{1}{2}\,O_2 \rightarrow 2\,CH_2{=}CHCl + H_2O \quad (4)$$

In a typical balanced plant producing vinyl chloride from ethylene dichloride, all the HCl produced in ethylene dichloride pyrolysis is normally used as the feed for oxychlorination. On this basis, EDC production is about evenly split between direct chlorination and oxychlorination, and there is no net production or consumption of HCl. The three principal operating steps used in the balanced process for ethylene-based vinyl chloride production are shown in the block flow diagram in Figure 1, and a schematic of the overall process for a conventional plant is shown in Figure 2. A typical material balance for this process is given in Table 2.

Direct Chlorination of Ethylene. Direct chlorination of ethylene to ethylene dichloride is conducted by mixing ethylene and chlorine in liquid EDC. The reaction is a homogeneous catalytic reaction in the liquid phase, but under typical process conditions the reaction rate is controlled by mass transfer with absorption of ethylene

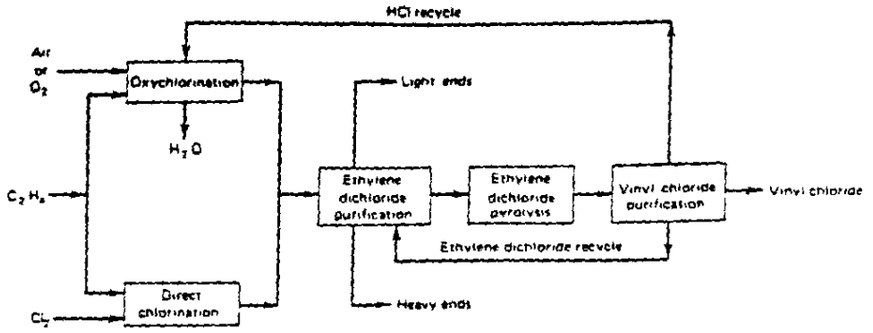

Figure 1. Principal steps in balanced vinyl chloride process.

as the limiting factor (61). Ferric chloride is a highly selective and efficient catalyst for this reaction and is used in most commercial processes (59). The addition reaction proceeds through a polar mechanism, by which the catalyst may polarize chlorine, as shown in equation 5. The polarized chlorine molecule then acts as an electrophilic

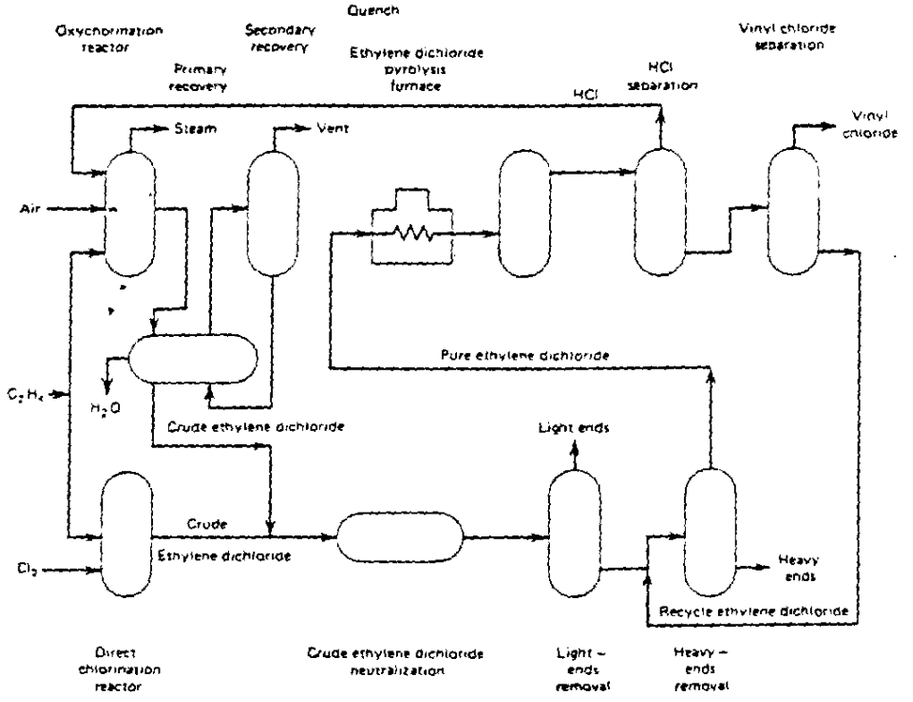

Figure 2. Typical balanced vinyl chloride process with air-based oxychlorination.

Table 2. Process[a]

Compon
C_2H_4
Cl_2
N_2
O_2
CO_2
CO
$ClCH_2Cl$
HCl
H_2O
NaOH
NaCl
lights
heavies
$CH_2=Cl$
Total kg/k chlo

[a] Ref. 60
[b] Inerts p
[c] Represe recycle

reagent 6):

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Table 2. Typical Material Balance for Vinyl Chloride Production by the Air-Based Balanced Ethylene Process[a]

Components, kg	Raw materials	Intermediates	By-products	Aqueous streams	Vent streams: Direct chlorination[b]	Vent streams: Oxychlorination	Vent streams: Distillation columns	Product
C_2H_4	0.4656				0.0025			
Cl_2	0.5871				0.0001		0.0001	
N_2	0.5782					0.5779	0.0003	
O_2	0.1537					0.0214		
CO_2	0.0003					0.0116		
CO						0.0032		
$ClCH_2CH_2Cl$		1.6370[c]	0.0029		0.0016	0.0017	0.0045	
HCl		0.6036						
H_2O	0.0171		0.1438	0.1196		0.0413		
NaOH				0.0008				
NaCl				0.0014				
lights			0.0029		0.0003	0.0025		
heavies			0.0023					
$CH_2{=}CHCl$			0.0008		0.0001	0.0012	0.0024	1.0000
Total, kg/kg vinyl chloride	*1.8020*	*2.2406*	*0.1527*	*0.1218*	*0.0046*	*0.6608*	*0.0073*	*1.0000*

[a] Ref. 60.

[b] Inerts present in chlorine feed are emitted in this vent stream.

[c] Represents EDC necessary for a stoichiometric balance, including that converted to by-products but no recycled EDC.

reagent to attack the double bond of ethylene, thus facilitating chlorine addition (eq. 6):

$$FeCl_3 + Cl_2 \rightleftharpoons FeCl_4^- \cdots Cl^+ \quad (5)$$

$$FeCl_4^- \cdots Cl^+ + CH_2{=}CH_2 \rightarrow FeCl_3 + ClCH_2CH_2Cl \quad (6)$$

The direct chlorination reaction may be run with a slight excess of ethylene or chlorine, depending on the methods available for handling effluent gases from the reactor. Conversion of the limiting component is essentially 100%, and selectivity to ethylene dichloride is greater than 99% (59). The main by-product is 1,1,2-trichloroethane, which probably forms through radical reactions beginning with homolytic dissociation of a small fraction of the chlorine. However, oxygen, which is frequently present as an impurity in chlorine, tends to increase selectivity to EDC by inhibition of free-radical reactions that produce 1,1,2-trichloroethane. Amides, eg, *N,N*-dimethylformamide also increase selectivity to EDC (62).

The heat of reaction is removed either through conventional water cooling for reactors that operate at moderate temperatures of 50–65°C, or by operating the reactor at the boiling point of ethylene dichloride and allowing the pure product to vaporize (63–65). For reactors equipped with liquid product removal, the EDC is usually treated to remove ferric chloride. The latter, which would lead to rapid fouling of the EDC cracking reactor, can be removed by washing with water or by adsorption on a solid (66–67). With dry feedstocks and good temperature control, carbon steel can be used in the direct chlorination reactor and auxiliary equipment (68). Compared with direct chlorination, the oxychlorination process is characterized by higher capital investment,

higher operating costs, and less-pure EDC product. However, the use of the oxychlorination process is dictated by the need to consume the HCl generated in EDC pyrolysis.

Oxychlorination of Ethylene. In the oxychlorination process, ethylene reacts with dry hydrogen chloride and either air or pure oxygen to produce EDC and water. Various commercial processes for oxychlorination differ somewhat because they were developed independently by several vinyl chloride producers (59,69). In general, however, the reaction is carried out in the vapor phase in either a fixed- or fluid-bed reactor containing a modified Deacon catalyst. However, oxychlorination of ethylene occurs readily at temperatures well below that required for the oxidation of hydrogen chloride in the Deacon process for chlorine production (70). Oxychlorination catalysts generally contain copper chloride as the main active ingredient, but they may also contain numerous additives impregnated on a porous support, eg, alumina, silica–alumina, diatomaceous earth, etc (71–72). Although the detailed catalytic mechanism is not known, copper(II) chloride is generally recognized as the active chlorinating agent. The copper(I) chloride produced during the ethylene chlorination step is rapidly reconverted to copper(II) chloride under reaction conditions, and the presence of some copper(I) is thought to be advantageous because it readily complexes with ethylene, bringing it into contact with copper(II) chloride for a long enough time for chlorination to occur (59). A very simple representation of this heterogeneous catalytic cycle is given in equations 7–9.

$$CH_2{=}CH_2 + 2\,CuCl_2 \rightarrow 2\,CuCl + ClCH_2CH_2Cl \quad (7)$$

$$\tfrac{1}{2}\,O_2 + 2\,CuCl \rightarrow CuOCuCl_2 \quad (8)$$

$$2\,HCl + CuOCuCl_2 \rightarrow 2\,CuCl_2 + H_2O \quad (9)$$

Another suggested mechanism involves initial formation of ethylene oxide as the possible rate-limiting step in the reaction (73).

Since commercial oxychlorination processes differ somewhat with either fluid- or fixed-bed reactors and either air or oxygen feed, the operating conditions, feed ratios, conversions, and yields also vary, depending on the particular combination used in production and on the methods employed for secondary recovery of feedstock and product. For any particular combination of reactor type and oxidant, however, good temperature control of this highly exothermic reaction is essential for efficient production of ethylene dichloride. Increasing temperatures in the reactor lead to increased by-product formation, mainly through increased combustion of ethylene to carbon oxides and increased cracking of EDC. Cracking, ie, dehydrochlorination, of EDC results in the formation of vinyl chloride, and subsequent oxychlorination and cracking steps lead progressively to by-products with higher levels of chlorine substitution. High temperatures can also lead to deactivation of the catalyst through increased sublimation of copper(II) chloride.

Fluidized-bed reactors typically are cylindrical vessels equipped with internal cooling coils for heat removal and either external or internal cyclones to minimize catalyst carry-over (see Fluidization). Fluidization of the catalyst assures intimate contact between feed and product vapors, catalyst, and heat-transfer surfaces and results in a uniform temperature within the reactor (74). Reaction heat can be removed by the generation of steam within the cooling coils or by some other heat-transfer medium. An operating temperature of 220–235°C and reactor gauge pressures of 150–500 kPa (22–73 psig) are typical for oxychlorination with a fluidized catalyst. With

these operating conditions, fluid-bed reactors are commonly constructed with a carbon-steel shell and a corrosion-resistant alloy for the internal parts (68).

Fixed-bed reactors resemble multitube heat exchangers with the catalyst packed in vertical tubes held in a tubesheet at top and bottom. Uniform packing of catalyst within the tubes is important to ensure uniform pressure drop, flow, and residence time through each tube. Reaction heat can be removed by the generation of steam on the shell side of the reactor or by some other heat-transfer fluid. However, temperature control is more difficult in a fixed-bed reactor than in a fluid-bed reactor because localized hot spots tend to develop in the tubes. The tendency to develop hot spots can be minimized by packing the reactor tubes with active catalyst and inert diluent mixtures in certain proportions so that there is low catalyst activity at the inlet but that the activity steadily increases to a maximum at the outlet (59). Another method is packing the tubes with catalysts having progressively higher loadings of copper chloride so as to provide an activity gradient along the length of the tubes. Multiple reactors are also used in fixed-bed oxychlorination primarily to control heat release by staging oxidant feed, ie, air or oxygen. Each successive reactor may also contain catalyst with progressively higher loadings of copper chloride. These methods of staging oxidant and of grading the catalyst activity tend to flatten the temperature profile and allow improved temperature control. Compared with the fluid-bed oxychlorination process, the fixed-bed process generally operates at higher temperatures (230–300°C) and gauge pressures (150–1400 kPa (22–203 psig)). With these operating conditions, a corrosion-resistant alloy is used for the reactor tubes; tubesheets and reactor heads are clad with nickel on steel; and the reactor shell is constructed of carbon steel (68).

In the air-based oxychlorination process with either fluid- or fixed-bed reactors, ethylene and air are fed in slight excess of stoichiometric requirements to ensure high conversion of HCl and to minimize losses of excess ethylene that remains in the vent gas after product condensation. Under these conditions, typical feedstock conversions are 94–99% for ethylene and 96–99% for HCl with EDC selectivities of 93–96%. Downstream product recovery involves cooling the reactor exit gases by either direct quench or with a heat exchanger and condensation of the ethylene dichloride and water, which are then separated by decantation (Fig. 2). The remaining gases still contain 1–5 vol % EDC, so they are further processed in a secondary recovery system involving either solvent absorption or a refrigerated condenser. In air-based processes operating with high ethylene conversion, the dilute ethylene remaining in the vent is generally incinerated; but in those operating at lower conversion, various schemes are first used to recover unconverted ethylene, usually by direct chlorination to EDC (75–76).

The use of oxygen instead of air in the oxychlorination process with either fixed- or fluid-bed reactors permits operation at lower temperatures and results in improved operating efficiency and product yield (69,76). Unlike the air-based process, ethylene is generally fed into an oxygen-based reactor in somewhat larger excess over stoichiometric requirements. Reactor exit gases are cooled, purified from traces of unconverted HCl, separated from EDC and water by condensation, recompressed to the reactor inlet pressure, reheated, and recycled to the oxychlorination reactor. Recycle of the effluent gases permits lower ethylene conversion per pass through the reactor with minimal loss in overall ethylene yield. A small amount of reactor off-gas, typically 1–5 vol %, is continuously purged from the system to prevent accumulation of im-

purities, eg, carbon oxides, nitrogen, argon, and unreacted hydrocarbons, which either form in the oxychlorination reactor or enter the process as impurities in the feed streams. An important advantage of oxygen-based oxychlorination technology over air-based operation is the drastic reduction of the vent-gas volume discharged by the oxychlorination process. Since nitrogen is no longer present in the reactor feed streams, only a small amount of purge gas is vented. On a volume comparison, the reduced purge-gas stream would typically amount to only 1–5% of the vent-gas volume for air-based operation. Air-based processes release significant quantities of vent gases to the atmosphere, generally after treatment by incineration and scrubbing. Typically, for every kilogram of EDC produced by oxychlorination, ca 0.7–1.0 kg of vent gases is emitted from the air-based process (see Table 2). Therefore, for an air-based, balanced, vinyl chloride plant with a rated capacity of 450,000 metric tons per year of vinyl chloride, the total vent-gas volume released to the atmosphere would be 7–10 m^3/s (245–353 ft^3/s). However, the vent gas consists mainly of nitrogen, some unconverted oxygen, and small amounts of carbon oxides. Depending on the type of oxychlorination process involved, however, there are differing levels of undesirable impurities, ethylene, and chlorinated hydrocarbons in the oxychlorination vent gas.

Chlorinated by-products of ethylene oxychlorination typically include 1,1,2-trichloroethane; chloral (trichloroacetaldehyde); trichloroethylene; 1,1-dichloroethane; *cis*- and *trans*-1,2-dichloroethylenes; ethyl chloride; vinyl chloride; 1,1-dichloroethylene (vinylidene chloride); mono-, di-, tri-, and tetrachloromethanes (methyl chloride, methylene chloride, chloroform, and carbon tetrachloride); and higher boiling compounds. All of these by-products present problems and their production should be minimized in order to lower raw-material costs, lessen the difficulties in ethylene dichloride purification, prevent fouling in the pyrolysis reactor, and minimize by-product handling and disposal. Chloral, in particular, should be removed because it tends to polymerize in the presence of strong acids forming solids which foul and clog operating lines and controls (59). Oxychlorination-reactor feed purity can also contribute to by-product formation. Normally, however, the only problem is with low levels of acetylene present in the HCl from the EDC cracking process. Since acetylene in the feed causes the formation of highly chlorinated by-products and tars, selective hydrogenation of this acetylene to ethylene and ethane is practiced by many companies (77).

Purification of Ethylene Dichloride for Pyrolysis. By-products contained in EDC from the three main processes must be removed; these include by-products in EDC from direct chlorination, and oxychlorination and recovered EDC from the cracking process. 1,2-Dichloroethane used for pyrolysis to vinyl chloride must be of high purity, ie, usually greater than 99.5 wt %, because the ethylene dichloride cracking process is exceedingly susceptible to inhibition and fouling by trace quantities of impurities (59,78). It must also be dry (no separate water phase and less than 10 ppm of total dissolved water) to prevent excessive corrosion downstream of the pyrolysis unit. Inadvertent moisture pickup, however, is always possible; in such cases, the corrosion of steel equipment tends to be the greatest in reboilers, the bottom section of distillation columns, bubble caps, plates, condensers, water separators, valves, pumps, and fittings (68).

Direct chlorination generally produces EDC with a purity greater than 99.5 wt % and, except for removal of the $FeCl_3$, little further purification is necessary. Ferric chloride can be removed by adsorption on a solid, or the EDC can be distilled from

the $FeCl_3$ in a boiling reactor. Alternatively, the ferric chloride can be removed by washing with water, usually in conjunction with EDC from the oxychlorination process.

Ethylene dichloride from the oxychlorination process is generally less pure than direct-chlorination EDC and, thus, is usually washed with water and then with caustic solution to remove chloral and other water-extractable impurities (79). Low boiling impurities and water are taken overhead in a first (light-ends) distillation column, and then pure dry EDC is taken overhead in a second (heavy-ends) column (see Fig. 2).

Ethylene dichloride recovered from the cracking process contains an appreciable number of impurities. Two of these, trichloroethylene and chloroprene (2-chloro-1,3-butadiene), are not readily removable by distillation and necessitate the use of other treatments (59). Chloroprene, if not altered by chemical treatment, concentrates in the light-ends column where it can polymerize to solid or rubbery materials which seriously foul this column (see Chlorocarbons, chloroprene). Trichloroethylene forms an azeotrope with EDC, boiling very close to EDC; if it is allowed to accumulate, it leads to inhibition of the cracking reaction and increased fouling rates (see Chlorocarbons, trichloroethylene). Both impurities can be removed by subjecting the recycle ethylene dichloride stream to chlorination prior to distillation (80–82). Treatments with HCl and hydrogenation have also been patented as methods for removal of chloroprene (83–86).

Ethylene Dichloride Pyrolysis to Vinyl Chloride. Thermal cracking of EDC to vinyl chloride and hydrogen chloride occurs as a homogeneous, first-order free-radical chain reaction. The accepted general mechanism involves the four steps shown in equations 10–13 (87–89):

Initiation	$ClCH_2CH_2Cl \rightarrow ClCH_2\dot{C}H_2 + Cl\cdot$	(10)
Propagation	$Cl\cdot + ClCH_2CH_2Cl \rightarrow ClCH_2\dot{C}HCl + HCl$	(11)
	$ClCH_2\dot{C}HCl \rightarrow CH_2{=}CHCl + Cl\cdot$	(12)
Termination	$Cl\cdot + ClCH_2\dot{C}H_2 \rightarrow ClCH{=}CH_2 + HCl$	(13)

Reactions 11 and 12 are the chain-propagation steps, because each elementary step consumes one of the two chain carriers and simultaneously produces the other. The net effect of reactions 11 and 12 is continuation of the chain by conversion of EDC to vinyl chloride. Thus, the two chain carriers are chlorine atoms and 1,2-dichloroethyl radicals. In general, anything consuming a chain carrier is an EDC cracking inhibitor and anything producing a chain carrier is a promoter. That is, any molecular or radical species that consumes a chain carrier without simultaneously producing either 1,2-dichloroethyl radicals or chlorine atoms is an EDC cracking inhibitor, eg, propylene. The allylic hydrogen atoms of propylene can be easily abstracted by one of the chain carriers, either 1,2-dichloroethyl radicals or chlorine atoms. The resulting allyl radical can then combine with a chlorine atom forming allyl chloride. Since the same sequence can occur two more times, one molecule of propylene can consume up to six chain carriers. Reaction initiators or accelerators include carbon tetrachloride, chlorine, bromine, iodine, or oxygen (87). More recently, however, exclusion of oxygen is claimed to result in considerably less fouling on the pyrolysis tube walls (90).

The endothermic cracking of ethylene dichloride is relatively clean at atmospheric pressure and temperatures of 425–550°C. Commercial operations, however, generally

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The endothermic cracking of ethylene dichloride is relatively clean at atmospheric pressure and temperatures of 425–550°C. Commercial operations, however, generally

operate at gauge pressures up to 2.5–3.0 MPa (360–435 psig) and temperatures of 500–550°C in order to provide better heat transfer, reduced equipment size, and easier separation of HCl from vinyl chloride by fractional distillation. Ethylene dichloride conversion levels per pass through the pyrolysis reactor are normally maintained at 50–60% at residence times of 2–30 s, with selectivities to vinyl chloride of 96 to >99% (59). Increasing cracking severity gives somewhat higher EDC conversion but also results in lower selectivities to vinyl chloride. Since some of the by-products generated during cracking act as inhibitors to the free-radical sequence, increasing cracking severity leads to progressively smaller increases in EDC conversion and progressively larger problems with pyrolysis-tube coking and downstream-product purification.

An important processing requirement in EDC cracking is rapid cooling or quenching of the reaction mixture. If cooling is done too slowly, substantial yield losses to heavy ends and tars result (84,91–95). Therefore, the hot effluent gases are normally quenched and partially condensed by direct contact with cold EDC in a quench tower. Although each producer of vinyl chloride has its own minor modifications in the HCl–vinyl chloride recovery section, in general the quench column effluent is distilled to remove first HCl and then vinyl chloride (Fig. 2). The vinyl chloride is generally further treated to produce specification product, recovered HCl is sent to the oxychlorination process, and unconverted EDC is purified for removal of light and heavy ends prior to recycle to the cracking furnace. The light and heavy ends either are further processed or are disposed of by incineration or other methods. By-products from EDC pyrolysis can include acetylene, ethylene, methyl chloride, butadiene, vinylacetylene, benzene, chloroprene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, and other chlorinated hydrocarbons (59). Most of these impurities remain in the unconverted ethylene dichloride fraction and are subsequently removed in EDC purification as light and heavy ends. Ethylene and acetylene codistill with the HCl and are routed back to the oxychlorination reactor after optional hydrogenation of the acetylene to ethylene. Methyl chloride and butadiene tend to codistill with the vinyl chloride, depending on the efficiency of the vinyl chloride fractional distillation system. Addition of chlorine or carbon tetrachloride to the cracker feed is claimed to suppress methyl chloride formation (96). Removal of butadiene, a contaminant which can interfere with polymerization of vinyl chloride, has been done by treatment with chlorine, anhydrous HCl, or selective hydrogenation (97–99).

By-Product Disposal. Disposal of by-products from vinyl chloride manufacturing processes involves a number of methods because a variety of gaseous, organic liquid, and aqueous streams must be handled. Vent-gas streams from various units may contain small amounts of HCl, vinyl chloride, chlorine, ethylene, methane, and carbon monoxide. These streams can sometimes be treated chemically or by scrubbing, sorption, or other methods to recover some chemicals when economically justified. For objectionable components remaining in the vent-gas streams, however, the common cleaning technique is either incineration or catalytic combustion followed by removal of HCl from the vent gases (see Incinerators; Exhaust control, industrial). Organic liquid streams include the light and heavy ends from ethylene dichloride purification (see Fig. 2 and Table 2). The light ends contain mainly ethyl chloride, *cis*- and *trans*-1,2-dichloroethylene, chloroform, and carbon tetrachloride. The heavy ends contain mostly 1,1,2-trichloroethane, lesser concentrations of tetrachloroethanes, chlorinated butanes, chlorinated aromatics, and many other compounds present in

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smaller amounts. These streams are sometimes fractionated to recover useful components, and the remaining by-products are incinerated and scrubbed to remove chlorine. Another method involves combining all liquid by-product streams and passing them along with air into a fluidized-bed, catalytic oxidation reactor (100). The resulting combustion product stream, consisting essentially of HCl, H_2O, N_2, O_2, and carbon oxides, is fed directly into an oxychlorination reactor where the HCl content is recovered as ethylene dichloride. Further, the heat of combustion is recovered as high pressure steam in a manner similar to that in fluid-bed oxychlorination processes. Process water streams from vinyl chloride manufacture are typically steam-stripped to remove volatile organics, neutralized, and then treated in an activated sludge system to remove nonvolatile organics remaining in the water (101).

Economic Aspects

Yearly U.S. production volumes and prices of vinyl chloride are listed in Table 3. The cost of vinyl chloride is not as vulnerable to the increasing cost of hydrocarbon, since 56% of the compound is chlorine. The cost of chlorine has not increased as rapidly as the hydrocarbon portion. The lower relative cost of poly(vinyl chloride) has allowed it to compete effectively with metals in the housing and automobile industries.

U.S. production and capacities are listed in Table 4. Worldwide production capacity of each country for vinyl chloride is listed in Table 5. With the global increase in vinyl chloride capacity in the industrialized nations, there will be little opportunity for significant increase in the exporting of vinyl chloride as 1,2-dichloroethane from the United States. Also, many poly(vinyl chloride) producers are manufacturing vinyl chloride.

Environmental Considerations

Vinyl chloride emissions in the balanced process occur from a number of sources, but the main ones are the vinyl chloride purification system vents and the product-loading facility vents. Losses from the purification system are continuous and those from the loading system are intermittent. In 1974, the EPA estimated typical vinyl chloride plant emissions in terms of the source and kilograms of vinyl chloride lost per 100 kg vinyl chloride produced as follows: vinyl chloride finishing column, 0.24

Table 3. U.S. Vinyl Chloride Production and Prices[a]

Year	Production, 1000 t	List price, ¢/kg
1955	240	23.1
1960	470	27.6
1965	907	17.6
1970	1833	10.5
1975	1903	19.8–26.5
1979	3422	33.1
1980	2933	48.5
1981	3005	48.5

[a] Ref. 102.

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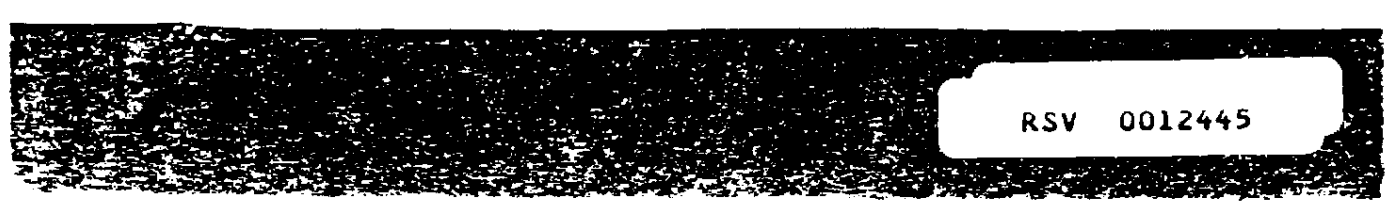

	Capacity, 1000 t	Remarks
	277	became sole owner of Monochem capacity, Jan. 1982
	318	Conoco purchased by E. I. du Pont de Nemours & Co., Inc., 1981
	68	
	340	
	567	
	136	
	136	purchased Imperial Chemical Industries, Ltd. plant, Dec. 1980
	240	
	454	
	454	
	454	purchased Diamond-Shamrock LaPorte plant, Jan., 1982
	0	scheduled startup of a 726,000-t/yr vinyl chloride plant at Convent delayed
	408	
	381	
	318	
	4551	

...n. 0.05 kg; oxychlorination process, 0.0364 ... of the toxicity of vinyl chloride, the EPA ... as the emission standards for vinyl chloride ... processes except oxychlorination must be reduced ... oxychlorination must be reduced to 0.02 kg ... from the oxychlorination process; preventable ... and fugitive emissions are to be minimized ... collection of the emissions (104). These ... of the 1974 estimated typical vinyl chloride ... best available technology. Compliance testing ... of 1978. Additional EPA and state actions ... hydrocarbon emissions from vinyl chloride ... actions were directed primarily against the ... gas from air-based units. The effect of these

various regulations has been to increase substantially the scope of add-on technology in vinyl chloride production plants, such as: installation of primary and redundant incineration facilities for vinyl chloride point-source and collected fugitive emissions, except oxychlorination; installation of HCl scrubbing and neutralization or recovery units in conjunction with the incinerators; installation of closed-process sewers, collection systems and larger or redundant wastewater strippers; replacement of single mechanical seals on pumps and agitators with double mechanical seals; leak-detection systems and portable monitors; enclosed sampling and analytical systems; and vapor-recovery systems for vinyl chloride loading, unloading, and equipment clearing (59).

Technology Trends. Recent developments in commercial vinyl chloride processes based on the balanced ethylene-feedstock route, which is used overwhelmingly worldwide, include boiling-liquid reactors for direct chlorination, a trend toward oxygen-based oxychlorination, and efforts to improve conversion and minimize by-product formation in the ethylene dichloride (EDC) pyrolysis process (59,63–65,69,76,105–106). Direct chlorination in liquid-boiling reactors offer advantages of energy savings and reduced product purification requirements, compared with conventional processes operating at lower temperatures. Energy savings arise by essentially using the reactor as a reboiler for the conventional EDC purification system. With this modification, the heat of reaction is used to provide most of the required column vapor load for fractionation. This results in lower steam and cooling-water usage requirements compared with the conventional process. In addition, the EDC is distilled from dissolved catalyst, thus facilitating product purification. Use of pure oxygen instead of air for the oxychlorination process offers a number of advantages, including improvements in ethylene and hydrogen chloride yields, reduced equipment requirements for secondary recovery of ethylene and EDC, and reduced emissions (69,76). The main advantage is the drastic reduction of the vent-gas volume discharged by the process. Therefore, destruction of the environmentally objectionable compounds in this stream is more manageable, and savings in incineration can be sufficient to pay for the oxygen raw-material requirement. With emission-control standards becoming more severe, it is expected that the ratio of oxygen-based to air-based plants will increase. For existing air-based plants, conversion to oxygen will depend on local emission standards, oxygen availability and cost, and alternative add-on systems available for cleaning the vent gas, eg, catalytic oxidation or sorption techniques. In terms of ethylene dichloride pyrolysis chemistry, it is expected that companies will continue their efforts in developing cracking promoters, by-product inhibitors, and improved feed purification techniques (89,93). Since current cracking technology limits EDC conversion to 50–60%, considerable energy and cost savings could be achieved through increased conversion levels without concurrent losses of EDC to undesirable side reactions and coking problems. Recent development of a laser-induced EDC cracking technique at the Max Planck Institute (Göttingen, FRG), for example, has provoked interest in the vinyl chloride industry (94–95). At temperatures comparable to those used in commercial operation, this laser-induced cracking process is claimed to increase conversion while concurrently decreasing by-product formation.

Vinyl chloride processes based on acetylene or mixed acetylene–ethylene streams are limited by local availability and relative costs of such feedstocks. However, the development of lower cost routes to acetylene will renew interest in this original manufacturing process. For example, development of a relatively new crude-oil

Table 5 (*continued*)

Country	Capacity, 1000 t/yr
Africa	
Algeria	40
Egypt	0
Libya	62
Morocco	27
Republic of South Africa	180
Senegal	0
Total	*309*
Australia	62
Grand total	*17,219*

[a] Ref. 103.

cracking process, which involves very high temperature steam as a heat-transfer fluid, produces substantial yields of acetylene along with ethylene (107). High temperature naphtha cracking also produces considerable amounts of acetylene and ethylene. Therefore, under certain economic and geographic conditions, these processes may provide acetylene or mixed hydrocarbon feedstocks for vinyl chloride production. Typical conditions for the hydrochlorination of acetylene are temperatures of 150–180°C, total pressures of ca 500–1500 kPa (5–15 atm), and the use of a carbon-supported mercuric chloride catalyst (108–109). With stoichiometric quantities of reactants, essentially complete conversion is obtained with selectivities of 98%. Ethylene does not react under these conditions; thus, mixed acetylene–ethylene streams can be used as feeds. Ethylene is easily recovered from the vinyl chloride product by fractional distillation and is then chlorinated yielding 1,2-dichloroethane. In addition to the three general types of vinyl chloride processes in commercial use, ie, those based on ethylene, acetylene, and mixed-gas feedstocks, various other process schemes based on ethane, ethylene, and methane have been described in the patent literature in recent years (59,110–115).

Specifications

Technical-grade vinyl chloride should not contain more than the amounts of impurities listed in Table 6.

Health and Safety Factors

Vinyl chloride is an OSHA-regulated material (117). Current OSHA regulations require that no employee be exposed to vinyl chloride concentrations greater than 1.0 ppm over any 8-h period, or 5.0 ppm averaged over any period not exceeding 15 min. Monitoring is required at all facilities where vinyl chloride is produced or PVC is processed. The monitoring may be discontinued for any employee only when at least two consecutive determinations, made not less than five working days apart, show exposures at or below the action level of 0.5 ppm. Contact with liquid vinyl chloride is prohibited. Chronic exposure to vinyl chloride at concentrations of 100 ppm or more is reported to have produced Raynaud's syndrome, lysis of the distal bones of the fingers, and a fibrosing dermatitis. However, these effects are probably related to

Table 6. Impurity Levels in Vinyl Chloride[a]

Impurity	Maximum level, ppm
acetylene	2.0
acidity, as HCl by wt	0.5
acetaldehyde	0.0
alkalinity, as NaOH by wt	0.3
butadiene	6.0
1-butene	3.0
2-butene	0.5
ethylene	4.0
ethylene dichloride (EDC)	10.0
nonvolatiles	150.0
propylene	8.0
water	200.0
iron, by wt	0.25

[a] Ref. 116.

continuous intimate contact with the skin. Chronic exposure is also reported to have produced a rare cancer of the liver (angiosarcoma) in a small number of workers after continued exposure for many years to large amounts of vinyl chloride gas (118). Toxicology data on vinyl chloride, eg, TC_{Lo} (human), TC_{Lo} (rat), LD_{50} (rat), and threshold limit values, are reported in ref. 8. Exposures to vinyl chloride can be readily reduced by feasible engineering controls or work practices to below the OSHA acceptable levels. Use of closed systems or laboratory hoods that have protection factors adequate to prevent worker exposure are recommended. Whenever exposure is above the permissible OSHA limit and cannot be reduced by feasible engineering practices, respirators are required and must be used in accordance with a standard respirator program (118).

Vinyl chloride is flammable when exposed to heat, flame, or oxidizing agents. Large fires of the compound are very difficult to extinguish. Vapors represent a severe explosion hazard. Peroxides can form on standing in air, especially in the presence of iron impurities. Vinyl chloride is generally transported in railroad tank cars and in tank trucks (119). Because of possible peroxide formation, vinyl chloride should be transported or handled under an inert atmosphere. The presence of peroxide from vinyl chloride and air can initiate polymerization of stored vinyl chloride; however, stabilizer can be added to prevent polymerization (48). Because of the worldwide production and transport of vinyl chloride, the higher temperatures of certain climates may require that small amounts of phenolic or other stabilizers be added to the vinyl chloride.

Uses

Vinyl chloride has gained worldwide importance because of its industrial use as the precursor to poly(vinyl chloride). It is also used in a wide variety of copolymers. The inherent flame-retardant properties, wide range of plasticized compounds, and the low cost of the polymers from vinyl chloride have made it a major industrial chemical (see Flame retardants, halogenated fire retardants). The use of vinyl chloride as a starting material for the synthesis of other industrial compounds will be in-

Lederer, *Angew. Chem.* 71, 162 (1959).
S. Pat. 4,062,925 (Jan. 21, 1977), D. E. Witenhafer, C. A. Daniels, and R. F. Koebel (to BFGoodrich
).
SSR Pat. 734,544 (May 15, 1980), V. A. Alferov and co-workers.
S. Pat. 2,060,303 (Nov. 10, 1936), H. P. A. Groll and G. Hearne (to Shell Oil Co.).
V. Suknanov, A. F. Revzin, and V. Y. Shtern, *Kinet. Katal.* 15, 551 (1974).
S. Dainton, D. A. Lomax, and M. Weston, *Trans. Faraday Soc.* 57, 308 (1961); P. B. Ayscough, A.
Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.* 57, 318 (1961).
I. Subbotin, V. S. Etlis, and V. N. Antonov, *Kinet. Katal.* 9, 490 (1968).
G. Rinker and W. H. Corcoran, *Ind. Eng. Chem. Fundam.* 6, 333 (1967).
S. Kharasch, J. A. Norton, and J. F. R. Mayo, *J. Am. Chem. Soc.* 62, 81 (1940).
Schmering, *J. Am. Chem. Soc.* 68, 1653 (1946).
M. Davidson and A. Lowry, *J. Am. Chem. Soc.* 51, 2979 (1929).
Boeseken and co-workers, *Rec. Trav. Chim.* 32, 184 (1911).
. Tsukervanik and K. Y. Yuldashev, *Zh. Obshch. Khim.* 31, 858 (1961).
S. Malinovskii, *Zh. Obshch. Khim.* 17, 2235 (1947).
S. Pat. 2,006,517 (July 2, 1935), G. W. Seymur (to Celanese Corp. of America).
Arundale and L. A. Mikeska, *Chem. Rev.* 51, 505 (1965).
S. Pat. 2,124,851 (July 26, 1938) and Brit. Pat. 465,467 (May 3, 1937), W. Fitzky (to I. G. Farben-
ustrie A.G.).
T. Vasil'eva and co-workers, *Izv. Akad. Nauk SSR Ser. Khim.* 7, 1584 (1980).
E. Weiss and K. A. Krieger, *J. Catal.* 6, 167 (1966).
H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 165 (1949).
M. O'Mara, L. B. Crider, and R. L. Daniel, *J. Am. Ind. Hyg. Assoc.* 32, 153 (1971).
W. McPherson, C. M. Starks, and G. J. Fryar, *Hydrocarbon Process.*, 75 (March 1979).
Sittig, *Vinyl Chloride and PVC Manufacture, Process and Environmental Aspects*, Noyes Data
rp., Park Ridge, N.J., 1978, p. 75.
N. Balasubramanian and co-workers, *Ind. Eng. Chem. Fundam.* 5, 184 (1966).
S. Pat. 3,338,982 (Aug. 29, 1967), H. S. Leach (to Monsanto Chemical Co.).
S. Pat. 3,911,036 (Oct. 7, 1975), L. DiFiore and B. Calcagno (to Soc. Italiana Resine).
S. Pat. 3,917,727 (Nov. 4, 1975), U. Tsao (to Lummus Co.).
S. Pat. 3,941,568 (March 2, 1976), B. D. Kurtz and A. Omelian (to Allied Chemical Co.); Ger. Pat.
24,610 (Jan. 1, 1982), E. Birnbaum and co-workers (to BASF A.G.).
S. Pat. 2,540,292 (March 17, 1977), W. Opitz and H. Hennen (to Hoechst A.G.).
S. Pat. 4,000,205 (Dec. 28, 1976), R. G. Campbell (to Stauffer Chemical Co.).
M. Schillmoller, *Hydrocarbon Process.*, 89 (March 1979).
E. Wimer and R. E. Feathers, *Hydrocarbon Process.*, 81 (March 1976).
orine—Its Manufacture, Properties and Uses, ACS Monograph Series No. 154, American Chemical
iety, Washington, D.C., 1962, pp. 250–260.
. Pat. Appl. 41,330 (Sept. 12, 1981), R. A. Kearley (to PPG Industries).
n. Pats. 81 159,148 (Dec. 5, 1981) and 82 2,224 (Jan. 7, 1982), (to Tokuyama Soda Co.).
V. Carruba and J. L. Spencer, *Ind. Eng. Chem. Process Des. Dev.* 9, 414 (1970).
S. Pat. 3,488,398 (Jan. 6, 1970), A. E. Van Antwerp, J. W. Harping, R. G. Sterbenz, and T. L. Kang
B.F. Goodrich Co.).
S. Pat. 4,046,822 (Sept. 6, 1977), F. T. Severino (to Stauffer Chemical Co.).
Reich, *Hydrocarbon Process.*, 85 (March 1976).
it. Pat. 1,189,815 (April 29, 1970), K. Miyauchi (to Mitsui Toatsu Chemical Co.).
f. 60, pp. 37–39.
S. Pat. 3,966,300 (Dec. 7, 1976), R. C. Ahlstrom, Jr. (to The Dow Chemical Co.).
S. Pat. 3,935,286 (Jan. 27, 1976), J. C. Strini and J. R. Costes (to Rhone-Progil).
S. Pat. 4,060,460 (Nov. 29, 1977), E. W. Smalley, B. E. Kurtz, and B. Bandyopadhyay (to Allied
hemical Corp.).
it. Pat. 1,266,676 (March 15, 1972), (to Knapsack Co.).
. Pat. 1,602,322 (Jan. 29, 1971), (to Solvay et Cie).
S. Pat. 3,484,493 (Dec. 16, 1969), A. Krekeler (to Knapsack Co.).
rit. Pat. 956,618 (1964), A. G. Jacklin (to Imperial Chemical Industries, Ltd.).; Fr. Pat. 1,343,501
Nov. 22, 1963), (to Imperial Chemical Industries, Ltd.).
er. Pat. 2,217,694 (Oct. 18, 1973), W. Froelich (to Hoechst A.G.).

87. D. H. R. Barton, *J. Chem. Soc.*, 148 (1949).
88. K. E. Howlett, *Trans. Faraday Soc.* 48, 25 (1952).
89. P. G. Ashmore and co-workers, *J. Chem. Soc. Faraday Trans. 1*, 657 (1982).
90. U.S. Pat. 3,896,182 (July 22, 1975), D. P. Young (to B.P. Chemicals, Ltd.).
91. Brit. Pat. 938,824 (Oct. 9, 1963), (to BFGoodrich Co.).
92. Jpn. Pat. 67 22,921 (June 30, 1967), (to Mitsui Chemical Industries).
93. Ger. Pat. 3,024,156 (Jan. 21, 1982), A. Czekay and co-workers (to Hoechst A.G.).
94. Ger. Pat. 2,938,353 (Sept. 21, 1979), J. Wolfrum (to Max Planck Institute (Göttingen, FRG)).
95. Ger. Pat. 3,008,848 (March 7, 1980), J. Wolfrum (to Max Planck Institute (Göttingen, FRG)).
96. Brit. Pat. 1,168,329 (Oct. 22, 1969), (to Monsanto Chemical Co.).
97. U.S. Pat. 3,125,607 (March 17, 1964), H. M. Keating (to Monsanto Chemical Co.).
98. U.S. Pat. 3,142,709 (July 28, 1964), E. H. Gause (to Monsanto Chemical Co.).
99. U.S. Pat. 3,125,608 (March 17, 1964), D. W. McDonald (to Monsanto Chemical Co.).
100. J. S. Benson, *Hydrocarbon Process.*, 107, 108 (Oct. 1979).
101. U.S. Pat. 3,557,229 (Jan. 19, 1971), H. Riegel (to Lummus Co.).
102. *Chemical Economics Handbook, Marketing Research Report on Polyvinyl Chloride Resins*, Stanford Research Institute International, Menlo Park, Calif., April 1982.
103. *1982 Vinyl Chloride Report*, World Petrochemicals Program, Stanford Research Institute International, Menlo Park, Calif., 1982, pp. 113-7, 113-8.
104. *U.S. Environmental Protection Agency Report No. EPA-450/2-75-009*, EPA, Research Triangle Park, N.C., 1975.
105. Ref. 60, pp. 8–15.
106. Ref. 60, pp. 72–89.
107. Ger. Pat. 2,217,694 (Oct. 18, 1973), W. Froelich (to Hoechst A.G.).
108. Brit. Pat. 977,578 (Dec. 9, 1964) and 1,068,793 (May 17, 1967), (to Kureha Chemical Industries); E. Ger. Pat. 150,985 (Sept. 30, 1981), J. Glietsch and co-workers.
109. Ref. 60, pp. 42–46.
110. Ref. 60, pp. 7, 15, 36, 47–68, 333–339.
111. U.S. Pat. 3,670,037 (June 13, 1972), J. J. Dugan (to Esso Research and Engineering Co.).
112. U.S. Pat. 3,799,998 (March 28, 1974), D. G. Mead (to Imperial Chemical Industries, Ltd.).
113. U.S. Pat. 4,115,323 (Sept. 19, 1978), C. G. Vinson, M. F. Lemanski, and F. C. Leitert (to Diamond Shamrock).
114. U.S. Pat. 4,102,935 (July 25, 1978), W. J. Kroenke, R. T. Carroll, and A. J. Magistro (to BFGoodrich Co.).
115. U.S. Pat. 4,100,211 (May 17, 1976), A. J. Magistro (to BFGoodrich); Can. Pat. 1,111,454 (Oct. 10, 1981), T. P. Li (to Monsanto Co.).
116. G. R. Black and D. B. Schrock, personal communications, BFGoodrich Co., Chemical Group; generally accepted, industry-wide specifications.
117. *OSHA Regulations* 1910.1017, June 19, 1980.
118. *Prudent Practices for Handling Hazardous Chemicals in Laboratories*, National Academy Press, Washington, D.C., 1981, pp. 150–152.
119. *Vinyl Chloride Monomer—Handling and Properties*, 3rd ed., PPG Industries Brochure, Pittsburgh, Pa., Sept. 1977.

General References

S. Patai, *Chemistry of the Carbon–Halogen Bond*, Parts 1–2, John Wiley & Sons, New York, 1973.
Vinyl Chloride Process Economics Program, Report Series No. 5, Stanford Research Institute, Menlo Park, Calif., May 1965.

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