Industrially Significant Organic Chemicals

Part 3

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Decyl alcohols	157	14.2
Di(2-ethylhexyl) phthalate (DOP)	350	38.5
Diisodecyl phthalate	123	14.8
Diisooctyl phthalate	85	10.2

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This third part of our series covers 14 chemicals, including chloroethane (vinyl chloride), which ranks seventh in sales among the top 100 organics and is manufactured by 12 U.S. companies.

Chloroethane (Ethyl Chloride)

Three-quarters of ethyl chloride production is used for the manufacture of tetraethyl lead, a use whose future is uncertain. Ethyl cellulose consumes about 10%: other uses, such as refrigerants, anaesthetics and other ethylations are trivial, even when considered all together.

Ethyl chloride can be made from ethyl alcohol (although this is not the preferred method), from ethylene and HCl (about 88% of production), and (along with a mixture of byproducts) from the light- or heat-catalyzed chlorination of ethane or ethane/methane mixtures:

$$C_2H_5OH + HCl \xrightarrow[98\%\ yield]{ZnCl_2} C_2H_5Cl + H_2O$$

$$CH_2CH_2 + HCl \xrightarrow{AlCl_3} C_2H_5Cl$$

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

$$C_2H_6 + CH_4 + Cl_2 \xrightarrow[100\text{-}200°C]{photo} C_2H_5Cl(85\%) + CH_3Cl(15\%) + 2HCl$$

*To meet the author, see Chem. Eng., Jan. 21, 1974, p. 132.

In 1970, seven U.S. firms (American Chemical, Dow, Du Pont, Hercules, Pittsburgh Plate Glass, Martin Marietta, and Ethyl Corp.) made 678 million lb priced at 6¢/lb. The current price is about 8¢/lb.

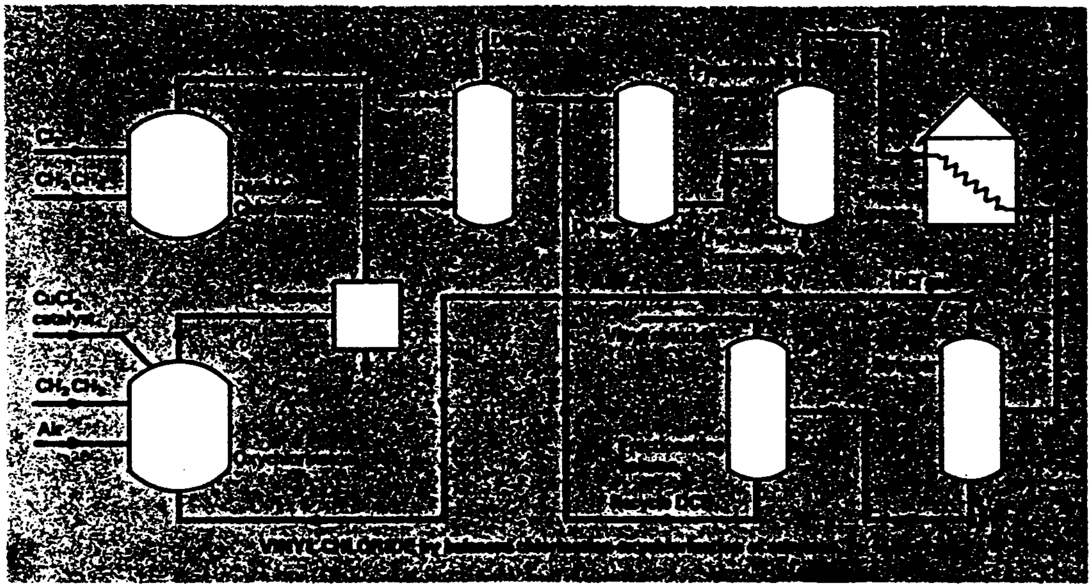
Chloroethylene (Vinyl Chloride)

Chemical principles indicate that the reaction, $CH_2CH_2 + Cl_2 \rightarrow CH_2CHCl + HCl$, offers a desirable way to make vinyl chloride. Yields from this reaction are low, however, and it has not been commercialized. Because the product vinyl chloride is in such great demand, research toward making this reaction economically attractive would seem promising.

Three commercial feedstocks yield vinyl chloride: naphtha, ethylene or acetylene. Oxychlorination, hydrochlorination, dehydrochlorination and combinations of these reactions all are used commercially.

The fine qualities of polyvinyl chloride plastic have brought about enormous demand for the monomer, and its production rate has been expanding at 10%/yr. It alone now accounts for nearly 15% of U.S. chlorine production. Because its price is low, the processes for its production must be efficient in their use of both energy and materials.

The usual procedure is to form dichloroethane (DCE), then dechlorinate DCE to vinyl chloride either by thermal cracking or the use of strong NaOH. Competition



in licensing the processes is keen. While there are important differences in handling heat and managing catalysts, temperatures, and yields, there are essentially four processing systems: acetylene hydrochlorination, balanced acetylene-ethylene chlorination, oxychlorination, and single-step chlorination and cracking.

From acetylene:

$$HCCH + HCl \xrightarrow[90\text{-}140^\circ C]{HgCl_2 \text{ on charcoal}} CH_2CHCl$$

Since ethylene costs approximately half as much as acetylene, considerable chemical manipulation can be justified to allow substituting ethylene for acetylene, so this process appears to be disappearing.

From balanced acetylene-ethylene: While no new plants using this process are being built, it represents a major step forward and solves two problems: (1) reducing the amount of acetylene consumed, and thus the feedstock costs, and (2) using byproduced HCl. Thermal cracking of the intermediate DCE must not proceed beyond 50%, or too many heavy ends are formed.

$$CH_2CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$$

$$CH_2ClCH_2Cl \xrightarrow[\text{pumice catalyst}]{480\text{-}510^\circ C} CH_2CHCl + HCl$$

$$HCCH + HCl \rightarrow CH_2CHCl$$

From ethylene by oxychlorination: This process uses an ethylene and chlorine feedstock for a normal chlorination to DCE, plus oxychlorination of ethylene and HCl to DCE by means of the HCl formed on decomposition of the DCE:

$$CH_2CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$$

$$CH_2CH_2 + 2HCl + \tfrac{1}{2}O_2 \rightarrow CH_2ClCH_2Cl + H_2O$$

$$CH_2ClCH_2Cl \xrightarrow[\text{pumice catalyst}]{480\text{-}510^\circ C} CH_2CHCl + HCl$$

Single-step chlorination and cracking (*Transcat*): Ethane is cheaper and more readily available as a feedstock than either ethylene or acetylene. There has been developed through the pilot plant stages a new process using a molten salt bath, in which such feedstock is cracked to ethylene, and in which chlorination, oxychlorination and dehydrochlorination of DCE all occur simultaneously. Copper oxychloride acts as an oxygen carrier in this process, and functions also in the HCl recovery process:

$$Cu_2Cl_2 + O_2 \rightarrow 2CuO \cdot CuCl_2$$

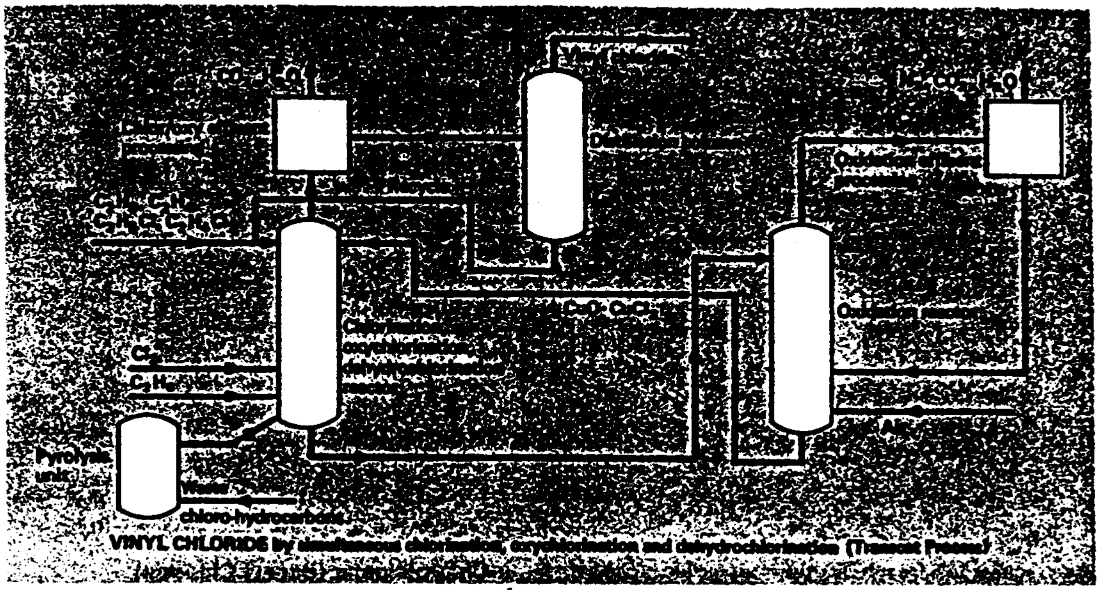
$$Cu_2Cl_2 + Cl_2 \rightarrow 2CuCl_2$$

$$Cu_2Cl_2 + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O$$

Vinyl chloride is produced at high purity, and with an overall yield of 80 mol% based on ethane and 90 mol% based on chlorine. Feeds can contain ethane, ethylene, mixed ethylene, chlorination products, and HCl in various mixtures, permitting recovery of values from such materials. Changing the reaction conditions permits the primary product to be vinyl chloride, chloromethanes, trichloro-ethylene or perchloroethylene.

Currently, the balanced oxychlorination process dominates the production of vinyl chloride, and it has several variations, involving fixed and fluid beds and different methods of heating and separation, all of which are economically and technically important. None of the processes is totally byproduct-free, but some are very good. Feedstock problems make the question of which process will dominate the future highly uncertain; ethane, ethylene (from naphtha) and acetylene are all in short supply. All the vinyl chloride goes into polymers.

In 1970, ten U.S. firms (Allied Chemical, American Chemical, Goodrich, Conoco Chemical, Diamond-Shamrock, Dow, Tenneco, Monochem, Pittsburgh Plate Glass, and Ethyl Corp.) made 4.04×10^9 lb for a price of around 4¢/lb. Production of 4.8×10^9 lb at $4\tfrac{1}{2}$¢/lb has



been predicted for 1973. The price is currently quoted at 5¢/lb.

Chloroform

This is an old product, which can be made in several ways, but the only significant quantity is made through chlorination of methane. Since this reaction produces a range of chlorinated compounds, depending on the ratio of chlorine to methane and the reaction conditions, methyl chloride, methylene chloride, chloroform and carbon tetrachloride are manufactured together. The flow diagram for making chloromethane (methyl chloride) suffices for all four products.

Two-stage chlorination gives the maximum yield of chloroform:

$$CH_4 + Cl_2 \rightarrow \text{mixed products including } CHCl_3$$

Some chloroform is also made from acetone and bleaching powder:

$$(CH_3)_2CO + 6CaClOCl\cdot H_2O \xrightarrow{60^\circ C} 2CHCl_3 + (CH_3COO)_2Ca + Ca(OH)_2 + 3CaCl_2 + 6H_2O$$

The yield is about 88%. Ethyl alcohol or acetaldehyde or mixtures of these can also be converted with bleaching powder, but the process appears to be uneconomical in most cases.

Most chloroform (55%) is used in making dichlorodifluoromethane, the principal refrigerant fluid in home air conditioners; 30% goes into fluorocarbon resins, such as polytetrafluoroethane, TFE, and FEP. There are also many small uses: it is an ingredient in liniment, cough syrup and perfume; it is a denaturant, and a solvent extractant in the manufacture of penicillin, steroids, vitamins, and nicotine; it is used in dye application; and it is used as propellant for aerosols, freezing-point depressant for carbon tetrachloride, and fumigating agent for grain.

In 1970, six U.S. manufacturers (Allied Chemical, Diamond-Shamrock, Dow, Du Pont, Vulcan Materials, and Stauffer) made 2.4 × 10⁸ lb, which sold at 16¢/lb. It is currently quoted at 17½¢/lb.

Chloromethane (Methyl Chloride)

Chloromethane is made either by the chlorination of methane or the hydrochlorination of methanol. By analogy with the oxychlorination of similar hydrocarbons, the reaction of methane with HCl and oxygen should be feasible, but yields are not sufficiently good to make this process attractive for methyl chloride at this time.

The hydrochloric acid byproduced by direct chlorination of methane can be used up as formed, by reacting it with excess methanol:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl + \text{(mixed products)}$$

$$CH_3OH + HCl \xrightarrow[340^\circ C]{\text{alumina}} CH_3Cl + H_2O$$

Either fluidized or fixed-bed catalysts are used with alumina gel or Cu_2Cl_2 and $ZnCl_2$ on active carbon or pumice, as well as H_3PO_4 on active carbon. The yield with alumina is about 95% on methanol. When methyl chloride is desired from the direct chlorination reaction, the Cl_2/CH_4 ratio should be below stoichiometric and the yield per pass minimal. Even with low Cl_2/CH_4 ratios, however, polychloro compounds are formed, and the methyl chloride yield does not exceed 40%. Unless a market for methylene chloride, chloroform and carbon tetrachloride exists, production of methyl chloride by the direct chlorination of methane is not practical.

Chloromethane's primary use (58% of production) is in the manufacture of methyl silicones. The manufacture of tetramethyl lead consumes 16%, the manufacture of