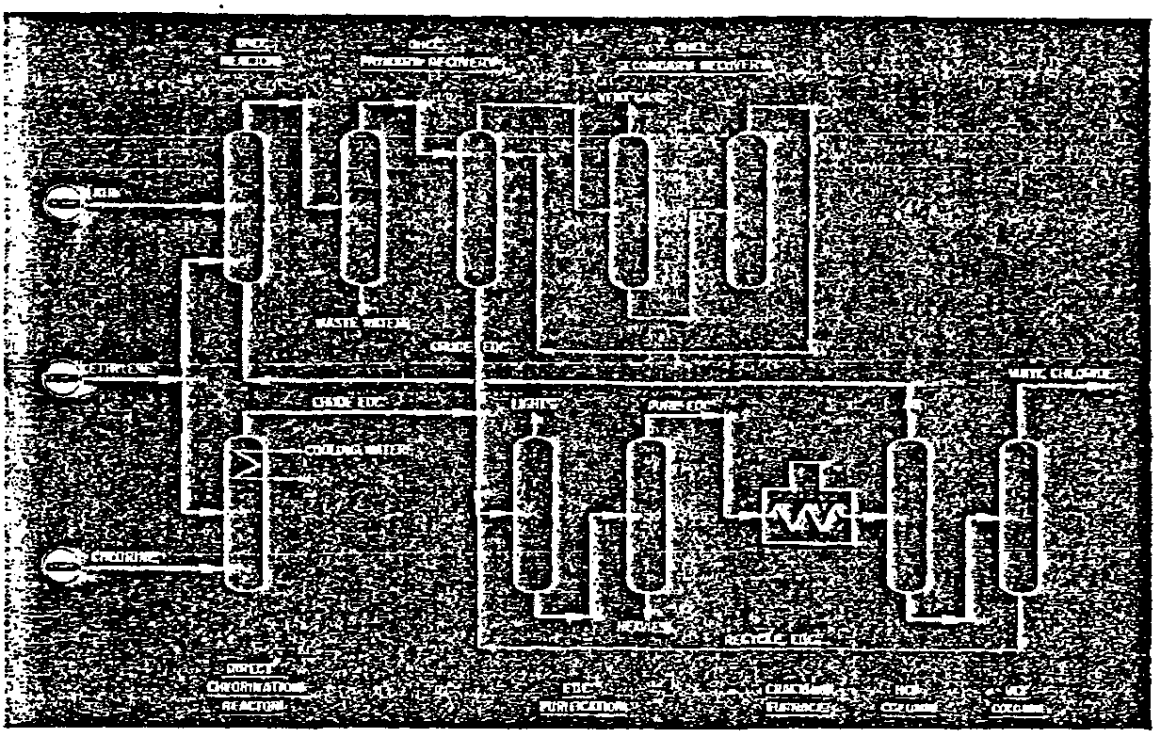
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Vinyl chloride — B. F. GOODRICH CHEMICAL CO.

Applications: A process to produce vinyl chloride monomer and ethylene dichloride (EDC) from ethylene, chlorine and air.

Descriptions: Vinyl chloride monomer is produced by thermal cracking of EDC according to the following equation:

$$C_2H_4Cl_2\ (EDC) \xrightarrow{\Delta} HCl + C_2H_3Cl$$

The feed EDC for this operation is supplied from two sources. In the first source, ethylene and chlorine are reacted in essentially stoichiometric proportions to produce EDC by direct addition thusly:

$$Cl_2 + C_2H_4 \rightarrow C_2H_4Cl_2$$

In the second source ethylene is reacted with the HCl produced from the thermal cracking operation to produce EDC by oxyhydrochlorination as follows:

$$C_2H_4 + 2\,HCl + 1/2O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

The oxyhydrochlorination reaction takes place in a fluid bed of copper chloride impregnated catalyst. Special reactor design and process conditions allow use of an all-carbon-steel reactor without risk of corrosion. The reaction products are efficiently recovered by condensation in the primary recovery unit and absorption in the secondary recovery unit. Unreacted HCl is discharged with the water of reaction as a dilute (less than 1%) hydrochloric acid stream which is easily neutralized and disposed of. The heat of reaction is removed by the generation of steam.

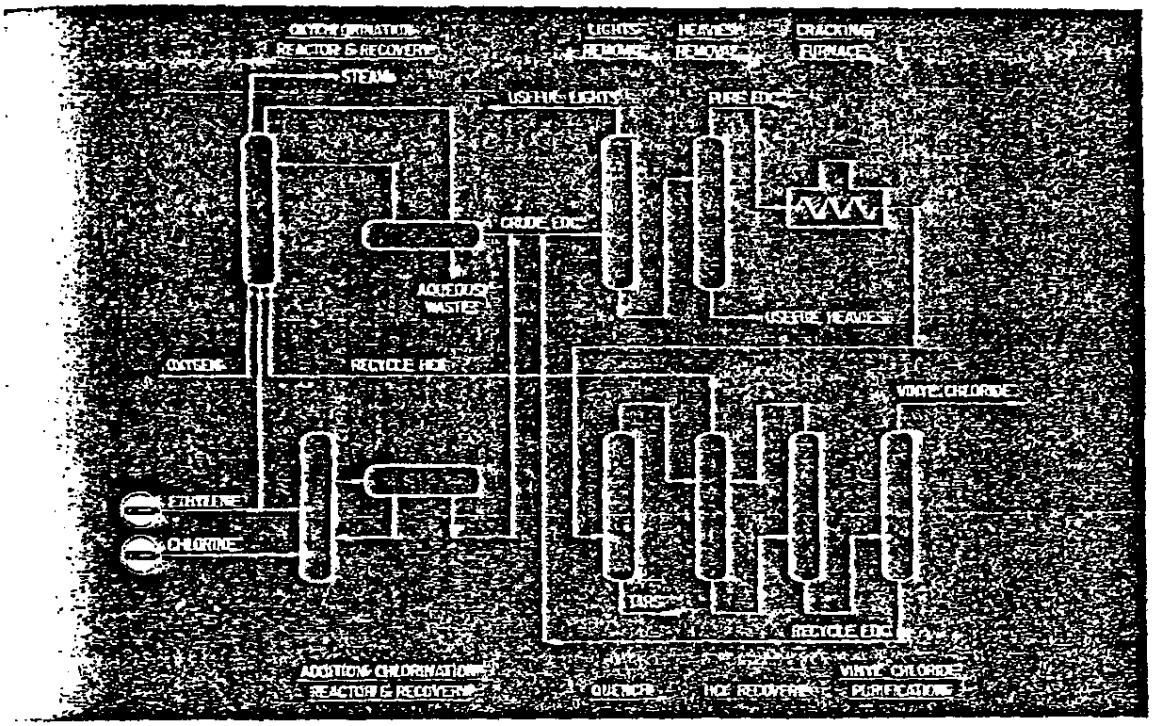
In the direct chlorination unit, the heat of reaction is removed with cooling water. The resultant crude EDC is combined with the crude EDC from the OHCl unit and recycle EDC from the cracking unit. The mixed stream is then fractionated to remove the small quantities of low boiling and high boiling contaminants.

The purified EDC is cracked in a furnace at elevated temperature and pressure. The hot effluent gases are rapidly quenched and distilled to remove first HCl and then VCl. Unconverted EDC is returned to the EDC purification train to remove small quantities of contaminants which would otherwise build up in the system.

Commercial Installations: The Badger Co., Inc., offers engineering design and construction services for plants using this combined process scheme. B.F. Goodrich Chemical Co. processes are in operation or construction at 31 locations throughout the world. Aggregate capacity of the plants exceeds 13 billion pounds per year of total EDC by oxyhydrochlorination and direct chlorination, and 11 billion pounds per year of vinyl chloride monomer.

References: U.S. patent 2,724,006 F. Hoechst; U.S. Patent 3,488,398 B. F. Goodrich; *Chemical Week*, Aug. 29, 1964, pp. 101-108; U.S. and foreign patents applied for.

AP00022065



Vinyl chloride — PPG INDUSTRIES, INC.

Application: A process to produce vinyl chloride monomer from ethylene, oxygen, chlorine and hydrogen chloride.

Description: The process as presented here is for a "balanced-integrated" vinyl chloride plant wherein vinyl chloride monomer (VCM) is the sole product, and all of the hydrogen chloride (HCl) produced from the cracking of ethylene dichloride (EDC) is recycled to the oxychlorination unit and no externally produced hydrogen chloride is used as feed. Under other circumstances, the process can be arranged to produce either one or both EDC and HCl as co-products. The process also is well able to receive externally produced hydrogen chloride as a feed.

In the "balanced-integrated" arrangement, EDC is produced in both direct chlorination and oxychlorination units.

In the direct chlorination unit, chlorine is combined with ethylene in the liquid phase by the addition reaction to produce EDC.

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

In the oxychlorination unit ethylene, oxygen and HCl are reacted in the vapor phase over a PPG-developed catalyst to produce EDC.

$$C_2H_4 + 2HCl + 1/2\ O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

The heat of reaction is recovered as high pressure steam and used in other portions of the process.

Due to the use of oxygen and the judicious choice of design and materials, the oxychlorination unit operates at a high onstream factor, under moderate pressure employing a simplified condensation system to provide high yields and essentially corrosion free operation.

The crude EDC from the oxychlorination and direct chlorination units is combined with the EDC recycled from the cracking unit and purified by distillation.

Vinyl chloride monomer is produced by thermally cracking the purified EDC at high temperature.

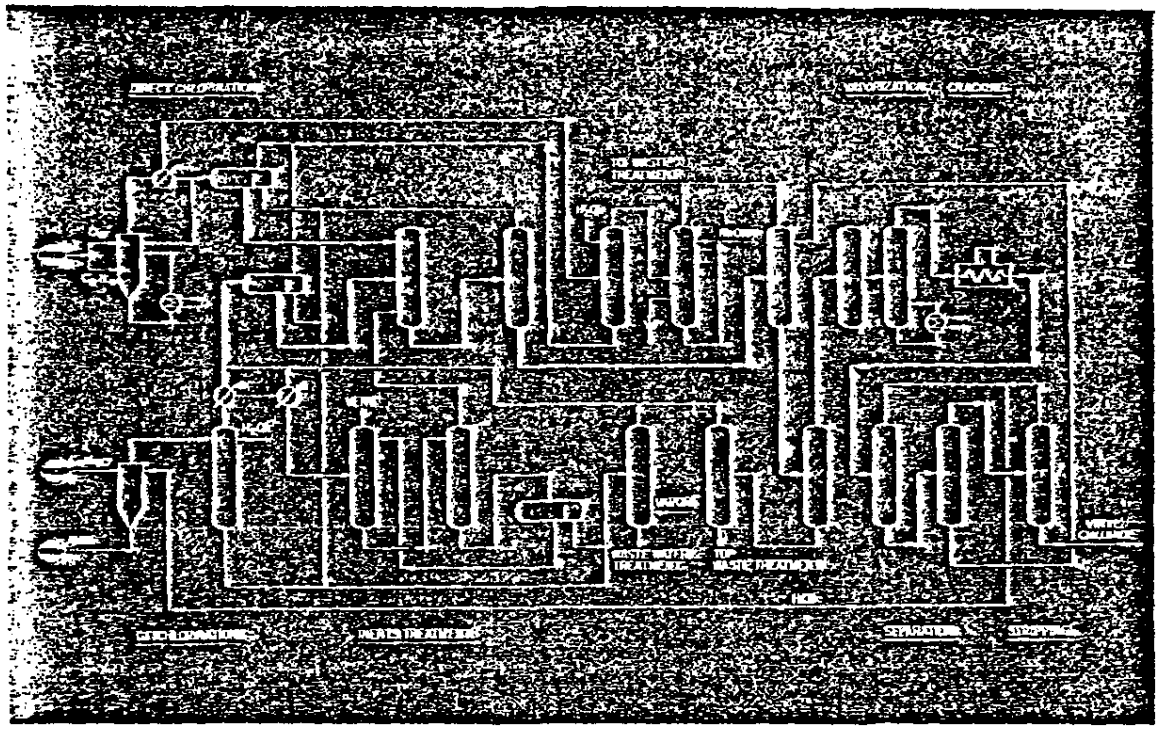
$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

The cracker effluent is quenched and the HCl separated and recycled to the oxychlorination unit. High purity polymer grade VCM is separated from the unreacted EDC. The unreacted EDC is recycled to the purification unit.

The process has been designed and automated for safe, low manpower, high yield and high stream factor operation over a broad range of turndown. In addition to producing high purity polymerization grade VCM, the process enjoys essentially corrosion free operation, low catalyst cost, infrequent decoking and low maintenance cost.

Commercial Installations: PPG holds more than 400 domestic and foreign patents on the subjects of oxychlorination and vinyl chloride. PPG's oxychlorination and VCM technology was developed in the early 1950s and commercialized in the early 1960s. Polymer grade VCM and EDC are produced by the PPG process in plants in the United States, Japan and Europe. The combined capacity of the plants now in operation and under construction is more than 3.8 billion pounds per year of EDC and 2 billion pounds per year of VCM.

AP00022066



Vinyl chloride— RHONE-POULENC S.A.

Application: A process to produce vinyl chloride monomer from ethylene, chlorine and air. Anhydrous hydrochloric acid may be either consumed or produced as well as EDC.

Description: Ethylene dichloride (EDC) is produced in two ways:

- Direct chlorination in which chlorine is reacted with ethylene in liquid EDC according to:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

- Oxychlorination in which hydrochloric acid recycled from the cracking unit reacts with air and ethylene according to:

$$C_2H_4 + 2HCl + \tfrac{1}{2}\,O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

A very efficient fluidized bed catalytic system has been developed.

EDC is then carefully purified and thermically cracked in a pyrolysis furnace: $C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$

(VCM)

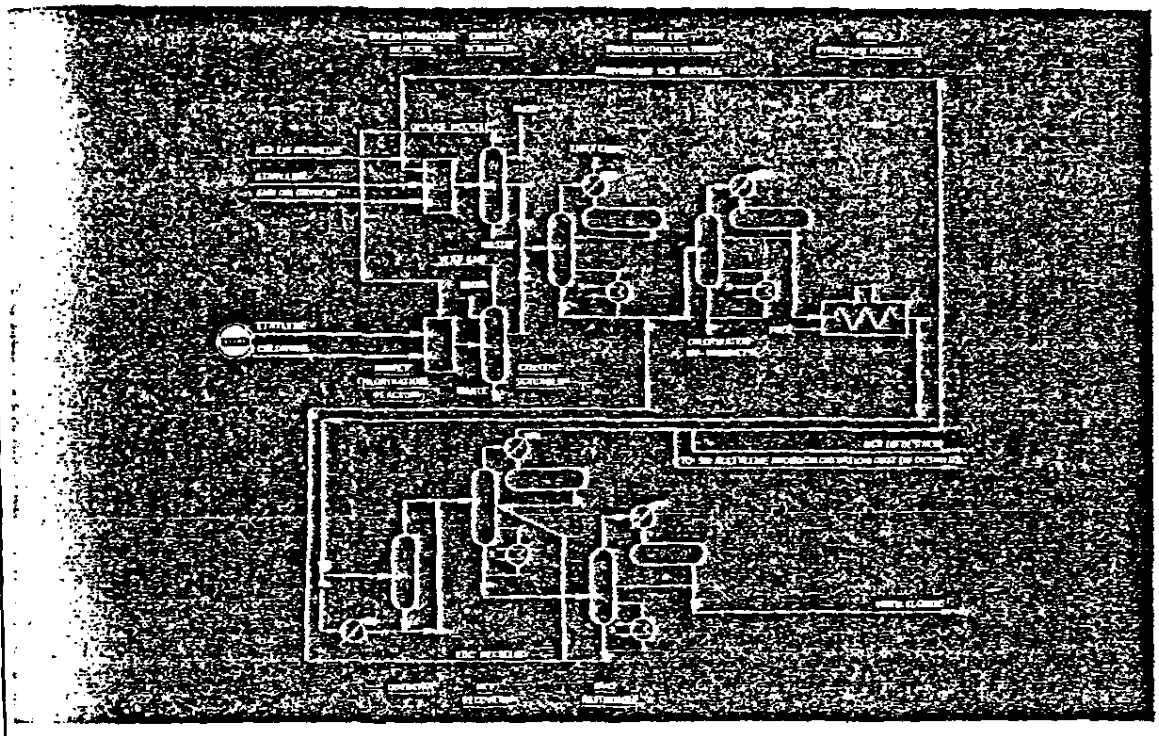
The products are separated, HCl is fed back to the oxychlorination section and VCM is purified and stored.

Features:

- High yield due to a selective oxychlorination catalyst
- High reliability due to a carefully purified EDC and pyrolysis conditions (no boilers or furnace clogging, decoking cycle: more than 12 months)
- No pollution: waste waters suitable for biological treatment, chlorinated wastes destroyed in Rhône-Poulenc incineration process (HCl recycled to oxychlorination).

Commercial operation: Rhone-Poulenc plant at Lavera, France: 350 to 500,000 tons/year MVC.

AP00022067



Vinyl chloride (Monsanto Co.) — SCIENTIFIC DESIGN CO., INC.

Applications: Processes for the manufacture of vinyl chloride monomer (VCM) from ethylene, chlorine, air or oxygen. Externally produced hydrogen chloride may also be fed.

Descriptions: The flowsheet presented represents a "balanced" vinyl chloride plant, wherein all hydrogen chloride produced as a coproduct of the cracking of ethylene dichloride (EDC) to monovinyl chloride (VCM) is recycled to the oxychlorination reactor. The latter may also receive externally produced hydrogen chloride as a feed.

Reactions:

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (Direct Chlorination)

$C_2H_4 + 2HCl + 1/2\ O_2 \rightarrow C_2H_4Cl_2 + H_2O$ (Oxychlorination)

$C_2H_4Cl_2 \rightarrow CH_2 = CHCl + HCl$ (Cracking)

The oxychlorination process is a vapor-phase reaction carried out in a carbon steel reactor operating at moderate pressures. In direct chlorination, ethylene and chlorine gases are charged to a reactor system containing liquid EDC as reaction medium and coolant. The EDC produced in the reaction system is then treated for removal of chlorine and HCl.

The crude EDC is purified by distillation and fed to pyrolysis furnaces where it is cracked to yield vinyl chloride and HCl. The anhydrous hydrogen chloride is recycled to the oxychlorination reactor. Vinyl chloride is refined to product meeting the highest industrial specifications.

Commercial Installations: Monsanto Co., Texas City, Texas; Electrochemical Industries (Frutarom) Ltd., Haifa, Israel; Mitsubishi Chemical Industries, Ltd., Mizushima, Japan; Mitsubishi Monsanto, Yokkaichi, Japan; Petroleos Mexicanos, Pajaritos, Vera Cruz, Mexico; Chinese Petroleum Corp., Kaohsiung, Formosa.

Reference: Ozero, B. J. and Schaffel, G. S., "The Monsanto-Scientific Design Vinyl Chloride Process," AIChE, Houston, March 1971.

AP00022068