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***Prepped by Candice Davis***

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*Chemical Products Synopsis*

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## PROPYLENE DICHLORI

II-I-16

FOCUS.....Propylene dichloride (PDC) is available commercially as an unavoidable co-product of PO manufacture by the chlorohydrin process. There is no deliberate or on-purpose commercial production of PDC. Twenty years ago, all propylene oxide producers, except Celanese, used chlorohydrin technology. Currently chlorohydrin technology is still used on a very large scale, but only by Dow. Dow sells a small percentage of its propylene dichloride co-product but uses most of it captively as a raw material for perchloroethylene and carbon tetrachloride.

During the early 1930's, both ethylene oxide and propylene oxide were made by the chlorohydrin process. In 1937, Union Carbide began commercial production of ethylene oxide by vapor-phase air oxidation of ethylene. The new direct-oxidation technology proved superior to chlorohydrin technology for ethylene oxide production. Direct-oxidation technology became available through license. EO producers built new plants using the new technology. However, chlorohydrin-process EO plants were not dismantled but instead converted to propylene oxide production. In 1969, Oxirane (now Arco) began commercial production of propylene oxide from propylene and isobutane hydroperoxide. Success of this new technology led to expansions by Arco and shutdowns by four chlorohydrin-process PO producers – Union Carbide in 1976, Jefferson (now Texaco) in 1980, BASF Wyandotte in 1981, and Olin in 1983. Dow continued to operate chlorohydrin-process PO plants, presumably because they are large, efficient, and totally integrated with Dow's other chlorine-related operations.

Throughout the 1970's, PDC output rose in proportion to PO production at those plants using chlorohydrin technology. Propylene oxide output rose steadily in response to increased demand for flexible polyurethane foams. During some years of the late 1970's, annual U.S. PDC production probably exceeded 100 MM pounds. However, PDC production declined in recent years following shutdowns of chlorohydrin-process propylene oxide plants. Also, trade sources believe that Dow has progressively reduced the percentage of co-product propylene dichloride formed in its plants. The last reported value for annual sales of propylene dichloride was 33 MM pounds in 1978, including sales by BASF Wyandotte, Dow, Olin, and Jefferson. BASF Wyandotte, Olin, and Jefferson apparently had no captive use for propylene dichloride and probably sold their entire output. Based on various analysis and estimates, Dow is currently co-producing about 60 MM pounds of total propylene dichloride. Dow is probably selling 5-10 MM pounds on the open market and using the rest captively.

Merchant sales of propylene dichloride are believed to be split between ion exchange resin production and reclamation of petroleum cracking catalysts. Dow sells PDC to only those customers with appropriate handling facilities and procedures. Dow reportedly will not sell PDC without first approving the customer's facilities and ensuring that employees have been trained in proper handling. Dow makes every effort to help the user avoid problems which might arise because of use of the material.

OUTLOOK.....Future propylene dichloride production will be a direct function of PO output by the chlorohydrin process. Split about 50–50 between Arco and Dow, propylene oxide production is expected to increase 7% in 1984, as compared with 1983, and then by 4% per year in the 1985–89 period. PO is used as a raw material for polyurethane polyols and also as a raw material for propylene glycol, a major component of unsaturated polyester resins. As long as Dow's share of the PO market continues to increase, availability of PDC should also rise.

PRICING.....Historically, the price of propylene dichloride has ranged from 45% to 60% of the price of propylene oxide. Propylene dichloride prices remained low throughout the 1960's and then doubled between 1970 and 1975 as a result of the 1973 OPEC crude oil price increase and its effect on hydrocarbon feedstock prices. In most previous years, average sales values for PDC were well below the published list price. With no significant competition in the merchant market, Dow is believed to be selling propylene dichloride at or near the list price. During the first four months of 1984, 224,000 pounds of propylene dichloride were imported from West Germany at 15 cents per pound (foreign port). Although this quantity is small, it still creates downward price pressure. As long as Dow has a significant alternate use for PDC in chlorinated solvent production, there should not be much of a problem in setting the best selling price on the merchant market.

**AVERAGE PRICE RANGE – PROPYLENE DICHLORIDE**

**Cents Per Pound – FOB Freeport TX – Bulk**

| | 1960 | 1965 | 1970 | 1975 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | 1987 | 1989 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Trade List | 7 | 7½ | 7½ | 15 | 22 | 22 | 22 | 26½ | 29 | 29 | 32 | 34 |

*Through the 1970's, list prices were on a delivered basis. In 1980 and following years, Dow became the dominant producer and changed the basis to FOB Freeport, TX.*

SUPPLY AND DEMAND.....Millions of Pounds.....Estimated.....Domestic U.S.

| | 1960 | 1965 | 1970 | 1975 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | 1987 | 1989 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Capacity | 40 | 75 | 135 | 150 | 120 | 100 | 90 | 85 | 85 | | | |
| Production (Demand) | 30 | 61 | 95 | 84 | 77 | 70 | 55 | 60 | 60 | 60 | 65 | 70 |

*Capacity and production figures are estimated as percentages of chlorohydrin–process propylene oxide capacity and production, with the exception that production figures for 1965, 1970, and 1980 are those reported by the U.S. International Trade Commission.*

AVAILABILITY.....PDC availability should be excellent over the next few years. Dow remains competitive in propylene oxide, based on large-scale production and the apparent excellent integration of PO facilities with other chlorine-related operations.

PRODUCERS AND CAPACITIES–PROPYLENE DICHLORIDE–MILLIONS OF POUNDS

| PRODUCTION | LOCATION | 1984 CAPACITY |
|---|---|---|
| Dow | Freeport, TX | 60 |
| Dow | Plaquemine, LA | 25 |
| | TOTAL | 85 |

*Dow's nominal 1984 capacity for PDC is estimated at 85 million pounds based on about 6% of propylene oxide capacity.*



END USES.....Propylene dichloride – PDC – (1,2-dichloropropane, density 9.6 pounds per gallon, boiling point 96° C) is a stable colorless liquid with a characteristic chloroform-like odor. The principal application for PDC is as a feedstock for chlorinated hydrocarbons. PDC can be used as a raw material for carbon tetrachloride and perchloroethylene. Non-catalytic chlorinolysis of propylene dichloride in an excess of chlorine at 500° C. yields carbon tetrachloride and perchloroethylene. Dow produces perchloroethylene and carbon tet at Plaquemine, LA, as well as Pittsburg, CA. Most carbon tetrachloride is consumed as a raw material for dichlorodifluoromethane (F-12), widely used as working fluids in air conditioners and refrigeration units. The chlorofluorocarbons are also used as blowing agents in both flexible and rigid polyurethane foams. Carbon tetrachloride is used to some extent as a solvent for oils, fats, and waxes, but in these applications its use is restricted by its toxicity. Perchloroethylene is used chiefly as a dry cleaning solvent. In this application, perc generally replaced carbon tetrachloride because of lower toxicity. The quantity of perchloroethylene used for dry cleaning has declined in recent years because of the installation of solvent reclamation equipment by dry cleaning establishments. Perchloroethylene is also used for metal degreasing and as a raw material for chlorofluorocarbons.

Propylene dichloride is used in the production of ion- exchange resins. A typical ion-exchange resin is a styrene-divinylbenzene co-polymer containing 1-5% divinylbenzene. Beads produced by suspension co-polymerization are soaked in a solvent. This swells them to more than twice their original volume and increases porosity, effectively increasing their active surface area. PDC is one of the swelling solvents used for this purpose. Propylene dichloride is also used by petroleum refiners. Although all fluid catalytic cracking units include a regenerator in which coke is burned off the catalyst by air, inevitably catalyst becomes spent. Some refiners reclaim it by treatment with propylene dichloride, which dissolves hydrocarbons, tar, and coke.

In past years, propylene dichloride was used as a metal degreasing agent, in paint strippers, and as a component of leaded gasoline additives, where it functioned as a lead scavenger. Because of the difficulty of regulating exposure to these materials, Dow as a policy no longer sells propylene dichloride for these applications.

END USE PATTERN–1984 ESTIMATE

| DERIVATIVE | PERCENT |
|---|---|
| Chlorinated Solvents | 90 |
| Other (Ion Exchange Resins, Catalyst Reclamation) | 10 |

MANUFACTURING.....The first step in the production of propylene oxide by the chlorohydrin process is the reaction of propylene, chlorine, and water in the liquid phase at atmospheric pressure and 35° C. Chlorine reacts with a large excess of water to form hypochlorous acid (HOCl) which in turn reacts with propylene to form propylene chlorohydrin (1-chloro-2-propanol). The chlorohydrin reactor is a tower, lined with rubber or acid-proof brick, which runs nearly full of liquid. A high external recycle of the reactor contents is maintained in order to promote contact in the reactor. Propylene and chlorine gases are mixed with this recycle stream and pumped into the base of the tower. The product overflows as an aqueous solution containing 4% propylene chlorohydrin. Propylene dichloride forms in this reactor. The vent gas from the top of the reactor consists primarily of unreacted propylene along with propylene dichloride and small amounts of hydrogen chloride and unreacted chlorine. The vapor is fed to a tower and scrubbed with chilled caustic soda solution to remove hydrogen chloride, chlorine, and propylene dichloride. PDC is flashed off the liquid leaving the base of this scrubber and then purified by distillation.

The presence of a liquid propylene dichloride phase in the chlorohydrin tower is undesirable because propylene and chlorine dissolve readily in propylene dichloride and there react readily to form more propylene dichloride. The liquid propylene dichloride phase tends to form because of the low solubility of propylene dichloride in water (0.3% at 35° C). Therefore, it is necessary to keep the PDC concentration in the reactor liquid below 0.3%. This is done by maintaining a high propylene recycle rate. The propylene strips the propylene dichloride out of the reactor. Trade sources speculate that Dow, through careful control of conditions in its chlorohydrin towers, has reduced the proportion of propylene dichloride co-product from 10% to 6%.

ENVIRONMENTAL.....Eye contact with propylene dichloride causes mild to moderate transient irritation. Prolonged skin contact may lead to mild irritation and scaling, but short contact produces no significant effect. Propylene dichloride is not likely to be absorbed through the skin in acutely toxic amounts. Single dose oral toxicity of propylene dichloride is low. OSHA standard and ACGIH recommended threshold limit value for inhalation is 75 ppm, time-weighted average for an 8-hour workday and a 40-hour work week.

Systemic human effects of propylene dichloride have not been established. For this reason, Dow restricts sales to applications where contact with the product can be carefully monitored and controlled.