VINYL CHLORIDE

SUPPLEMENT B

A private report by the

PROCESS ECONOMICS PROGRAM

STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

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Supplement

VINYL CHLORIDE

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CONTENTS

CONTENTS

CONTENTS

ILLUSTRATIONS

TABLES

TABLES

TABLES

2 SUMMARY

General Aspects

The worldwide plant capacity for vinyl chloride monomer was approximately 12 million metric tons per year in 1974. About 17% of this capacity was new in 1974. Capacity additions in the United States, Western Europe, and Japan in 1974 amounted to only about 10% of the total for that year.

Major future additions to vinyl chloride capacity have been announced for all parts of the world, with the notable exception of the United States. The largest percentage expansion is to take place in Eastern Europe, where announced future new capacity will be double the 1974 capacity of 700,000 metric tons per year. Also some of the major petrochemical complexes being planned in OPEC countries will include production of vinyl chloride. With all the new capacity and a slowing of demand for polyvinyl chloride, the supply of vinyl chloride monomer will probably be ample at least for the immediate future.

The incidence of a form of liver cancer (angiosarcoma) in workers exposed to vinyl chloride monomer has resulted in severe restrictions in the United States and Sweden on maximum allowable concentrations of vinyl chloride in the work area. The problem is much less serious in monomer plants than in polymer plants because most of a monomer plant is out-of-doors and nearly all streams are enclosed. The principal sources of emissions from a monomer plant are tank car loading, vents, and leaks from pumps and flanges. The U.S. Environmental Protection Agancy (EPA) has estimated that, in the past, total emissions from a monomer plant could have amounted to as much as 0.1% of the production.

Ten companies or groups of companies offer basically similar balanced ethylene chlorination-oxychlorination processes for license. No one licensor has a patent structure covering all parts of any one overall

process; much of the technology seems to be based on know-how. As far as can be discerned from the patent and trade literature, the most distinguishing difference among the various processes is the use of fixed or fluid bed reactors in the oxychlorination step. Several licensors use chlorination to recover unreacted ethylene in oxychlorination offgases. Also, oxygen rather than air is used for oxychlorination in some processes; the greatly reduced volume of offgases would be a significant advantage if the offgases have to be incinerated for hydrocarbon pollution abatement.

A few of the licensed processes are distinctly different. The Rhone-Progil process is a balanced ethylene chlorination and oxychlorination process, but employs nonselective chlorination; chlorinated solvents are coproducts. The Lummus Transcat process is also basically a balanced chlorination and oxychlorination process, but it uses a molten salt as the catalyst and ethane as the hydrocarbon feedstock. Chlorinated by-products can be recovered as chlorinated solvents, or they can be burned in the process along with other by-products to recover their chlorine values. The Transcat process has not yet been commercialized for vinyl chloride, but the process will be used for chloromethane production in a plant now under construction.

The only extant process based on hydrochlorination and chlorination of ethylene-acetylene streams is offered by Kureha-Chiyoda. The process uses high-temperature cracking of crude oil or naphtha to produce an equimolar mixture of ethylene and acetylene.

There are no new processes starting from ethylene that seem likely to challenge the conventional balanced ethylene chlorination and oxychlorination process. However, it is possible that feedstock prices and availability as well as increased investment costs could alter the economics among processes using different feedstocks. Hence in this report, costs have been estimated for the balanced ethylene chlorination and oxychlorination process and for acetylene-ethylene hydrochlorination and chlorination, with crude oil as the feedstock. These costs and the

updated costs for ethane chlorination-oxychlorination by the Transcat process are compared in Table 2.1.

The capital investment needed for vinyl chloride production from crude oil acetylene-ethylene is much greater than that for ethylene chlorination-oxychlorination because the former includes the investment in crude oil cracking and cracked gas purification. The allocated battery limits investment for ethylene production from gas oil amounts to about $35 million. Thus the total battery limits investment for vinyl chloride production with gas oil cracking and balanced ethylene chlorination-oxychlorination amounts to about $54 million. This investment is significantly greater than that for the crude oil acetylene-ethylene process and is more than double that for ethane chlorination-oxychlorination. On this more comparable basis, both the crude oil acetylene-ethylene process and the ethane chlorination and oxychlorination process seem attractive.

Hydrocarbon feedstock costs are one of the most important elements in vinyl chloride production costs. Those indicated above are on a mutually consistent basis for U.S. conditions and are derived from SRI's energy studies (see Process Economics Reviews, Report X-1). Some advantage is indicated in net operating costs for the crude oil acetylene-ethylene process over those for the ethylene chlorination and oxychlorination process. However, this advantage is greatly dependent on the value of the oil by-products obtained from crude oil cracking. The values assigned are mainly fuel values less desulfurization costs. It might also be noted that in parts of the world where crude oil prices are higher than they are in the United States, the crude oil acetylene-ethylene process would probably be less favorable. Feedstock costs for this process are directly proportional to crude oil price. Ethylene costs and prices also would be higher, but not in direct proportion to crude oil price.

The production cost estimates indicate a greater than 2¢/lb differential in favor of ethane oxychlorination as compared with ethylene oxychlorination. However, according to SRI's projections, future world

Table 2.1

VINYL CHLORIDE MONOMER MANUFACTURE

COMPARISON OF PROCESS ECONOMICS

Plant Capacity: 600 Million lb/yr
(272,000 metric tons/yr) at 0.9 Stream Factor
CE Cost Index: 180

	Ethylene Oxychlorination	Crude Oil Ethylene	Ethane Oxychlorination
Capital investment at CE Cost Index=180 ($ million)			
Battery limits	$19.1	$ 38.5	$23.4
Fixed capital	32.4	61.5	37.8
Total investment, less land	48.3	82.8	53.6
Production costs (¢/lb)			
Direct operating cost			
Labor	0.20¢	0.34¢	0.22¢
Crude oil (at $7.46/bbl)		3.32	
Ethane at 2.84¢/lb			1.71
Ethylene at 7.9¢/lb	3.75		
Chlorine at 5¢/lb	3.03	3.06	2.87
Other materials	0.18	0.24	0.15
Utilities	1.06	1.03	0.99
Total direct operating cost	8.22¢	7.99¢	5.94¢
Indirect operating cost	1.21	2.16	1.38
Total production cost	9.43¢	10.15¢	7.32¢
By-product credit			
Recovered HCl	-0.04	-0.04	
Cracking by-products		-1.01	
Net production cost	9.39¢	9.10¢	7.32¢
Confidence rating*	C	C	C

*The confidence rating (A is the highest) is SRI's appraisal of the reliability of the technical and economic input for the evaluation. The bases for these ratings are explained in detail on pages D-7, 8 in the July 1974 Index for the Process Economics Program.

crude oil prices (in constant dollars) will be lower than at present. This will be reflected in reduced ethylene prices, whereas ethane prices will steadily increase in the United States. On this basis, the differential would decrease to about 0.6¢/lb by 1980. On the other hand, if the ethane were obtained as a by-product from steam cracking, its value should be proportional to that of ethylene, and a large differential could remain. An even larger differential would exist in regions that are rich in natural gas.

The above costs do not include provisions for compliance with the new regulations on allowable ambient concentrations of vinyl chloride. According to one survey, the added investment to keep within a 10 ppm limit would be about $2.4 million for a 600 million lb/yr monomer plant, and operating costs would increase by about 0.3¢/lb. Extrapolation of the survey results to the 5 ppm ceiling (1 ppm 8-hour average) now required in the United States and Sweden indicates an added capital investment of about $3.5 million and increased operating costs of 0.6¢/lb or more.

Technical Aspects

Other than giving general process descriptions, this discussion of technical aspects is restricted to significant developments that have occurred since the previous reports were issued.

Vinyl Chloride by Balanced Ethylene Chlorination-Oxychlorination

In this process, ethylene dichloride is produced by addition of chlorine to ethylene in the liquid phase (ethylene dichloride) and in the presence of iron as a catalyst. Ethylene dichloride also is produced by the oxychlorination of ethylene over a copper-bearing catalyst. The streams from these steps are combined with recycled ethylene dichloride and purified by neutralization and distillation. The pure ethylene dichloride is then pyrolyzed to vinyl chloride. Hydrogen chloride produced in the pyrolysis is used in the oxychlorination step, and unconverted ethylene dichloride is recycled to the purification section.

Probably the most significant developments in ethylene chlorination are a number of new catalysts that appear to be superior to the usual iron catalysts. These include inorganic salts of metals such as lithium, tin, bismuth, and tellurium, as well as organic compounds such as sulfoxides and substituted phenols such as o-cresol. The substituted phenols in particular are claimed to give marked improvements in product purity and to reduce corrosion.

Patents on ethylene oxychlorination do not reveal appreciable changes or improvements in technology since the previous reports were issued. However, one patent reported extraordinarily high selectivities (99% and better, both on hydrogen chloride and ethylene) by use of a 100% excess of ethylene. Unconverted ethylene is recovered by chlorination.

New chemical methods have been developed for treating ethylene dichloride to facilitate removal of troublesome impurities, such as chloroprene, trichloroethylene, benzene, and butadiene. Among these methods are hydrogenation, chlorination, and treatment with aluminum chloride.

In ethylene dichloride pyrolysis, a selectivity to vinyl chloride of 99.7% at a conversion of 100% is attained by use of a catalyst composed of active carbon impregnated with chromium salts. However the life of the catalyst is not indicated. Also, it has been found that the exclusion of oxygen reduces coking (even though oxygen is specified as a pyrolysis accelerator) and that the addition of nitric oxide to deoxygenated ethylene dichloride reduces coke formation still further.

Vinyl Chloride from Acetylene and Mixed Acetylene-Ethylene Streams

Vinyl chloride was originally produced by the hydrochlorination of acetylene derived from calcium carbide over a mercury catalyst. The process is still in use today on a limited scale. The overall process has been modified by generating acetylene from hydrocarbons. A further modification has been to produce a mixed stream of ethylene and acetylene by cracking hydrocarbons followed by hydrochlorination of the contained acetylene and then chlorination of ethylene to ethylene dichloride. The

Appendix C

SAFETY

All chlorinated hydrocarbons are toxic to some degree. In general, toxicity increases with increased halogentation, and saturated compounds are usually more toxic than their unsaturated analogs. Therefore, vinyl chloride and other toxic products such as tetrachloroethane and 1,1,2-trichloroethane are present in vinyl chloride system. The threshold limit of vinyl chloride was at 500 ppm. It has been set at 50 ppm on a temporary 6-month emergency basis by Occupational Safety and Health Administration since the January announcement by B.F. Goodrich Chemical Company of the deaths of several employees from angiosarcoma of the liver.

A number of companies have observed physiological effects of vinyl chloride monomer at concentrations above 50 ppm in laboratory animals. A report by Biochemical Research Laboratory, Dow Chemical in 1961 indicated (2019) that repeated exposure to vinyl chloride monomer caused liver and kidney injury. Repeated 7-hour exposure at 200 ppm for six months results in micropathological changes in the livers of rabbits and statistically significant increases in the average weight of the livers of male and female rats, but no detectable changes in dogs and guinea pigs. At 100 ppm, slight increases in the average weight of rat livers were observed. All species studied tolerated repeated, daily 7-hour exposures to 50 ppm for six months with no detectable injury. Recently, Professor Cesare Maltoni of Instituto di Oncologia, Bologna, Italy has experimentally created liver angiosarcoma in rats inhaling vinyl chloride down to 250 ppm level, but so far not at 50 ppm level (90549). He also found that vinyl chloride monomer administered to rats by inhalation results in zymbal gland carcinomas, kidney nephroblastomas, and skin carcinomas and probably hepatomas and neuroblastomas (90550). A preliminary test at Industrial Bio-Test Laboratories, Inc. for the Manufacturing Chemists Association confirms the findings of Cesare Maltoni (90548).

Currently, OSHA has proposed a no-detectable level for exposure for monomer, polymer, and fabricating operations as determined by a sampling and analytical technique capable of detecting vinyl chloride concentration of 1 ppm with ±50% accuracy. SPI, however, proposed a ceiling of 40 ppm for vinyl chloride monomer for 1974, 25 ppm in 1975 for polyvinyl chloride resin plants, and a ceiling of 25 ppm for vinyl chloride monomer this year, 10 ppm in 1975 for VCM plants.

In addition to chlorinated compounds, an accidental release of hydrogen chloride or chlorine also could be hazardous to operating personnel.

Highly inflammable gases such as acetylene, ethylene, and hydrogen are present in vinyl chloride operations, and vinyl chloride itself has a flash-point of 108.4°F (-78°C) with explosive limits in air of 4 to 22% (B-8).

In common with many other monomers, accidental initiation of polymerization can result in a dangerous liberation of heat. The presence of water, acids, or air accelerates polymerization and the formulation of shock-sensitive peroxides (B-8).

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