

VCM AND PVC MANUFACTURE

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The Department of Labor has issued a Permanent Standard regulating the exposure of employees to vinyl chloride monomer (VCM). This Standard requires that VCM exposure levels in manufacturing plants be maintained at less than a time weighted average of one part per million (ppm) and a maximum level of 5 ppm effective January 1, 1975. This Standard encompasses all operations where vinyl chloride monomer is present above 0.5 ppm and thus covers vinyl chloride monomer plants, polymerization plants and fabrication facilities. It demands an unrealistically low level for polyvinyl chloride (PVC) producers and fabricators and raises questions as to the ability of some segments of this industry to survive.

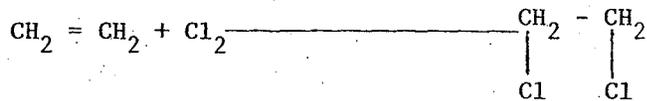
This paper will review the manufacture of vinyl chloride monomer and its use in polymerization plants, the plant problem areas which contribute to escape of VCM during these manufacturing operations, past and present levels of exposure in typical VCM and PVC plants and what can be expected in terms of exposure levels in the future. Further, since some VCM remains occluded within the polymer providing a chance for VCM release during transportation and downstream processing steps, the last section of this paper will review historical levels of VCM contained in PVC, as well as to outline what are felt to be technically achievable in this regard in the future.

Vinyl chloride is a colorless gas at ambient conditions of temperature and pressure. It has a relatively high odor threshold and although some variations exist in the data, experimenters now generally agree that it cannot be detected by smell below a level of 1200 - 2000 parts per million.<sup>(1)</sup> It has approximately twice the density of air and consequently tends to concentrate at grade level. These physical properties make it both difficult to detect by odor and to disperse in VCM and PVC manufacturing facilities. Consequently, concentrations of VCM have been, and are now, above those prescribed by OSHA in the Permanent Standard.

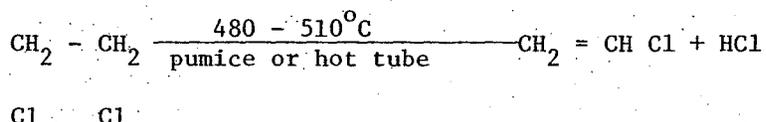
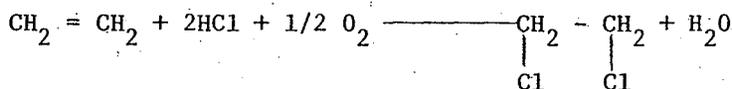
#### VINYL CHLORIDE MONOMER

During 1973, VCM was produced at a level of 5.3 billion pounds in fifteen plants in the United States. These facilities range in capacity from 175 million pounds per year to one billion pounds per year. Thirteen of these monomer plants utilize ethylene as a feedstock and two use acetylene.

Where ethylene is used as a feedstock, the most practical route is to employ a "balanced process" so as to fully utilize the chlorine values. A schematic diagram of this process is given in Figure 1. In this route ethylene is chlorinated to ethylene dichloride in the first step and subsequently cracked to VCM and HCl. The HCl is then utilized to produce additional ethylene dichloride by carrying out an oxychlorination step. The pertinent equations are given below:



DCE (dichloroethane)  
ethylene dichloride



The overall reaction is thus:



The most recently constructed VCM plants are large, highly automated facilities such as Shell Chemical Company's 600 million pound per year plant at Norco, Louisiana. In such plants all the reaction steps are carried out continuously with essentially no opening of the system except for periodic maintenance. Thus, the chances of escape of reactants is relatively low and VCM levels in the operating areas of the plants have been low. Consequently, the SPI recommendations presented at the June, 1974 OSHA hearings in Washington, D. C. were that operations in VCM plants be at below an exposure level of 10 ppm TWA with a 25 ppm ceiling starting October 5, 1974, with this dropping to a 5 ppm TWA, 10 ppm ceiling on October 5, 1976.

Dow Chemical, one of the leading manufacturers of VCM, early in 1961 dropped the then accepted standard of 500 ppm voluntarily to 50 ppm. Dow has stated that now they are "currently operating under conditions that limit worker exposure to less than 10 ppm on an 8 hour time weighted average." Data supplied by other VCM manufacturers to Foster D. Snell during their recent study for the Department of Labor corroborate this. (2) Typical levels of VCM as reported in this study are given in Table I where it can be seen that under normal conditions of operation exposure would be minimal.

Major causes of VCM leakage which contribute to these levels within monomer facilities are as follows:

- Leaks from pumps, valves and flanges
- Process purge streams containing VCM
- Storage and loading systems
- Maintenance operations

Currently, many VCM loading operations are carried out by men in fresh air supplied masks since short-term levels of VCM as high as 200 ppm sometimes occur in disconnecting lines after filling operations. Also, fresh air masks are utilized in some maintenance operations while the equipment is being purged and opened, and until it can be determined that VCM levels are acceptable.

VCM levels in monomer plants will be further reduced in time as manufacturers develop means to minimize and/or eliminate leakage from mechanical equipment so that exposure in the synthesis and purification areas will eventually be below the "action level" specified by OSHA, i.e., 0.5 ppm. Fortunately, the design of monomer plants is generally such that the operating units are widely spaced with the control room and ancillary facilities far enough removed from the processing units that respiratory equipment will not be required in the former areas. For those areas or operations as product loading and "make ready" for maintenance, respiratory equipment will continue to be necessary.

#### POLYVINYL CHLORIDE

PVC and copolymers of vinyl chloride monomer with vinyl acetate are currently produced in 36 plants in the U.S. with 1973 production at 4.6 billion pounds. Plants range in size from 20 million pounds per year to over 300 million pounds per year. The facilities vary greatly as to age with some plants having been built over 25 years ago.

PVC and copolymers are manufactured by four processes - suspension, emulsion, bulk or mass polymerization and the solution process. The problems of VCM exposure are somewhat different for each process. As the suspension process comprises over 80 percent of the U.S. annual output of PVC, it will be the one to which most attention will be devoted here.

A schematic flow diagram of a typical suspension process plant is given in Figure 2. The heart of the process is the polymerization reactors which operate on a batch cycle. Demineralized water is first charged to the reactors along with measured amounts of suspending agents such as hydroxymethyl cellulose and other additives used in the industry. Since VCM is essentially insoluble in water, the suspending agents and agitation provide a fine suspension of VCM in water thus giving the desired particle size. VCM and catalysts, such as lauroyl peroxide, are then added and the batch polymerized for 5 - 8 hours. In order to produce high quality resin, conversion of monomer is generally limited to about 80 - 90% and the unreacted monomer is recovered under vacuum. Stripping to recover the unreacted monomer can be done either in the reactor or in a separate vessel.

At this point in the process, the PVC slurry, substantially stripped of monomer, contains about 33% solids. Most of the water is then removed in a continuous centrifuge and the wet cake, containing about 25% water by weight, dried with hot air. Both rotary

and fluid bed dryers are currently used in the industry.

The dried resin is screened to remove the oversize material and then conveyed pneumatically to bulk siloes. The product is shipped either in bag or bulk, with bulk shipments being made by either truck or rail hopper car.

The batch nature of the PVC manufacturing process, and the layout of most PVC plants result in high VCM exposure levels within the plant. Figure 3 presents a photograph of a typical PVC plant with physical location of the following operational and support areas designated:

- 1) VCM unloading and storage
- 2) Bulk resin storage
- 3) VCM polymerization, stripping of monomer, slurry dewatering
- 4) Packaging, shipping and bagged resin storage
- 5) Polymer drying
- 6) Maintenance facilities
- 7) Laboratory and office building
- 8) Utilities

Although the physical layout of one plant may vary from another, all have these particular functions on each site. Thus, with geographical distances between operations relatively short, generally 400 feet at the most, VCM loss in one area of the plant will adversely affect downwind areas. Consequently, office, quality control, utility and maintenance personnel are often exposed to detectable levels of VCM.

Vinyl Chloride Unloading and Storage - VCM is shipped from the monomer plant to the polymerization facility by rail, tank car, tank truck, barge, ship and pipeline with rail tank car being the predominant mode at this time. Rail shipment is in tank cars of 26,000 and 38,000 gallons capacity, however, there are some smaller capacity cars in limited service. Barge and ship movements of vinyl chloride, either under pressure or refrigerated, are not particularly common. It is believed, however, that this type of transportation will be used in the future wherever possible. Pipeline delivery of monomer is undoubtedly the most desirable method of transport as it offers the least chance of monomer escape. Its use is limited, however, since the majority of existing polymer plants are located in the northern part of the country far removed from the Gulf Coast monomer production.

As discussed under VCM production, the unloading of monomer rail tank cars is difficult to accomplish without the escape of monomer to the atmosphere and hence, is one of the main problem areas in PVC plants. A PVC plant of 200 million pounds per year capacity will require the unloading of up to 4 cars per day with connection and disconnection of lines required for each car. The attendant losses of VCM associated with this operation can be reduced by purging or evacuating the transfer line before it is

disconnected, however, since there is always an opportunity for high localized concentrations of VCM during this operation, producers generally mandate fresh air masks be used at this time.

It is the usual procedure for the vapor pressure of VCM to be used to push the liquid VCM from the tank car to the pump, and then to the storage spheres. The VCM vapor remaining in the car is then reduced to 5 psig by a compressor. As the compressor and associated piping, valves, etc. provide sources for leaks, it has been proposed that the cars be emptied down to only the VCM vapor pressure. Although more VCM is returned in the car to the supplier by this procedure, use of the compressors is obviated. The quantity of residual VCM will vary dependent on ambient temperature, however, a 26,000 gallon car can be emptied to within 3,000 pounds via this method. Although the credit for a "heel" of this magnitude has not been accepted by all the monomer producers as yet, it would seem to offer a means of minimizing VCM losses. Despite a cost penalty, this procedure should find favor in the long run.

The unloading and storage areas are located outside and in many plants distant from the polymerization operation and ancillary facilities. It is an area of myriad pumps, compressors, valves, etc. which require constant maintenance to keep the escape of VCM to a minimum. Reduction in the number of flanges and valves, where possible, and the use of canned pumps to minimize leakage are means of reducing exposure in these areas. To obtain low VCM levels within a polymerization plant with many potential points of leakage is an extremely complex and difficult problem since only one pound of VCM if uniformly dispersed over a five acre plant site to a height of 30 feet would give a level of 2 ppm.

Polymerization -In the early days of PVC manufacture, it is reported that the odor of VCM was noticeable in the polymerization building most of the time indicating exposure levels could have been as high as 2000 ppm on a regular basis. Levels of VCM exposure currently observed in the polymerization area and other parts of a typical PVC plant are given in Table II. As can be seen, levels of VCM in the polymerization section have been reduced considerably, however, they still can be quite high and this area is the major problem in most facilities today.

The technology of suspension VCM polymerization has not changed fundamentally over the past 25 years. The industry still uses a batch process, with all the problems inherent in such operations, despite efforts to develop continuous processing techniques. With the technology practiced in most industry plants, it is necessary to open the reactor between batches, or at least after several batches, to remove polymer which adheres to the walls of the reactor during polymerization. These deposits must be kept to a minimum to permit reaction heat to be removed through the walls of the reactor and to maintain polymer quality.

Besides reactor cleaning, there are numerous other tasks in the typical polymerization building which must be carried out by the operator necessitating his physical presence in this area. These are charging reactants and additives, dumping of the products and checking instruments. In many of the older plants, the control room is an integral part of the polymerization building which increases the number of operators working in this environment.

Given time, control functions can to some extent be carried out remotely, thereby minimizing the number of operators that would have to wear respiratory equipment. Currently, the opening of the reactors and the cleaning of polymer from the reactor walls are usually performed by operators wearing fresh air supplied masks.

Recent engineering developments offer the promise that VCM leakage from the reactor opening and cleaning operation might be greatly minimized and/or eliminated. Solvent cleaning of reactors has been successfully practiced in several plants and can be considered commercial. The solvents used or recommended in some cases are expensive, i.e., THF and N-methylpyrrolidone, and thus solvent losses must be carefully monitored and controlled. Although solvent cleaning successfully applied can help to reduce VCM exposure, plant operators must control releases to the atmosphere of the solvents since they too are toxic.

Secondly, automated high pressure cleaning devices as Goodrich's HRC system have been developed which can remotely remove the polymer from inside the reactor. At the present time it is necessary to open the reactor to insert such devices permitting some monomer to escape, however, it is feasible that the cleaning could be accomplished without opening the reactor vessel.

Additionally, proprietary systems have been commercialized which prevent polymer from adhering on the walls of the reactor and thus obviating cleaning entirely. This approach is certainly the most promising and is being incorporated in the Tenneco plant now under construction at Pasadena, Texas.

An important factor in minimizing leakage is reactor size. Obviously, for any given production volume the number of flanges, valves, fittings, pumps, etc. which must be maintained decreases proportionately with reactor size. The early PVC plants utilized reactors of 1,100 gallon capacity while the newest domestic plants have installed reactors in the 20,000 - 35,000 gallon range. A 50,000 gallon reactor has been developed in Europe, but as of today has not been used commercially in the U.S.

Unfortunately, the majority of the U.S. PVC plants are old and consequently, have the problems inherent in old plants, i.e., small reactors, equipment inside buildings with poor ventilation and close proximity between process operations. As can be seen from Figure 3, the majority of PVC plants will utilize reactors in the 5,000 gallon range and below. Consequently, several years will be required before today's capacity can be converted to the larger reactors with the associated health and economic advantages.

Stripping, Centrifuging and Drying - Since VCM is not completely stripped from the slurry after completion of the polymerization cycle, VCM continues to diffuse from the resin while in the slurry tanks and during centrifugation. Slurry tanks are generally not designed for containing the released VCM and escape of VCM here adds to the total background level in the plant. A high percentage of the VCM remaining in the centrifuge cake is then removed in the dryer where from 30,000 - 40,000 CFM is used to lower the moisture level to less than 0.5 percent. Typical VCM levels in the dryer exhaust stream are 2,500 ppm. The dryer exhaust is usually vented above the dryer building and thus, under adverse atmospheric conditions, can be the cause of high concentrations of monomer in the area.

Reduction of the VCM content of the slurry prior to drying offers the dual advantage that VCM can be recovered in a closed system before it is diluted with air to the point where recovery is virtually impossible and secondly, it permits the production of a final resin with low VCM content. The latter would greatly minimize VCM release during downstream bagging, transport and fabrication. If ultimately successful to the point where no detectable level of VCM was in the resin, it would permit the processor to receive resin and fabricate it without any concern as to VCM exposure of his employees or his customers.

Since it is believed that reduction of the VCM content of the resin is of tremendous import, Tenneco has committed its resources to initially lowering the VCM level of all the resins it produces to below 50 ppm, and ultimately to the non-detectable level.

Table III depicts the levels of residual VCM in typical Tenneco resins before the OSHA Temporary Standards were issued in early 1974. Additional data on copolymer resins are given in Table IV. It is believed these historic data are also representative of levels of VCM in resins produced throughout the industry. Also set forth on Tables III and IV are the current obtainable levels, all less than 50 ppm, which have been demonstrated on a commercial scale.

More specifically, the next Table, Table V, shows VCM content data for copolymer resins taken over a three month period at our Burlington, N.J. plant where new operating techniques have been instituted. Similar results have been obtained in the plant with homopolymer resin as shown in Table VI. Tenneco 10.5R is a low molecular weight resin with a relative viscosity of 1.80. Tests in the laboratory and pilot plant have successfully lowered the VCM content of the product resin consistently to the non-detectable level, however, these developments still must be translated to the plant.

The above accomplishments, although perhaps not industry wide, do demonstrate that PVC resin can be produced at substantially reduced levels of residual VCM, i.e., less than 50 ppm in the short-term, and ultimately at the no-detectable level of VCM. This, when achieved, will offer PVC processors the ability to operate at minimum levels of exposure in their plants.

The reduction in VCM content of the resin has been accomplished in most cases at the sacrifice of some product quality and plant capacity. Overall discoloration is apparent in some grades of resin and, generally, a loss of porosity leading to reduced plasticizer adsorption. The latter will require longer processing times and possibly the need for the processor to modify his formulations in the short-term to accommodate resin of different quality.

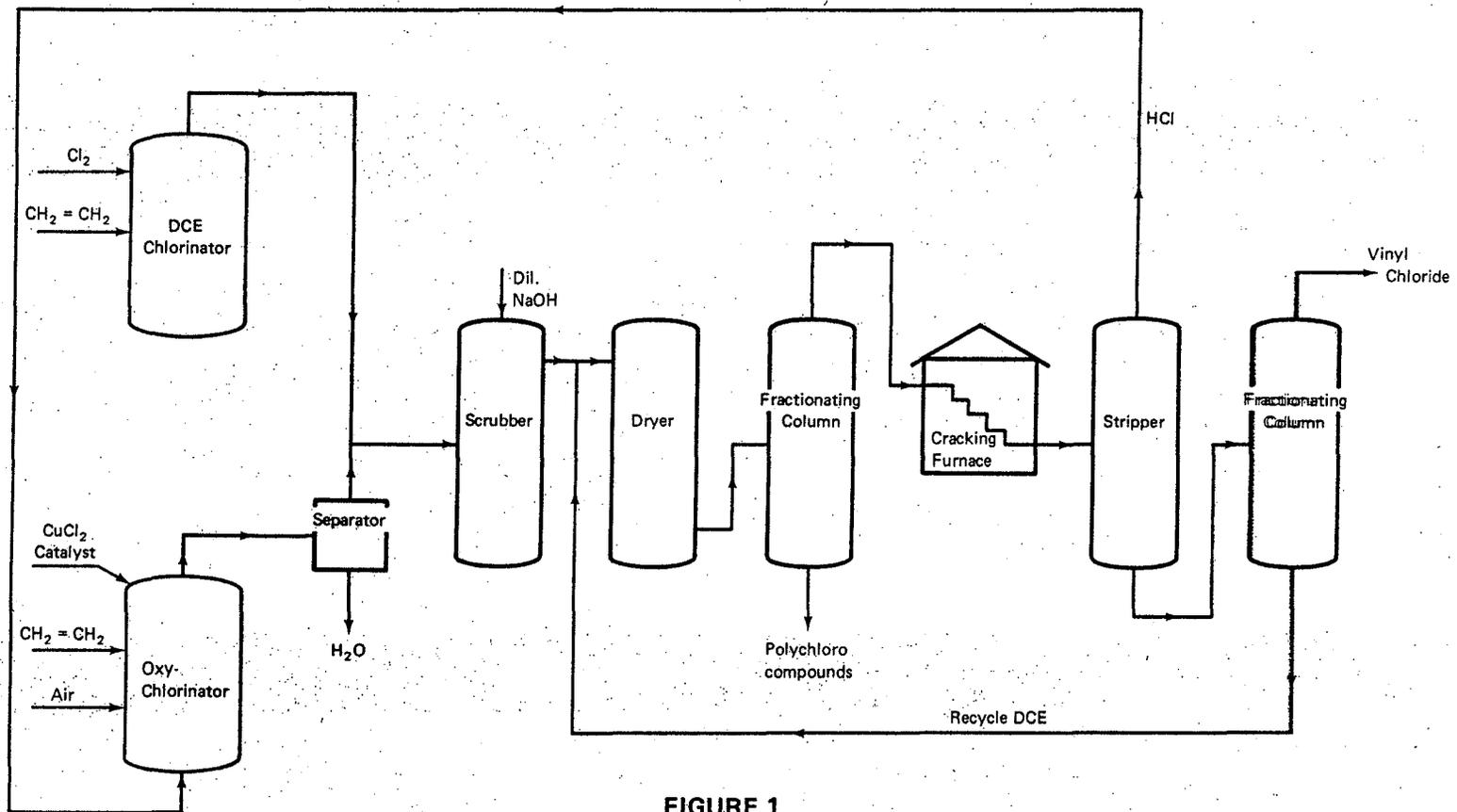
#### SUMMARY

In summary then, the VCM exposure levels in monomer and polymer plants have decreased and will decrease further in time as manufacturers continue to modify their processes and mode of operation.

Resin manufacturers will continue to strive to reduce, and will ultimately succeed in eliminating, any residual VCM in the product resin. This reduction may be at the expense of quality and product output although technical efforts are directed at developing processing techniques which will retain all quality parameters. As a result of these operational changes, resin prices may increase to reflect the associated higher manufacturing costs. It is believed, however, that complete removal of VCM from the resin at the polymer plant is the ultimate answer in solving the current problems facing the PVC processing industry.

B I B L I O G R A P H Y

- (1) Manufacturing Chemists Association, Washington, D. C.  
August 8, 1974.
- (2) Foster D. Snell, Inc. "Economic Impact Studies of  
the Effects of Proposed OSHA Standards for Vinyl  
Chloride," Contract No. L/A 74-167, Florham Park, N.J.,  
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- (3) Disch, G. E., "Plastics Raw Materials to End Markets,"  
167th National American Chemical Society Meeting,  
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**FIGURE 1**  
**FLOW SHEET**

**BALANCED CHLORINATION – OXYCHLORINATION OF ETHYLENE TO VINYL CHLORIDE**

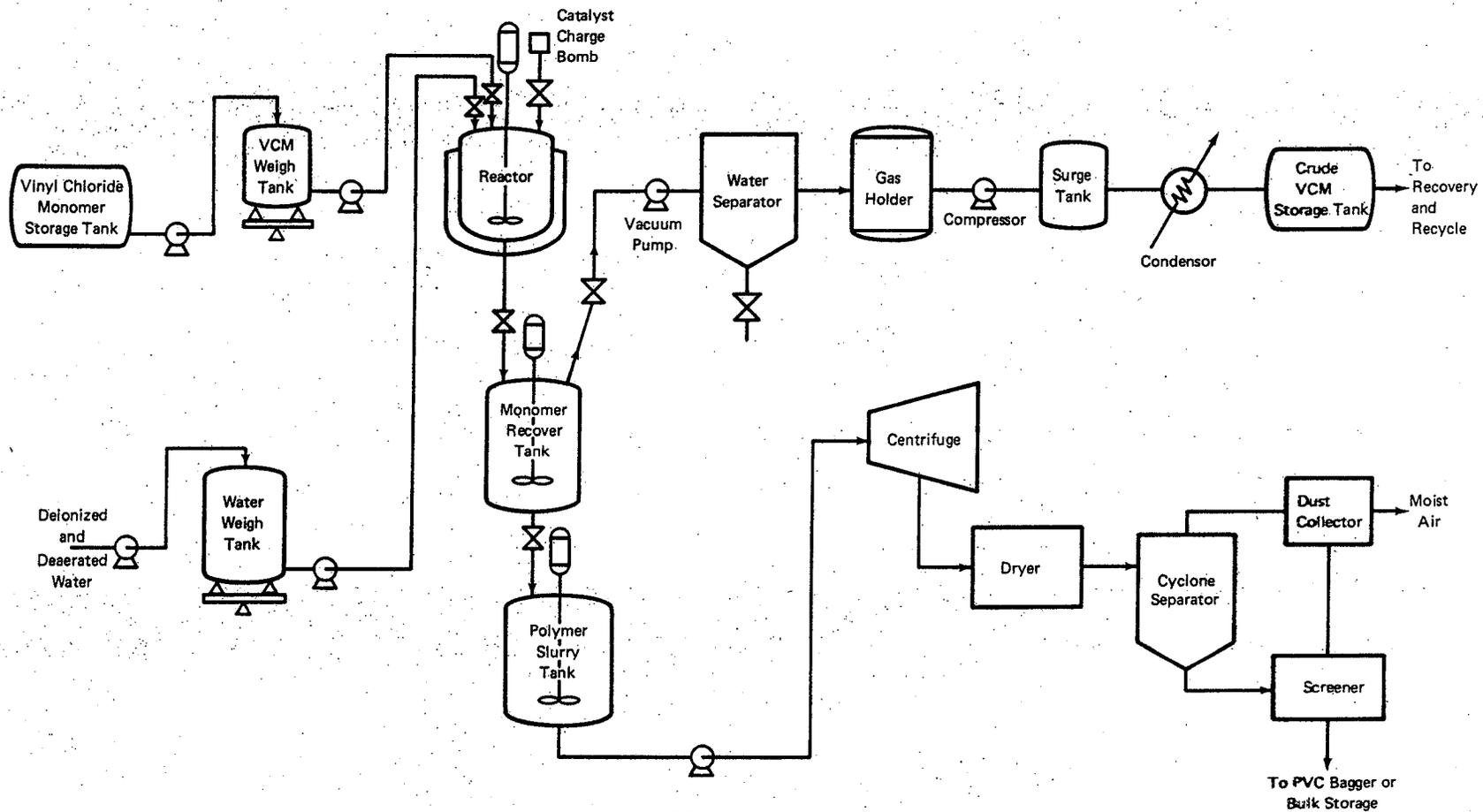
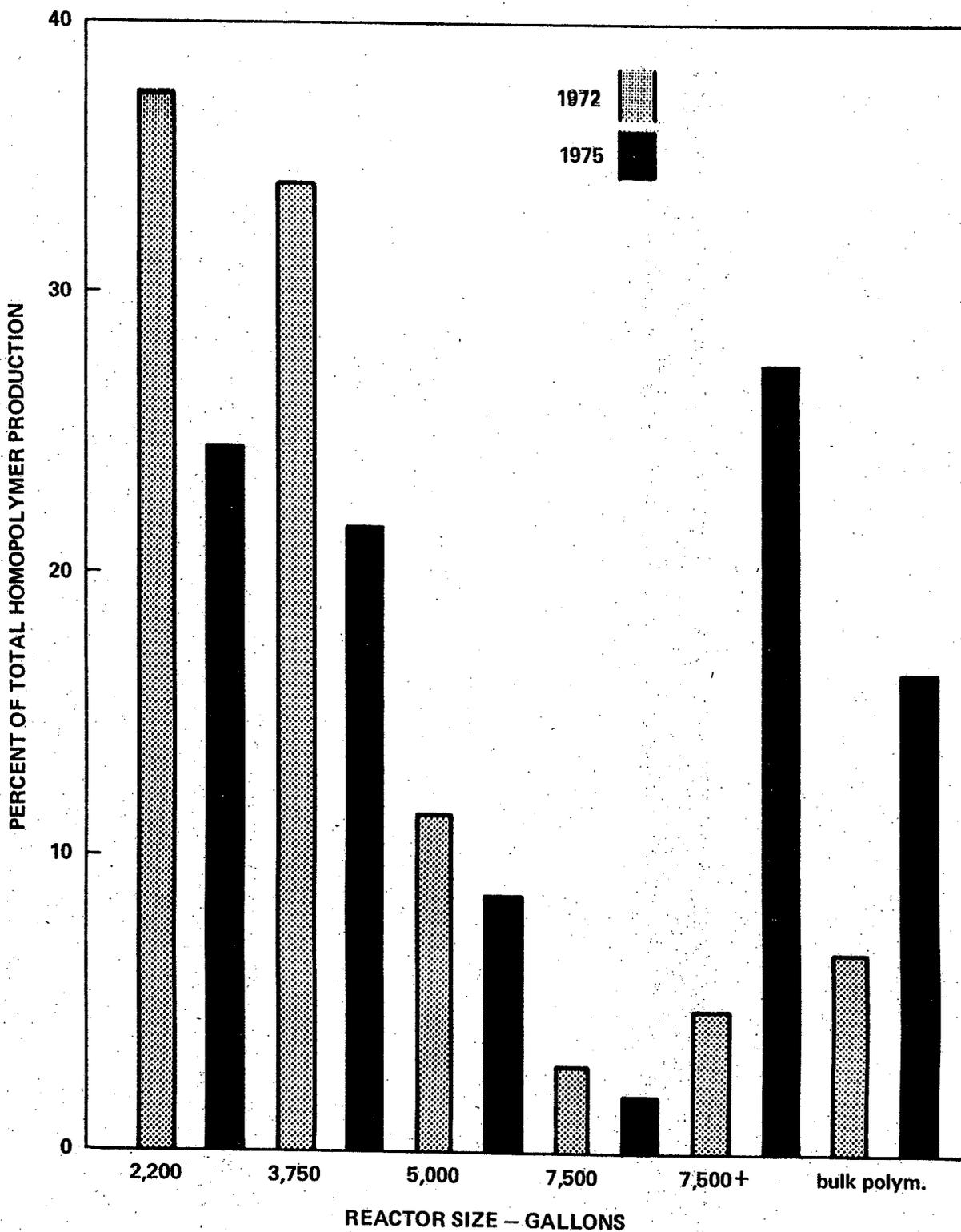


FIGURE 2

FLWSHEET FOR SUSPENSION POLYMERIZATION OF POLYVINYL CHLORIDE

FIGURE 3

PVC HOMOPOLYMER PRODUCTION IN VARIOUS SIZE REACTORS



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FIGURE 4

TABLE I

TYPICAL VCM LEVELS  
IN  
VCM MANUFACTURING PLANTS (2)

<u>PLANT AREA</u>	<u>VCM LEVEL, PPM</u>
SYNTHESIS	0.5 - 10
PURIFICATION	0.3 - 2
VCM LOADING	6 - 16

TABLE II

TYPICAL VCM LEVELS  
IN  
PVC SUSPENSION PLANTS (2)

<u>PLANT AREA</u>	<u>VCM LEVEL, PPM</u>
VCM UNLOADING RACK	5 - 200
POLYMERIZATION	5 - 50*
DRYING	2 - 20
PRODUCT WAREHOUSE	2 - 7
QUALITY CONTROL LABORATORY	1 - 4

\*Peaks to 500 ppm as reactors opened between batches

Table III

RESIDUAL VCM CONTENT

IN

TENNECO RESINS

<u>HOMOPOLYMER RESIN</u>	<u>TYPICAL VALUES PRIOR TO 1974 (PPM)</u>	<u>CURRENTLY ACHIEVABLE (PPM)</u>
LOW MOLECULAR WEIGHT R.V. 1.75 - 1.85	1,000	< 50
MEDIUM LOW MOLECULAR WEIGHT R.V. 2.00 - 2.08	500	< 50
MEDIUM MOLECULAR WEIGHT R.V. 2.25 - 2.32	500	< 50
MEDIUM HIGH MOLECULAR WEIGHT R.V. 2.31 - 2.39	500	< 50
HIGH MOLECULAR WEIGHT R.V. 2.40 - 2.51	500	< 50
BLENDING RESIN	1,000-3,000	< 50

Table IV

RESIDUAL VCM CONTENT

IN

TENNECO RESINS

<u>COPOLYMER RESIN</u>	<u>TYPICAL VALUES PRIOR TO 1974 (PPM)</u>	<u>CURRENTLY ACHIEVABLE (PPM)</u>
MEDIUM MOLECULAR WEIGHT 14.5% VINYL ACETATE R.V. 1.53 - 1.58	200	< 50
HIGH MOLECULAR WEIGHT 10.5% VINYL ACETATE R.V. 1.81 - 1.87	200	< 50
BLENDING RESIN	1,000-3,000	< 50
<u>DISPERSION RESIN</u>	100	< 25

Table V

RESIDUAL VCM CONTENT

OF

TENNECO 315 COPOLYMER

<u>DATE</u>	<u>LOT NO.</u>	<u>VCM CONTENT OF RESIN, PPM</u>
6-13-74	614024	6
7-1-74	614027	14
7-2-74	614027	13
7-24-74	614029	14
7-29-74	614030	30
8-1-74	614030	21
8-4-74	614032	41
8-20-74	614034	14
8-28-74	614035	48
9-1-74	614035	ND
9-8-74	614036	10
9-12-74	614037	0.1
9-18-74	614038	32
9-22-74	614039	ND

ND = non-detectable

Table VI

RESIDUAL VCM CONTENT  
OF  
TENNECO 10.5R HOMOPOLYMER

<u>DATE</u>	<u>LOT NO.</u>	<u>VCM CONTENT OF RESIN, PPM</u>
8-14-74	494044	4
8-15-74	494045	29
8-16-74	494045	28
8-17-74	494046	18
8-17-74	494046	19
8-18-74	494047	12
8-18-74	494048	2
9-7-74	494049	26
9-8-74	494050	22
9-9-74	494051	23
9-9-74	494051	17
9-12-74	494053	17
9-12-74	494054	9
9-13-74	494055	7
9-15-74	494056	16
9-15-74	494057	13
10-7-74	494058	37