

Poly(vinyl Chloride) Processes and Products

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Poly(vinyl chloride) resins are produced by four basic processes: suspension, emulsion, bulk and solution polymerization. PVC suspension resins are usually relatively dust-free and granular with varying degrees of particle porosity. PVC emulsion resins are small particle powders containing very little free monomer. Bulk PVC resins are similar to suspension PVC resins, though the particles tend to be more porous. Solution PVC resins are smaller in particle size than suspension PVC with high porosity particles containing essentially no free monomer. The variety of PVC resin products does not lend itself to broad generalizations concerning health hazards. In studying occupational hazards the particular PVC process and the product must be considered and identified in the study.

Poly(vinyl chloride) is a ubiquitous part of our environment today, in that it appears in clothing, upholstery, flooring, wire insulation, food containers, phonograph records and an almost infinite variety of other items. Despite this wide application and the size of the industry there is little public understanding of the term. A part of this confusion stems from the human inclination to abbreviate terms—thus, we say PVC when discussing poly(vinyl chloride) resins, poly(vinyl chloride) latexes, poly(vinyl chloride) compounds, poly(vinyl chloride) film and so forth. This confusion has been accentuated by governmental regulators, who define PVC as a polymer containing any amount of vinyl chloride. On taking these two factors into account it has become almost impossible to distinguish what is meant when the term PVC is used in the various media. In order to study possible PVC industry-related health problems one must know something of the various processes and products to properly evaluate study results. Many study results can have significance only if the source and composition of the PVC is stated.

Manufacture of synthetic resins from vinyl chloride and other monomers involves reacting these monomers in agitated pressure vessels in the presence of catalysts and converting these liquids and/or gases to solid resins. A considerable amount of heat

is generated by the reaction. This is removed by cooling the vessel. As the monomer is converted to polymer during the reaction, the rate of reaction slows down; thus, after some optimum reaction time, the unconverted remaining monomer is removed from the reacting mass by heat and vacuum and the resin (PVC) is recovered as a dried white powder or as a liquid latex or solution. This polymerization reaction may take place in pure monomer, in a solution, in a water-monomer emulsion or in a water suspension of monomer. The nature of the polymerization process determines the nature of the subsequent recovery process, and the nature of the resin particles produced. Currently there are four basic vinyl chloride polymerization techniques which give use to the following four processes: (1) suspension polymerization, (2) emulsion polymerization, (3) bulk polymerization, and (4) solution polymerization.

Suspension polymerization is the major process used for the manufacture of PVC resins and is used for about 82-85% of U.S. production (Fig. 1). It involves the charging of one or two parts water and one part vinyl chloride monomer or comonomer mixture to an agitated reactor along with initiator and suspending agents such as poly(vinyl alcohol). The mass is reacted at 50-65°C until about 85-90% of the contained monomer is converted to resin. The resin-water mixture is heated, sometimes under vacuum, until the unconverted monomer is substantially removed. The resin is then removed

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moldings produced is remote.

All PVC processes have a problem with reactor system fouling to some degree. The conversion of a liquid monomer to a high molecular weight solid polymer while contacting reactor walls, baffles and so forth results in the deposition of some of that solid polymer on surfaces. This deposition or fouling interferes with the reactor operation so that periodically it has to be removed. In earlier times, this was removed manually by a man working in a shutdown reactor. These reactor cleaners were exposed to very high concentrations of vinyl chloride monomer (several thousand ppm). It was within the group of men in this cleaning operation that the excess of angiosarcoma was observed by Creech (1). More recently, techniques to minimize fouling and techniques for cleaning such as solvent washing and hydroblasting have reduced or eliminated the need for reactor entry and cleaning.

Emulsion polymerization is the second most widely used process for the manufacture of PVC resins and comprises 10–12% of total U.S. production. One of the important things to understand about emulsion polymerization is that it is not a single process but a large family of processes, each producing specialized products that are defined or specified in terms of performance in a particular application. In the interest of brevity, the two major process families will be discussed: the water-soluble initiator system and the oil-soluble initiator system (Fig. 2).

In the water-soluble initiator system, one to two parts water, one part monomer, 0.01 to 0.03 parts surfactant and water-soluble initiator (a redox system or a persulfate salt) are charged or fed to an

agitated reactor and reacted at 30–60°C to form a synthetic latex. The reactor agitation must be sufficiently vigorous to emulsify the monomer-water mixture but not so vigorous that the latex is coagulated. When 80–95% of the monomer is converted to polymer, the latex may be gently stripped of the unconverted monomer with heat and vacuum, or it may be subjected to a second initiator treatment and reacted to essentially 100% monomer conversion. The product of this polymerization may be simply filtered and shipped to consumers as a latex for coatings, mastics, and the like, or the polymer may be recovered as a dry resin. Recovery techniques vary. The most commonly used is simply spray-drying of the latex, though some resins are recovered by coagulating the latex and dewatering with subsequent drying of the coagulum (resin).

In the oil-soluble initiator system, one part monomer containing an organic peroxide is emulsified in one to two parts water containing 0.01 to 0.03 parts surfactant. The resulting emulsion is reacted at 30–60°C to form a synthetic latex. Approximately 80–90% of the monomer is converted to polymer. After reaction, the latex is gently heated and vacuum-treated to remove the unconverted monomer. After stripping, the latex may be shipped as a product though most of it is converted to a dry powder by spray-drying. The basic difference between the oil-soluble initiator process and the water-soluble initiator is that the size of the emulsified monomer particle determines the resin particle size in the oil-soluble initiator process, while polymerization technique determines the resin particle size

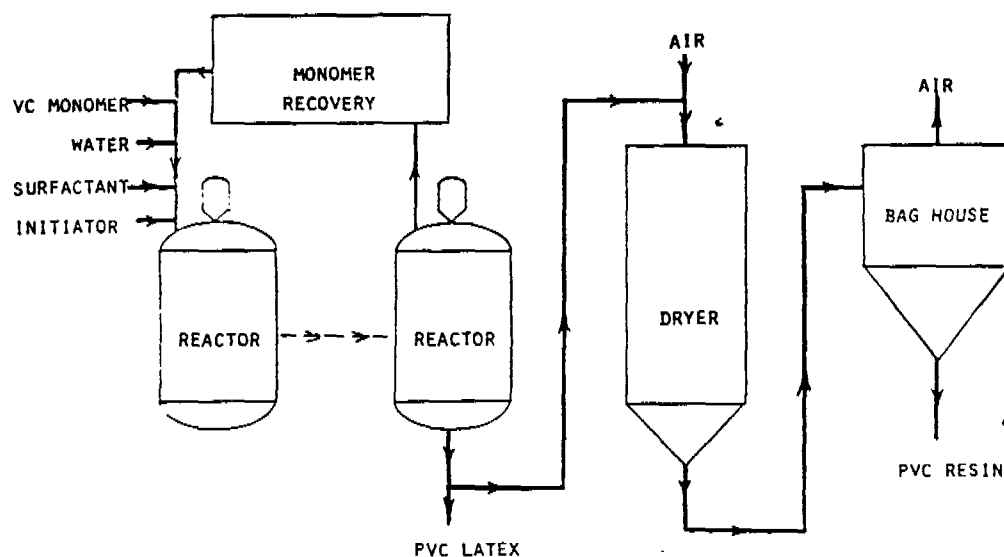


FIGURE 2. Emulsion polymerization process.

ss and poorer removal of residual VCM. These bulk process resins are generally directly competitive with suspension process PVC homopolymers.

The relatively large porous resin particles (50 to 150 μm) tend not to retain monomer, thus removal of residual VCM is theoretically easy. The transfer of heat from the reactor wall to the resin particle for stripping is poor thus offsetting the advantages gained by the high particle porosity in removing residual VCM. In the early 1970s, residual VCM in this type of resin was of the order of 1000 ppm when produced, but more recently these resins have less than 50 ppm in residual VCM when produced.

Solution polymerization is a process unique to Union Carbide Corporation and accounts for about 2% of the total resin produced (Fig. 4). Vinyl chloride monomer, comonomer, solvent and initiator are fed to a continuous reactor system. The polymer formed is soluble in the reacting mass so that the reactor product is a viscous resin solution. This solution is distilled to remove the unconverted vinyl chloride monomer, and the resin product is recovered by treating the resin solution with water and drying the product. The resin particle is very porous, is always a copolymer, is free of soaps and suspending agents, has a median particle size of 75 μm and contains less than 0.2 ppm residual VCM. Manufacturing investment is high, and the product finds its greatest use as a coating material, i.e.,

paints and lacquers, that utilize its good dissolving qualities. It is used in relatively small quantities, and is nearly always shipped in bags rather than bulk.

In addition to the basic PVC resins described earlier, there is a wide variety of resin powders, pellets, liquids and latexes in commerce that fall under the general designation of PVC. These are chemically or mechanically converted PVC resins such as post-chlorinated resins and compounded resins containing plasticizers, stabilizers and the like. As a general rule, the additional processing has removed essentially all of the residual VCM and agglomerated the dusts. Converted PVC resins have no involvement with problems related to vinyl chloride monomer exposure.

Conclusions

Poly(vinyl chloride) resins are produced by four basic techniques: suspension, emulsion, bulk and solution polymerization.

The variety of PVC resin products does not lend itself to broad generalizations concerning hazards to worker health.

In evaluating occupational hazards, the PVC process, the PVC product and other materials present must be considered before valid conclusions can be reached.

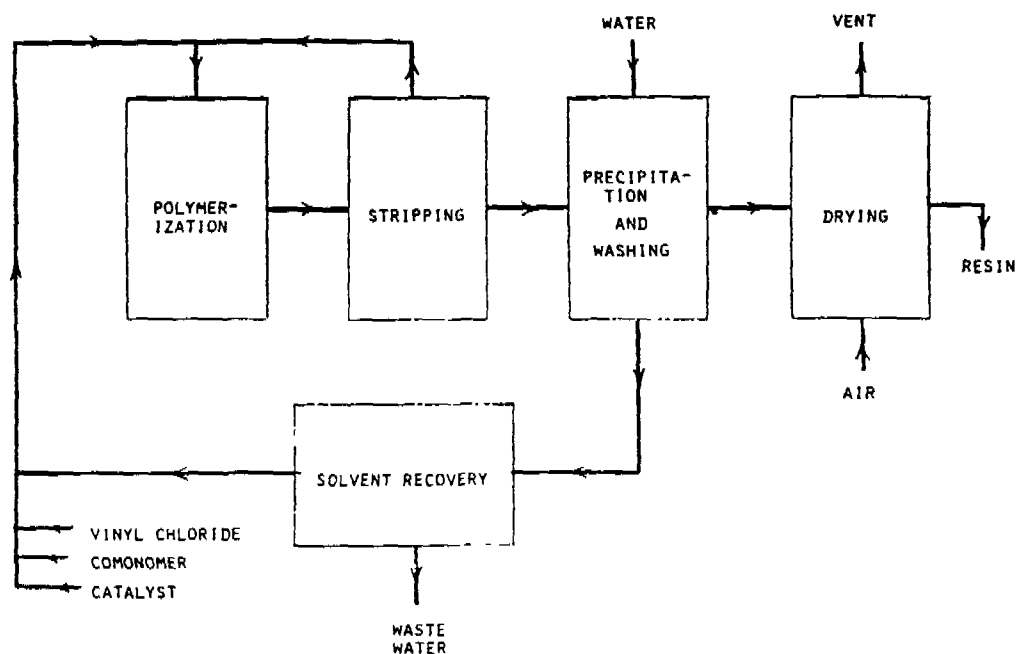


FIGURE 4. Solvent vinyl resin process.

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SPECIALTY VINYL CHLORIDE RESIN PROCESSES

EFFECTS OF GOVERNMENTAL REGULATIONS

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September 1, 1976

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3. Reactor product changeovers were made without equipment cleanup; thus, any VCM contained in the reactor was reacted into a non-PVC latex. This technique requires careful study and product selection to maintain overall product quality.
4. Emissions during monomer unloading were reduced by inert gas purging of the unloading hoses to the supplier's truck and using dry disconnect couplings. These couplings contain check valves that close automatically when the hose is disconnected; thus, the VCM is held in the hose rather than emitted to the air. This is a feasible solution when small hoses can be used.

Items which are troublesome under the OSHA standard and will be affected by the proposed EPA standard are:

1. All rotary pumps handling VCM or mixtures of VCM will have to be equipped with double mechanical seals instead of their present single seals. No measureable change in VCM emissions is expected though, theoretically, emissions caused by seal failure are lower with double seals.
2. Revision of reciprocating compressor and pump packing glands in a manner acceptable to EPA. As mentioned earlier, this portion of the proposed EPA standard is unclear. No measureable change in emissions is expected.
3. VCM emissions caused by control of equipment maintenance for items in monomer service is awaiting promulgation of the EPA standard. Since only the monomer storage tank and piping are involved, the investment will be minimal.

The effect of the VCM health and air emission regulations on latex plants has been to tax the engineers ingenuity to the utmost. Many of the controls used make full utilization of available facilities and knowledge. This is one advantage of the program discussed earlier in that investment for control equipment is optimized.

CONTINUOUS BULK POLYMERIZATION - UCC NONSOLVENT PROCESS

Continuous bulk polymerization of vinyl chloride produces a fine, very porous resin particle containing no surfactants, suspending aids or other extractible material. The porous fine particle gives up residual vinyl chloride monomer very readily; thus, these resins as sold contain 0 to 10 ppm vinyl chloride monomer. The resins find use in plastisols, slush and powder coatings and in medical devices such as blood bags.

The flow diagram (Figure III) shows four steps: polymerization, monomer stripping, dewatering and drying. The process operates on the principle that polyvinyl chloride is insoluble in vinyl chloride. Vinyl chloride, catalyst and comonomer are fed to an agitated reactor; as the monomer polymerizes the polymer precipitates so that the reaction mass is a slurry of resin suspended in monomer. Some heat of reaction is removed by jacket cooling, but most is removed by evaporation of monomer. Resin slurry is removed to the stripper where it contacts hot water driving off the unconverted monomer and yielding a resin water slurry. This is vacuum stripped to remove more monomer. The resin is dewatered and dried in an air drier.

The major problem contributing to emissions is equipment fouling with resin deposits. These deposits must be removed manually from the reactor and accessory pipelines. Reactor cleaning is required about every five days.

The continuous bulk polymerization is relatively old in terms of technology and plant. The fact that it is still operating is indicative of the unique properties of its resins. Age has, however, not prevented progress toward meeting the current and proposed regulations. Table IX shows the change in personal exposure from 1973 to 1976.

TABLE IX

CONTINUOUS BULK PVC PERSONAL VCM EXPOSURE

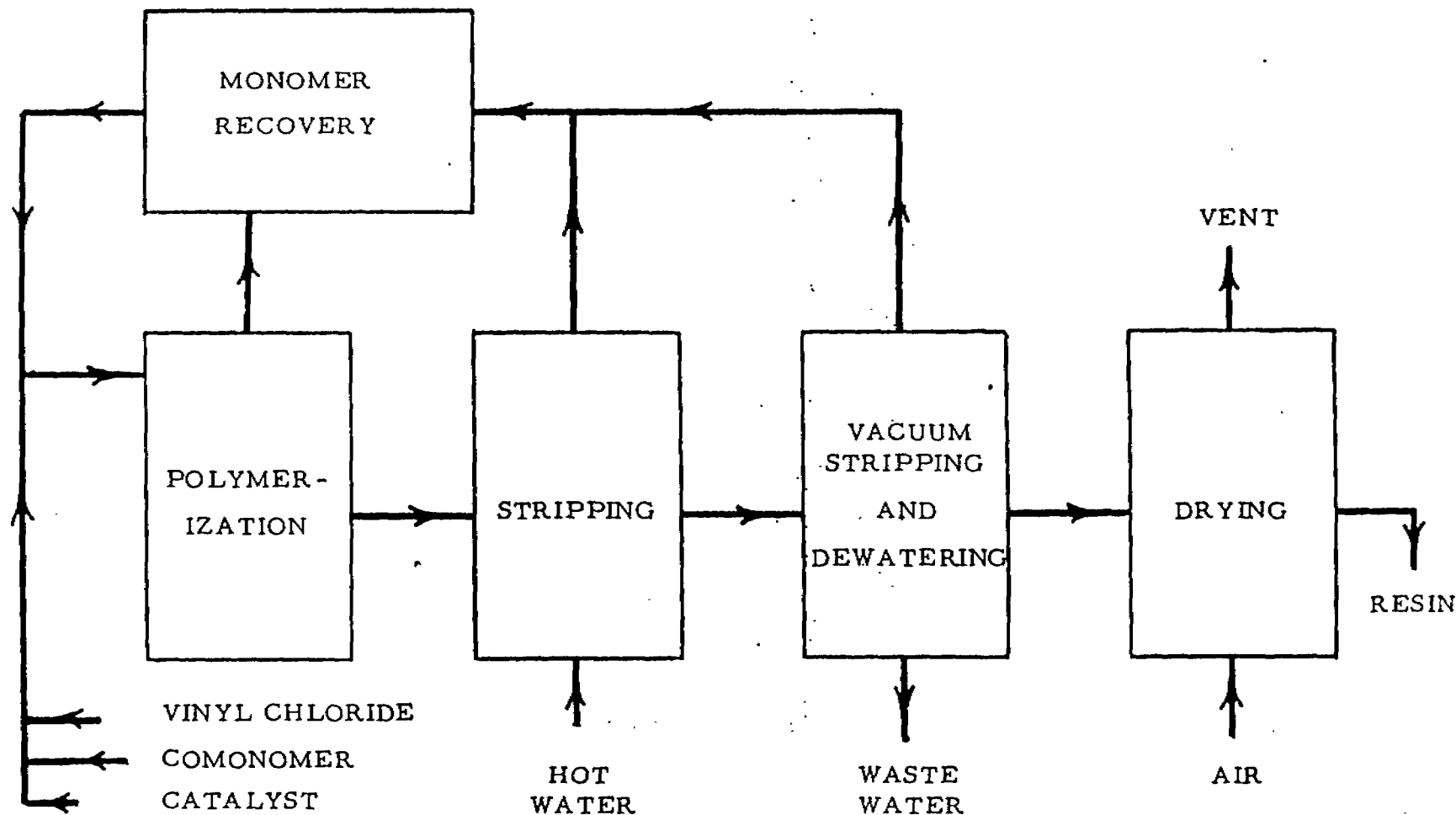
<u>Operator</u>	<u>Year 1973</u>	<u>Year 1976</u>
Number 1	7.9 ppm	0.5 ppm
Number 2	3.6 ppm	0.05 ppm
Number 3	7.95 ppm	0.43 ppm
Number 4	2.4 ppm	0.14 ppm
Number 5	16.6 ppm	0.14 ppm

The low TWA exposures for 1976 raise a question. The OSHA standard states that TWA exposures of less than 0.5 ppm require no control action yet on the day these measurements were made four out of the five men wore a respirator for a part of the day. The plant, as a safety policy, chooses to avoid employee exposure if there is a possibility of an emission.

The continuous bulk polymerization plant is a part of a larger suspension resin operation; therefore, no specific data on ambient air emissions is available.

Operational changes caused by the regulations are as follows:

FIGURE 14
CONTINUOUS BULK VINYL RESIN PROCESS



1. Solvent scrubbing of the monomer recovery system vent reduced the VCM concentration of this stream to less than 0.5%. The vent from this system was then incinerated in the local steam power plant. The solvent scrubbing system operates at 100 psi cleaning 400 pounds of vent gas per hour with methyl ethyl ketone.
2. The process control rooms where the operators spend most of their time were pressurized and ventilated with air from a remote location. When an operator has to go to a particular plant location he checks the VCM monitor and uses a respirator if the need is indicated.
3. All rotary pumps in vinyl chloride service were equipped with double mechanical seals as required by the proposed EPA standard. In this plant there was a decrease in the work space air concentration as a result of the change from packing and single seals to double seals.

Process development and new investment remain to be done in this process to achieve full compliance with the OSHA standard and the proposed EPA standard. Major items for further work are:

1. Improved resin slurry stripping. The present two-stage continuous system is barely meeting the minimum EPA limit for stripping. The monomer left in the very porous resin particle readily leaves the resin in the drier; thus, the resin leaves the process in the 0 to 10 ppm RVCM range. Improved stripping would reduce the dried resin to 0 ppm RVCM and would reduce potential employee VCM exposure in the drying area. The number of stripping stages and operating conditions are not yet fully determined.
2. Improved monomer recovery. Replacement of the existing reciprocating compressors with rotary units is in the engineering stage. This change will be a part of an overall revision of the recovered monomer system to provide more surge capacity, to reduce safety hazards caused by vacuum operation, to reduce vinyl chloride emissions and to reduce the energy requirements of the process. This low conversion process has a major portion of its investment in monomer recovery and handling equipment; thus, this could be said to be a large project.
3. Reactor agitator stuffing box revision. The proposed EPA standard requires that agitator packing consist of double mechanical seals with a pressurized sealing fluid between the seals. Since the reacting material has the potential for complete conversion

to polymer, mechanical seals quickly become inoperative. The present system uses dual sets of mechanical packing with a sealing fluid which hopefully EPA will accept as equivalent.

4. Equipment maintenance. As in the preceding discussion of other processes the application of EPA's proposed regulation to maintenance of equipment is not wholly clear; thus, a problem of interpretation and application of the regulation remains.

As in the solvent and latex processes the continuous bulk process has many other smaller emission problems that have been or are being corrected.

This discussion of the effect of governmental regulations on the specialty PVC processes is more of a brief progress report than it is a technical presentation. The industry has many problems that are similar to the larger segment of the PVC and it also has some problems that are peculiar to its operations. A great deal of progress has been made, but the end is not yet in sight.

In summary, the specialty vinyl chloride resin area has attempted to respond to the need for public and worker safety as well as to the resulting governmental regulations. The key factors in this response have been and will continue to be:

1. Availability of technical and financial resources.
2. Personal commitment on the part of the people involved.
3. Aid and cooperation of the regulatory bodies.

With these tools almost any problem including vinyl chloride control can be overcome with a lot of hard work.