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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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from the water and dried in rotary, flash or fluid bed dryers by exposure to heated air. The dried resin is transferred to storage silos, whence it is shipped to fabricating plants in bulk containers or in paper bags. If only vinyl chloride monomer is reacted, the product is PVC homopolymer. If a monomer such as vinyl acetate is mixed with the vinyl chloride then a PVC copolymer is produced.

The advantages of the suspension resin process are its high productivity per unit reactor volume, its flexibility with regard to polymer composition and resin particle characteristics and the granular nature of its product. The relatively large resin particles (50 to 150 μm) cause problems in removing unconverted vinyl chloride monomer. The monomer tends to diffuse slowly from the center of the resin particle to the surface, where it is removed by the monomer recovery operation; thus removal often is incomplete. In the past, residual vinyl chloride monomer concentrations in suspension PVC resins ranged as high as 2000 ppm by weight until improved methods were developed in response to recognized need for lower residual levels.

The process produces a wide variety of products, each of which presents different monomer release characteristics as well as differing suitability for particular fabricating operations. As a general rule, small particle size resins have lower residual monomer than large particle size; porous particle resins have lower residual monomer than nonporous particle resins; and resins containing little or no comonomer have lower residual monomer than resins with significant amounts of comonomer. The

relatively large suspension resin particle, while retaining monomer from the manufacturing process, results in a product that has excellent handling properties such as bulk flow. Recent improvements in monomer stripping technology have resulted in most PVC suspension homopolymer resins containing about 10 ppm residual vinyl chloride monomer at the time of shipment while the residual vinyl chloride monomer in most copolymers ranges from 25 to 200 ppm at the time of shipment.

The stress on residual monomer content at the time of shipment in the preceding paragraph is purposeful. Vinyl chloride monomer is not soluble in the PVC nor is it absorbed or adsorbed in the resin particle. It is entrapped, and, given an opportunity, it escapes to the ambient air. Heating tends to accelerate this escape. PVC resin in a bulk container loses its residual monomer at a rate of 25 to 50% per month. PVC resin in a paper bag loses its residual vinyl chloride monomer at an approximate rate of 75% per week. Once the residual monomer is gone, there is no source of monomer from the PVC resin, i.e., the resin does not decompose to yield significant amounts of monomer. If heated, the resin gives off hydrogen chloride and turns black. Thus a year-old PVC resin contains almost no residual monomer; on heating until it blackens it will always give off hydrogen chloride. PVC resin fabricating operations drive off the free residual monomer in the first heating step; thus the probability of a toxic response from vinyl chloride monomer contained in the vinyl film or

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

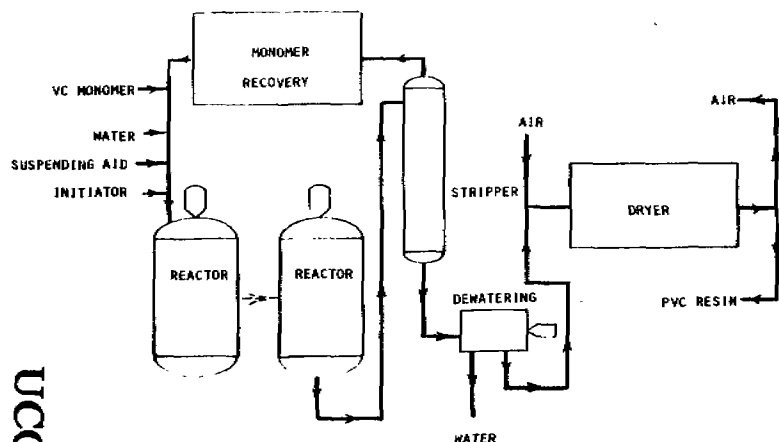


FIGURE 1. Suspension polymerization process.

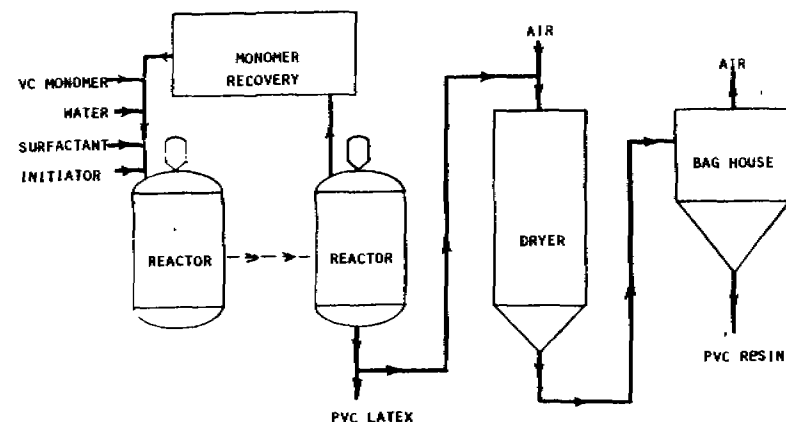


FIGURE 2. Emulsion polymerization process.

in the water initiator process. The resin particles formed during emulsion polymerization range in size from 0.05 to 2 μm . In the course of recovery and drying these may be agglomerated to particles as large as 30 μm . For some uses the agglomerates may be ground to a median particle size of about 2 μm . The small particle size results in rapid loss of residual vinyl chloride so that the resin contains about 1 ppm free monomer as produced. Because of handling problems, nearly all the resin is bagged, letting the small amount of monomer retained escape easily before it arrives at a fabricating plant.

Nearly all dried emulsion process PVC resin is utilized by paste or dispersion fabrication techniques. The resin, pigments and other additives are stirred into plasticizer, yielding a thick viscous liquid plastisol. This plastisol is spread on a cloth or a paper or poured into molds. The coated mold or cloth is heated, causing the resin and plasticizer to fuse into a solid forming the finished plastic article. In this fashion, the small manufacturer or the producer of elaborate shapes or highly styled items can make a product with a minimum capital investment.

The emulsion polymerization process, in addition to the reactor fouling problem noted for suspension polymerization, has less flexibility with regard to changes in process conditions. Each change in reaction, stripping or drying has an identifiable effect on product properties and quality. Some of these properties are well known, and quality tests keep them under control. Others are not well known and are recognized when customers com-

plain. Emulsion process resins cost more to produce, and plant operators tend to be very conservative in the approach to process changes. Because of this difficulty, emulsion process plants tend to emit more vinyl chloride monomer to the ambient air per pound of resin produced. In Europe particularly there have been reports of worker dermatitis from surfactants and possible pneumoconiosis from resin dust inhalation in the emulsion process plants (2-4).

Bulk polymerization is the third major process in terms of volume for the manufacture of PVC resins but supplies only about 5% of U.S. production (Fig. 3). The process involves the charging of vinyl chloride monomer and initiator to a first-stage polymerizer, where about 10% of the monomer is converted to polymer. This batch is then transferred to a second-stage polymerizer where additional monomer, and sometimes initiator, are added. The polymerization is continued until about 80-85% of the container monomer is converted to polymer. The unreacted vinyl chloride is removed by heat and vacuum and the finished resin product transferred to storage bins for later shipment to fabricating plants. The absence of water in the polymerization stage eliminates the need for the drying step and provides some economy in capital and operating costs.

The advantages of the bulk process are its simplicity, the uniformity of the resin particle size, the high porosity of the resin particles and the purity of the polymer (no soaps or suspending aids). The disadvantages are: less flexibility in product mix (homopolymers only) than the suspension pro-

cess 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 hazard to worker health.

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

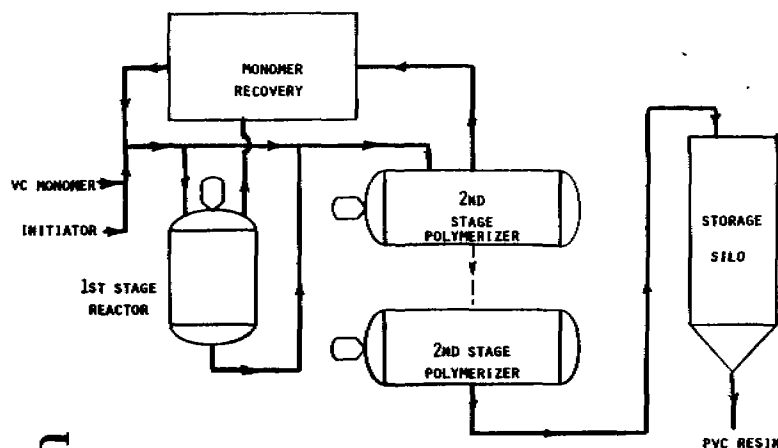


FIGURE 3. Bulk polymerization process.

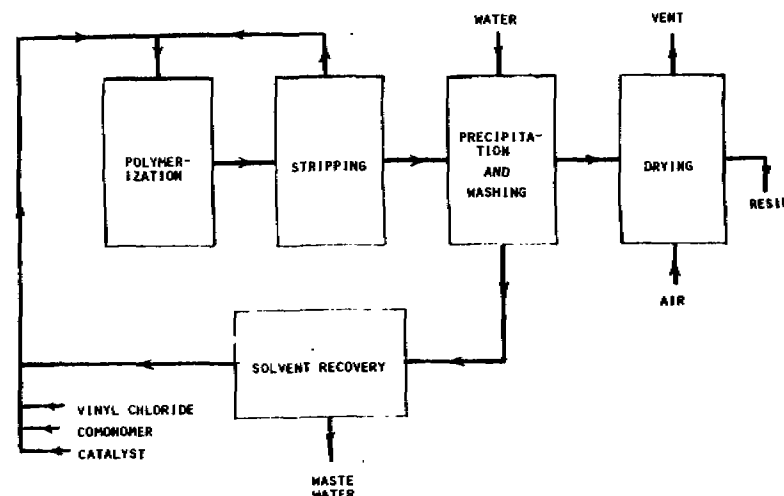


FIGURE 4. Solvent vinyl resin process.

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