POLLUTION CONTROL IN THE PLASTICS AND RUBBER INDUSTRY

Pollution Control in the Plastics and Rubber Industry

Marshall Sittig

NOYES DATA CORPORATION
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FOREWORD

This book is No. 18 in our Pollution Technology Review Series. It has become increasingly evident that much can and must be done by industry during the early stages of manufacture of raw materials, intermediates, and even of end products to control environmental pollution and improve waste removal techniques.

Therefore, the present volume is not just a book on pollution control in the plastics and rubber industries, but also a comprehensive treatise on plastics and rubber manufacturing processes and product finishing. The point of view is an integrated one: New and timely reviews of industrial practice are given together with constant attention to air pollution, water pollution, and solid waste problems.

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The Table of Contents is organized in such a way as to serve as a subject index and provides easy access to the information contained in this book. There is also an index of patentees and a valuable list of references to government reports which are hard to find via ordinary bibliographic search tools.

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CONTENTS AND SUBJECT INDEX

INTRODUCTION

The plastics and rubber industries—the polymer industries—have been among the fastest growing sectors of our economy. With growth, however, has come the responsibility for disposal of increasing quantities of air and water pollutants and especially solid wastes.

One aspect of this which can be mentioned at the outset is that plastics (particularly thermoplastics rather than thermosets) are recyclable whereas rubber is essentially not recyclable (vulcanized rubber perhaps being considered as more analogous to thermosetting resinous materials).

Today, some 10 million tons of plastics are used annually in products ranging from automobile components to artificial heart valves. Some of these plastics products—in fact the great majority—are used in applications that require long service. Some plastics, however, are used in forms that will be discarded after short-term use. The growing use of these short-term applications has led to speculation about contributions plastics may make to pollution.

In packaging, plastics have replaced other materials because of a number of advantages. Plastics in packaging aid in display of products, eye appeal and are lightweight. Plastics are used to package many household products including cosmetics, shampoos, bleaches, liquid detergents and a wide variety of food. Packaging plastics are those which primarily are discarded after serving their useful purpose within a year of manufacture. Ecologically, it is interesting to note that the same quantity of products packaged in most materials other than plastics would mean a larger contribution from packaging to the solid waste load—larger on a weight basis and, in most cases, on a volume basis according to Ethyl Corporation (1).

However in 1970, plastic packaging waste was estimated at 1.8 million tons compared to all other plastic solid waste of 0.75 million tons according to National Industrial Pollution Control Council (2), so the problem is there—and growing.

The plastics and rubber industry is unique in that is presents fairly massive problems of air pollution, water pollution and solid waste disposal. The air pollution problems result from manufacturing processes to some extent but more from possible products of incineration of plastics and rubber wastes. The water pollution problems are primarily a product of manufacturing operations. The solid waste disposal problems are perhaps the greatest of the three.

As pointed out by Ethyl Corporation (1), the volume of plastics in all solid waste is not large, but it is growing since the uses of plastics are growing. One recent study showed that the solid waste generated in the U.S. in a year was in the range of 300 million tons. Realistic estimates indicate that all plastics account for about three million tons of solid waste a year. Based on weights of refuse collected, the percentage of plastics, on average, is between 1.5 and 1.7% while paper products, for example, account for about 33% of the total. Food wastes comprise about 16% of the solid waste load with textiles and garden trash accounting for about 18% of the total. About 85% of the solid waste is disposed of via landfills and 10% via incineration.

According to H.H. Connolly, then Acting Deputy Commissioner, Solid Waste Management Office, U.S. Environmental Protection Agency in an address delivered to Palisade Section, Society of Plastics Engineers, Cherry Hill, New Jersey, October 1970, however, there is good reason to believe that the figures for plastic wastes could be as much as 12% by 1980.

In 1969, according to the EPA (3), the rubber industry consumed 3.2 million tons of rubber. The rubber industry consumption includes new rubber as well as reclaimed rubber and old tires consumed by retreaders and tire splitters. Tire splitting is a clear case of reuse, analogous to wiping cloth production from old textiles. Retreading is a more ambiguous case and could be viewed either as recycling or reuse. The table below shows recent patterns of rubber consumption in the United States.

Rubber Usage in the United States
'000 Long Tons

	1971	1972	1973	1974
Total new rubber	2,999	3,161	3,453	3,311
Reclaim	199	191	201	151
Retread	276	259	245	na*

na = not available

Source: Rubber Manufacturers Association

In reclaiming, obsolete and new rubber wastes are reduced to a uniform size by shredding and cracking; metals and fibrous materials are removed; the rubber is mixed with reclaiming oils, softened, and mixed with compounding agents; and after further refining and milling operations, the reclaimed rubber is sold in slabs or bales.

The tire splitting industry engages in the production of various industrial products die-cut from obsolete tires. Typical products are gaskets, shims, insulators, doormats, conveyor rollers, belt pieces, and the like.

Rubber wastes, usually in the form of obsolete tires and inner tubes, are handled by secondary materials dealers; some are rubber specialists, but this is a disappearing breed because rubber waste handling is not a very profitable business. Rubber dealers, who once paid waste generators for tires, are converting their operation to a new basis—whereby the generators pay them to remove the tires. Since tires occur in relatively small concentrations at garages and filling stations, the sales price is usually insufficient to cover a dealer's costs of picking up tires, removal and disposal of unacceptable tires (excessively worn tires, studded snow tires, steel-wire reinforced tires), and delivery or freight to the reclaimer. He must be paid for the removal service in order to stay in business.

Reclaimers, who can best use rubber wastes that are already free of metals and fibers, pay considerably more for such wastes than for tires.

Conventional recycling and reuse of rubber products is thus a limited activity. Rubber waste recycling and reuse depends in large measure on retread tire sales. The bulk of rubber production reaches the discard state in the form of tires which, though largely rubber, are composites of several materials, including textiles and metals. The reprocessing of this rubber by removal of impurities is usually less costly than production of virgin rubber, but the cost advantages have not been for the most part sufficiently great in light of the technical limitations of reclaim, to cause greatly increased use of reprocessed rubber.

Rubber in mixed municipal wastes usually also occurs as a component of products—soles and heels on footwear, rubber backings on textiles, wire coatings, gaskets and insulation in small appliances, etc. Some rubber is pure (water bottles, rubber bands, toys) but this is an insignificant portion of the total. Removal of these materials from mixed wastes for recovery appears impractical. Furthermore, a critical cost and logistics problem seems to be the collection of tires to central processing locations.

The most practical use for rubber, particularly old tires, appears to be raw materials recovery by distillation or energy recovery.

PLASTICS MANUFACTURE

Some idea of the environmental impacts of the manufacture of specific plastics in terms of air pollution, water pollution and solid waste disposal (as well as indications of environmental imports due to energy consumption and transportation), are given in Tables 1 through 5. These were taken (with permission) from *Plastics: Resource & Environmental Profile Analysis,* Washington, D.C., Manufacturing Chemists Association (June 28, 1974)(4).

TABLE 1: DATA FOR MANUFACTURE OF 1,000 POUNDS OF POLYVINYL CHLORIDE

Raw Materials	
(Vinyl chloride monomer 1,030 lb)	
Peroxides, stabilizers, antioxidants and hydrocarbons	3.0 lb
Energy	
Electric	84.0 kwhr
Natural gas	160.0 scf
Distillate oil	52.0 gal.
Water Volume	1,000.0 gal.
Process Solid Wastes	3.0 lb
Process Atmospheric Emission	
Hydrocarbons (as vcm)	30.0 lb
Particulates	0.34 lb
Waterborne Wastes	
BOD	0.45 lb
COD	2.25 lb
Suspended solids	0.45 lb
Transportation	
Rail	400 ton-miles
Truck	100 ton-miles

Source: Manufacturing Chemists Association (4)

TABLE 2: DATA FOR MANUFACTURE OF 1,000 POUNDS OF HIGH DENSITY POLYETHYLENE

Raw Materials--lb	
(Ethylene - 1,040)	
Solvent	45.7 lb
Additives	3.0 lb
Energy	
Electric	390.0 kwhr
Natural gas	2.5 scf
Water Volume	1,780.0 gal.
Process Solid Wastes	2.4 lb
Process Atmospheric Emissions	
Hydrocarbons	5.0 lb
Waterborne Wastes	
BOD	0.37 lb
COD	2.04 lb
Suspended solids	0.62 lb
Transportation	250 ton-miles

TABLE 3: DATA FOR MANUFACTURE OF 1,000 POUNDS OF LOW DENSITY POLYETHYLENE

Raw Materials--lb	
(Ethylene--1,047)	
Additives	35.0
Energy	
Electric	580.0 kwhr
Natural gas	5,000.0 scf
Diesel	0.02 gal.
Gasoline	0.05 gal.
Water Volume	262.0 gal.
Process Solid Waste	9.0 lb
Process Atmospheric Emissions	
Particulates	1.3 lb
Hydrocarbons	3.0 lb
Waterborne Wastes	
BOD	0.23 lb
COD	0.61 lb
Suspended solids	0.28 lb
Transportation	
Rail	250 ton-miles

Source: Manufacturing Chemists Association (4)

TABLE 4: DATA FOR MANUFACTURE OF 1,000 POUNDS OF ABS RESIN

Raw Materials	
(styrene - 680, acrylonitrile - 237, polybutadiene - 71)	
Material process addition	12.0 lb
Energy	
Electric	206 kwhr
Natural gas industrial heat	2,386 scf
Water Volume	2,841 gal.
Process Solid Wastes	1.0 lb
Process Atmospheric Wastes	
Hydrocarbons	2.70 lb
Waterborne Wastes	
BOD	0.46 lb
COD	2.36 lb
Oil	0.02 lb
Suspended solids	0.49 lb
Chromium	0.0016 lb
Iron	0.016 lb
Aluminum	0.016 lb
Nickel	0.008 lb
Cyanide	0.0008 lb
Transportation	
Rail	125.0 ton-miles
Truck	125.0 ton-miles

TABLE 5: DATA FOR MANUFACTURE OF 1,000 POUNDS OF HIGH IMPACT POLYSTYRENE RESIN

Raw Materials	
(Styrene - 989, Polybutadiene - 52)	
Material process addition	30.0 lb
Energy	
Electric	170.0 kwhr
Natural gas	1,471 scf
Water Volume	1,160 gal.
Solid Waste Process	5.0 lb
Atmospheric Hydrocarbons	2.9 lb
Waterborne Wastes	
BOD	0.19 lb
COD	0.87 lb
Suspended solids	0.24 lb
Oil	0.01 lb
Transportation	
Rail	250 ton-miles
Truck	250 ton-miles

Source: Manufacturing Chemists Association (4)

AIR POLLUTION

The major sources of possible air contamination in resin manufacturing are the emissions of raw materials or monomer to the atmosphere, emissions of solvent or other volatile liquids during the reaction, emissions of sublimed solids such as phthalic anhydride in alkyd production, emissions of solvents during thinning of some resins, and emissions of solvents during storage and handling of thinned resins. Table 6 lists the most probable types and sources of air contaminants from various resin-manufacturing operations.

In the formulation of polyurethane foam, a slight excess of tolylene diisocyanate (TDI) is usually added. Some of this is vaporized and emitted along with carbon dioxide during the reaction. The TDI fumes are extremely irritating to the eyes and respiratory system and are a source of local air pollution. Since the vapor pressure of TDI is small, the fumes are minute in quantity and, if exhausted from the immediate work area and discharged to the outside atmosphere, are soon diluted to a nondetectible concentration. No specific controls have been needed to prevent emission of TDI fumes to the atmosphere.

The finished solid resin represents a very small problem–chiefly some dust from crushing and grinding operations for molding powders. Generally the material is pneumatically conveyed from the grinder or pulverizer through a cyclone separator to a storage hopper. The fines escaping the cyclone outlet are collected by a baghouse-type dust collector. The collector should be designed for a filter velocity of about 4 fpm or less.

Most of the contaminants are readily condensable. In addition to these, however, small quantities of noncondensable, odorous gases similar to those from varnish cooking may be emitted. These are more prevalent in the manufacture of oil-modified alkyds where a drying oil such as tung, linseed, or soya is reacted with glycerin and phthalic anhydride. When a drying oil is heated, acrolein and other odorous materials are emitted at temperatures exceeding about 350°F (see further discussion under Varnish Cookers). The intensity of these emissions is directly proportional to maximum reaction temperatures.

TABLE 6: PRINCIPAL AIR CONTAMINANTS AND SOURCES OF EMISSION FROM RESIN-MANUFACTURING OPERATIONS

Resin	Air contaminant	Possible sources of emission
Phenolic	Aldehyde odor	Storage, leaks, condenser outlet, vacuum pump discharge
Amino	Aldehyde odor	Storage, leaks
Polyester and alkyds	Oil-cooking odors Phthalic anhydride fumes Solvent	Uncontrolled resin kettle discharge Kettle or condenser discharge
Polyvinyl acetate	Vinyl acetate odor Solvent	Storage, condenser outlet during reaction, condenser outlet during steam distillation to recover solvent and unreacted monomer
Polyvinyl chloride	Vinyl chloride odor	Leaks in pressurized system
Polystyrene	Styrene odor	Leaks in storage and reaction equipment
Petroleum and coal tar resins	Monomer odors	Leaks in storage and reaction equipment
Polyurethane resins	Tolylene diisocyanate	Emission from finished foam resulting from excess TDI in formulation

Source: EPA (5)

Thus, the intensity of noncondensable gases from resin formulation should be considerably less than that of gases from varnish cooking since the reaction temperature is approximately 100°F lower.

Control of monomer and volatile solvent emissions during storage before the reaction and of solvent emissions during thinning and storage after the polymerization of the resin is relatively simple. It involves care in maintaining gastight containers for gases or liquefied gases stored under pressure, and condensers or cooling coils on other vessels handling liquids that might vaporize. Since most resins are thinned at elevated temperatures near the boiling point of the thinner, resin-thinning tanks, especially, require adequate condensers. Aside from the necessity for control of air pollution, these steps are needed to prevent the loss of valuable products.

Heated tanks used for storage of liquid phthalic and maleic anhydrides should be equipped with condensation devices to prevent losses of sublimed material. An excellent device is a water-jacketed, vertical condenser with provisions for admitting steam to the jacket and provisions for a pressure relief valve at the condenser outlet set at perhaps 4 ounces pressure.

During storage the tank is kept under a slight pressure of about 2 ounces, an inert gas making the tank completely closed. During filling, the displaced gas, with any sublimed phthalic anhydride, is forced through the cooled condenser where the phthalic anhydride is deposited on the condenser walls. After filling is completed, the condensed phthalic anhydride is remelted by passing steam through the condenser jacket.

Addition of solids such as phthalic anhydride to other ingredients that are above the sublimation temperature of the phthalic anhydride causes temporary emissions that violate most air pollution standards regarding opacity of smoke or fumes. These emissions subside somewhat as soon as the solid is completely dissolved but remain in evidence at a reduced opacity until the reaction has been completed. The emissions can be controlled fairly easily with simple scrubbing devices. Various types of scrubbers can be used.

A common system that has been proved effective consists of a settling chamber, commonly called a resin slop tank, followed by an exhaust stack equipped with water sprays. The spray system should provide for at least 2 gallons per 1,000 scf at a velocity of 5 fps. The settling chamber can consist of an enclosed vessel partially filled with water capable of being circulated with gas connections from the reaction vessel and to the exhaust stack. Some solids and water of reaction are collected in the settling tank, the remainder being knocked down by the water sprays in the stack. Here the vapors from a polyester resin process kettle are first passed through a spray chamber type precleaner followed by a venturi scrubber.

This system effectively reduces visible emissions. Scrubber water may be recirculated or used on a once-through basis, depending primarily upon the available wastewater disposal system. The scrubber water can be odorous and should be discharged to a sanitary sewer.

Many resin polymerization reactions, for example, polyvinyl acetate by the solution method, require refluxing of ingredients during the reaction. Thus, all reactors for this or other reactions involving the vaporization of portions of the reactor contents must be equipped with suitable reflux- or horizontal-type condensers or a combination of both. The only problems involved here are proper sizing of the condensers and maintaining the cooling medium at the temperature necessary to effect complete condensation.

When noncondensable, odor-bearing gases are emitted during the reaction, especially with alkyd resin production as already mentioned, and these gases are in sufficient concentration to create a public nuisance, more extensive air pollution control equipment is necessary. It includes equipment for absorption and chemical oxidation, adsorption, and combustion, both catalytic and direct-flame type.

As regards the intermedia aspects of the plastics manufacturing industry, water pollution control can give rise to some air pollution problems. If incineration of waste sludges is employed, for example, there is potential for air pollution, principally particulates and possibly nitrogen oxides, although the latter should be minimal because incineration of sludges does not normally take place at temperature levels where the greatest amounts of nitrogen oxide are generated. Odors from the wastewater treatment plants may cause occasional problems since wastewaters are sometimes such that heavy, stable, foams occur on aerated basins and septicity is present. But, in general, odors are not expected to be a significant problem when compared with odor emissions possible from other plant sources.

Polyvinyl Chloride Manufacture

The general types of emissions, emission control techniques and control costs have been described by B.H. Carpenter of Research Triangle Institute (6).

The problems of vinyl chloride monomer (VCM) emission have of course reached almost panic proportions in the public press due to disclosures of the involvement of vinyl chloride in deaths from liver cancer (angiosarcoma). As a consequence, the U.S. Occupational Safety and Health Administration (OSHA) has proposed rules for vinyl chloride exposure. However, as pointed out in *Chemical Week* for January 15, 1975, the proposed OSHA rules are already in litigation in the courts.

The Society of the Plastics Industry (SPI) and several of its member companies are opposing OSHA's recently issued regulation stating that employees must not be exposed to air in which the vinyl chloride content is more than one part per million. The new standard was stated to go into effect in January 1975 but the Second Circuit Court of Appeals in New York granted a stay pending a decision on the merits of the SPI objection. Meanwhile an earlier standard of 50 ppm remains in effect.

In PVC production, as reported by Carpenter (6), the pounds of VCM losses per pound of PVC are at least an order of magnitude higher than those from VCM production. Most producers report PVC production as 3 to 4% lower than VCM intake, and some producers report 1 to 1.5% of PVC production lost as fines to the atmosphere. Thus, the actual VCM losses (2 to 3%) result from the batch operation of the polymerization and in the filtration and the drying of the polymer. Direct reduction to 50% of this level seems possible, but a 90% reduction without process changes in some existing PVC plants is likely to be beyond control techniques and acceptable costs. However, intensive stripping at the end of the suspension reaction may achieve the 90% reduction at acceptable costs.

Controls appraised for VCM production sources include recycling of vent streams, condensation with refrigeration, compression, adsorption with carbon, incineration, oxidation with ozone, absorption (scrubbing), and venting to flares. Monomer loading (and unloading) involves special controls: vapor collection adapters with recycling, thermal level detectors with recycling, and magnetic gauges. The PVC production sources can benefit from the same controls plus vacuum stripping of crude product, steam stripping, and carrier airstream recycling. Fugitive sources require use of better valves, packings, etc. A typical PVC plant includes the following operations:

[1] Receiving and storage of VCM and catalysts.
[2] Polymerization of VCM: measuring and charging, and reaction.
[3] Stripping and recovery: reactor blowdown and recovery, and slurry handling and storage.
[4] Centrifugation or filtration.
[5] Drying.
[6] Pneumatic conveying and storage.
[7] Packaging and shipping.
[8] Blending.
[9] Waste treatment.

Compounding, which may be done in a PVC resin plant or in separate facilities, is not included in this study.

Total PVC output for 1972-73 is attributed to four process types: suspension polymerization, 78%; emulsion polymerization, 12%; bulk polymerization, 6%; and solution polymerization, 4%. All polymerizations in the United States are batch operations, which probably contribute strongly to the severity of the VCM emissions problem.

Suspension polymerization (Figure 1) uses a water media, a suspension agent such as polyvinyl alcohol, and an oil-soluble catalyst. A typical recipe is 100 parts VCM, 200 of water, 0.1 to 0.2 of catalyst, and 0.005 to 0.0 of suspension agent. The VCM-water ratio can be varied over a wide range; the limiting factor is sufficient fluidity of the final PVC-water slurry, for adequate dissipation of the heat evolved during polymerization. Oil-soluble catalysts such as dibenzoyl peroxide, acetyl benzoyl peroxide, or dibutyl peroxide are preferred to the water soluble persulfate catalyst. Persulfate is slower, and it produces particles too fine to be handled in conventional filtering and drying equipment.

Commercial suspension resins show little or no retention on a 100-mesh (U.S. standard) screen and from 30 to 80% retention on a 200-mesh screen. Such a particle size is achieved by rapid agitation in glass-lined autoclaves at 35° to 45°C. Vigorous agitation suspends VCM as fine droplets in water, controls size, and gives a granular polymer for better filtering and drying.

During polymerization, alkaline buffers such as sodium carbonate, bicarbonate, and phosphate have been used to maintain the pH at 5 to 8 to prevent formation of hydrochloric acid. Use of an inert substance such as nitrogen increases reaction rate, reduces the amount of hydrochloric acid evolved, and thereby increases the stability of the polymer.

There is little published information on molecular weight distribution and chain branching of vinyl chloride polymers. However, chloride polymers in general have narrow molecular distributions, especially compared to those of polystyrene.

The major advantage of suspension polymerization is the excellent heat transfer rate attainable in conventional equipment. The major disadvantage is that water must be separated from the polymer, usually by centrifugation and drying.

In Table 7 the VCM emissions rates are given for the sources shown in Figure 1; the table is restricted to those plants for which data have been supplied.

Fugitive emissions account for 12 to 46% of total emissions. Vacuum stripping of the crude product would reduce these emissions 50 to 80%; carbon adsorption, 50 to 99%; condensation with refrigeration, 40 to 60%; incineration, 50 to 99%; and adsorption, 50 to 90%.

Collectively, the dryer vents, the air conveyor vent, the storage bin vent, and the centrifuge vent provide 35% of the total emissions. Vacuum stripping could achieve 50 to 80% reduction, and either carbon adsorption, ozone oxidation, incineration, steam stripping, or recycling to compressors would reduce emissions 40 to 99%. Air recycling should reduce these emissions 40 to 80%.

Blend surge tanks account for 11% of total emissions. Carbon adsorption, ozone oxidation, and incineration should give 50 to 99% reductions. Vacuum stripping and absorption are expected to give 50 to 80%; recycles to compressors, 40 to 60%.

The emulsion process (Figure 2) is similar to the suspension process (Figure 1). In emulsion, the particle size is smaller. Emulsifiers and additives maintain a nonsettling emulsion during polymerization. At least four components are needed—water, VCM, water soluble initiators, and an emulsifying agent. Water is the continuous phase; VCM is the discontinuous phase. Low concentrations of emulsifiers (either anionic or cationic) behave essentially as electrolytes because they are uniformly distributed between the water-VCM phases. When the concentration is increased, the surface tension between the phases decreases and the conductivity of the mixture increases.

FIGURE 1: SIMPLIFIED FLOW DIAGRAM OF PVC SUSPENSION PROCESS

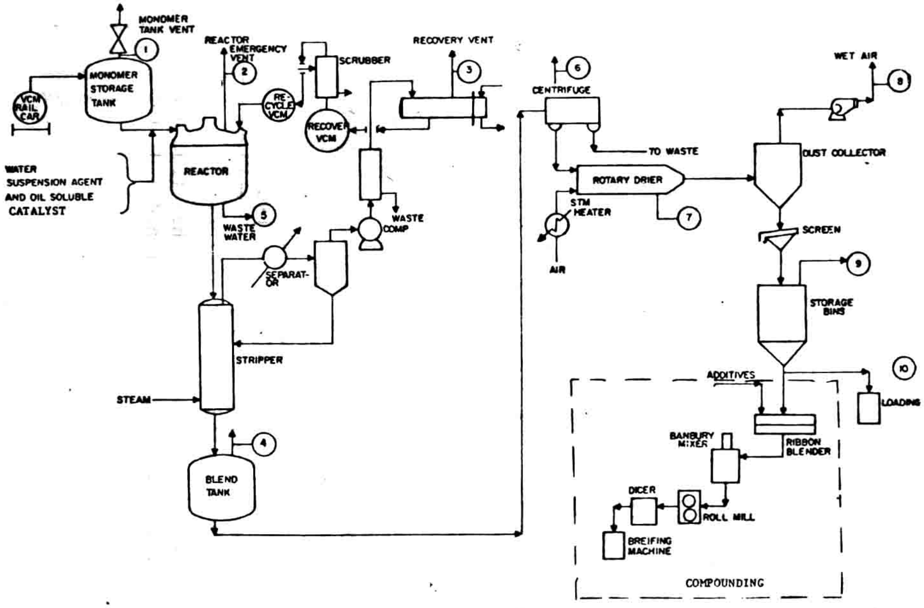
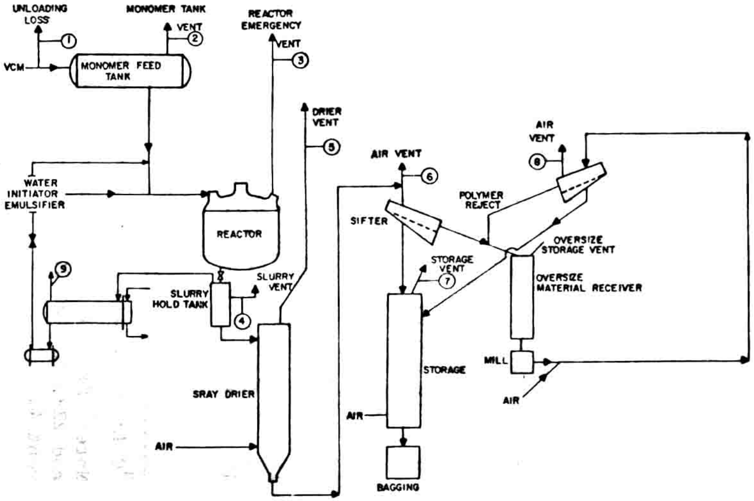


FIGURE 2: SIMPLIFIED FLOW DIAGRAM FOR BATCH EMULSION POLYMERIZATION OF VINYL CHLORIDE



Source: B.H. Carpenter (6)