A.I.Ch.E.

1964

SEMINAR

POLYVINYL CHLORIDE

MANUFACTURE

AND TECHNOLOGY

SPONSORED BY

THE AMERICAN INSTITUTE

OF CHEMICAL ENGINEERS

PRESENTED BY

THE GENERAL TIRE & RUBBER COMPANY

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AMERICAN INSTITUTE OF CHEMICAL ENGINEERS TEACHING SEMINAR
PRESENTED BY THE GENERAL TIRE & RUBBER COMPANY

AGENDA

October 16, 1964

8:00 - 8:30 A.M.	Registration, Conference Room Falls-Akron Motel
8:30 - 8:40	Welcome, J. H. Koffolt for A.I.Ch.E.
8:40 - 8:50	Welcome, P. E. Jacobs for General Tire
8:50 - 9:00	Briefing, E. E. Gruber, Director of Research and Development
9:00 - 9:30	History of PVC, A. J. Beber, Manager, Chemical Pilot Plant
9:30 - 10:00	Theory of Polymerization, R. Milkovich, Group Leader, Polymer Research
10:00 - 10:15	Break
10:15 - 10:45	Vinyl Chloride Synthesis, P. R. Sayre, Tech. Supt., Ashtabula, Chemical Division
10:45 - 11:15	General Tire Suspension Process, W. J. Hanlon, Technical Manager, Chemical Division
11:15 - 11:45	PVC Fabrication and Applications, G. Hackim, Vice President - Sales, Chemical-Plastics Division
11:45 - 1:30 P.M.	Luncheon, Falls-Akron Motel
1:30	Buses depart for tours at Pilot Plant and R & D Center
3:30 - 4:30	Panel discussion at R & D Cafeteria
4:30	Buses depart for Falls-Akron Motel
5:30	Buses depart for Women's City Club
6:00 - 7:00	Social Hour
7:00 - 8:00	Banquet
8:00	Welcome, M. G. O'Neil, President, General Tire
Speaker	Sam Salem, President, Chemical-Plastics Division
Remarks	By representative of the A.I.Ch.E.

GENERAL INTRODUCTION

The program being presented by The General Tire & Rubber Company for the members of A.I.Ch.E. in this one day seminar is concerned only with "Polyvinyl Chloride, Manufacture and Technology." The importance of this plastic in the United States is evidenced by a consumption now approaching nearly two billion pounds per year. We have attempted to set up the day's program to carry you through the early history of PVC, present day technology, including vinyl chloride monomer synthesis, polymerization theory, and plant scale manufacturing of polyvinyl chloride resin. Some of the technology used to produce useful end products is discussed. We have tried to make this presentation, which includes much proprietary engineering data, the most up-to-date and comprehensive treatment of this subject matter available.

General Tire entered the plastics fabrication field in the early 1950's on a large scale by acquisition of several manufacturing facilities located in Ohio, Pennsylvania, and Massachusetts. These facilities made General Tire the largest calender operator for vinyl in the United States. Products manufactured in these plastic plants include calendered, printed, and embossed supported and unsupported vinyl film and sheeting for the home furnishings, marine, shoe, and automotive accessory industries. A new plant in Columbus, Mississippi, a multimillion dollar investment in plastic operations, went on stream late in 1963.

In 1954, General Tire built a plant at Ashtabula, Ohio, to produce vinyl chloride from acetylene and hydrochloric acid and to produce polyvinyl chloride resins by the suspension polymerization method. This plant is now undergoing its third major expansion.

General Tire is thus vertically integrated in the vinyl field from monomer synthesis through polymerization and, finally, is a supplier of all types of plastic end products or accessories to several major industries. General Tire's capabilities in plastic fabrication, in addition to vinyl applications, include reinforced polyester plastics, thermoplastic end products, and polyurethane plastic foam for all kinds of cushioning applications.

BIOGRAPHY

Dr. Elbert E. Gruber received his B.S. in Chemistry at Xavier University, Cincinnati, Ohio, in 1932. He was awarded degrees of M.S. and Ph.D. in Organic Chemistry in 1934 and 1937 respectively at the University of Illinois where he also served as Graduate Assistant in Chemistry during 1935-1937. Upon completion of his graduate work, Dr. Gruber joined the Research Division of the B. B. Goodrich Company in 1937 advancing to the position of Research Supervisor in 1946. During the war years of 1943-1946 he served on a committee on modifiers in the Copolymer Research Group, Office of Rubber Reserve. In 1950 he joined the Central Research Laboratories of The General Tire & Rubber Company as Head of Plastics Research and in 1955 was named Assistant Director for Exploratory Research, and in 1962 became Director of Research and Development. In addition to his duties at General Tire, Dr. Gruber serves as a member of the Solid Committee of the Large Rocket Committee of the Aerojet-General Corporation, Azusa, California.

HISTORY OF POLYVINYL CHLORIDE

by

A. J. BEBER

BIOGRAPHY

A. Joseph Beber is a native of Montana. Graduated from Montana State College in 1930 with a Bachelor of Science degree in Chemical Engineering, he received his Master's degree in Chemical Engineering, 1932, and a Ph.D. in Chemistry and Physiology, 1937, from the University of Minnesota. Until 1942, Dr. Beber was associated with Southwest Missouri State College as instructor in General, Analytical, and Organic chemistry. He then joined B. F. Goodrich Company as Research Chemist, working on organic synthesis of rubber chemicals. In 1949, Dr. Beber came to The General Tire & Rubber Company, serving in the analytical and pilot plant sections of research. He now acts as Manager of the Company's chemical pilot plant at Mogadore, Ohio.

HISTORY OF POLYVINYLCHLORIDE

The first billion-pounds-per-year plastic product, polyvinylchloride, is designated by the term "vinyls" or "vinyl resins." It is produced on a global basis and is marketed under many trade names such as PVC, Vinylites, Geons, Corvic, Vinidur, Vinnol, Pliovic, Marvinol, Opalon, and General Tire's Vygens.

That PVC has risen to such an important place in the economies of several nations is due to a great deal of technical work done in this field. The need of a rubber substitute as well as artificial leather and another celluloid started the research in Germany. With the advent of the war, England likewise was required to find a rubber substitute, particularly for the wire and cable industry.

The development of special forms of the polymers such as plastisols during the later war years led to the coating of textiles for the manufacturer of leather-like cloth products. By the end of the war, good plastisol polymers were available and from 1948 the standard types of PVC suspension, emulsion, polymers and copolymers were being made in increasing tonnage.

The period 1950-1955 throughout the world saw the development of improved polymers. Following this period, major price reductions were made and this, together with the improved polymers for special applications and improved process techniques, have all contributed to the amazing growth in consumption over the past twenty years.

The early beginnings can be traced back to 1835 when M. V. Regnault[1] published his findings on the reaction of an alcoholic solution of caustic potash on the ethylene dihalides to yield the monomer vinyl chloride according to the following equation:

$$CH_2Cl\text{-}CH_2Cl + KOH \rightarrow CH_2 = CHCl + H_2O + KCl$$

He also observed that when the mixture was allowed to stand for a time, and subsequently heated and exposed to sunlight, a white precipitate formed. Several reviews[2][3][4] have covered in considerable detail the development of polyvinylchloride. M. Kaufman[5] presents an interesting review of the development of polyvinylchloride in England. Almost 40 years later, 1872, Dr. E. Baumann[6] published his obaervations that vinyl bromide as well as vinyl chloride in sealed tubes exposed to sunlight, changed from liquids to light-colored solids. He also observed that these materials were extremely chemically resistant to acids, alkalies, and solvents.

The next significant steps are described in papers by I. Ostromislensky.[7][8] The first one, published in 1912, was entitled "Concerning the Structure of Polymerized Vinyl Bromide and Its Rubber." He observed the reaction of ultraviolet light on the polymerization of vinyl chloride and vinyl bromide to yield three different modifications, and on the basis of their solubilities, he divided them into alpha, beta, and gamma forms and considered that the degree of polymerization was the highest with the most insoluble or gamma form. The most insoluble or gamma isomer was called Kaupren bromide and Kaupren chloride, and served for the basis of determining the cryoscopic molecular weight and resulted in the empirical formula ($C_{32}H_{48}Br_{16}$) or ($C_{32}H_{48}Cl_{16}$) which showed that 16 vinyl halides had been definitely combined.

$$16\ CH_2 = CHCl \rightarrow C_{32}H_{48}Cl_{16}$$

$$16\ CH_2 = CHBr \rightarrow C_{32}H_{48}Br_{16}$$

At about the same time, 1912, Ostromislensky and others[9] applied for a British Patent entitled "A Process for Obtaining Rubber or Similar Substances from Polymerized Vinyl Bromide or Polymerized Vinyl Chloride and Their Methyl Homologs." It was stated that the polymerized vinyl chloride or vinyl bromide is identical in all its properties with the chloride or bromide of the "Butadiene" rubbers. They also noted the action of sunlight and the absence of oxygen in accelerating this reaction. It was observed that the polymerization could easily be effected in solution, in bromobenzene, toluene, xylene or carbon disulfide. Later Ostromislensky[10] received a patent on a process for obtaining vinyl chloride from acetylene. Also in 1929, he received a British Patent[11] "The Preparation of PVC and the Application of Plasticizers such as dichlorbenzene, chlorinated naphthalene in order to work the material into plastic masses and films."

In 1912, F. Klatte[12] was issued a German Patent for "The Synthesis of Vinyl Chloride by the Reaction of HCl and Acetylene." In an analogous reaction, he likewise made vinyl acetate. These syntheses still today are the main ones for the commercial production of these monomers.

Klatte and others[13] obtained a Patent for the "Processing and Preparation of Horny Materials, Films, Synthetic Fibers, Lacquers, and Working of Plastic Materials." They also recognized at this time that, with or without additives, through pressure or with solvents, PVC could be softened or dissolved so that it could be worked into a desirable shape or form.

In 1928, three groups working independently developed vinyl chloride copolymers. The use of vinyl acetate as a copolymer in the polymerization of vinyl chloride greatly increased the use of the vinyl polymers because it solved the processing difficulties of the straight homopolymers. The three groups: E. W. Reid[14] from Carbide and Carbon, Voss and Dickhauser[15] from I. G. Farbenindustrie, and W. E. Lawson from DuPont,[16] all obtained patents on their processes.

A little later, W. L. Semon[17] disclosed that a rubber-like gel structure could be obtained by intimately mixing a high boiling point material like tritolylphosphate into the polymer. This was later followed by other plasticizers and resulted in a product called "Koroseal"[18] and has served as a basis for the development of this new class of materials.

The first commercial polymerization process of vinyl chloride resulting from technical applications is credited to Lawson and Werntz of E. I. DuPont deNemours[19] who, in the year 1928, showed that peroxide catalysts such as ozone, benzoyl peroxide and barium peroxide could be used. In the earlier patents only the action of light and heat were described. The DuPont process could likewise be used in organic solvents.

The application of emulsion processes for vinyl chloride polymerizations resulted in a rapid development of PVC preparation and applications. The oldest emulsion polymerization process of vinyl chloride is that of Mark, Fikentscher, Hengstenberg, and V. Susich.[20] A further advance was the I. G. process of Bappert and Wick[21] for "Continuous Emulsion Polymerization."

The effect of oxygen or air on the course of the polymerization was later recognized by Schonfeld.[22]

The oldest suspension process, although not using vinyl chloride, appears to be that of Crawford and McGrath,[23] who developed a suspension process for a series of acryl and vinyl esters. The first suspension PVC resins were made by Dr. Berg[24][25] of Wacker-Chemie in 1935 in which he employed partially saponified polyvinyl acetate (polyvinyl alcohol) as the protective colloid. In the suspension process, the PVC is formed in polymerization into a granular powder in an easily-filterable form.

The future of PVC as well as the past is linked to the appropriate balance of research and development. Further expansion and growth of the PVC industry is dependent on a greater knowledge of its basic behavior and improved processing techniques.

Where the industry now stands in this country is shown in the following Tables 1 and 2 of monomer and polyvinyl chloride resin production capacities.

Table 1

Estimated Vinyl Monomer, U. S. Capacity, 1964

	Capacity-Millions of Pounds Annually
B. F. Goodrich	400
Union Carbide	280
Ethyl Corporation	240
Dow Chemical	200
Tenneco (Cary Chemical)	170
Allied Chemical	150
Monochem (Borden & U. S. Rubber)	150
Monsanto	150
Diamond Alkali	90
Goodyear	45
Cumberland Chemical (Airco)	60
General Tire	30
American Chemical	40
	2025

Table 2

Estimated Polyvinyl Chloride Resin, U. S. Capacity, 1964

	Capacity-Millions of Pounds Annually
B. F. Goodrich	325
Union Carbide	275
Monsanto Chemical	150
Cary Chemical	140
Firestone Tire & Rubber	125
Diamond Alkali	120
Air Reduction	115
U. S. Rubber	110
Goodyear Tire & Rubber	80
Borden Chemical	80
Thompson Chemical	65
General Tire & Rubber	55
Pantasote Company	50
Dow Chemical	40
Escambia Chemical	40
Atlantic Refining	25
Atlantic Tubing	25
Keysor Chemical	25
Great American Plastics	15
American Chemical	12
Rubber Corporation of America	10
Minnesota Mining & Manufacturing	5
	1887

Literature References

(1) M. V. Regnault, Liebigs Ann. Chem. 15 (1835) 63
(2) C. E. Schildknecht, "Vinyl and Related Polymers," Wiley and Sons (1952)
(3) F. Kainer, "Polyvinylchlorid and Vinylchlorid-Mischpolymerisate," Springer-Verlag (1951)
(4) Karl Krekeler and Georg Wick, "Kuntstoff-Handbuch" Band II Teil 1, Karl Hanser-Verlag (1963)
(5) M. Kaufman, "The First Century of Plastics," P. 74, Plastics Institute, London, 1963
(6) E. Baumann Liebigs Ann. Chem. 163 (1872) 312
(7) I. Ostromislensky, J. Russ. Phys. Chem. Ges. 44 (1912) 204-239, Chem Zentral, 1912, I, 1980
(8) I. Ostromislensky, J. Russ. Phys. Chem. Ges. 48 (1916), 1132-51, Chem Zentral, 1923, IV, 606
(9) B. P. No. 6299 (Ostromislensky and Others) (1912)
(10) U.S.P. No. 1,541,174 (Ostromislensky) (1925)
(11) B. P. No. 255,837 (Ostromislensky) (1925)
(12) D.R.P. No. 278,249 F. Klatte (1912)
(13) D.R.P. No. 281,877 F. Klatte (1913)
(14) U.S.P. No. 1,935,577 E. W. Reid (1928)

(15) U.S.P. No. 2,012,177 Voss and Dickhauser (1935)
(16) U.S.P. No. 1,867,014 W. E. Lawson (1928)
(17) U.S.P. No. 2,188,396 W. L. Semon (1940)
(18) U.S.P. No. 1,929,453 W. L. Semon (1933)
(19) B. P. No. 319,591 Lawson and Werntz (1928)
(20) U.S.P. No. 2,068,424 Mark, Fikentscher, Hengstenberg, and Susich (I. G. Farben ind.) (1937)
(21) D.R.P. No. 679,897 Bappert and Wick (1936
(22) U.S.P. No. 2,168,808 Schonfeld (B. F. Goodrich) (1937)
(23) U.S.P. No. 2,108,044 Crawford and McGrath, ICI (1933)
(24) D.R.P. No. 750,428 Berg (Wacker-Chemie) (1935)
(25) D.R.P. No. 755,028 Berg (Wacker-Chemie) (1935)

THEORY OF POLYMERIZATION

by

R. MILKOVICH

BIOGRAPHY

Ralph Milkovich is a native of Clairton, Pennsylvania. He was graduated from Duquesne University with a Bachelor of Science degree in Chemistry in 1951. After four years in the research laboratories of the Koppers Company, he attended State University of New York, receiving a Master's degree in Physical and Organic Chemistry in 1957. He received a Ph.D. in Polymer Chemistry from the University of Akron in 1959. Returning to industry, Dr. Milkovich first accepted a position with The Shell Chemical Company in California. He was active in the Polymer Group of the Southern California Section of the American Chemical Society, serving as Chairman of both the Arrangements and the Executive Committees, and was instrumental in the establishment of the Gordon Research Conferences on the West Coast. He was also instructor of Polymer Chemistry at the University of California, Los Angeles, before joining The General Tire & Rubber Company in 1963. Dr. Milkovich presently serves as Group Leader of Polymer Preparation in Plastics Research.

THEORY OF POLYMERIZATION

Introduction

This paper is an introduction to polymerization terminology as applied to the kinetics and mechanisms involved in the synthesis of macromolecules. The presentation will be of a general nature to help you better understand the following presentations which deal specifically with the commercial preparation of polyvinyl chloride.

Definition

Polymers are high molecular weight materials consisting of chains of many repeating units. The process connecting such units (monomers) into a chain is called polymerization. Through the process of polymerization, a variety of reactive gases, liquids, and solids are converted into high molecular weight materials which have been found to have unique physical properties of commercial importance as shown in Table I.

There are two main classes of reactions which are responsible for the formation of these useful materials, polycondensation and addition polymerization. The similarities of these two classes of reactions are that they both lead to the formation of long chains. The differences are based on the reactions involved, which are dependent on the type of monomer employed. Polycondensation reactions proceed in a stepwise fashion involving intermolecular condensation of dissimilar functional groups, e.g., esterification to produce Dacron. Addition polymerization is a fast chain reaction involving monomers having one functional group such as carbon-carbon double bonds to produce such materials as polyethylene. In addition polymerization, an active center rather than an organic functional group is responsible for the growth of the chain. Polymer molecules are formed from the beginning of the reaction and almost no species intermediate between monomer and high molecular weight polymer are found. The synthesis of polymeric chains having molecular weights of several million are possible in addition polymerization. There are three different types of active centers which can provide mechanisms of addition polymerization. These are:

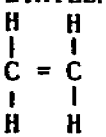
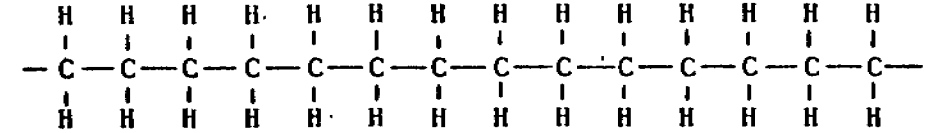
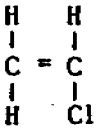
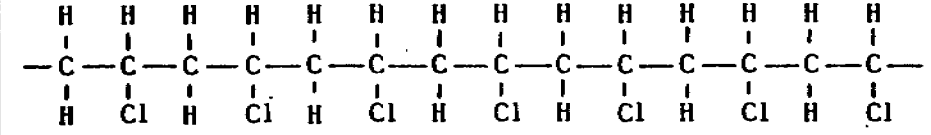
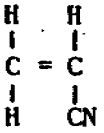
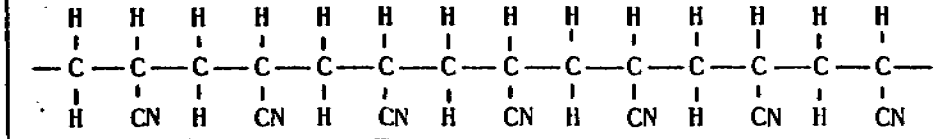
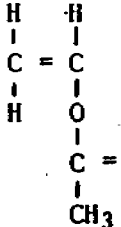
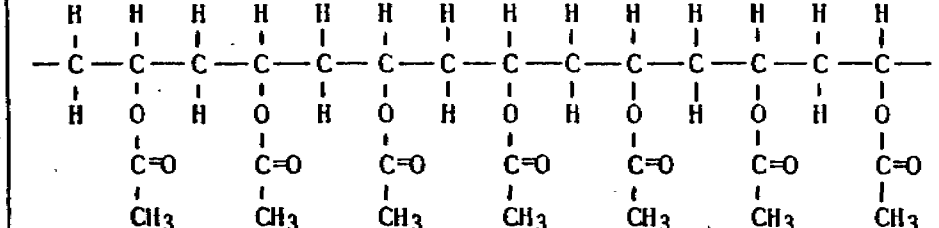
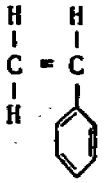
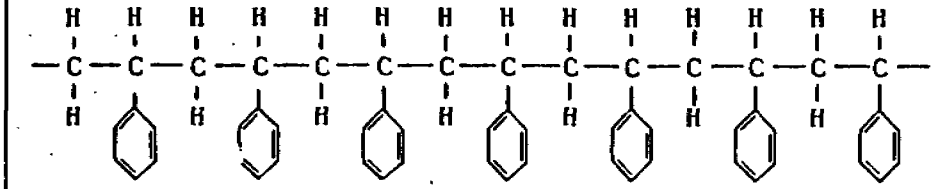
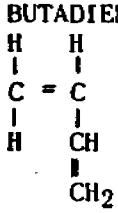
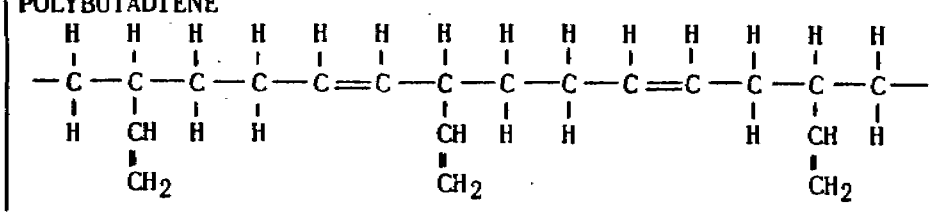
Free Radicals	$R\cdot$
Cations	$R^{\oplus}$
Anions	$R^{\ominus}$

Suspension Polymerization

The traditional avenues by which monomers are converted to polymers by a free radical mechanism are:

TABLE

ADDITION POLYMERS

MONOMER	POLYMER	PRINCIPAL USES
ETHYLENE 	POLYETHYLENE 	1. FILMS 2. TUBING 3. MOLDED OBJECTS 4. ELECTRICAL INSULATION
VINYL CHLORIDE 	POLYVINYL CHLORIDE 	1. SHEETS 2. PHONOGRAPH RECORDS 3. COPOLYMER WITH VINYL ACETATE TO MAKE FLOOR COVERINGS, LATEX PAINTS, ETC.
ACRYLONITRILE 	POLYACRYLONITRILE 	1. FIBERS; E.G., ORLON, ACRILAN
VINYL ACETATE 	POLYVINYL ACETATE 	1. CHEWING GUM 2. ADHESIVES 3. TEXTILE COATINGS 4. TO MAKE POLYVINYL ALCOHOL (ON TREATMENT WITH ALKALI)
STYRENE 	POLYSTYRENE 	1. MOLDED OBJECTS 2. ELECTRICAL INSULATION 3. COPOLYMER WITH BUTADIENE TO MAKE BUNA-S AND GR-S RUBBER 4. TO MAKE ION-EXCHANGE RESINS (ON TREATMENT WITH SULFURIC ACID)
BUTADIENE 	POLYBUTADIENE 	1. BUNA RUBBER

A. Bulk Polymerization

A polymerization system containing only monomer and an initiating species.

B. Solution Polymerization

A polymerization system in which the monomer is polymerized in the presence of a solvent.

C. Emulsion Polymerization

This polymerization system is distinguished by the fact that the monomer is solubilized in water by a soap into microscopic particles called micelles, to form a stable colloidal emulsion. The polymerization reaction is initiated in the micelles. The final product is an emulsified polymer system called a latex.

D. Suspension Polymerization

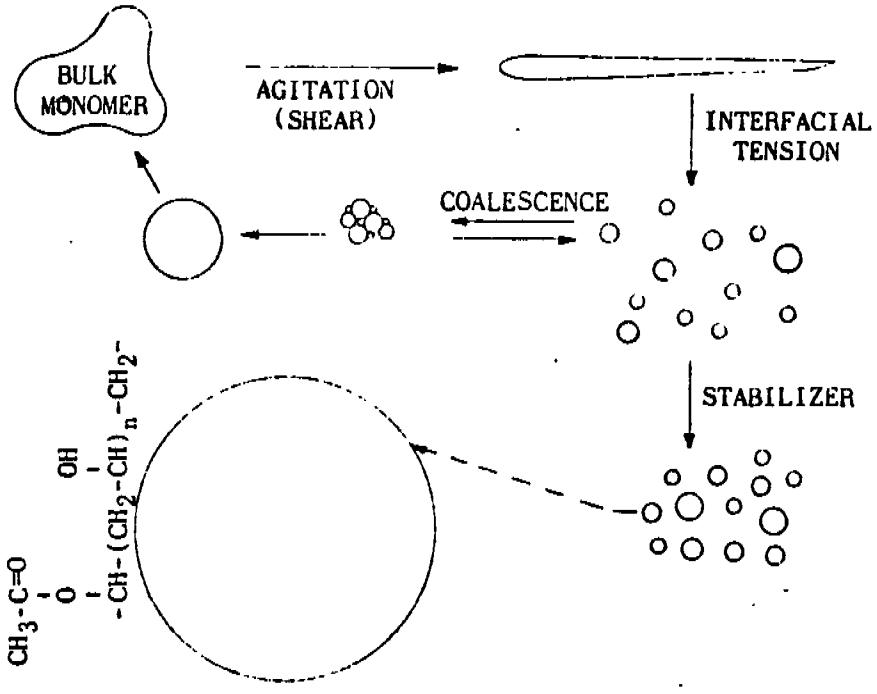
The dispersed monomer phase in water is of macroscopic size and is the site of the polymerization reaction. The final product is in the form of beads.

The General Tire & Rubber Company employs the suspension polymerization process for the commercial preparation of polyvinyl chloride. Polymerization of a monomer in suspension is achieved by dispersing the monomer in the form of small droplets in a nonsolvent medium (usually water) by strong mechanical agitation and subjecting this monomer suspension to polymerizing conditions. The size of the suspended monomer droplets can be varied over a wide range (0.01 - 0.5 cm) and is dependent on the monomer-to-water ratio, the rate of mechanical agitation and the interfacial tension of the monomer droplets (which can be controlled by suspension stabilizers).

The mechanics of forming suspensions of insoluble monomers in an aqueous system is illustrated schematically in Figure 1. Mechanical agitation subjects the monomer to a viscous drag causing elongation to a thread-like form with subsequent degeneration into drops. Simultaneously, through the reverse process of coalescence, the drops tend to revert to the original monomeric mass. In a simple mechanical suspension under a constant overall rate of shear, a dynamic equilibrium is quickly established. Clusters of globules held together by weak residual forces, but not fused, tend to disperse under the disruptive stress of an agitated system. Effective surface-active agents will deflocculate these aggregates. With the onset of polymerization and the accompanying increase in viscosity within the monomer droplets, there is greater resistance to distortion of droplets due to viscous drag but, unfortunately, a greater tendency toward aggregation through collisions with neighboring globules. The latter phenomenon is minimized by suspension stabilizers which are selectively adsorbed at the interface forming a protective film of molecular proportions. This is illustrated schematically by the enlarged droplet in Figure 1 supporting an adsorbed film of a suspension stabilizer.

The mechanism of polymerization in suspension is fundamentally identical to the other modes of polymerization processes already mentioned.

FIGURE 1. SCHEMATIC DIAGRAM OF STATES OF DISPERSION IN SUSPENSION POLYMERIZATION



However, the kinetics of polymerization of vinyl chloride varies greatly with the process employed except in the cases of the bulk and suspension systems where they are virtually identical.

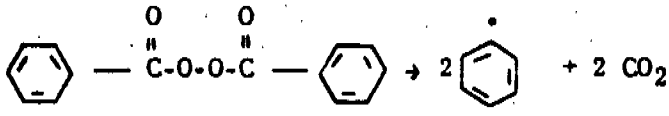
Free Radicals

A free radical can be defined as a molecular species having an odd number of electrons, consequently an unpaired electron. Such molecular species do not normally have a formal electronic charge as represented above for cations or anions.

Free radicals can be produced in a number of ways including thermal or photochemical decomposition of such compounds as:

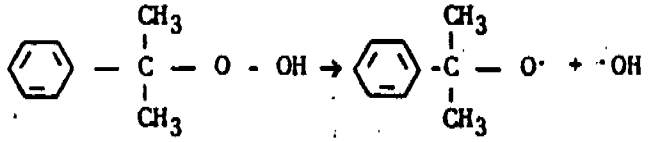
a. Organic Peroxides

Benzoyl Peroxide



b. Hydroperoxides

Cumene Hydroperoxide

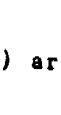


c. Azo Compounds

Azobisisobutyronitrile

$$(CH_3)_2 - \underset{\underset{C \equiv N}{|}}{C} - N = N - \underset{\underset{C \equiv N}{|}}{C}(CH_3)_2 \rightarrow 2(CH_3)_2\overset{\overset{C \equiv N}{|}}{C}\cdot + N_2$$

The stability of the radical formed will determine its rate of reaction with a monomer unit to initiate the polymerization reaction. Primary free radicals are less stable and more reactive than secondary free radicals, which are in turn less stable than tertiary free radicals. Phenyl radicals

() are more reactive than benzyl radicals (), and allyl radicals

($CH_2 = CH - CH_2 \cdot$) are so stabilized that they are quite unreactive.

Polymerization of Vinyl Monomers by Free Radicals

It has been established that the scheme of reactions is as follows: The radical is generated thermally or by radiation and initiates polymerization by adding to the monomer. The new radical formed grows by successive additions of monomer molecules to form a polymer chain radical. This polymer radical ceases to grow when two radicals interact and are rendered inactive. There are also other ways in which a polymer radical can react. The polymer molecule can attack a monomer in such a way as to transfer the radical activity to the monomer but not add it to the chain. This is called chain transfer to monomer. Another reaction can occur when one polymer radical attacks another polymer radical or an inactive polymer chain and transfers its radical activity. This will result in branches being formed on the backbone of a polymer chain. When such reactions occur to a high degree, crosslinked molecules are formed. Chain transfer of a polymer molecule to monomer is very prevalent in vinyl chloride polymerization as we will see later.

Mechanism of Free Radical Polymerization of Vinyl Monomers

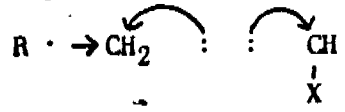
All addition polymerization reactions have three basic mechanistic steps in common, whether the reaction is carried out in bulk in the presence of a solvent or in a heterogeneous system such as an emulsion or suspension. These steps are: (a) Initiation, (b) Propagation, and (c) Termination.

When a free radical is generated in the presence of a monomer, the radical will attack the double bond of the monomer in the following way:

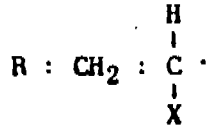
$$R - R \text{ (radical source)} \xrightarrow{\text{energy}} 2\,R\cdot \quad \text{(free radical)}$$

$$R\cdot + CH_2 = \underset{\underset{X}{|}}{CH} \qquad R - CH_2 - \overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}\cdot$$

As the radical approaches the double bond of the vinyl monomer, one of the bonds splits into two radicals:

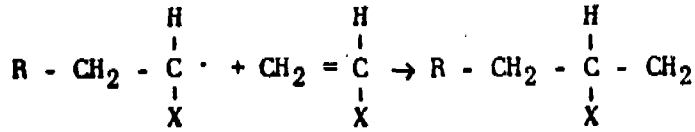


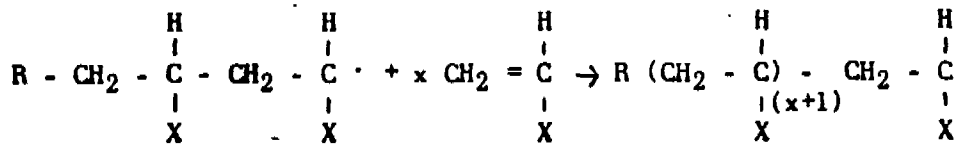
The attacking radical combines with one of the electrons forming a bond, and a new free radical results.



This then is the initiation step: The attack of a free radical on a monomer molecule.

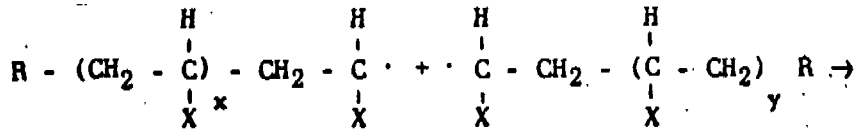
The propagation step is very similar in that the new radical formed in the initiation step attacks a second monomer unit and the radical is now propagated along a chain by successive monomer additions.

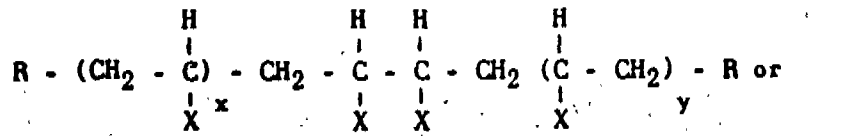




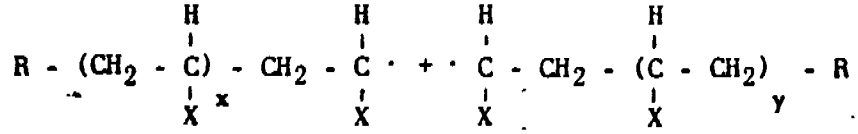
Termination of the propagation step can occur in a number of ways.

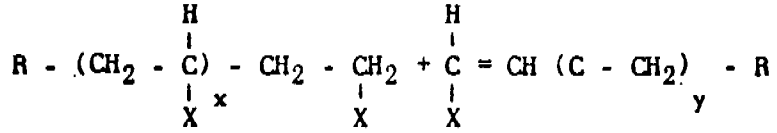
a. Two free radical chains may simply combine.



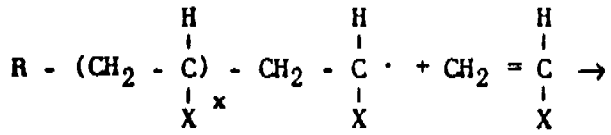


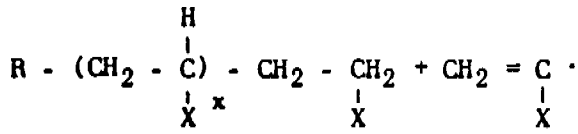
b. A disproportionation reaction may occur in which case one of the polymer chains will have an unsaturated end group:





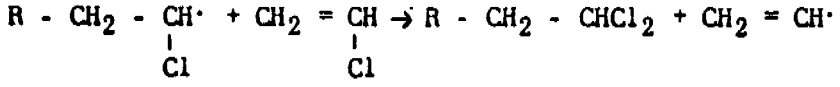
c. The polymer chain may transfer its radical to a monomer unit.





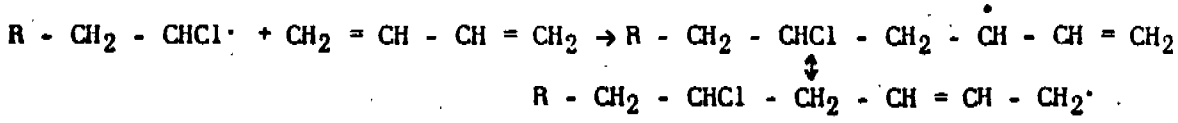
This is the generalized mechanism of free radical addition polymerization. Vinyl chloride is thought to deviate slightly in the termination steps.

It is known that transfer plays a very large part in the polymerization of vinyl chloride, and hence it seems likely that any termination by monomer will take the form of a degradative transfer reaction. The first step is probably the abstraction of a chlorine atom from the monomer[2].



The $CH_2 = CH\cdot$ radical may initiate the polymerization of vinyl chloride and thus constitute a true chain transfer step of polymer to monomer. If it dimerizes, butadiene will be formed which would then act as a chain terminator because when the butadiene is attacked by a polyvinyl chloride radical, the resulting species would be a resonance stabilized allyl radical.

The stability of this allyl-radical is such that it will not initiate polymerization of vinyl chloride monomer.



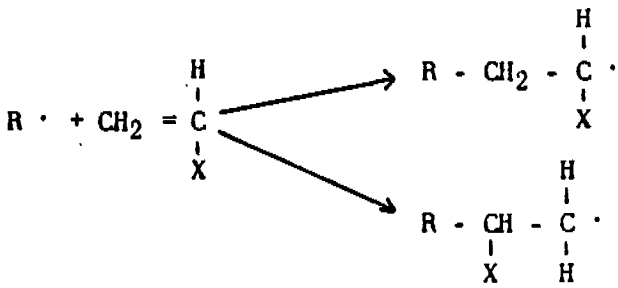
Another way in which the vinyl radical may disappear is by combination with a growing radical. In effect, each degradative chain transfer would then stop two chains: $R - CH_2 - CHCl\cdot + CH_2 = CH\cdot \rightarrow R - CH_2CHCl - CH = CH_2$.

This structure is the same as is formed if mutual termination of the growing radical takes place by a disproportionation reaction, and would not be expected to take any further part in the polymerization reaction:

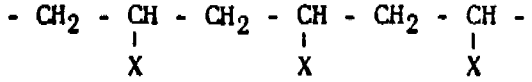
$$R - CH_2 - CHCl \cdot + R - CH_2 - CHCl \cdot \rightarrow R - CH_2 - CHCl_2 + R - CH = CH_2$$

The Arrangement of Monomer Units in the Chain

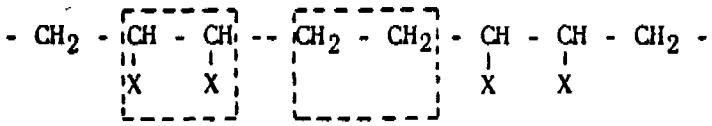
In the previous section on the mechanism of polymerization, the initiation step was shown to be an attack of a free radical on the double bond of the monomer. There are two ways in which this may occur.



As is generally true in free radical reactions, the reaction leading to the more stable product will be favored. The occurrence of either reaction exclusively would lead to a head to tail structure in which the substituent (X) would be on alternating carbon atoms.

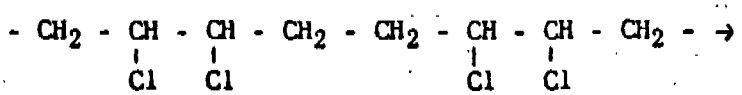


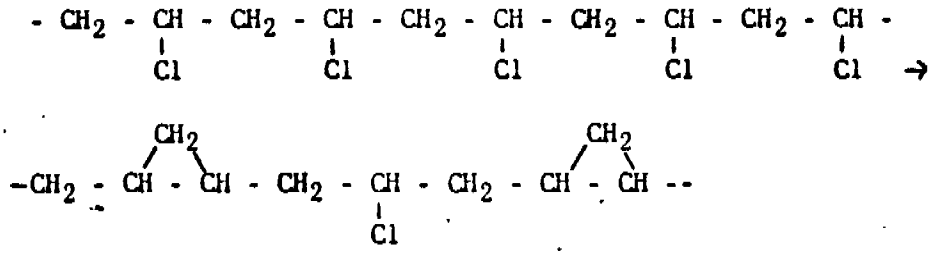
Alternate possibilities are head-to-head, tail-to-tail structures,



or a random structure containing both arrangements. The possibility of obtaining a regular head-to-head, tail-to-tail structure exclusively is quite remote, but it appears that an occasional monomer unit may enter the chain in a reverse manner to provide a single head-to-head, tail-to-tail linkage.

The question of orientation of vinyl chloride units in polyvinyl chloride has been resolved by treating the polymer with zinc. The head-to-head structure would leave an unsaturated polymer while the head-to-tail structure would yield cyclopropane rings[3].





Since only 84-86 per cent of the chlorine could be removed, this fits the theoretical calculations for a head-to-tail polymer.

The theoretical calculations are based on statistically derived probabilities for pairs of chlorine groups in a chain which might react with each other to form ring closures. The calculated values are that 86.47 per cent of the chlorine groups will react in pairs and that 13.53 per cent will be isolated.[4,5,6]

Kinetics of Initiated Polymerization

Initiation of addition polymerization in the presence of an initiator I may be considered in two steps.

1. The decomposition of the initiator into free radicals. R·

$$I \xrightarrow{k_d} 2\,R\cdot$$

where "k_d" is the rate constant for the decomposition step.

2. The addition of a monomer unit to form a chain radical M_1·

$$R\cdot + M \xrightarrow{k_a} M_1\cdot$$

where "k_a" is the rate constant for the attack of an initiator radical on a monomer unit.

The growth or propagation of a polymer chain is the repetitive step of the monomer radical attacking available monomer.

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$

$$M_x\cdot + M \xrightarrow{k_p} M\cdot(x+1)$$

All of the propagation steps are shown with the same rate constant "k_p" because radical reactivity is presumed to be independent of chain length and dependent only on the nature of the monomer radical.

The termination step involves the mutual annihilation of the activity of two radicals by either combination or disproportionation.

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{k_{t_c}} M_{(x+y)}$$

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{k_{t_d}} M_x + M_y$$

"k_{t_c}" and "k_{t_d}" represent the rate constant of termination by combination and disproportionation respectively. We now have the fundamental equations showing the various kinetic steps occurring in a free radical polymerization except for chain transfer, which will be treated later.

The rate equations of the three basic polymerization steps can now be written in terms of the concentrations of the species involved.

$$\text{Rate of Initiation} = v_i = \frac{(d\ [M^{\cdot}])}{(\ dt\ )_i} = 2\ f\ k_d\ [I]$$

This equation simply states that the rate of polymer radicals formed with time is equal to the concentration of the initiator [I] times the rate which the initiator decomposes. The efficiency factor (f) represents the fraction of the radicals formed that initiate polymerization.

$$\text{Rate of Termination} = v_t = -\frac{(d\ [M^{\cdot}])}{(\ dt\ )_t} = 2\ k_t\ [M^{\cdot}]^2$$

The rate of termination of polymerization as given in the above equation states that the rate of disappearance of free radical chain species is equal to the square of the radical concentration. The rate constant "k_t" in this case represents all modes of radical annihilation where two radicals are involved.

We now have the rate equations for the initiation and termination of polymeric radicals. At an early stage of polymerization the rates of radical formation and termination become constant and equal to each other. When this happens, a steady state condition is established. The use of the steady state assumption enables us to calculate the overall rate relationships of polymerization to initiator and monomer concentration.

$$v_i = v_t$$

$$2\ f\ k_d\ [I] = 2\ k_t\ [M^{\cdot}]^2$$

$$\frac{(f\ k_d\ [I])^{1/2}}{(\ k_t\ )} = [M^{\cdot}]$$

The quantity $[M\cdot]$ is the steady state concentration of radicals which, when substituted in the kinetic rate expression for the propagation step of the polymerization, gives us the following relationship:

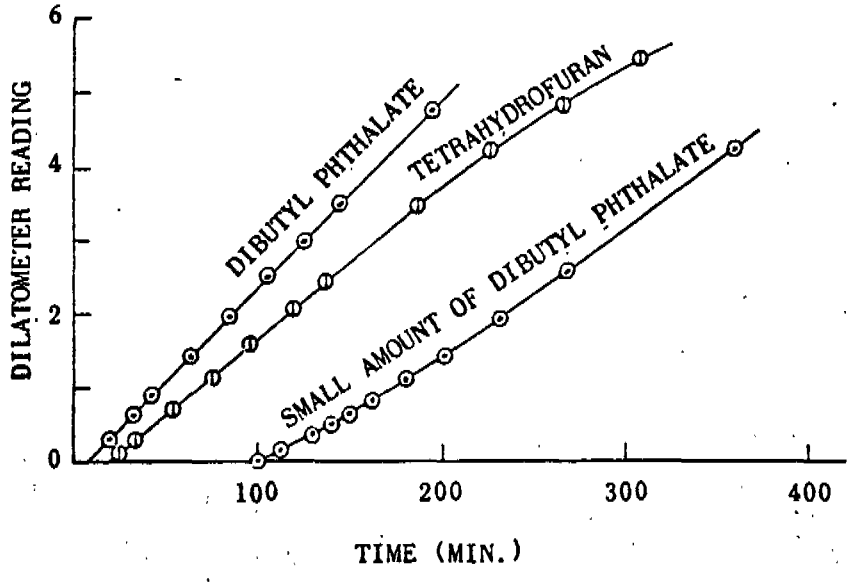
$$\text{Rate of Propagation} = v_p = -\frac{d\,[M]}{dt} = k_p\,[M]\,[M\cdot]$$

$$v_p = -\frac{d\,[M]}{dt} = k_p\,\left(f\,\frac{k_d}{k_t}\,[I]\right)^{1/2}\,[M]$$

Thus the overall rate of free radical polymerization should be, in the early stages, proportional to the square root concentration of the initiator. In the above equation, the overall rate is shown to be proportional to the first power of the monomer concentration. This will be true if the efficiency factor (f) is independent of the monomer concentration which would require (f) to be nearly one. If the efficiency factor is low, then (f) may be proportional to the monomer concentration and this would make the overall rate expression $[v_p \propto [M]3/2]$ proportional to the three halves power of the monomer concentration.

In order to observe the experimental verification of these theoretical kinetics, a per cent conversion (dilatometer reading) vs. time plot is first obtained as shown in Figure 2 to obtain the rate of polymerization.

FIGURE 2. POLYMERIZATION OF VINYL CHLORIDE IN THE PRESENCE OF SOLVENTS FOR THE POLYMER



The variation of the rate of polymerization with vinyl chloride concentration as determined in tetrahydrofuran solvent at constant initiator concentration (2,2'-azo-isobutyronitrile) is shown in Figure 3. The slope of the line shows that the rate of polymerization is related to the three halves power of the monomer concentration[2]. The actual slope as determined by the method of least square was found to be 1.46.

FIGURE 3. VARIATION OF RATE WITH VINYL CHLORIDE CONCENTRATION

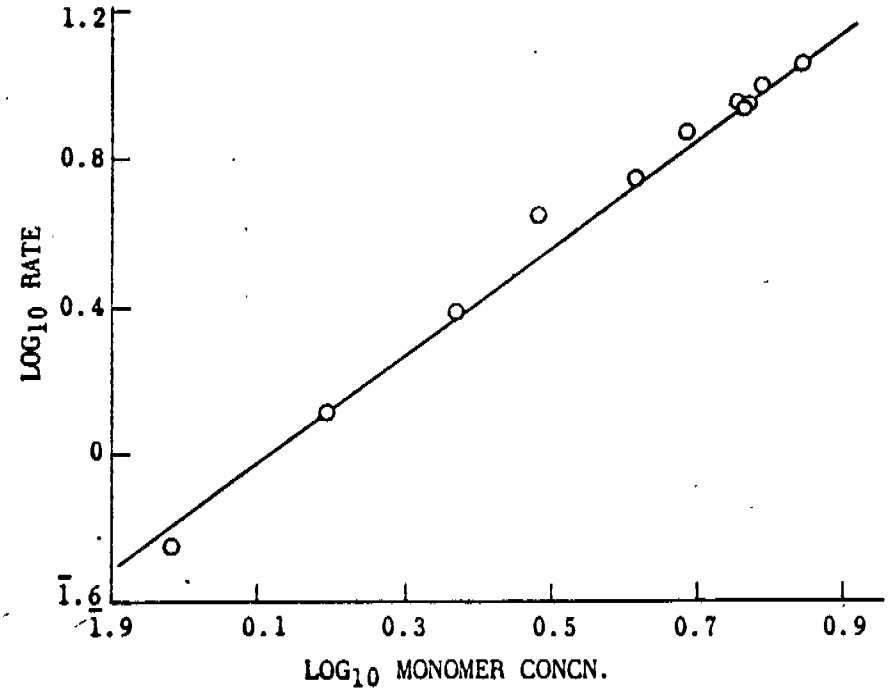
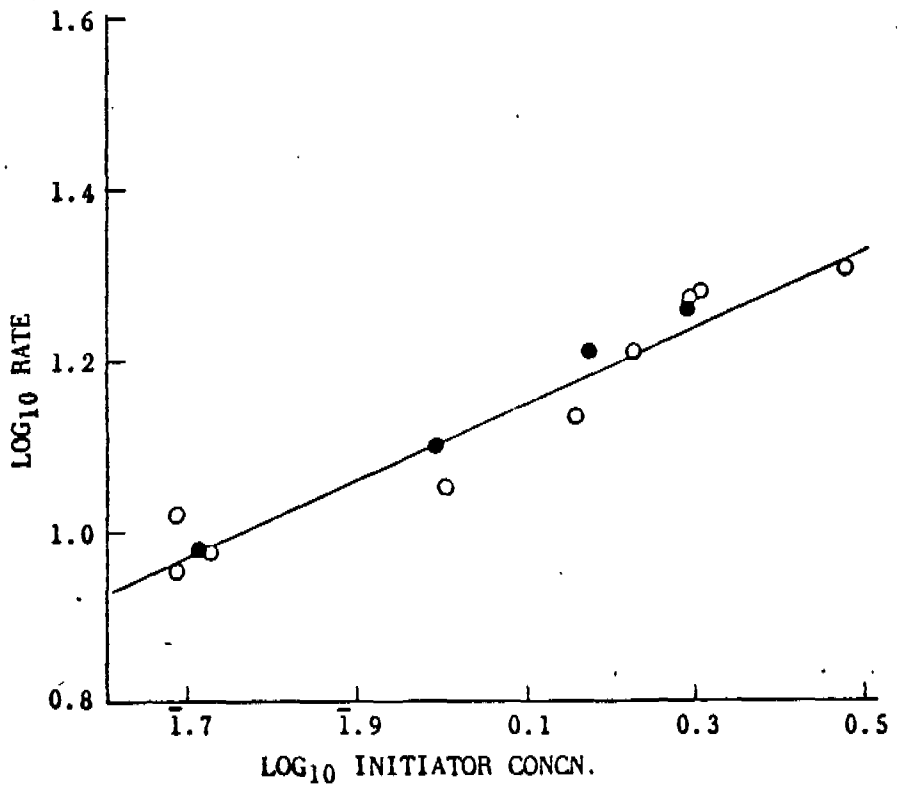


Figure 4 is a plot showing the relationship of rate of polymerization to varying initiator concentration at constant monomer concentration. The slope of the line for points obtained using tetrahydrofuran containing peroxides, as determined by the method of least squares, is 0.45. That for peroxide free tetrahydrofuran is 0.48. In this case, as shown in the theoretical rate expression previously, the rate of polymerization is dependent on the square root concentration of the initiator concentration.

FIGURE 4. VARIATION OF RATE WITH SENSITIZER CONCENTRATION (1-azo-bis-cyclohexane nitrile)

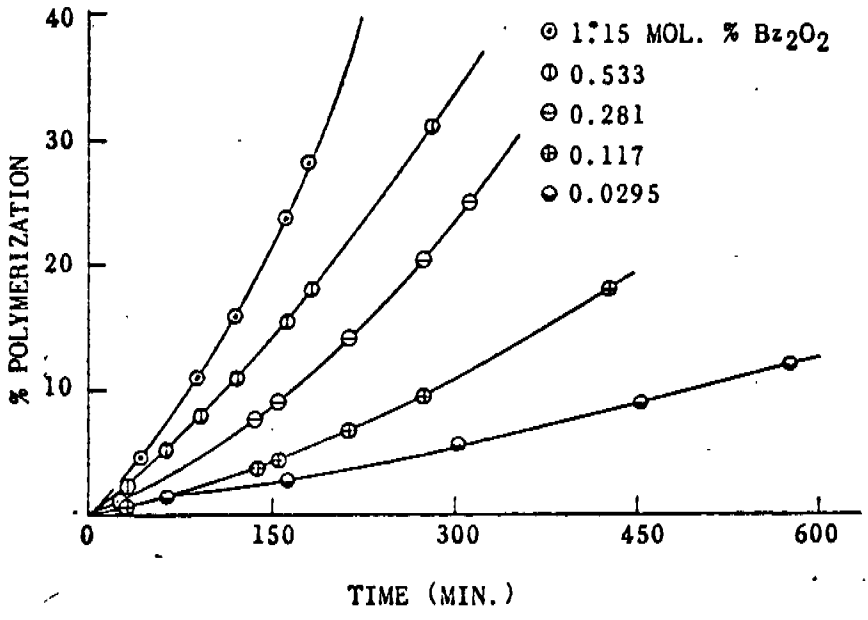


Thus far, we have shown that the polymerization of vinyl chloride via a free radical mechanism in a solvent for the polymer, i.e., tetrahydrofuran, follows the predicted theoretical kinetic scheme. However, when vinyl chloride is polymerized in a media in which the polymer is not soluble, such as in the case of suspension polymerization, deviations from the predicted theoretical kinetics are observed.

Heterogeneous Polymerization of Vinyl Chloride

When vinyl chloride is polymerized in the presence of a nonsolvating media for the polymer, a peculiar effect on the rate of polymerization is noted. For example, let us examine Figure 5 for the case of bulk polymerization of vinyl chloride initiated by benzoyl peroxide[7].

FIGURE 5. EFFECT OF BENZOYL PEROXIDE CONCENTRATION ON POLYMERIZATION OF VINYL CHLORIDE AT 47°C

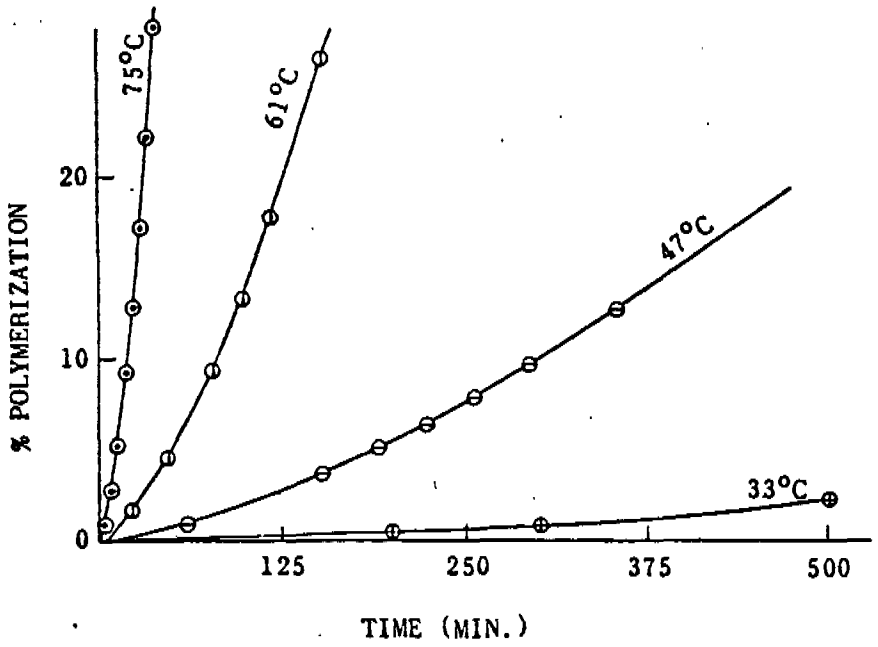


It can be seen from Figure 5 that throughout the first 30 to 40% polymerization, the rate of polymerization continually increases. This increase in rate is more marked in the early stages (e.g., from 0 to 5% polymerization).

The rate of polymerization increases or decreases with increase or decrease in concentration of benzoyl peroxide. The general "autocatalytic" shape of the curve, however, is not affected even when the concentration of benzoyl peroxide employed is varied from 0.025 to 1.0 mol %.

If now the concentration of benzoyl peroxide is kept constant, and the temperature is varied, it is found that the rate increases markedly with increase in temperature. This will be apparent from Figure 6 which shows the course of the polymerization of vinyl chloride catalyzed by 0.115 mol % benzoyl peroxide at temperatures of 33, 47, 61, and 75°C.

FIGURE 6. EFFECT OF TEMPERATURE ON THE POLYMERIZATION OF VINYL CHLORIDE CATALYZED BY 0.115 MOL % BENZOYL PEROXIDE



The polymerization thus appears to be autocatalytic over the range of catalyst concentration from 0.025 to 1.0 mol % benzoyl peroxide, and over range of temperature from 33 to 75°C.

Degree of Polymerization

An indication of the way in which the degree of polymerization varies with the mode and conditions of preparation of the polymer can be obtained by determining the relative viscosities of dilute solutions of the polymer. The equivalent viscosity, λ, is defined as the ratio $(\ln\eta_r)/c'$, where η_r is the relative viscosity of the solution and c' the concentration of the solution in monomoles per litre. It was shown that for vinyl chloride polymers

$$\lambda = \lambda_o(1 - \beta\lambda_o c')$$

where λ_o is the limiting equivalent viscosity for zero concentration and β is a constant which was found to be of low value; thus for very dilute solutions we have $\lambda = \lambda_o$. Furthermore, they showed that λ_o is proportional to the molecular weight. The value of the function $(\log \eta_r)/c$, where c is the concentration of the solution in g. of polymer per 100 ml. of solution will,

therefore, also be proportional to the molecular weight of the polymer. It is shown in Table 2 that there is little variation in the value of this function throughout the reaction.

TABLE 2

VARIATION OF DEGREE OF POLYMERIZATION WITH PERCENTAGE POLYMERIZATION, IN THE POLYMERIZATION OF VINYL CHLORIDE, CATALYZED BY 0.625 MOL. PERCENTAGE BENZOYL PEROXIDE, AT 47°C

Percentage Polymerization	$(\log\eta_r)/c$
4.5	0.41
9.0	0.41
20.0	0.41
33.0	0.41
48.5	0.41
64.0	0.41
88.0	0.39

The concentration (c) of the polymer solutions, used in the above experiments, is 0.25 g. of polymer per 100 ml. of tetrahydrofuran.

Similar results are obtained if vinyl chloride is polymerized in the presence of 10 mol. % dibutyl phthalate and 0.50 mol. % benzoyl peroxide. The degree of polymerization in this case, however, is somewhat lower than when dibutyl phthalate is absent from the system. It is interesting to note that no marked increase in rate of polymerization, or in degree of polymerization was observed, although the polymerizing mixture at 30% polymerization was a firm gel, from which the vinyl chloride escaped very slowly, even when left at room temperature; the results are shown in Table 3.

TABLE 3

VARIATION OF DEGREE OF POLYMERIZATION WITH PERCENTAGE POLYMERIZATION FOR VINYL CHLORIDE CATALYZED BY 0.5 MOL. PERCENTAGE BENZOYL PEROXIDE, IN THE PRESENCE OF 20 MOL. PERCENTAGE DIBUTYL PHTHALATE AT 47°C

Percentage Polymerization	$(\log\eta_r)/c$
3.6	0.28
8.4	0.29
15.0	0.34
26.0	0.33
35.0	0.30
46.3	0.29
66.5	0.28
85.0	0.29

Vinyl chloride, catalyzed by 0.115 mol. % benzoyl peroxide was polymerized at various temperatures to an extent of about 10% polymerization. Table 4 gives a comparison of the degree of polymerization at temperatures from 33 to 85°C. It is seen that at 85°C the value of the average molecular weight is about one-third of the value obtained at 33°C.

TABLE 4

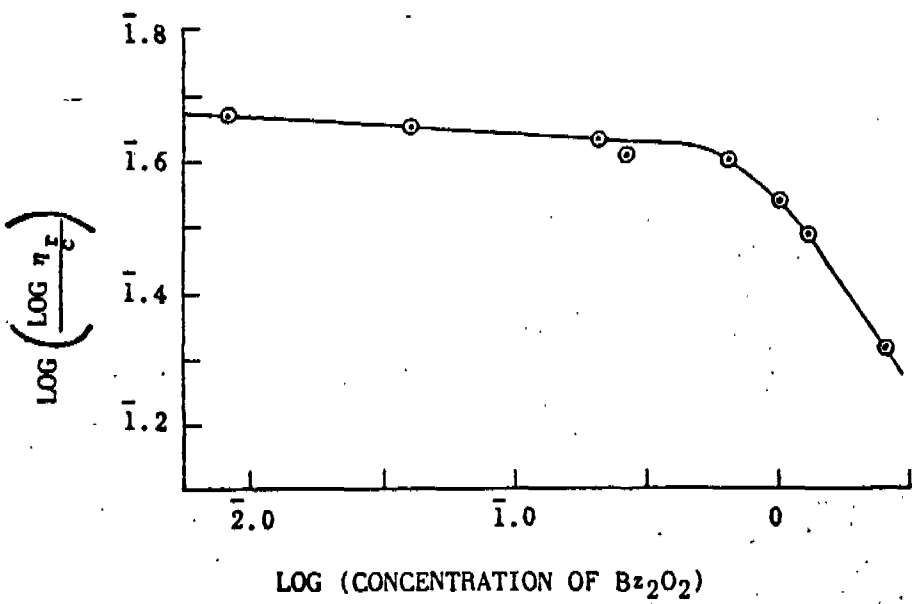
EFFECT OF TEMPERATURE ON THE DEGREE OF POLYMERIZATION

Temperature, °C	$(\log\eta_r)/c$
33	0.68
47	0.45
61	0.39
75	0.28
85	0.22

The variation of degree of polymerization with catalyst concentration was determined for polymerizations of vinyl chloride at 47°C. The concentration of benzoyl peroxide was varied from 0.008 to 2 mol. %, all polymerizations being stopped at about 10% conversion of the monomer to the polymer.

It is seen from Figure 7 that the degree of polymerization varies only slightly over a wide range of catalyst concentration. At concentrations higher than 0.5 mol. %, however, the average molecular weight becomes much more dependent on the concentration of the catalyst. At very high catalyst concentration it tends toward the familiar inverse proportionality between the average molecular weight and the concentration of the catalyst.

FIGURE 7. EFFECT OF CHANGE IN CATALYST CONCENTRATION ON THE AVERAGE MOLECULAR WEIGHT



Summary

1. When vinyl chloride is polymerized in the presence of a solvent for the polymer, the theoretical polymerization kinetics are obeyed, i.e., the rate of polymerization is proportional to the square root of the initiator concentration and to the three-halves power of the monomer concentration. The plot of per cent polymerization versus time, Figure 2, shows a linear relationship in the early stages of the polymerization reaction.

2. Whereas increasing the rate of polymerization by either increasing the initiator concentration or temperature is expected to reduce the molecular weight of the polymer formed, it is shown that in the case of vinyl chloride that the chain transfer effect is very strong in that initiator concentration had very little effect on the molecular weight, whereas, the temperature effect was very pronounced.

3. When vinyl chloride is polymerized in bulk, an auto acceleration is noted which begins in the initial stages of the polymerization reaction. This auto accelerated effect is also noted when insufficient solvent is present to solvate all of the polymer formed as indicated in Figure 2, in the case of a small amount of dibutyl phthalate. Periods of acceleration are also exhibited in the polymerization of monomers which are solvents for their polymers. This so-called "gel effect" does not appear until later stages of the reaction when the system has become viscous, and so differs from the period of acceleration which, in the polymerization of vinyl chloride, occurs from the very beginning of the reaction and is closely associated with the separation of the solid polymer phase. Again, in the polymerization of vinyl chloride, the average molecular weight of the polymer formed during the reaction remains constant, but with monomers which give rise to the "gel effect," it increases with increase in rate of polymerization. The "gel effect" has been explained as due to a reduction in the rate of the termination reaction, resulting from the great increase in viscosity of the medium, probably supplemented by the coiling of the growing polymer chains.

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THE GENERAL TIRE SUSPENSION PROCESS

by

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J. L. WEAVER

BIOGRAPHIES

Duane J. Clark is a native Ohioan. He was graduated in 1962 from Carnegie Institute of Technology with a Bachelor of Science degree in Chemical Engineering. He immediately accepted a post with The General Tire & Rubber Company as a technical trainee and was initially assigned to the Company's Ashtabula plant. In 1963, he moved to the Mogadore plant as Process Engineer, a position he still holds. Mr. Clark is a member of the American Institute of Chemical Engineers.

In 1949, William J. Hanlon was graduated from Syracuse University with a Bachelor of Science degree in Chemical Engineering. He was affiliated with the J. T. Baker Chemical Company and Olin-Mathieson Chemical Company prior to joining The General Tire & Rubber Company in 1952 as General Foreman of the Mogadore latex plant. He then served as Chief Process Engineer at the Ashtabula facilities until appointed to his present position as Technical Manager in 1960. Mr. Hanlon is a member of the American Institute of Chemical Engineers, the American Chemical Society, and numerous other professional and business groups.

J. L. Weaver graduated from Purdue in 1958 with a Bachelor of Science degree in Chemical Engineering. He joined The General Tire & Rubber Company's training program that same year and was assigned to the Ashtabula vinyl resin plant in 1959 as Process Engineer. He was made Senior Process Engineer at Ashtabula in 1961 and Development Engineer on the Chemical Division staff in 1964. Mr. Weaver is a member of the American Institute of Chemical Engineers.

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I. Introduction

"The General Tire Suspension Process" will be concerned with the suspension method for polymerizing vinyl chloride; with the technological advances made in the past ten years and their effects on plant design; with the existing facilities and planned expansion of General Tire's Ashtabula plant; and the exacting quality control and product improvements of Vygen resins.

Since 1954, when the Ashtabula plant first came on stream, important advances have been made in nearly every phase of PVC production. The result has been a constant modernization to remain economically competitive.

II. Suspension Polymerization

A. Selection

The Ashtabula plant was designed to make suspension type polyvinyl chloride (PVC) for the following reasons:

1. The General Tire & Rubber Company had a considerable internal demand for suspension PVC.

2. The polymer obtained from a suspension system is relatively free of impurities and consequently more stable as opposed to emulsion polymers which invariably contain emulsifier and other residues.

B. Recipe

The recipe given below is typical of that used throughout the industry to make suspension PVC.

	Parts by Weight
Vinyl Chloride	100
Water, Deionized	200
Alperox C (lauroyl peroxide)	0.1 INIT.
Elvanol 50-42 (polyvinyl alcohol)	0.1 PROT. COLLOID

The various producers may use a different initiator, a different colloid, or even a different water to monomer ratio; however, all suspension PVC recipes contain monomer, water, a free radical initiator and a protective colloid.

The type of initiator and the colloid used in the recipe must be chosen with extreme care. The choice of initiator is determined by its ability to produce an acceptable polymerization rate and not leave residues in the polymer that have a detrimental effect on heat stability. The choice of colloid is governed by several factors. First, the colloid should aid in stabilizing the monomer droplets which in turn become polymer particles. A good colloid must protect the particles from agglomerating and at the same time should minimize buildup of polymer in the reactor. As with the initiator, the colloid should not impair heat stability. Further, since the major portion of the PVC produced is plasticized, the colloid film which remains on the particles should not interfere with the absorption of plasticizer.

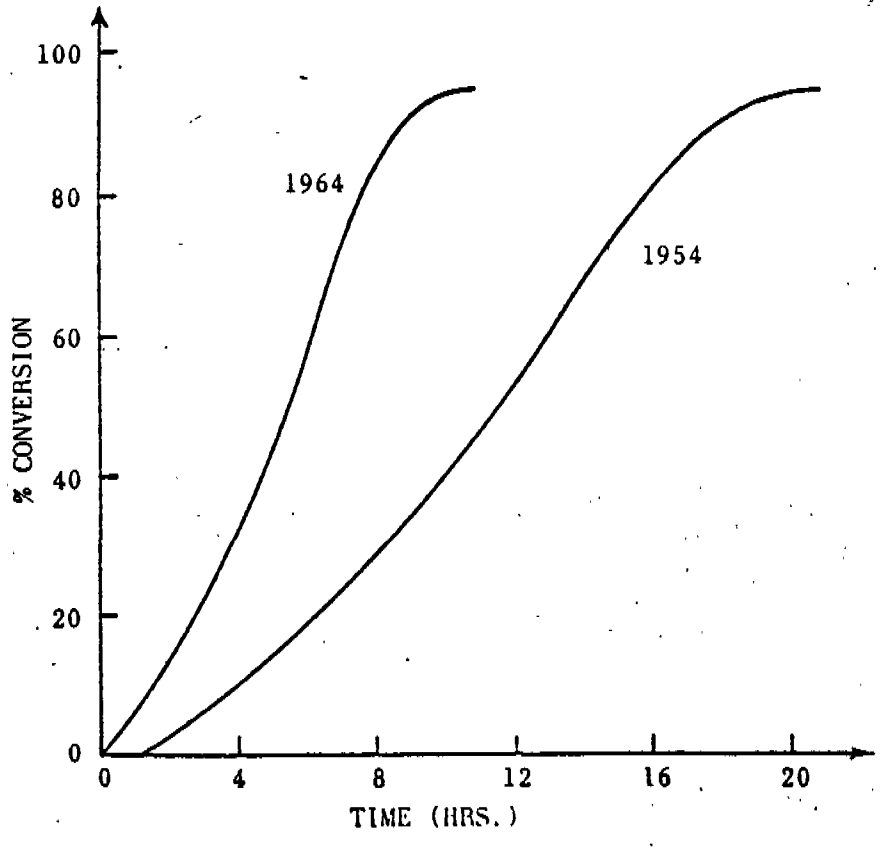
C. Controllable Characteristics

The emphasis of the technical program at Ashtabula has been to control molecular weight, molecular weight distribution, particle size distribution and polymer purity. The molecular weight of PVC polymers is controlled by the polymerization temperature. The higher the reaction temperature, the lower is the molecular weight. Molecular weight distribution can be adjusted by temperature programming; that is polymerizing part of the charge at one temperature, then changing the temperature as often as necessary to obtain a desired molecular weight distribution. Particle size distribution is controlled by the amount of colloid charged to the reactor and the type of agitation used during the reaction. Polymer purity can be controlled by taking extreme precautions that foreign materials are not introduced into the product and by washing the product prior to drying.

D. Reaction Characteristics and Design Data

The mechanism of free radical polymerization involving formation, propagation and termination has been covered previously. Full length polymer molecules are present in every step of the PVC reaction. The rate of polymerization of a suspension system follows the predicted proportionality involving the square root of the initiator concentration. Typical curves of time versus % conversion of a vinyl chloride polymerization reaction are shown in Figure 1.

FIGURE 1. REACTION PROFILE COMPARISON



The time period in which no reaction occurs, commonly called the induction period, is one in which the reaction is inhibited. This period arises from the presence of very small traces of impurities. Inhibitors combine with active centers of polymerization or with the initiator.[1]

The improved initiators practically eliminate the induction period and maintain a linear rate through a great portion of the reaction. A comparison of the reaction profile of the early 1950's with a typical reaction today is shown in Figure 1. The effect this advance has had upon plant design will be considered in detail in a later section.

The manner in which pressure changes with extent of conversion is illustrated in Figure 2.

FIGURE 2. PRESSURE VS. % CONVERSION

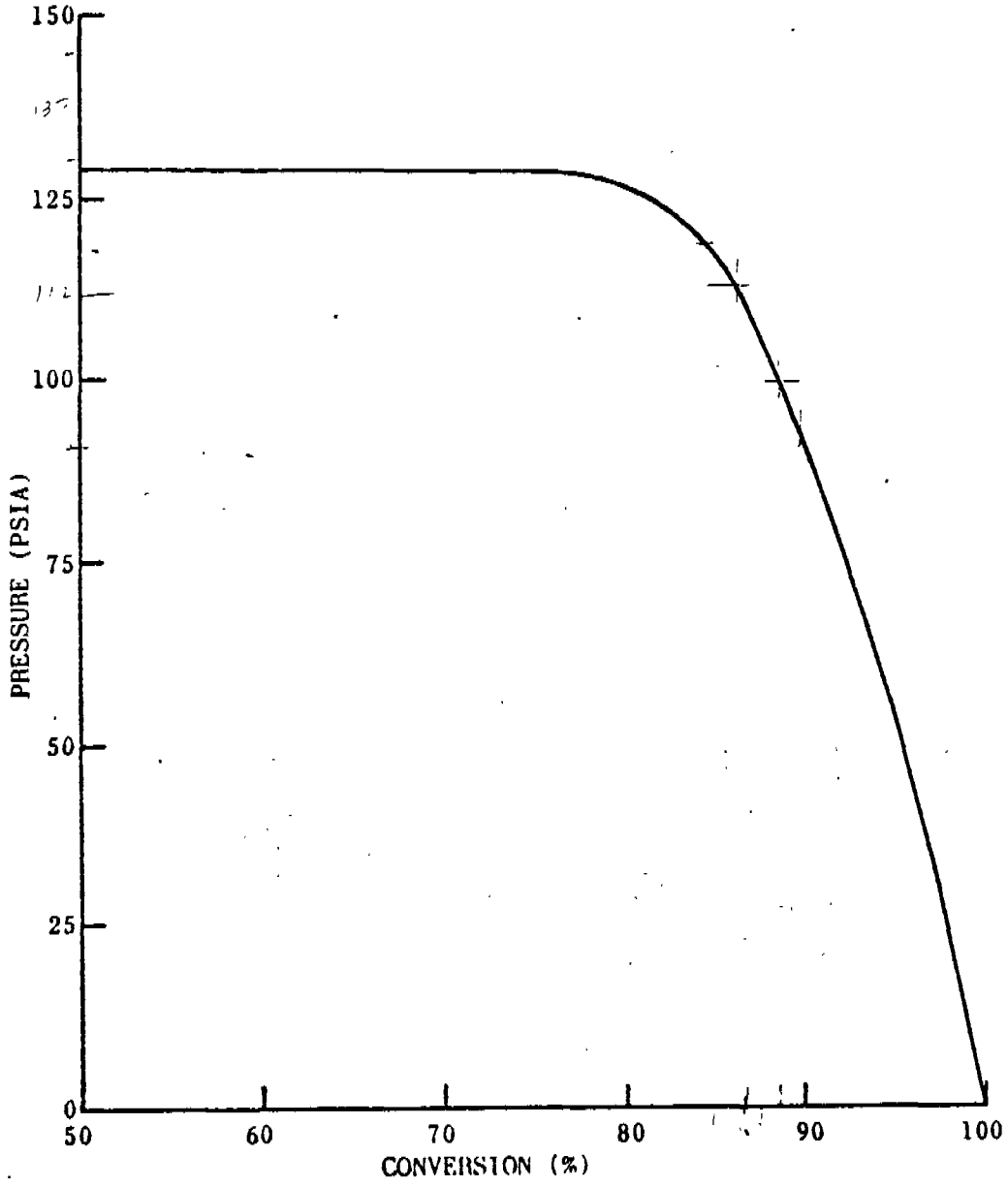
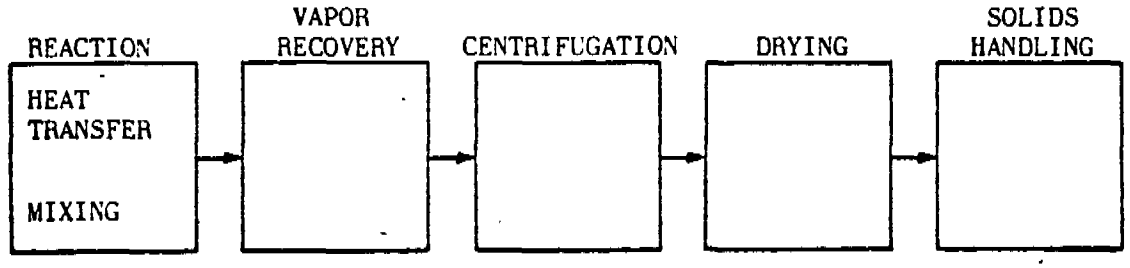


Figure 2 shows that there is a useful relationship between pressure and extent of conversion in the interval from 70% to 100% conversion. Below 70% conversion, the rate of reaction can be roughly estimated by the temperature differential between the batch and the jacket cooling water. This temperature differential becomes greater as polymerization progresses indicating an accelerating rate of polymerization up to about 70% conversion.

III. The Basic Unit Operations

For reasons previously discussed, PVC is to be produced by reaction in a suspension of water and is to be sold as fine, dry particles ranging in size from 75-250 microns (about 60-200 U.S. mesh) with the majority at about 100 microns. The unit operations of fluid flow, heat transfer, mixing, centrifugation, drying and solids handling are immediately recognized. Most chemical reactions are not economically feasible to run to completion so that an efficient design must consider vapor recovery methods. The auxiliary storage operations are defined by the design of the major equipment. A preliminary block diagram is shown in Figure 3. The immediate design problem is to determine whether a continuous or batch-wise reaction should be pursued.

FIGURE 3. PRELIMINARY BLOCK DIAGRAM



A. Batch Vs. Continuous Reaction

At the time of this writing, no commercial producing plant is known to be using a continuous suspension technique. However, the advantages of a continuous system are sufficient to warrant close investigation. Until this time, there have been three major stumbling blocks to continuous polymerization. Unless the first vessel or zone has sufficient hold-up time for particle formation (completion of the induction period), it is difficult to maintain proper particle-size control. Secondly, PVC has a pronounced tendency to adhere to even the most polished surfaces. The pumping of a partially polymerized slurry at low velocity results in plugged lines necessitating frequent clean-out. Last, a serious quality problem - the formation of "fish-eyes" which are hardened, solid particles so named for their appearance in a calendered sheet, and incapable of absorbing plasticizer or pigment - is observed when reaction vessels begin to get dirty.

A patent on continuous polymerization granted to General Tire[2] utilizes only three reactors but takes advantage of maximum conversion rates to almost double the output of batchwise production. It is known that the polymerization rate of VCl increases to a maximum at 70% conversion. At that point, pressure drop occurs and the polymerization rate falls off. In this patent, two reactors are continuously operating at the peak rate while the third serves in a "clean-up" capacity. A sketch of the process as outlined in the patent is shown in Figure 4. The relatively large volume hold-up in the first vessels allows sufficient time for particle formation, and extended runs have shown that the number of fish eyes did not increase with the time of reaction. It is concluded that continuous suspension reactions are feasible from a quality standpoint. The problem of line plugging has not been resolved.

B. Continuous Dewatering and Drying

Continuous dewatering and drying techniques have been used since the inception of PVC manufacture because of an advantage in good quality control and inherently economic operation. With large slurry hold tanks, several reactor batches can be blended, reducing batch-to-batch variances and providing a buffer zone between the variable reactor production rates and the constant rate dewatering and drying procedure.

C. Process Description

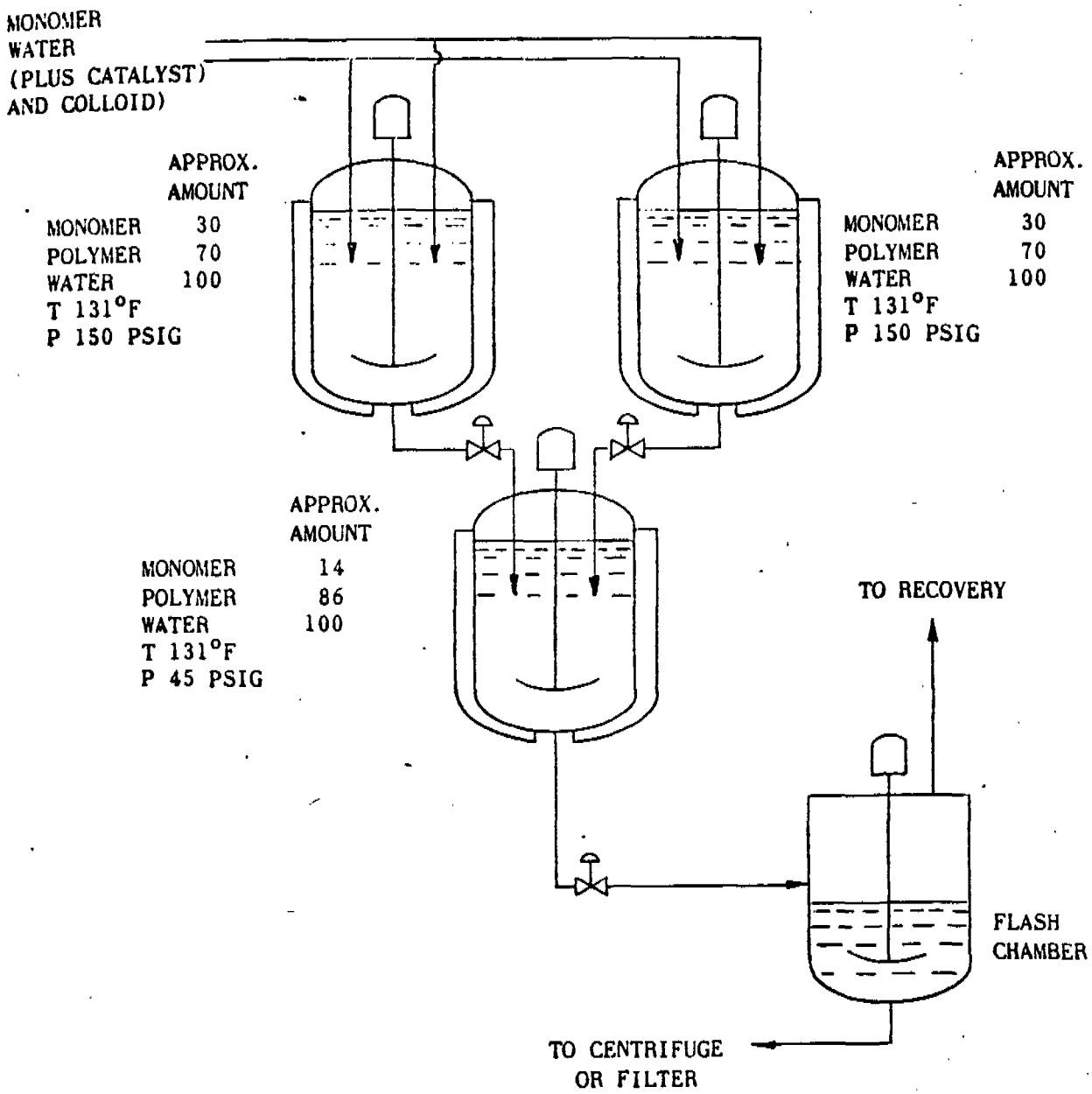
This section will very briefly describe the existing Ashtabula PVC production process. Each of the manufacturing steps mentioned will be discussed in detail in Section IV, Design Criteria.

Vinyl chloride monomer is pumped from a field storage tank to a weigh scale in the polymer area, and a weighed amount is then added to the reactor. The preheated process water is added after the monomer. A weighed amount of the colloid solution is pumped into the reactor along with the process water. Other ingredients are added through a charge bomb located on the top of each reactor. The reactants are agitated and the temperature of the reaction is controlled by regulating the temperature of the water in the jacket. The reaction is terminated when the desired conversion is obtained as indicated by a specific pressure.

The batch is then dropped to one of three agitated dump tanks. In the dump tank the unreacted monomer is stripped from the polymer slurry (75% water and 25% PVC) through a water sealed vacuum pump and is returned to the monomer area for purification and reuse. The stripped slurry is pumped to slurry storage tanks where it is blended before being pumped to the resin finishing area.

In the resin finishing area, the slurry is de-watered in a continuous solid-bowl horizontal centrifuge. The resin, after dewatering, contains about 25% moisture as it is fed by a screw conveyor into a rotary drier. The dried product is then sieved and packaged.

FIGURE 4. THE GENERAL CONTINUOUS SYSTEM



IV. DESIGN CRITERIA

A. Reactor

1. Design Considerations

The reactor is the focal point in producing PVC and its design is a subject for close study. We must consider materials of construction, productive cycles, heat transfer, and optimum sizing. The subject of agitation, although not a separate operation, will be considered in the next section.

a. Materials of Construction

There are two types of reactors in use for producing suspension PVC - stainless steel and glass-lined. The stainless reactors give superior heat transfer, while experience has taught that they also afford a surface on which polymerization will readily take place. A metal surface, even highly polished, is irregular enough to provide surfaces which become polymerization sites. Once a site is provided, the polymer builds up rapidly to a large size and hand-cleaning is required. The presence of reactor scale has a direct relation to the number of fish-eyes produced in a batch. Wall deposits also drop the heat transfer rate sharply. This combination of poor product quality due to fish-eyes and the reduction of heat transfer necessitates frequent reactor clean-out. With spray nozzles installed at the top of the reactor and a flush given after every polymerization, several batches can be produced before cleaning a glass-lined vessel. With stainless reactors, cleaning is more frequent and more difficult. The expense of cleaning that is incurred dictates the use of glass-lined vessels. In a similar fashion, the agitator and agitator shaft are subject to build-up and the use of glass-coated equipment is preferred.

b. Sizing

Glass-lined autoclaves are available in various sizes with some large vessels of 10,000 gallons and above. Beyond 5,000 gallons, pressure requirements are important in determining the maximum size attainable. In PVC polymerization, the highest pressure attained is due to the equilibrium vapor pressure of VCl. At 150°F., a pressure of 151 psig is experienced. A safety range must exist in which relief valves can operate. A 200 psi rated vessel is the minimum consistent with safety.

c. Productive Cycles

For the production of 75 million pounds per year of PVC, the number of reactors needed will depend on the reactor size, reactor loading, equipment downtime, yields, and reaction cycle. It will be assumed that reactor loadings are a constant 90% of nominal reactor capacity, that clean-out time does not vary with

size, that equipment downtime due to malfunctions is constant over a year's time, and that reaction cycles are identical for all reactor sizes if sufficient batch cooling is available. The following cycle calculation, based on plant experience, can be made:

Table 1

Typical Cycle Calculation

Preparation for Charging	0.5 hrs./batch
Reaction Time	13.0 hrs./batch
Drop and Flush Time	0.5 hrs./batch
Scheduling and Turn-Around	2.0 hrs./batch
	16.0 hrs./batch
Reactor Cleaning and Maintenance	2.0 hrs./batch
Equipment Malfunctions	200.0 hrs./yr.
Plant Shutdown	14.0 days/yr.

C_n = the number of batches per year in a single reactor

$$16\ C_n + 2\ C_n = \left[365\ \frac{\text{days}}{\text{yr.}} \times 24\ \frac{\text{hrs.}}{\text{day}}\right] - \left[14\ \frac{\text{days}}{\text{yr.}} \times 24\ \frac{\text{hrs.}}{\text{day}}\right] - 200\ \frac{\text{hrs.}}{\text{yr.}} \quad \text{-- (I)}$$

C_n = 457 batches per reactor per year

The following table can now be made:

Table 2

Number of Reactors Needed

Nominal Reactor Cap. (Gal.)	Assumed Loading (Gal.)	# MVC Charged	# PVC Produced At 95% Yield	# PVC Produced Per Reactor-Yr.	No. of Reactors For 75×10^6 #/Yr.
2,000	1,800	5,094	4,839	2.21×10^6	34
3,000	2,700	7,641	7,259	3.32×10^6	23
4,000	3,600	10,188	9,679	4.42×10^6	17
5,000	4,500	12,735	12,098	5.53×10^6	14

d. Heat Transfer

A glass-lined reactor used for PVC polymerization exhibits an average overall heat transfer coefficient of 46 $\frac{\text{BTU}}{\text{hr.ft.}^2{}^\circ\text{F}}$.

The heat of polymerization of vinyl chloride is approximately 650 BTU/# (H = -650 BTU/#). At its maximum, experience has shown the reaction to attain 16% conversion per hour at 72% total conversion.

Using these figures, the heat liberated per unit volume can be equated to the reactor jacket temperature and heat transfer area:

Heat Liberated at Maximum Conversion Rate

V = Volume
ρ = Density of monomer-water mixture = 7.88 #/gal.
Q = Heat liberated per hour
$Q = \rho V \Delta H$ x wt. % reacting per unit time ---------- (II)

$$= 7.88 \frac{\#\ \text{mix}}{\text{gal.}} \times V \times 650 \frac{\text{BTU}}{\#\text{VCl}} \times 0.16 \frac{1}{\text{hr.}} \times \frac{100\ \#\ \text{VCl}}{282\ \#\ \text{Mix}}$$

$$= 290.6\ V \frac{\text{BTU}}{\text{hr. gal.}}$$

Heat Transferred Through the Reactor Walls

$$Q = UA\Delta t = 46\ A\Delta t \qquad \text{---------- (III)}$$

Equating

$$Q = 46\ A\Delta t = 290.6\ V \qquad \text{---------- (IV)}$$

$$\frac{V}{A} = \frac{46\Delta t}{290.6} \frac{\text{gal.}}{\text{ft.}^2}$$

For various fluid coolant temperatures, the following table results:

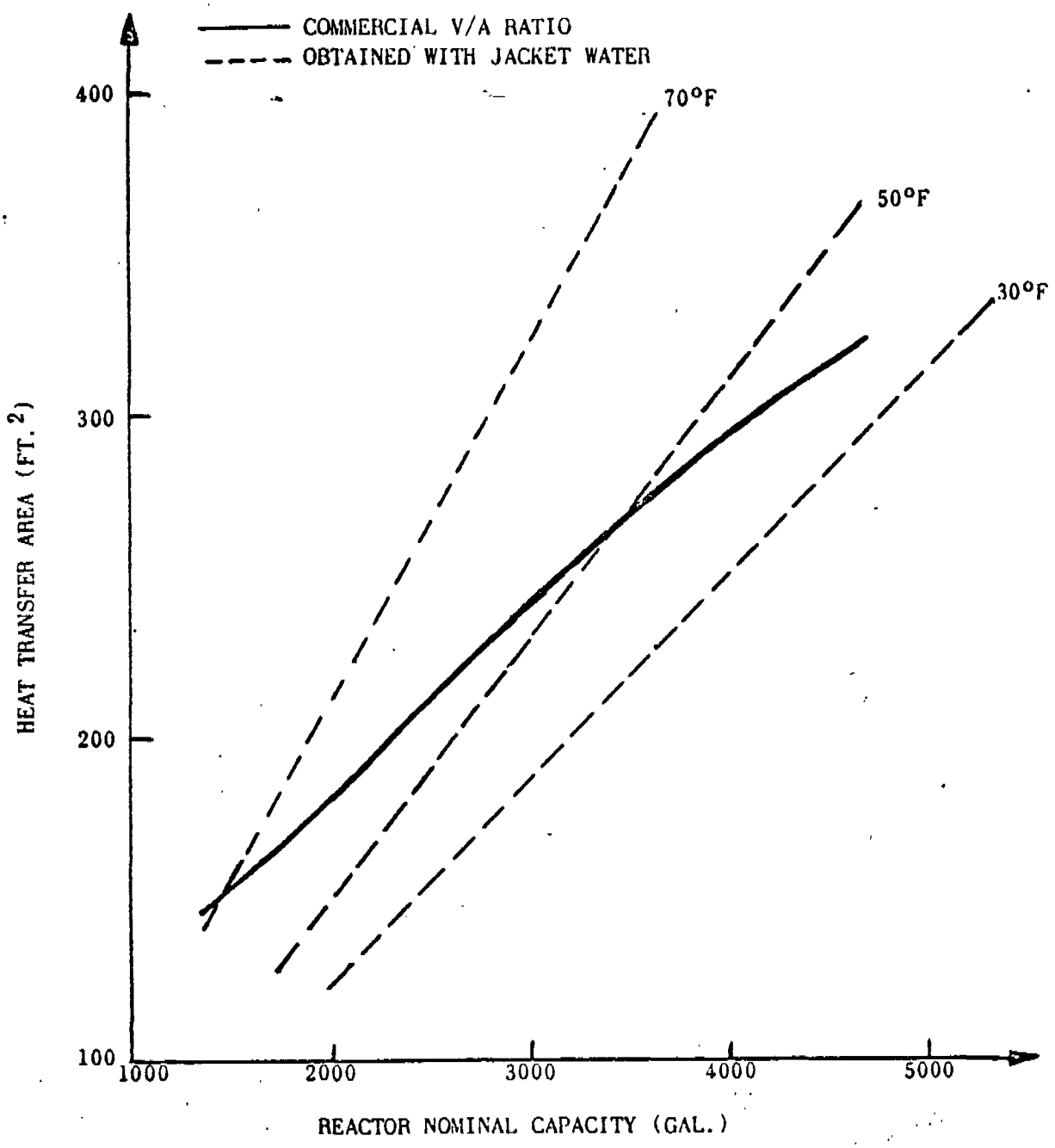
Table 3

V/A Ratios for Various t's at 130°F Batch Temperature

Average Cooling Water Temperature	70°F	60°F	50°F	40°F	30°F
Average Δt Across the Reactor Wall	60°	70°	80°	90°	100°
$46\Delta t$	2760	3220	3680	4140	4600
V/A	9.5	11.1	12.7	14.2	15.8

By plotting the reactor nominal capacity vs. the heat transfer area and by using the values obtained above for parameters, the necessary cooling water temperature can be obtained (Figure 5).

FIGURE 5. REACTOR NOMINAL CAPACITY VS. HEAT TRANSFER AREA



The 70°F water from a cooling tower will not maintain control over the batch if the only heat transfer surface available is the jacket wall. Accordingly, methods for extending the heat transfer area have been investigated. These take the form of external heat exchangers through which the slurry is recirculated or reflux condensers mounted on top of the reactors which continually condense VCl vapors. The former method has proved

impractical. If external pumping velocity is high, the resin particle size is disturbed; and if the pumping velocity is low, plugged lines result.

Early work with reflux condensers was concerned with the effect on product quality and the efficiency of heat transfer. The results were heartily encouraging with respect to product quality, and overall heat transfer coefficients in excess of 100 BTU/hr.^{o}F sq. ft. were reported. But as the condensers were used on larger vessels, serious fouling problems were noted. It was determined that cleaning would be excessive and that maintenance costs would offset any capital advantages over refrigerated water.

e. Optimum Sizing

Assuming that glass-lined reactors must be used, that they are available in various sizes, and that cooling costs will change somewhat with varying volume to area ratios, the optimum reactor size (200 psi) can be determined on the basis of bare equipment costs. The following table can be prepared:

Table 4

Reactor Equipment Costs for 75 x 10^6 #/Yr.

Nominal Reactor Capacity	F.O.B. Cost of Reactor and Agitator (per reactor)	Instrumentation Costs (per reactor)	No. of Reactors	F.O.B. Cost For Reactors, Agitators, And Instrumentation
2,000 gal.	$20,500 (3)	$3,100	34	$802,400
3,000 gal.	25,200	3,100	23	650,900
4,000 gal.	28,400	3,100	17	535,500
5,000 gal.	35,000	3,100	14	533,400

The cost of cooling equipment can be found by assuming a scheduling rate. The peak load is normally 16% conversion per hour and the nominal load 9% conversion per hour. Further assume that the 16% figure is based on the total monomer charged, the 9% figure is based on 95% yield, and that all reactors are on a 16-hour cycle with a 3-hour nonproductive time.

Table 5

Refrigeration Duty

Nominal Reactor Capacity (gal.)	# PVC Produced Per Batch	# PVC Produced At Peak Rate/Hr.	# PVC Produced At Avg. Rate/Hr.	No. Reactors Idle	No. Reactors At Peak Rate
2,000	4,839	815	436	6.4	2.1
3,000	7,259	1,223	653	4.3	1.4
4,000	9,679	1,630	891	3.2	1.0
5,000	12,098	2,038	1,089	2.6	0.9

No. Reactors At Nominal Rate	Peak Heat Load BTU/Hr.	Average Heat Load BTU/Hr.	Total Heat Load BTU/Hr.	Total Load in Tons of Refrigeration
25.5	11.1×10^5	7.22×10^6	8.33×10^6	694
17.3	11.1×10^5	7.34×10^6	8.45×10^6	704
12.8	10.6×10^5	7.42×10^6	8.53×10^6	711
10.5	11.9×10^5	7.44×10^6	8.56×10^6	713

Combining the refrigeration load with the temperature requirements of Figure 5, the refrigeration equipment costs can be estimated.

Table 6

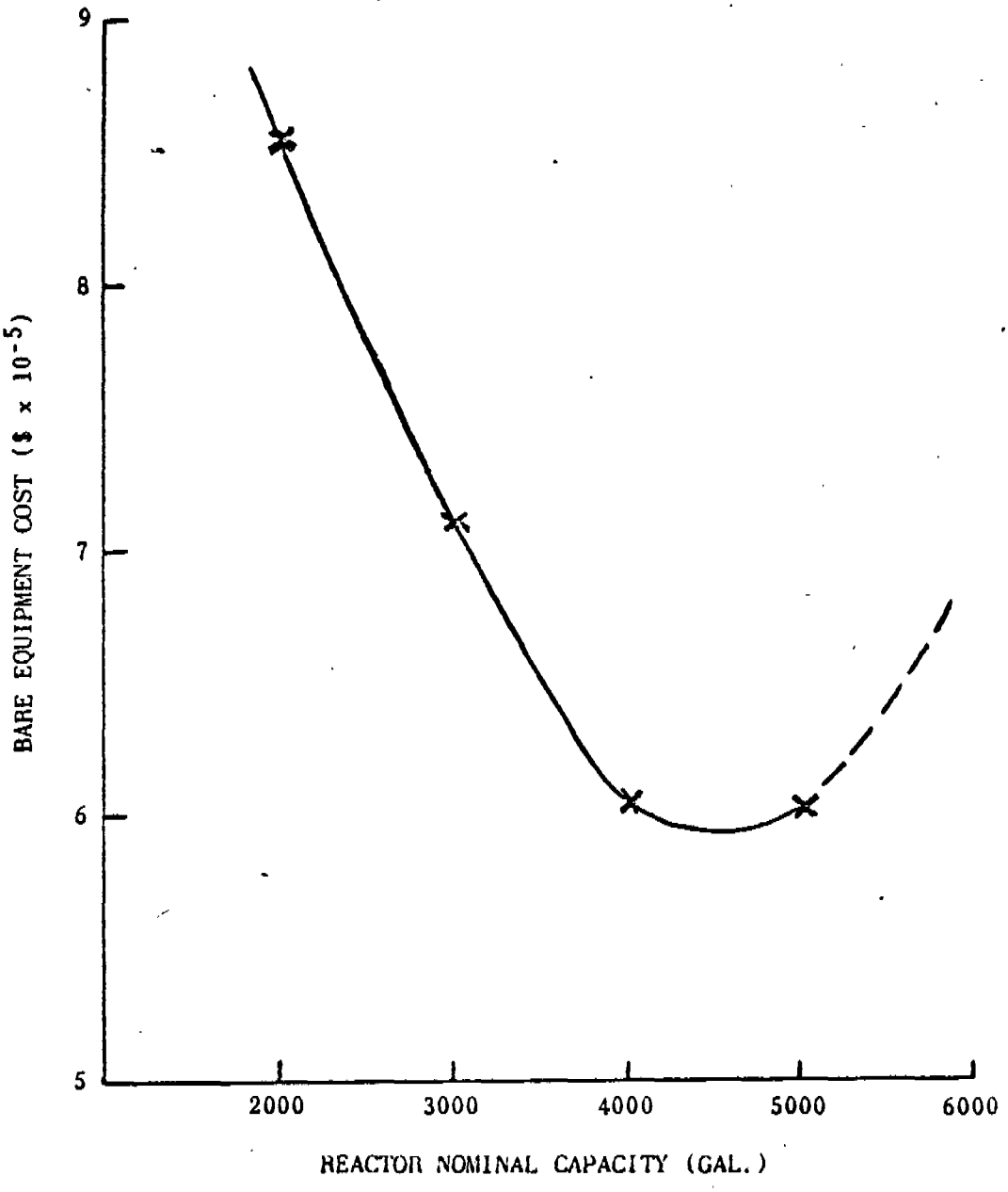
Cost of Cooling Equipment

Nominal Reactor Capacity	Tons of Refrigeration	Temperature Required	Refrigeration Equipment Cost, F.O.B.
2,000 gal.	694	50°F	$50,000
3,000	704	40°F	66,000
4,000	711	40°F	67,000
5,000	713	40°F	68,000

Using Tables 4 and 5, the equipment costs (F.O.B.) for refrigeration and reactors is known. A plot of the combined costs is shown in Figure 6.

The presented curve indicates a broad minimum between 4,000 and 5,000 gallon reactors. For a 6,000 gallon reactor, fabrication costs would rise steeply, causing the formation of a very definite minimum.

FIGURE 6. BARE COSTS VS. REACTOR SIZE



2. Ashtabula Design

The Ashtabula PVC Plant of The General Tire & Rubber Company was designed and constructed in 1954 by Scientific Design Company. The original plan called for a 24 million pound per year polymer facility utilizing ten 3,500 gallon reactors arranged in two banks of five reactors each. Reactor cooling was provided by a cooling tower and was generally successful with the 20-24 hour reaction times obtained with 1954 technology. All reactors were glass-lined.

By 1956, the demand for PVC caused General Tire to expand the polymer area by 50%. A new line of five reactors was added. In

the past several years, both the demand for PVC and the technology of manufacture have advanced. New catalyst systems have lowered reaction times to 10-16 hours (depending on the product) and markets have expanded.

B. Agitation

1. Design Considerations

The size of a particle made by the suspension method is a function of the protective colloid and the fluid regime. The agitation variables are primarily:

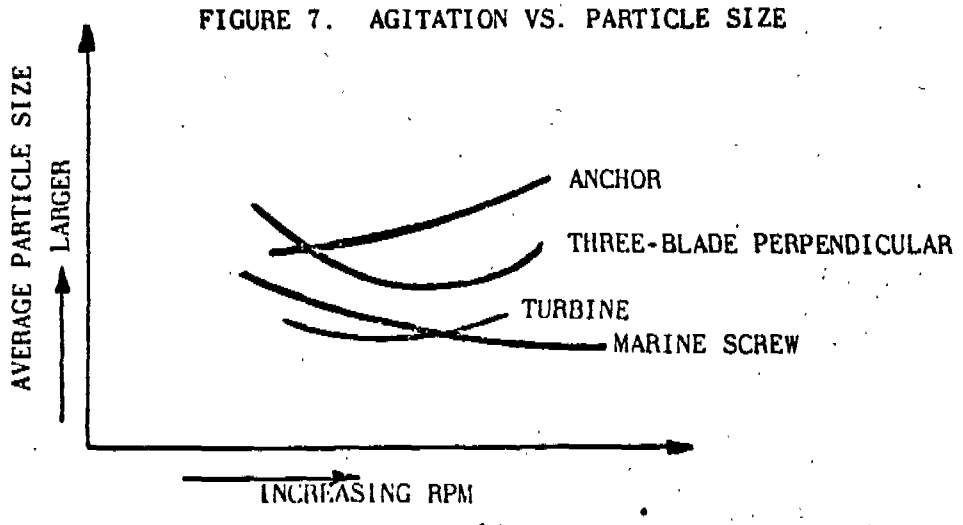
a. Agitator speed.
b. Impeller size and design.
c. Number of baffles and their design.
d. Material of construction.

The material of construction follows the requirements laid down in the reactor design.

Theoretical aspects of impeller design, baffling requirements, and motor sizing have been investigated by numerous workers since 1880. A complete equation, describing the geometry of the system, impeller Reynold's number, vortexing effect (Froude number) and baffling would include some ten dimensionless groups.[5] It is possible, following the method of Rushton,[6] to scale up an important variable if at least two smaller systems, geometrically similar, are used. In practice, it is common to scale up using trial and error techniques based on the commercial designs available. Initial pilot investigations at General Tire dealt with a variety of impeller and baffle designs. The tubular finger baffle was found most suited to PVC operations.

Five gallon reactor studies on the anchor, turbine, 45° marine screw and three-bladed perpendicular blades led to the conclusion that the speed of agitation and type of agitator had a decided effect on the particle (Figure 7).

FIGURE 7. AGITATION VS. PARTICLE SIZE



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Only with the marine screw agitator did particle size continue to decrease with increased speed. The optimum particle size distribution is also related to the agitator design.

The same result was obtained in the 3,500 gal. reactors by using a three-blade retreating blade impeller which does not have the deep vortex and large baffling requirements of the marine screw system. It is postulated that both the successful systems have an action resembling a centrifugal pump. The liquid is pulled downward and against the reactor sides, then flows up the walls and down for a repeat cycle. This gives very satisfactory heat transfer and with the retreat blade system there is minimal scale formation.

After the reaction is complete, the suspension is emptied through a transfer line to a receiver tank for unreacted monomer removal. If high-speed agitation is maintained, this operation is slowed greatly by the creation of a vortex. Cessation of agitation will result in phase separation and complete plugging of the reactor outlet valve. The solution is to equip all reactors with two-speed agitators, the lower speed used only while transferring.

2. Ashtabula Design

The Ashtabula plant presently has two-speed, 15 H.P., retreating blade agitators. The original ten reactors were equipped with a single, three-finger wall baffle. The five reactors added in 1956 have been successfully run with a single small blade baffle. The same recipe in the two types of reactors will produce a slightly different resin particle.

C. Recovery System

1. Design Considerations

The reaction for Vinyl resins attains an average 95% conversion in the reactor. The importance of the recovery system can be shown by a simple example:

Assume 75×10^6 lb./yr. production; then the unreacted monomer with no recovery at 95% conversion would be:

$$\frac{75 \times 10^6}{0.95} \text{ lbs./yr.} - 75 \times 10^6 \text{ lbs./yr.} = 3.9 \times 10^6 \text{ lbs./yr.}$$

At current market prices (8¢/lb.), this represents:

$\$0.08 \times 3.9 \times 10^6 = \$312,000$

Obviously the recovery system is no small part of the overall profit picture.

Vinyl chloride is nearly insoluble in water, and the bulk of the unreacted monomer is in a dispersed state within the water phase or in the vapor phase over the batch. Since VCl exhibits a volume

shrinkage of 35% during polymerization and the reactors are not fully loaded initially, the vapor in the free space is considerable (pressure is 30 to 50 psig). To a lesser extent, some residual monomer (about 0.4% of the amount charged) is solvated in the resin particle. The unreacted monomer is difficult to remove from the PVC particles because diffusion of monomer through the particle is time-temperature dependent.

Simple vacuum flashing suffices to remove the free monomer at a rate dependent on the size of the vacuum pump and recovery compressor and the batch temperature. The latter will drop off sharply unless the heat of vaporization is continually replaced. This heat may be supplied in a variety of ways but, if the boiler feed water is sufficiently pure, it is best to inject live steam into the batch. This must be carefully done to avoid product degradation but gives the added advantage of intimately contacting the polymer, leading to a lowered residual VCl level within the particle.

The drop tanks must be fully agitated to prevent phase separation and must be rated for full vacuum and a minimum of 100 psig. Since they are the site of only a minor amount of polymerization, stainless vessels are satisfactory. To reduce liquid entrainment in the recovery system due to foaming, the vessels should be at least 30% larger than the reactors.

The number of drop tanks is selected so that there will be no production scheduling holdups between batches. Since the completion of a PVC batch reaction is determined by pressure drop and not by time control, some latitude must be allowed and it is most economical to provide an adequate number of drop tanks. Based on plant experience, a single batch can be transferred into a drop tank in one-half hour, stripped in one hour, and transferred from the drop tank in one-half hour. For a system of N reactors operating at 16 hours turn-around per reactor and scheduled charging, there will be one batch available for monomer removal every N/16 hours. The number of drop tanks would then be given by the equation:

No. Tanks = Stripping time (hr./batch) x Prod. Rate (batches/hr.)

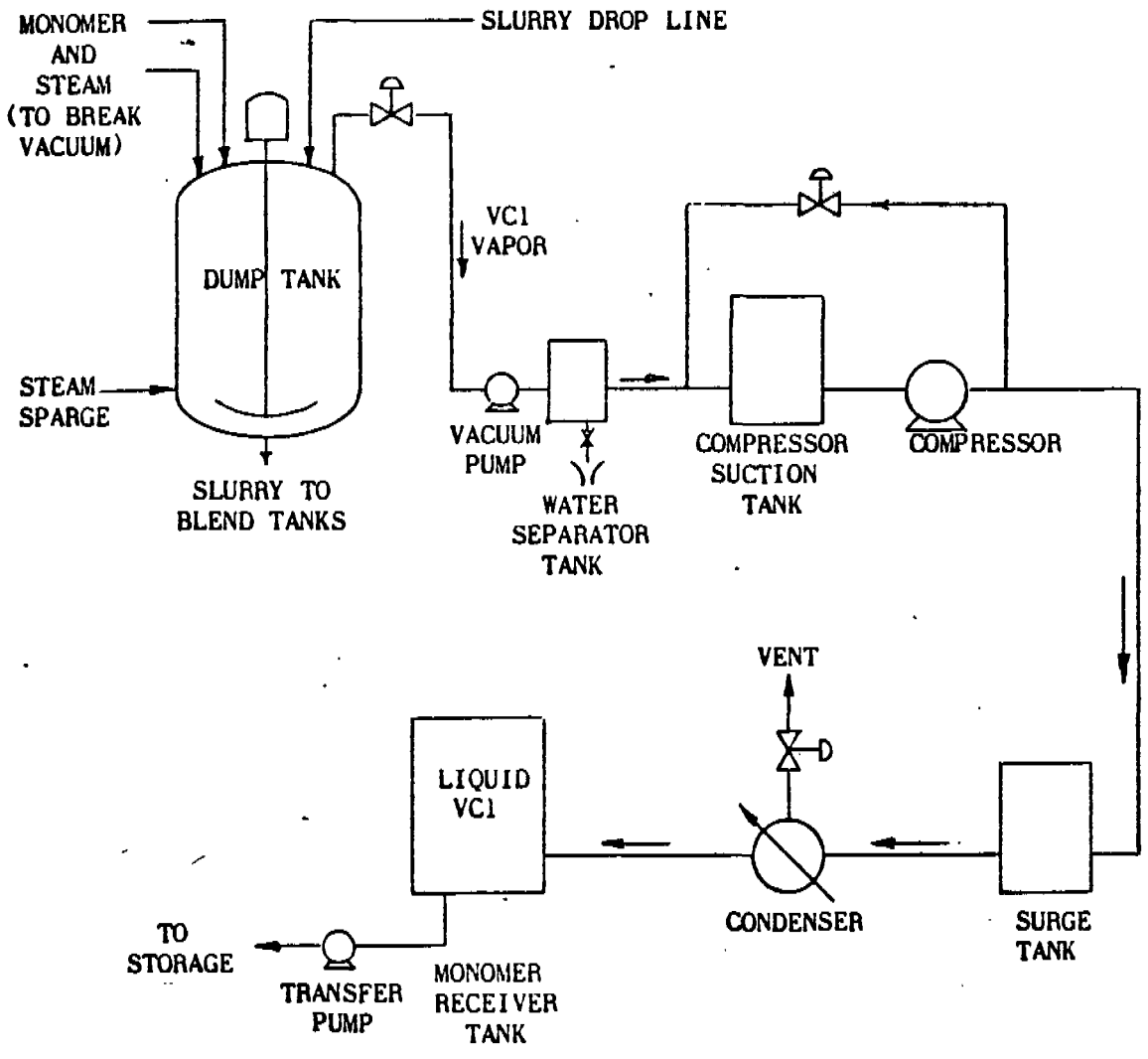
---------- (V)

$$\text{No. Tanks} = 2.0 \frac{\text{hrs.}}{\text{batch}} \times \frac{N}{16} \frac{\text{batches}}{\text{hr.}} = \frac{N}{8}$$

The conclusion is reached that one drop tank is needed for every eight reactors. This analysis does not allow for batch-to-batch variations in cycle time. For these reasons, a safer figure would be one drop tank for every six reactors. The physical arrangement of equipment may also help determine the number of drop tanks needed per reactor.

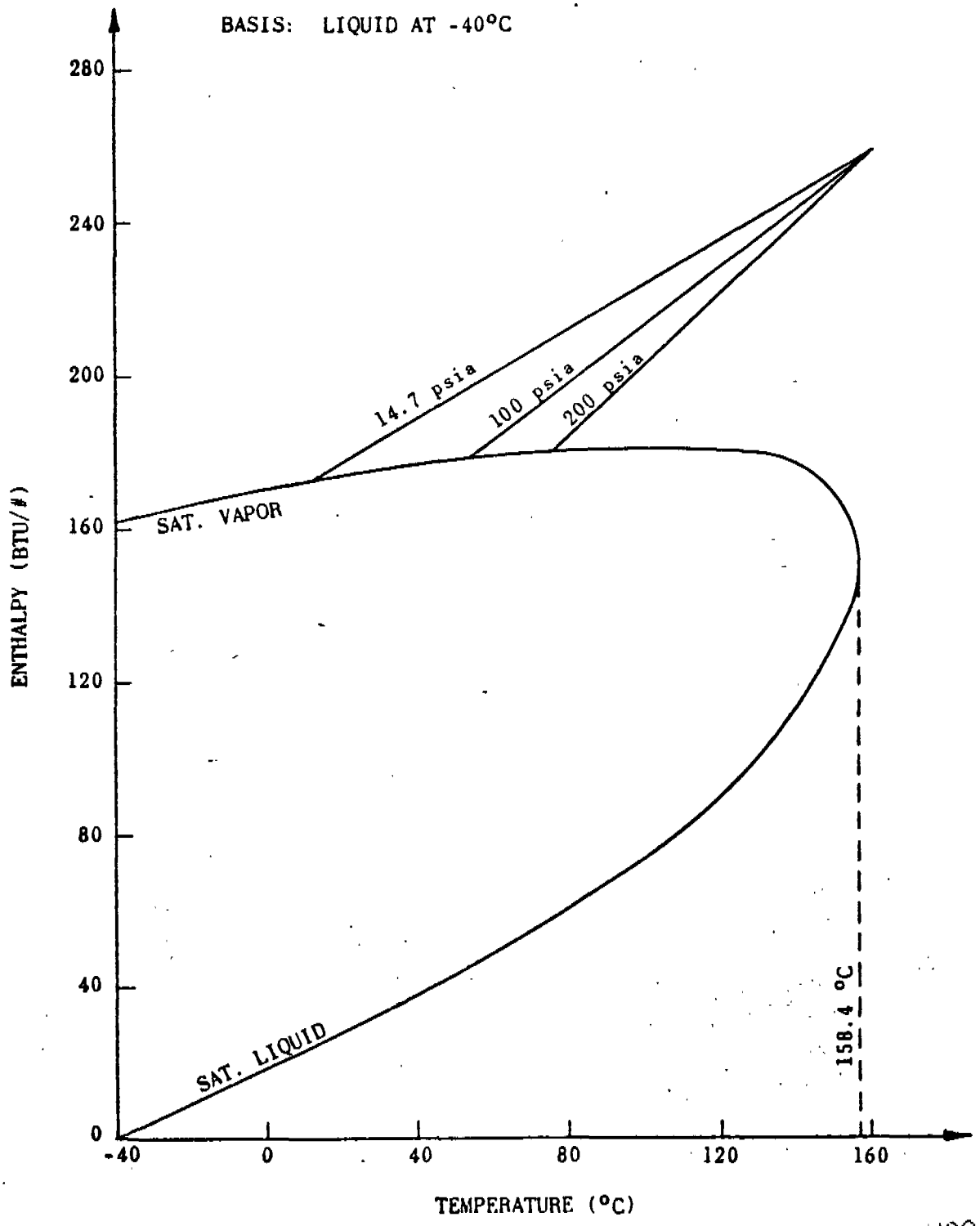
The general layout of a dump tank-recovery system is given in Figure 8.

FIGURE 8. DUMP TANK - RECOVERY SYSTEM



Using the enthalpy curves for VCl (Figure 9), the heat duty for the recovery condenser can be calculated. The storage conditions for VCl are normally 80°F and equilibrium vapor pressure.

FIGURE 9. ENTHALPY OF VCl



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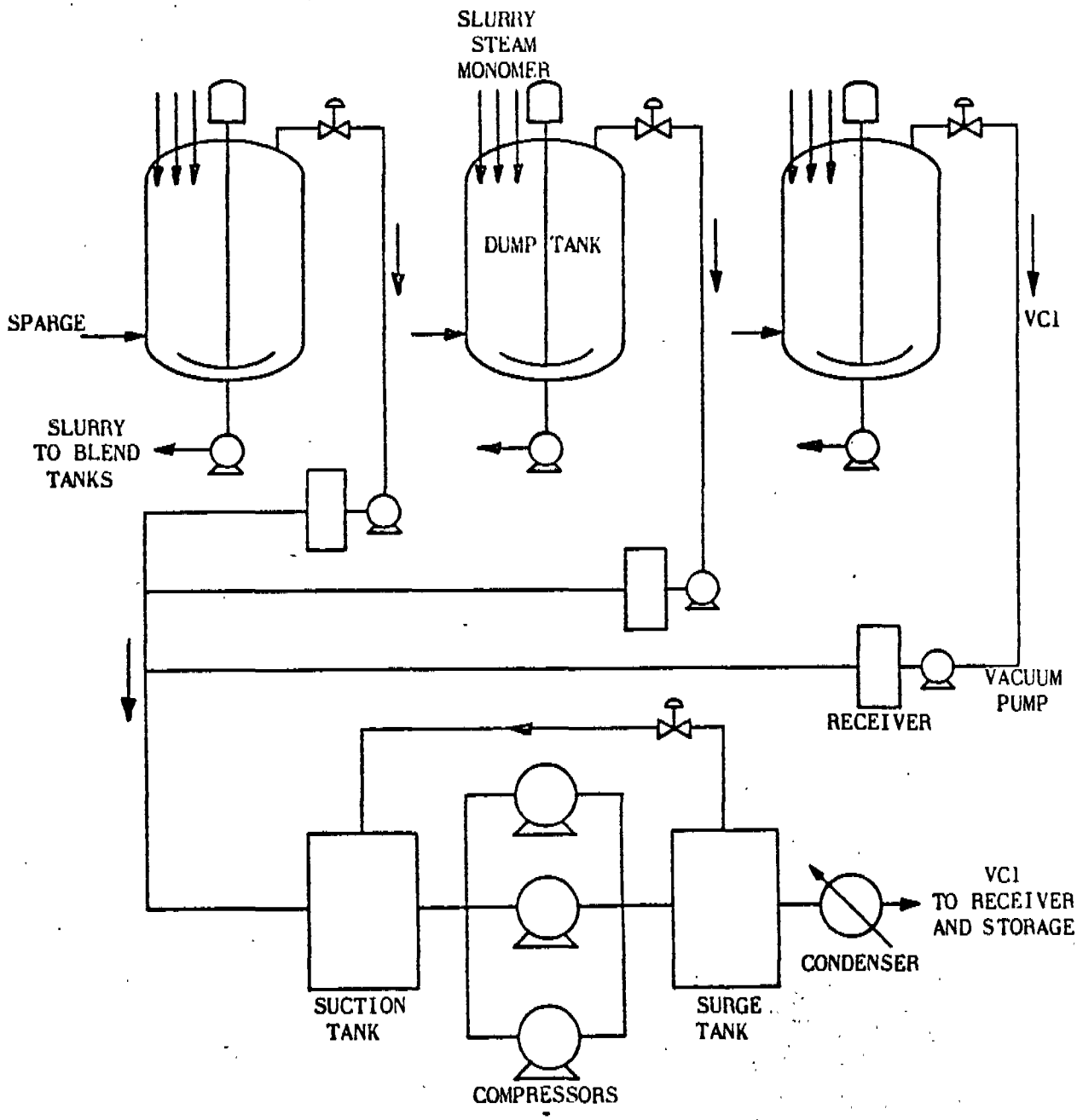
2. Ashtabula Design

The Ashtabula recovery system consists of three dump tanks, two of 7,000 gal. and one of 5,000 gal. capacity. Each has a vacuum pump and recovery compressor feeding a common recovery condenser. The system is given in Figure 10.

FIGURE 10. ASHTABULA RECOVERY SYSTEM



D. Storage

1. Design Considerations

As defined in this section, storage will mean the raw monomer being held for polymerization and the reactor slurry being held for continuous drying. The volume of the former is determined by the source of monomer (i.e., is it being continually produced, is it being shipped in, or a combination), and by the rate of production. Slurry storage is determined by the number of different products being produced simultaneously, the number of drying lines, and quality control. Several batches should be blended before drying to assure product uniformity in day-to-day operation.

2. Ashtabula Design

a. Monomer Storage

The original design for Ashtabula consisted of three monomer tanks of 15,000 gal. capacity each. Two were 304 stainless clad, and the third made of carbon steel. The stainless tanks were to hold purchased and produced monomer for feed to the reactors. The carbon steel tank received recovered monomer and served as a feed vessel to the monomer refining column. Iron contamination is removed in the refining step and the stainless tanks were to prevent any iron from being picked up after the refining step. It was soon found necessary to use a tank in conjunction with the continuous monomer production. This led to the purchase of a fourth, carbon steel, tank.

Time proved that the choice of 304 stainless clad tanks for Ashtabula-produced monomer was unfortunate. Trace quantities of HCl and water led to extensive corrosion problems and iron pickup in the monomer. The existing 304 stainless steel clad tanks have been repaired, and a glass-lined vessel is being purchased in the current expansion.

b. Slurry Storage

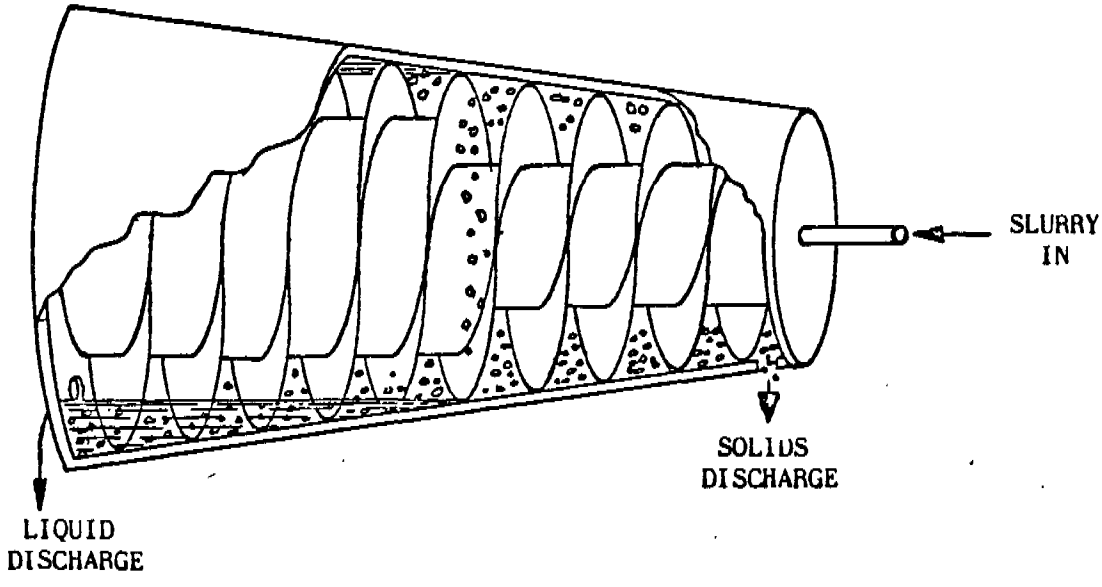
The slurry storage tanks ("blend" tanks) of the original Ashtabula design consisted of three 15,000 gal. 304 stainless steel tanks. Continuous agitation is provided to prevent phase separation. The transfer lines are constantly recirculated to prevent line plugging and to further increase the blending efficiency when the tanks are not feeding the dryers. During the 50% plant expansion of 1956, two more 15,000 gal. tanks were added, and three more are being installed with the current expansion.

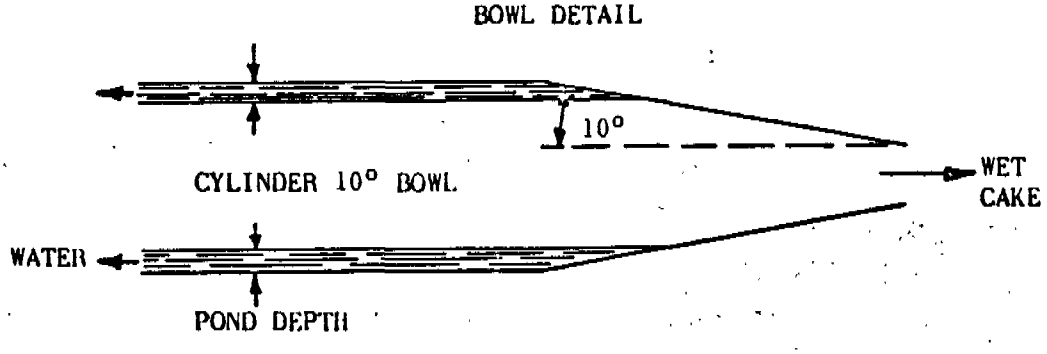
E. Dewatering

1. Design Considerations

Slurry from storage contains an average of 25% PVC with actual values varying with the basic recipe, reactor wash, and water added to facilitate pumping. All water used in the process is deionized. A combination technique of dewatering and drying is required for PVC. The method best suited is a continuous solid-bowl centrifugal separation with the solids discharge feeding directly into the drying system. Utilizing this, standard products can be consistently concentrated to 76% - 77% solids before entering the dryer. Figure 11 illustrates a commercial centrifuge commonly used.

FIGURE 11. COMMERCIAL CENTRIFUGE





A feed pipe running along the horizontal axis of the centrifuge distributes the slurry. The plow mechanism rotates in the same direction as the bowl but at a reduced speed, thus conveying solids to the small end of the bowl where they are discharged. Normal bowl rotational speeds range from 2000 RPM and above for small units, down to 500 RPM on large ones. Liquid level (the "pond") is maintained by adjustment of the outlet dams.

Both the depth of the pond and the angle of the bowl relative to the horizontal axis is important to the efficiency of operation. The deeper the pond, the more efficient the phase separation (less solids material in the effluent). Correspondingly, the deeper the pond, the more moisture in the wet cake discharge. The former means less loss of product to the plant, while the latter means an overload of the drying system with subsequent reduction in production rates. The net effect of the bowl configuration is to change the characteristics of the curve relating feed rate to discharge moisture content.

Electrical grade resins requiring low ion content for insulation applications are easily handled in commercial centrifuges with the use of a deionized wash water technique. Deionized water is introduced into the centrifuge, and is brought in contact with the resin through the churning action of the blade. Both the volume of wash water and the water temperature have an effect on the removal of soluble ions. With 120°F process water, the experimental wash water efficiency is given in Figure 12.

2. Ashtabula Design

Ashtabula has two driers rated for 25 million pounds per year each. Plans have been laid to install a third line with its attendant centrifugal dewatering system. The two existing driers each have two centrifuges developing 760xG at 1750 RPM with a feed of 4000 #/hr. on each line. Based on the drying capacity being installed, it is desired to maintain 5000 #/hr. on standard resins.

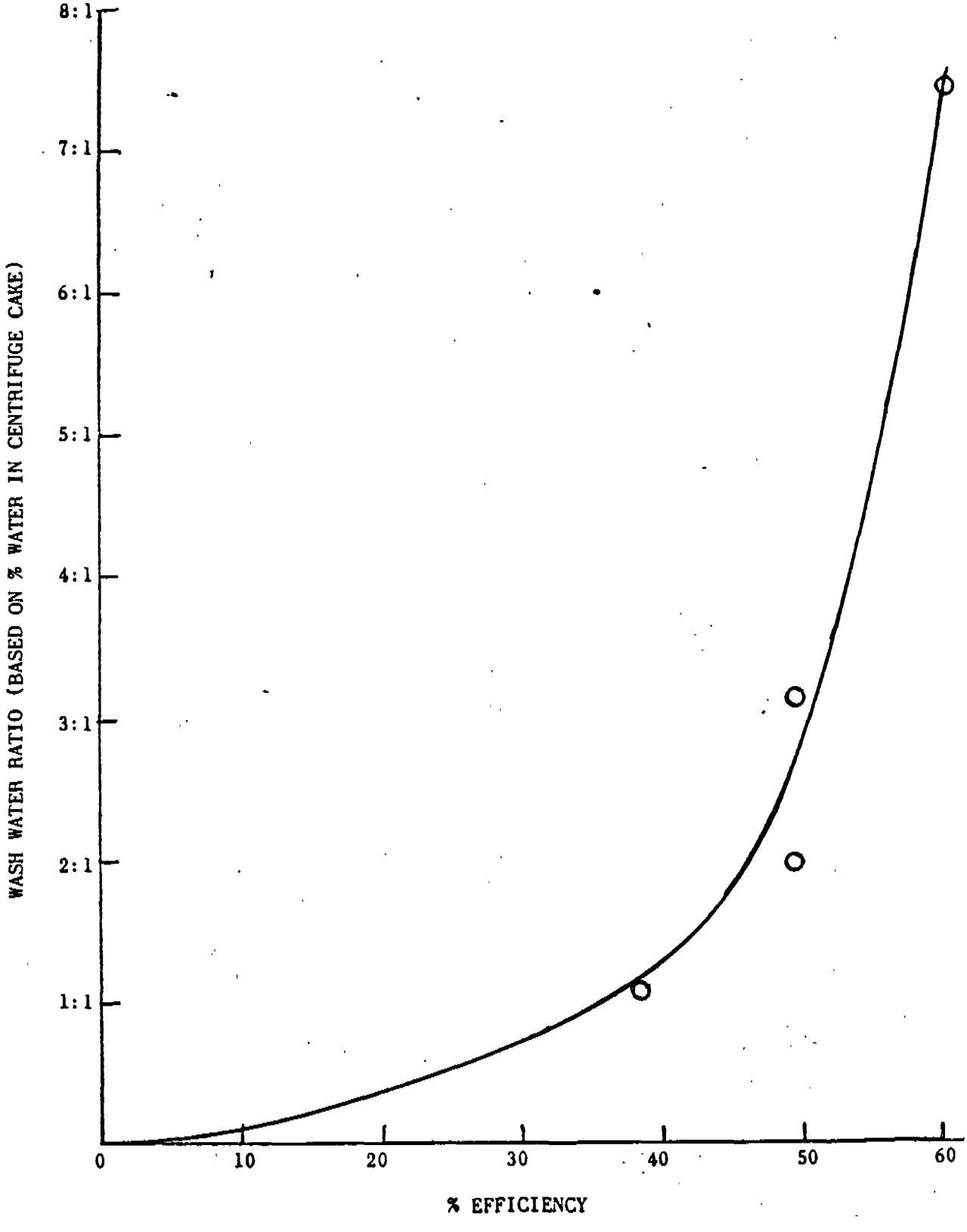
The specific centrifuge design for economic plant operation depends on the two factors mentioned previously, e.g., on the sum of the effluent losses and on the variable cost of drying for differing wet cake moistures.

F. Dryers

1. Design Considerations

The prime considerations in drying PVC are to avoid product degradation and to obtain low moisture content. At about 150°F degradation of the product will occur, resulting in discoloration of a milled sheet. In addition, PVC is subject to a cumulative "heat history"; the length of time at moderately elevated temperatures will affect quality. This necessitates the use of a co-current drying system or one in which exposure time of the polymer

FIGURE 12. WASH WATER EFFICIENCY



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to heat is minimized. The two types in use for PVC are rotary and flash. The rotary drier is used by General Tire.

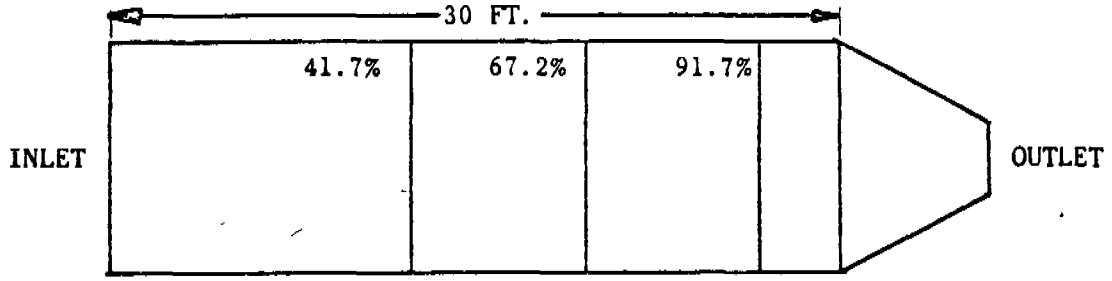
2. Ashtabula Design

The 1954 Ashtabula design consisted of a single 10' diameter x 30' long stainless steel, cocurrent rotary drier, rated for 25 million pounds a year. A finned-tube heat exchanger delivered approximately 3×10^6 BTU/hr. to the air stream. At normal operating rates, some 4,000 dry pounds could be produced per hour at an overall thermal efficiency of about 50%.

During the 50% plant expansion of 1956 a second, identical drier was installed. This pushed the drying capacity to 50 million pounds a year. With further reactor expansion planned to put plant capacity to 75 million pounds per year, a third will be required. Accordingly, the existing system was completely evaluated.

The following data and Figure 13 are extracts from a General Tire report bearing on factors affecting drier capacities.

FIGURE 13. DRIER SAMPLE POINT AND BAFFLE LOCATION



SAMPLE POINTS 1, 2 AND 3 LOCATED AT 28.3%, 54.3%, AND 90.0% OF DRIER LENGTH.

Table 7

No. 1 Drier

Fraction of Drier	0	.283	.543	.90	1.13
Air Temperature	300	209	200	190	146
Solid Temperature	120°	102°	108°	112°	136°
Solid Moisture:					
Wet Basis	24.3	17.9	8.2	0.3	0.25
Dry Basis	32.2	21.8	9.0	0.3	0.25
Humidity	.009	.0203	.0343	.0443	.0443
Wet Bulb Temp.	108°	102°	107.5°	112.3°	107°
Air Rate Through Drier	- 54,800 lbs./hr.				
Velocity Within Drier	- 198 ft./min.				
Heat Input by Coils	- 3,060,000 BTU-hr.				
Slurry Feed Rate (dry basis)	- 4,350 lbs./hr.				

From the preceding data, the overall volumetric heat-transfer coefficient was determined following Perry, Chemical Engineer's Handbook, Third Edition, p. 831 and Fourth Edition, p. 20-19:

$$q_t = U_a V (\Delta t)_m \quad \text{---------- (VI)}$$

q_t = Total heat transferred, BTU/hr.

U_a = Volumetric heat transfer coefficient, BTU/Hr.Ft.^{3}$^\circ$F

$(\Delta t)_m$ = True mean temperature difference between hot gases and material, $^\circ$F

$$\frac{1}{(\Delta t)_m} = \frac{q_p}{q_t (\Delta t)_p} + \frac{q_v}{q_t (\Delta t)_v} + \frac{q_s}{q_t (\Delta t)_s} \quad \text{---------- (VII)}$$

q_p = Heat transferred to wet material while heating to the air wet-bulb temp., BTU/hr.

q_v = Latent heat transferred to the material while moisture is being evaporated at constant temp., BTU/hr.

q_s = Sensible heat transferred to the dry material while heating it to the discharge temp., BTU/hr.

q_t = Total heat transferred in the drier, BTU/hr.

$(\Delta t)_v$ = Mean temp. difference between the air and the material at constant temp., $^\circ$F

$(\Delta t)_s$ = Mean temp. difference between the air and the material while heating to its discharge temp., $^\circ$F

$(\Delta t)_p$ = Mean temp. difference between the air and the material while heating to the wet-bulb temp., $^\circ$F

Evaluation of Equation VII

C_p (PVC) = 0.25 $\frac{\text{BTU}}{\# \ ^\circ\text{F}}$ $\quad$ C_p (H_2O) = 1.0 $\frac{\text{BTU}}{\# \ ^\circ\text{F}}$

Solids temp. = 120°F inlet, 136°F outlet
Air temp. = 300°F inlet, 146°F outlet
Air wet-bulb temp. = 107°F
Dry product production rate = 4,350 #/hr.
Water content of feed = 24.3%
Constant drying rate period = 20% to 1% moisture
Basis = 1 hour
Total moisture in feed = $\frac{4,350}{1.0 - 0.243}$ - 4,350 = 1,400 lbs.

$$q_p = (mC_p)_{PVC}\,\Delta t_p + (mC_p)_{H_2O}\,\Delta t_p$$

$$q_p = (4{,}350 \times 0.25)\,(107\text{-}120) + (1{,}400 \times 1.00)\,(107\text{-}120)$$

$$q_p = -3.23 \times 10^4 \text{ BTU}$$

$$q_v = (m_v \Delta H)_{H_2O} = \frac{.20 - .01}{1.00 - .757} \times 1{,}400 \times 1{,}030$$

$$q_v = 1.13 \times 10^6 \text{BTU}$$

$$q_s = (mC_p)_{PVC}\,\Delta t_s = (0.25 \times 4{,}350)\,(136\text{-}107)$$

$$q_s = 3.15 \times 10^4 \text{ BTU}$$

$q_t = q_p + q_v + q_s$ + heat of evaporation of unsteady-state moisture removal

Ignoring the last term:

$$q_t = -3.23 \times 10^4 + 1.13 \times 10^6 + 3.15 \times 10^4$$

$$q_t = 1.13 \times 10^6 \text{ BTU}$$

	Symbol	Value
Air temp. at inlet	T_{A1}	300°F
Air temp. at beginning of constant drying period (20% moisture)	T_{A2}	230°F
Air temp. at end of constant drying period (1% moisture)	T_{A3}	195°F
Air temp. at drier exit	T_{A4}	146°F
Material initial temp.	T_{M1}	120°F
Material constant drying temp. (wet bulb)	T_{M2}	107°F
Material final temp.	T_{M3}	136°F

$$(\Delta t)_p = \frac{T_{A1} + T_{A2}}{2} - \frac{T_{M1} + T_{M2}}{2} \qquad (\Delta t)_p = \frac{300 + 230}{2} - \frac{120 + 107}{2} = 151°F$$

$$(\Delta t)_v = \frac{T_{A2} + T_{A3}}{2} - T_{M2} \qquad (\Delta t)_v = \frac{230 + 195}{2} - 107 = 106°F$$

$$(\Delta t)_s = \frac{T_{A3} + T_{A4}}{2} - \frac{T_{M2} + T_{M3}}{2} \qquad (\Delta t)_s = \frac{195 + 146}{2} - \frac{107 + 136}{2} = 49°F$$

$$\frac{1}{(\Delta t)_m} = \frac{-3.23 \times 10^4}{1.13 \times 10^6 \times 151} + \frac{1.13 \times 10^6}{1.13 \times 10^6 \times 106} + \frac{3.15 \times 10^4}{1.13 \times 10^6 \times 49}$$

$$\frac{1}{(\Delta t)_m} = 9.81 \times 10^{-3}$$

$$(\Delta t)_m = 102^\circ F$$

Evaluation of Equation VI

$$q_t = U_a V (\Delta t)_m$$

Drier is 10' diam. x 30' long

$$V = \pi r^2 l = \pi(5)^2 \times 30 = 2.36 \times 10^3 \text{ ft.}^3$$

$$U_a = \frac{q_t}{V (\Delta t)_m} = \frac{1.13 \times 10^6 \text{ BTU/hr.}}{2.36 \times 10^3 \text{ ft.}^3 \times 102^\circ F} \qquad U_a = 4.70 \frac{\text{BTU}}{\text{ft.}^3 \text{hr.}^\circ F}$$

The above result was compared to the correlation of Friedman and Marshall:[7]

Comparison With Friedman-Marshall Correlation

$$U_a = \frac{20\ G^{0.16}}{D} \qquad \text{---------- (VIII)}$$

where G = air mass velocity, lbs./hr.ft.^{2} = 54,800 lbs./hr.

D = drier diam., ft. = 10 ft.

$$U_a = \frac{20}{10} \frac{(54,800)^{0.16}}{(25\pi)} = 5.70 \frac{\text{BTU}}{\text{hr. ft.}^3 {}^\circ F}$$

The Friedman-Marshall equation is admittedly only an approximation but it does show a fairly good correlation with the rotary driers in use at the Ashtabula plant.

G. Separation of the Product from Air

1. Design Considerations

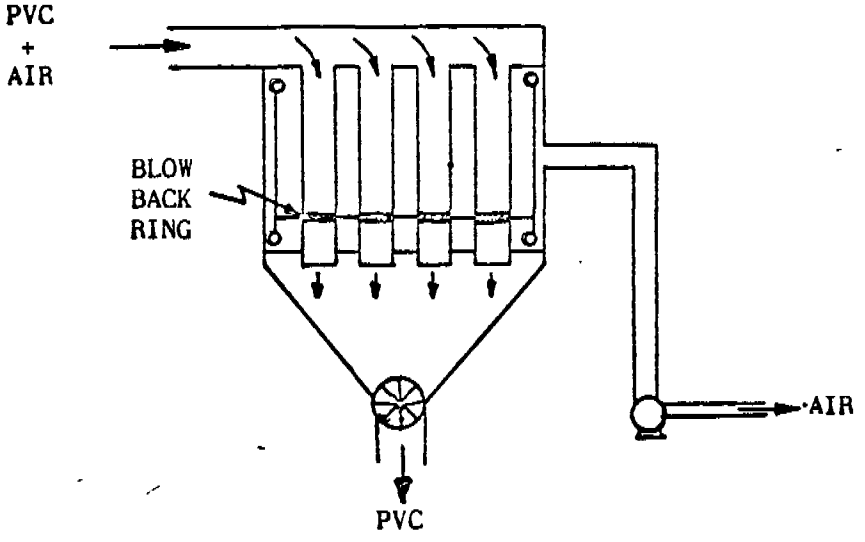
The product may be discharged from a rotary drier either directly from the lower end with the use of a breeching ring, or it may be intentionally entrained in the exit gases by restricting the exit area and thereby increasing the air velocity. The latter method is most common because (1) the breeching ring method is not highly efficient, since it requires a backup filter for the exhaust air, and (2) entrainment allows convenient conveying to any point in the plant. The fluidized particles must then be separated from the air stream for packaging or storage.

Air separation devices have normally been of three types: (1) cloth or bag filters, (2) cyclone separators, or (3) a combination of cyclone and cloth filters. The primary design criteria is overall collection efficiency. Even the loss of one-tenth of one per cent of the product in a 75 million pound plant represents a loss of $12,000 per year. The various methods of recovery are discussed below, along with their characteristic limitations.

a. The Bag Filter

From General's experience, a bag filter maintains an average 99.95% collection efficiency in retaining PVC particles. A typical installation is shown in Figure 14.

FIGURE 14. BAG FILTER



With this device the inlet air, laden with PVC particles, is distributed into a header feeding the interior of several rows of bags. A partial vacuum is maintained on the exterior of the bags, pulling the air out to the atmosphere. Most of the PVC drops to bins below, but some PVC particles are left clinging to the interior and must be removed. This is accomplished with the use of a blow-back ring mounted on a movable carriage. The carriage continually traverses the length of the bag with small jets of air shaking the PVC loose to drop in the bin below. A rotating star valve maintains an air seal while allowing the free-flowing polymer granules to pass through.

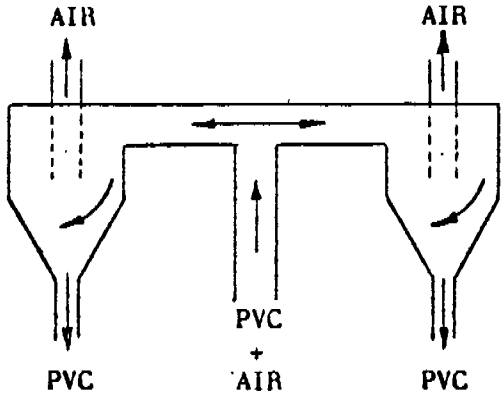
There are several disadvantages to the bag filter. Relatively high capital and operating costs are combined with operational limitations which periodically produce low-grade product. The filter media (commonly Orlon) plugs and can only be opened by more violent means than the blow-back rings. Successive release and re-establishment of the vacuum on the exterior of the

bags will cause firmly adhering PVC to drop off. The product garnered in this manner is primarily "fines" (smaller than 270 mesh) and is designated as off-specification material. This method is not successful indefinitely and bag replacement is frequent. Continual wear on the cloth from the mechanical carriage leads to eventual rupturing, further raising maintenance costs and the loss of top grade product.

b. Cyclone Separator

The cyclone separator operates with no moving parts, is inexpensive and relatively free of maintenance. Collection efficiencies have not been theoretically correlated to the degree of accuracy needed for firm design, necessitating experimental work. Such work has been done at the Ashtabula plant. The coarser resins could be collected at an efficiency of 99.93%, while the finer resins were gathered at efficiencies ranging down to 99.4%. By using two or more small-diameter cyclones in parallel, it is estimated that a high collection efficiency can be achieved. The system is shown in Figure 15.

FIGURE 15. DUAL CYCLONE COLLECTOR

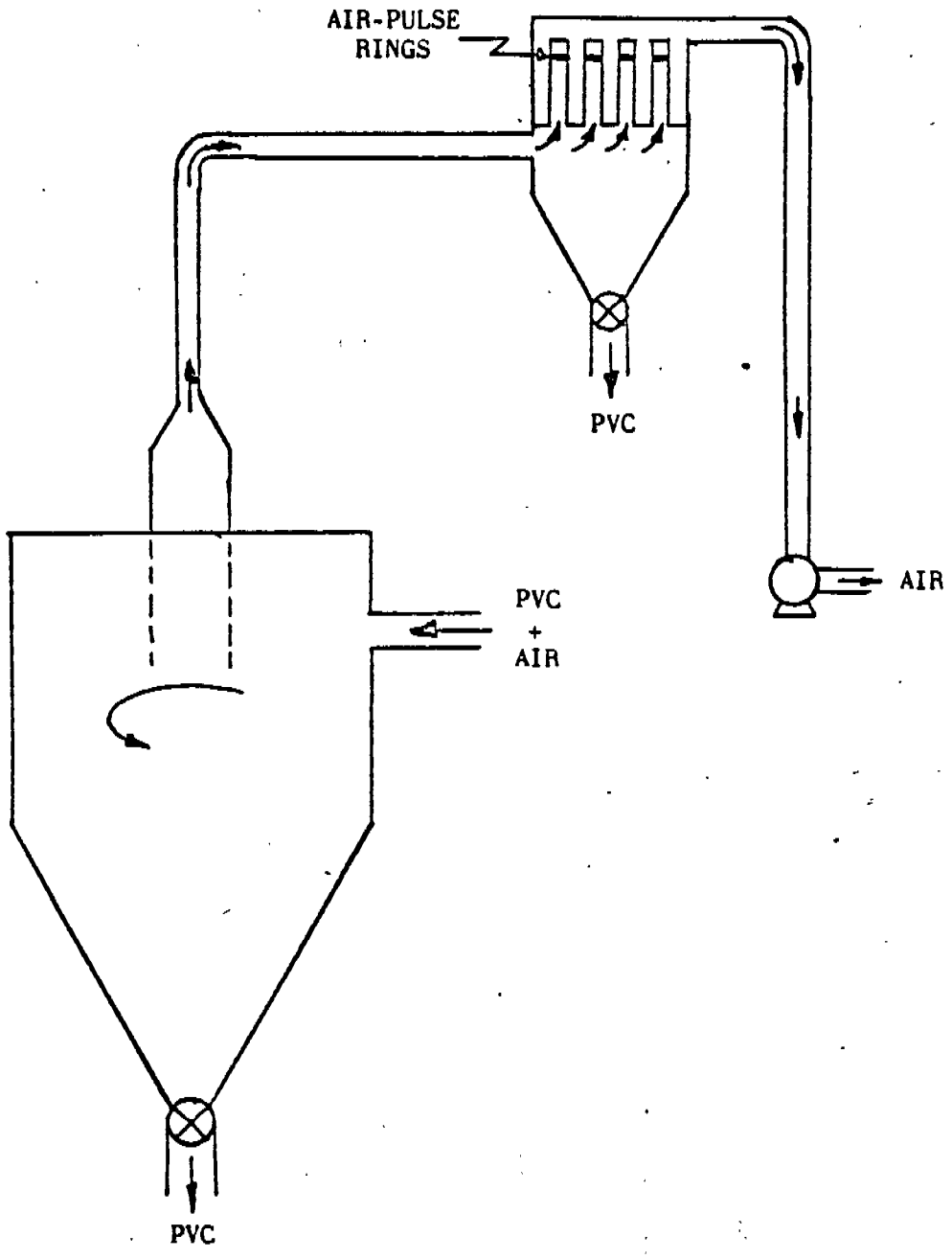


c. Combination of Cyclone and Cloth Filter

Various combinations of cyclone filters with cleanup cloth filters exist. One such arrangement is given in Figure 16.

In this separator, the incoming stream enters a conical separator where the majority of particles settle by the cyclone deaccelerating effect. Above the cyclone chamber are rows of cloth filters with a partial vacuum maintained on the inside. The air stream, rising up the center of the chamber, is drawn through the cloth to the asmosphere. The entrained product is retained on the outside of the cloth. The filter is cleaned by regulated pulses of air striking the neck which sets up a sinusoidal pattern violent enough to loosen adhering particles. The system has the high collection efficiency of the sock filter without great attendant mechanical difficulties.

FIGURE 16. COMBINATION FILTER



2. Ashtabula Design

The original Ashtabula design consisted of a bag filter identical to the type described above. During the 1956 expansion, an additional bag filter unit was installed with the new drying line. Since that time, cyclone separators have been improved and in the third drying line it is planned to switch to the use of cyclones.

H. Screening

1. Design Considerations

After the product is obtained in a free-flowing granular form, quality considerations dictate careful screening. This operation serves the dual purpose of removing foreign objects and oversize particles. The operation is accomplished by the use of a series of vibrating screens which automatically dump screened material into a storage bin. It is possible to design an arrangement which will give several classifications of the product.

2. Ashtabula Design

At the discharge of the bag filters there are two vibrating, triple-deck screens. All oversize particles must pass over all the screens before being discharged into a holding bin. Product obtained in this manner is designated off-specification and sold at a lower price. This method has been quite satisfactory and will be duplicated on the new drying line.

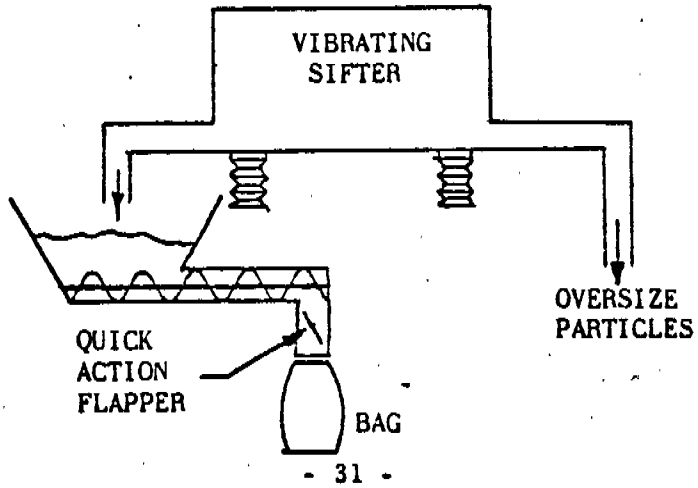
I. Dry Polymer Handling

1. Design Considerations

After screening classification, the dry polymer is ready for packaging and shipment. In the past, the operations of bagging, palletizing, and loading have been areas largely neglected by chemical engineers. But in high-volume products, packaging and handling contribute significantly to manufacturing costs. In the last twenty years, new methods for transporting PVC to the consumer have been steadily emerging, supplanting to a considerable extent the standard 50 lb. bag. The most economical shipping method is by railroad hopper cars which reduces filling, handling, storage, and container costs by two-thirds.[8]

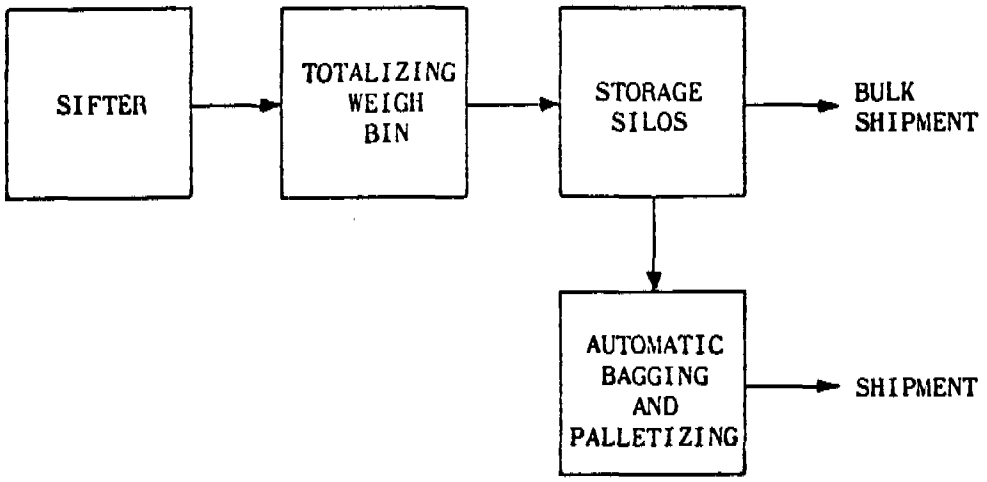
The use of these new methods has completely changed the process flow after the screening operation. Figure 17 illustrates the typical installation common a few years ago.

FIGURE 17. BAGGING STATION



Dry polymer is discharged from the sifter into a hopper fitted with a bagging machine. The new bulk handling methods utilizing pneumatic conveying have changed this procedure radically. PVC fluidized with small quantities of air can be moved rapidly to and from storage. Automated bagging stations operating at nominal speeds of 20 bags/min. perform the operations of bagging, closing, palletizing, and movement to the warehouse. Manpower is required only to remove the loaded pallets. Bulk storage silos store the various resins for shipment by railcar and truck. A typical installation utilizing bulk storage, bulk loading, and automatic bagging is shown in Figure 18.

FIGURE 18. BULK HANDLING



2. Ashtabula Design

The General Tire plant was originally set up for one bagging operation at the discharge of the bag filters. The 50% expansion of 1956 duplicated the original installation and allowed continuous bagging of two product lines simultaneously. Realizing the economics of the new bulk shipment methods and their convenience to the customer, General Tire has laid plans for the installation of storage silos and bulk loading equipment. An automated bagging machine used in conjunction with a bulk storage silo will allow all bagging to be done in short periods of time.

V. Ashtabula Operations

A. Standard Products

The Ashtabula, Ohio, plant has been producing PVC resins since 1954. Trade-named "Vygen," these PVC resins are a basic raw material in the production of many plastic products, both consumer and industrial.

There would be many advantages, to both the manufacturer and the consumer, of making a single, all-purpose vinyl resin that would be suitable for all applications. However, due to the number of methods of processing and end products, this is impossible. No single type of resin could possibly span the variety of specifications required by the industry. Hence, our research and development efforts are continually directed towards developing and manufacturing a family of specialized vinyl resins to meet the requirements of the processor.

While the Vygen resins were designed for various types of processes and uses, they all have the following essential characteristics:

Superior heat stability
Excellent light stability
Minimum of gelled particles
Consistency of performance
Dependable quality

B. Quality

We feel that quality and consistency of performance are the most important attributes of our Vygen resins. These are maintained by careful control of the raw materials, process conditions controlled by modern instrumentation, and by an extensive and exacting in-process and finished product quality control program. A brief description of our quality control program and facilities includes the following:

1. Pipeline Raw Materials (C_2H_2 and HCl) are metered and sampled as they enter the plant. Tests for purity are run, some on a continuous basis, so that at any time we can predict and set the gas flow ratio to our vinyl chloride producing reactors. In addition, a C_2H_2 purification system is in continuous operation to increase the efficiency and life of the monomer reactor catalyst beds.

2. Other Raw Materials are sampled as they enter the plant and must be released by the Quality Control group before being used in production.

3. Vinyl Chloride Monomer quality is carefully gauged by a system of process control instrumentation and frequent sampling at intermediate and final check-points. Chromatographic analysis of refined vinyl chloride is accomplished before the material is released for production use and contaminant levels in the parts-per-million range are readily detected.

4. The Water used in the suspension polymerization phase must be extremely pure. An efficient water treatment system consisting of carbon filters and deionizers is used and process water is continuously monitored for conductivity.

5. Polymer quality is initially controlled by monomer purity and the proper selection of other polymerization ingredients and conditions. Accurate weighing or metering of all recipe materials is accomplished

into a clean, purged polymerization kettle and precise batch temperature control is maintained to produce the desired polymer. A polymer sampling schedule is in effect to make sure the produced PVC has the correct properties (intrinsic viscosity, bulk density, fish eyes, particle size distribution, etc.).

6. The Polymer Dewatering and Drying Conditions are established and controlled to produce the desired low moisture content and to be sure the resin is not burned during the drying operation. Frequent (two-hour) samples of the drier polymer are taken and tested for dirt particles, per cent of moisture, and bulk density, and a test for fish eyes is run three times per day.

7. The Finished Product Testing Program is placed into effect after the resin is bagged into convenient lot sizes (usually 100,000 lbs.), but before it is shipped to the consumer. This extensive program is the final quality check and must be accomplished before shipment. Tests run on each lot include:

   Intrinsic Viscosity
   Bulk Density
   Plasticizer Take-Up
   Irreversible Plasticizer Take-Up (Blotter Resins)
   % Moisture
   Conductivity - (Electrical grade resins)
   pH (Electrical grade resins)
   Mill Stability
   Clarity
   Fish Eyes (Gelled particles)
   Foreign Particles (Dirt)
   Particle Size Distribution
   Press Stability

   In addition, special tests such as blended resin funnel flow, color drift and rheological (melt flow) studies are conducted as the situation warrants.

Vygen resins have become well known throughout the trade as being the most reproducible from lot to lot of all the PVC resins manufactured. This consistency of performance is accomplished by raw material purity and selection, an extensive and vigorous in-process testing scheme, a highly automated and accurate system of process control instrumentation and a comprehensive finished product resin testing program. This combination of factors is responsible for the reputation of quality that the Vygen "family of resins" has come to enjoy.

C. Productivity and Yields

Continued efforts to increase plant efficiency and productivity have been made at the Ashtabula plant in order to meet the increasing demand for Vygen resins and to maintain our competitive position in the industry. These efforts have been rewarded in excellent fashion, and have resulted in increasing our production from 36 million pounds

in 1959 to an estimated 50 million pounds this year with no major capital expenditure. During this same time period, the plant yield increased 3.5%.

In addition, a $2 million programmed expansion program was announced on May 14, 1964, which is expected to increase production of the plant by an estimated 50%. This expansion will include the installation of a new drying line, increased polymerization capacity, and improved bulk handling facilities.

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