A.I.Ch.E.
1964
SEMINAR

Polyvinyl Chloride Manufacture and Technology

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

GENC 000374

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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.

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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.

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HISTORY OF
POLYVINYL CHLORIDE

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HISTORY OF POLYVINYL CHLORIDE

by

A. J. BEBER

GENC 000380

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.

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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 observations 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.

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

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

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."

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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

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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)

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(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)

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THEORY OF
POLYMERIZATION

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THEORY OF POLYMERIZATION

by

R. MILKOVICH

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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:

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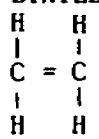
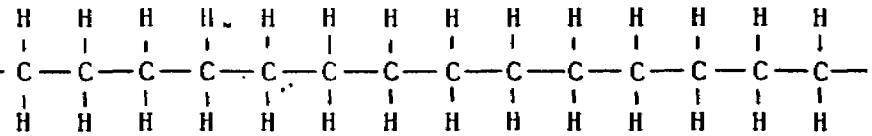
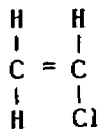
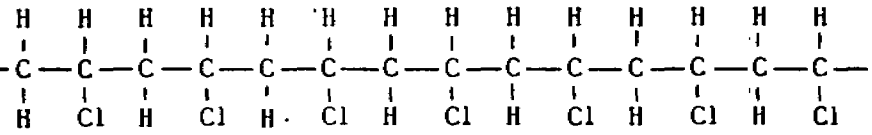
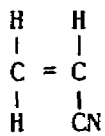
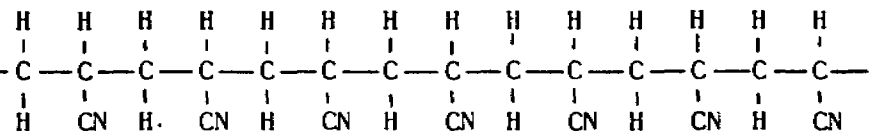
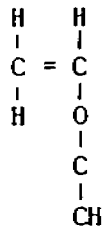
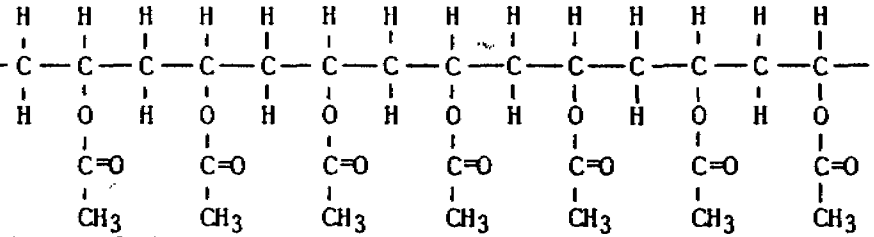
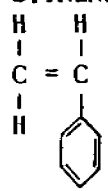
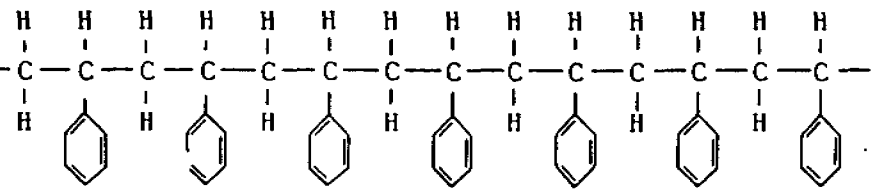
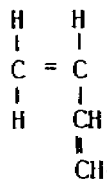
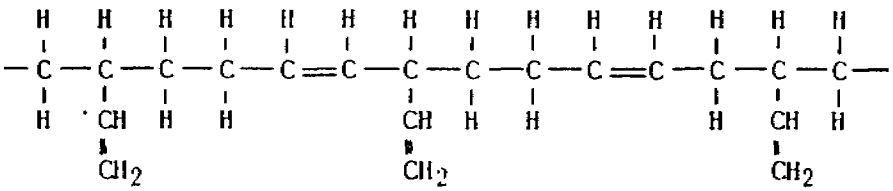
TABLE I

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.

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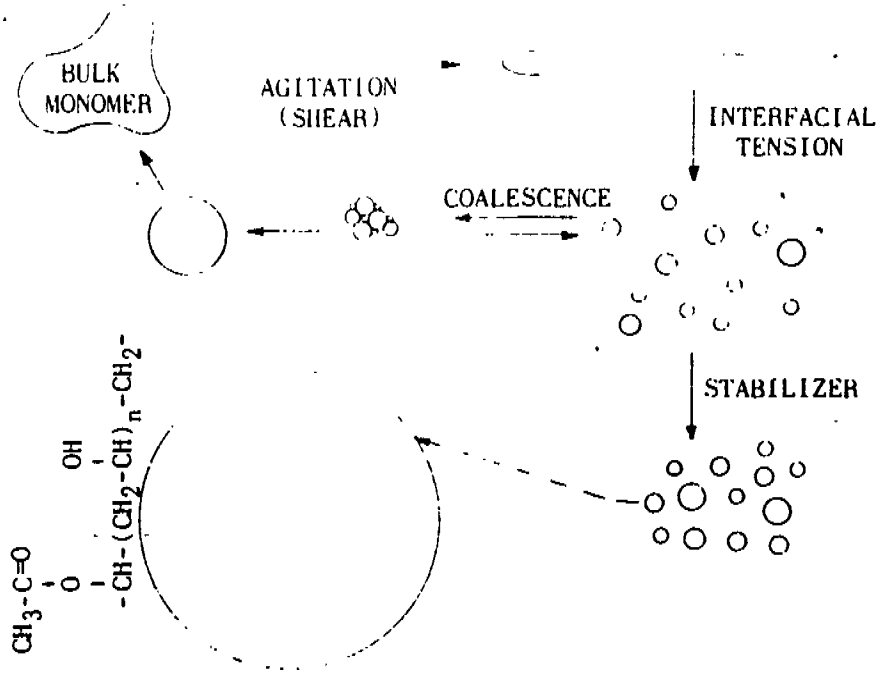
FIGURE 1. SCHEMATIC DIAGRAM OF STATES OF DISPERSION IN SUSPENSION POLYMERIZATION



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.

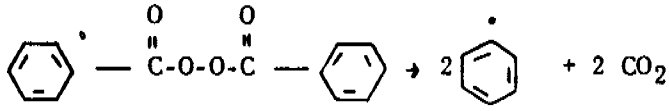
Free Radicals

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.

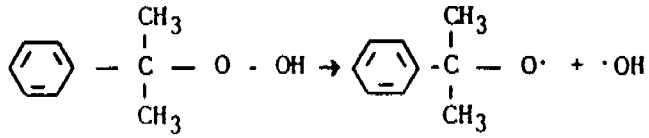
Free radicals can be produced in a number of ways including thermal or photochemical decomposition of such compounds as:

a. Organic Peroxides

Benzoyl Peroxide



b. Hydroperoxides

Cumene Hydroperoxide 

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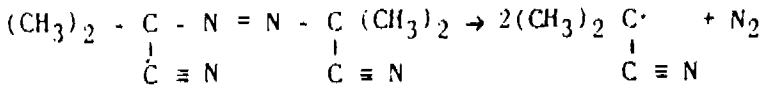
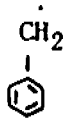
c. Azo Compounds

Azobisisobutyronitrile



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.

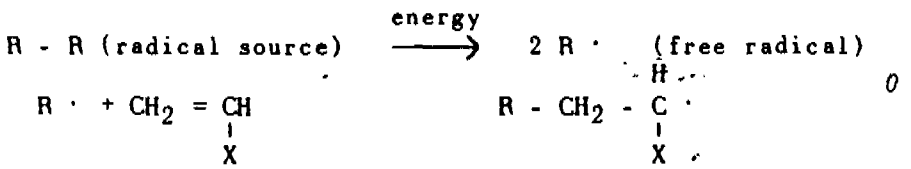
Polymerization of Vinyl Monomers by Free Radicals

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:



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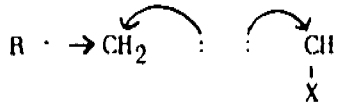
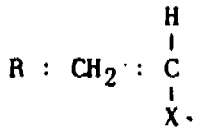
As the radical approaches the double bond of the vinyl monomer, one of the bonds splits into two radicals:

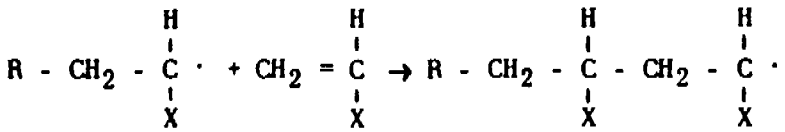


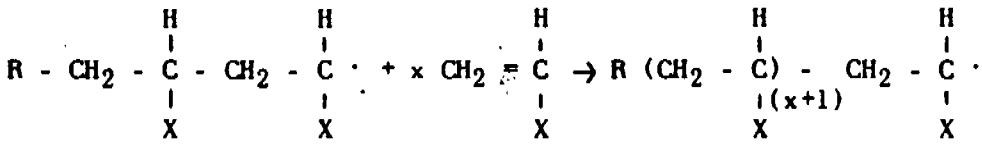
The attacking radical combines with one of the electrons forming a bond, and a new free radical results.



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

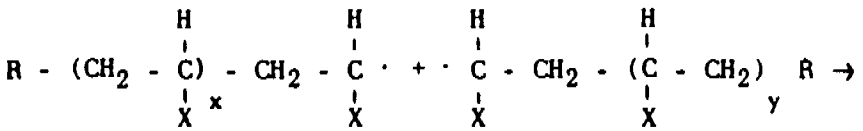
The propagation step is very similar in that the new radical formed in the initiation step attacks a second monomer unit and the radical is now propagated along a chain by successive monomer additions.

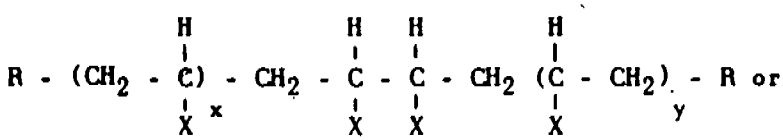




Termination of the propagation step can occur in a number of ways.

a. Two free radical chains may simply combine.





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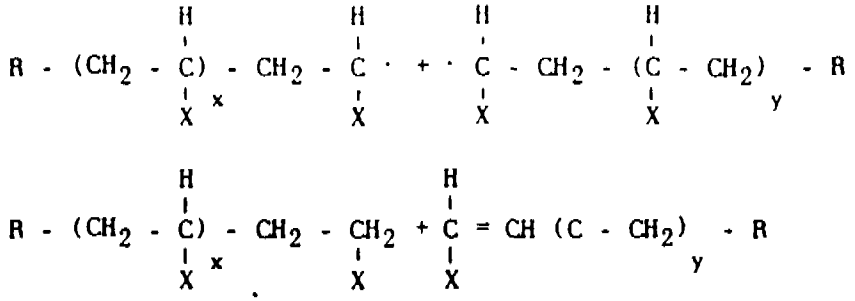
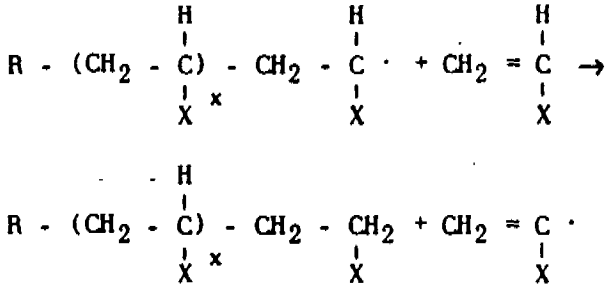
b. A disproportionation reaction may occur in which case one of the polymer chains will have an unsaturated end group:

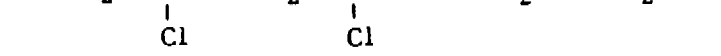


c. The polymer chain may transfer its radical to a monomer unit.



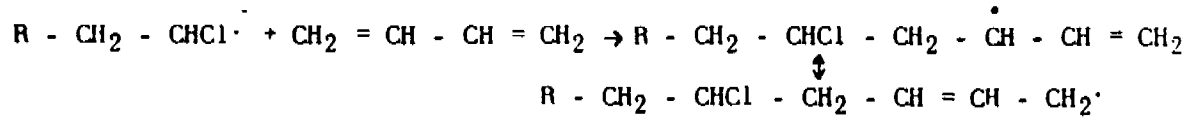
This is the generalized mechanism of free radical addition polymerization. Vinyl chloride is thought to deviate slightly in the termination steps.

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: $R - CH_2 - CHCl\cdot + CH_2 = CH\cdot \rightarrow R - CH_2CHCl - CH = CH_2$.

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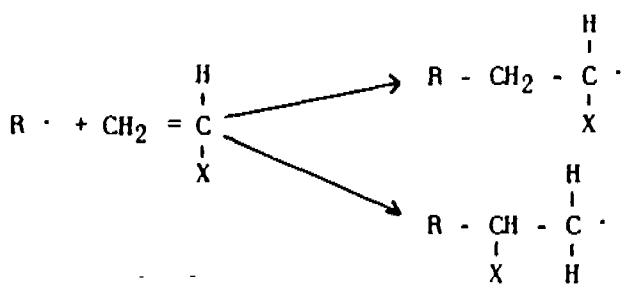
This structure is the same as is formed if mutual termination of the growing radical takes place by a disproportionation reaction, and would not be expected to take any further part in the polymerization reaction:

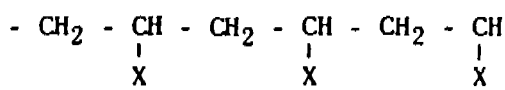
$$R - CH_2 - CHCl\cdot + R - CH_2 - CHCl\cdot \rightarrow R - CH_2 - CHCl_2 + R - CH = CH_2$$

The Arrangement of Monomer Units in the Chain

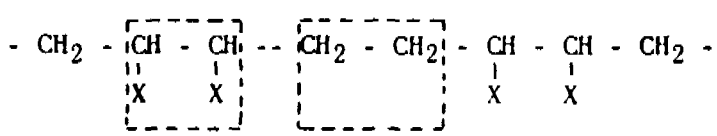
In the previous section on the mechanism of polymerization, the initiation step was shown to be an attack of a free radical on the double bond of the monomer. There are two ways in which this may occur.



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.

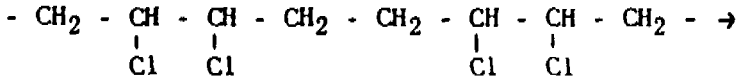


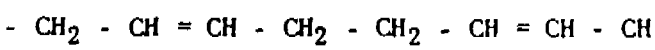
Alternate possibilities are head-to-head, tail-to-tail structures,



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].





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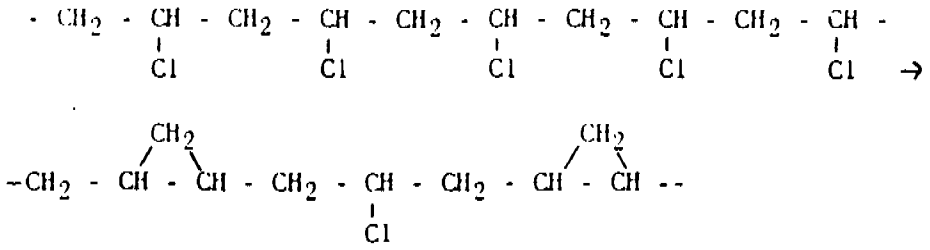

Since only 84-86 per cent of the chlorine could be removed, this fits the theoretical calculations for a head-to-tail polymer.

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.

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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.

$$v_i = v_t$$

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

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

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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:

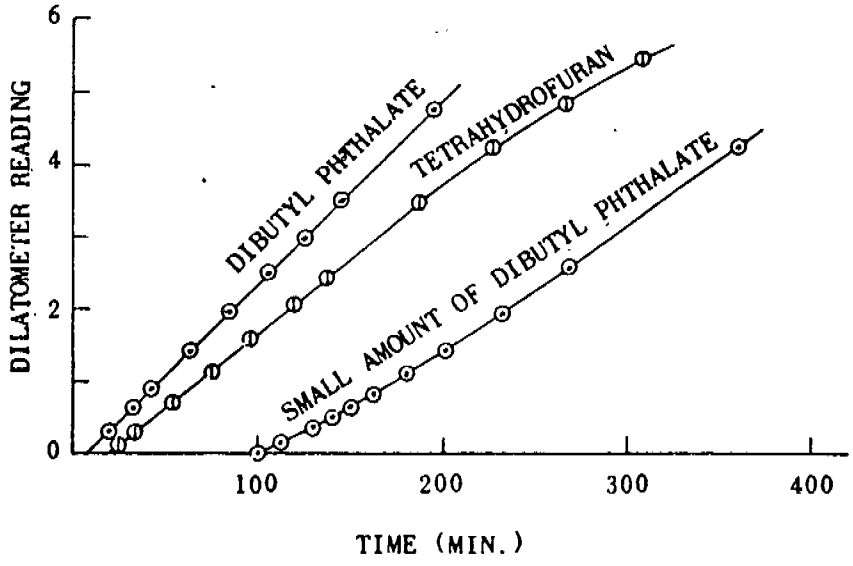
$$\text{Rate of Propagation} = v_p = -\frac{d[M]}{dt} = k_p [M] [M\cdot]$$

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

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



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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$^{\frac{3}{2}}$. 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

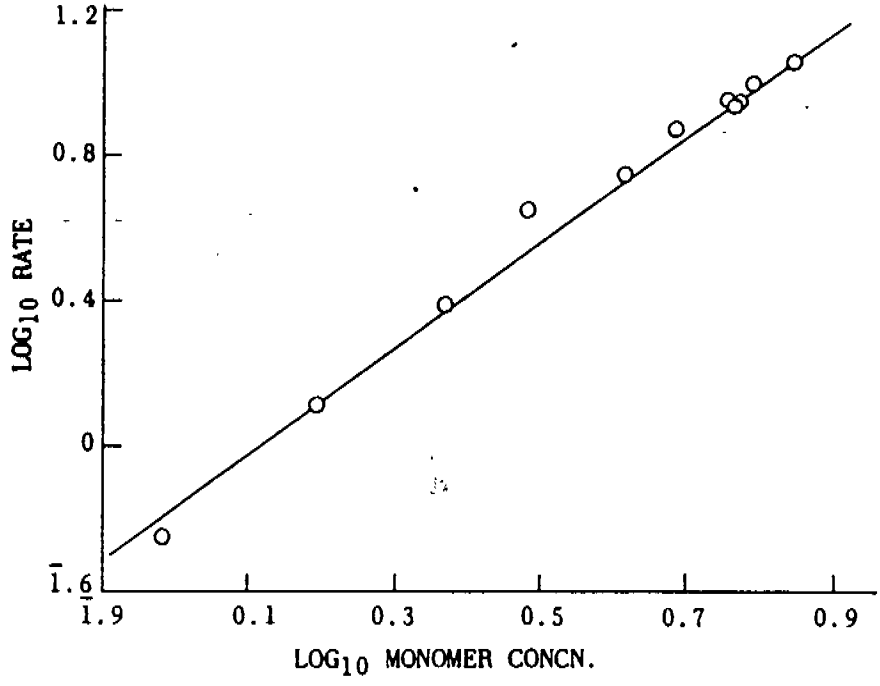

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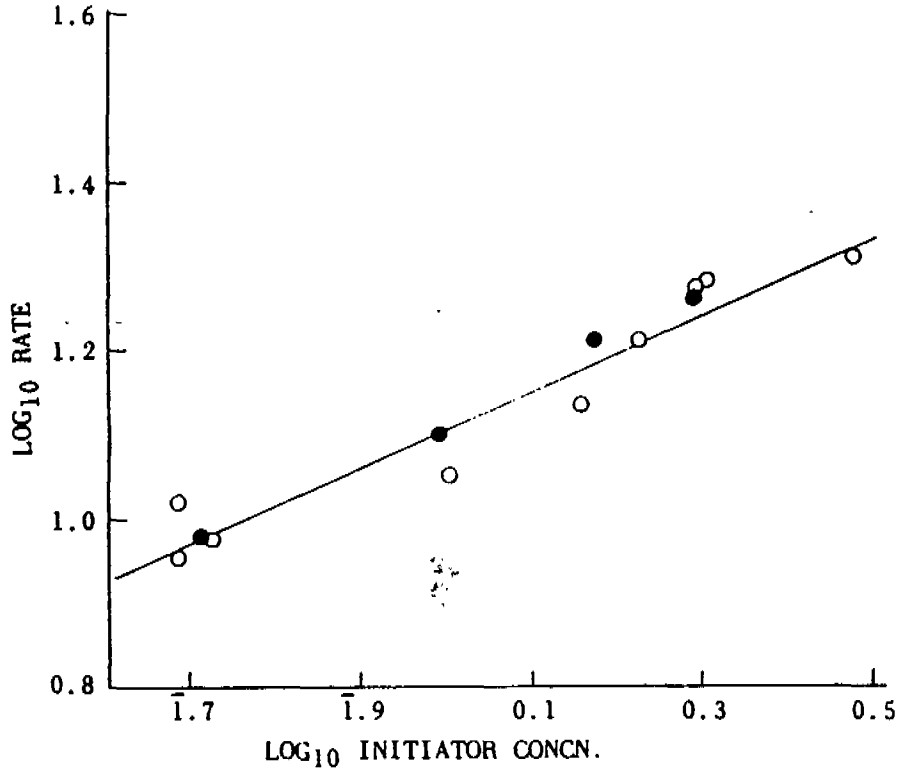
Figure 4 is a plot showing the relationship of rate of polymerization to varying initiator concentration at constant monomer concentration. The slope of the line for points obtained using tetrahydrofuran containing peroxides, as determined by the method of least squares, is 0.45. That for peroxide free 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.

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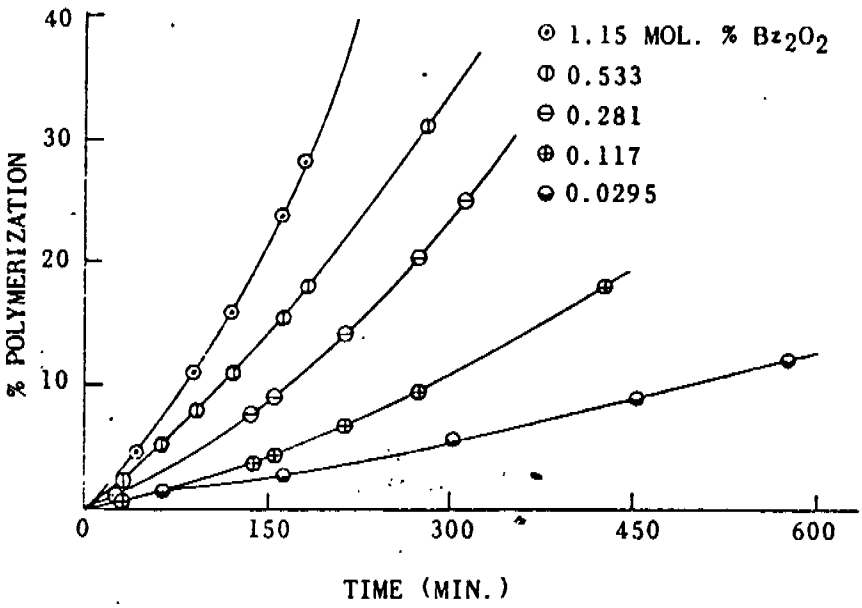
Heterogeneous Polymerization of Vinyl Chloride

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 %.

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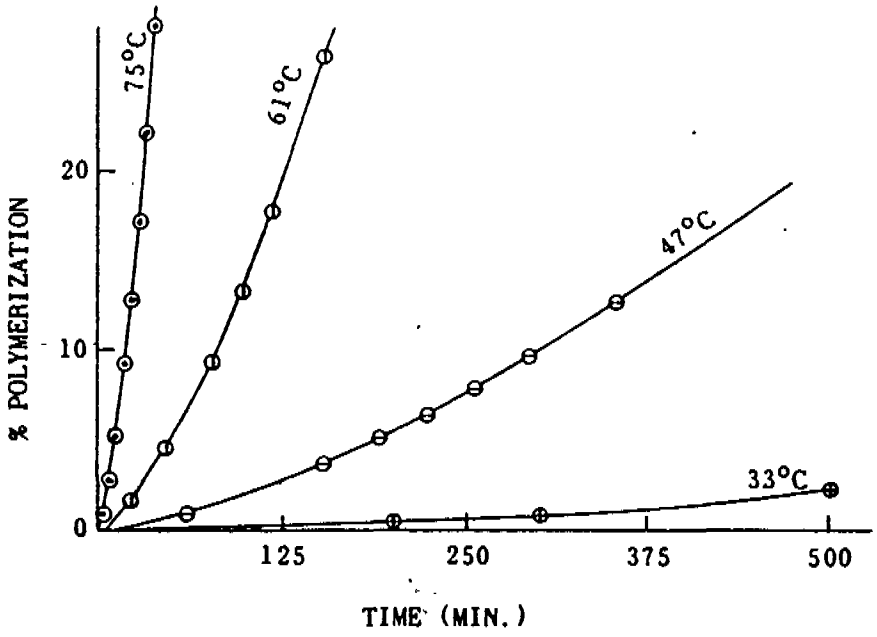
If now the concentration of benzoyl peroxide is kept constant, and the temperature is varied, it is found that the rate increases markedly with increase in temperature. This will be apparent from Figure 6 which shows the course of the polymerization of vinyl chloride catalyzed by 0.115 mol % benzoyl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

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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

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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

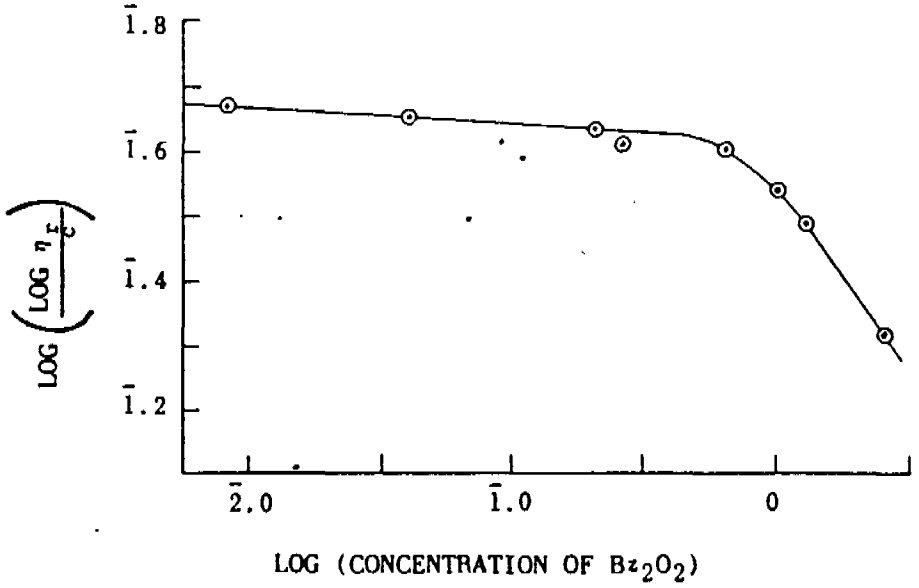
EFFECT OF TEMPERATURE ON THE DEGREE OF POLYMERIZATION

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



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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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REFERENCES

1. F. H. Winslow and W. Matreyek, Industrial and Engineering Chemistry, Page 1108, (May 1951)

2. G. M. Burnett and W. W. Wright, Proceedings of the Royal Society of London - Series A 221, Pages 28-36 (1954)

3. C. S. Marvel, J. H. Sample and M. F. Roy, J.A.C.S. 61 , Page 3241 (1939)

4. P. J. Flory, J.A.C.S. 61, Page 1518 (1939)

5. F. T. Wall, J.A.C.S. 62, Page 803 (1940) and J.A.C.S. 63, Page 821 (1941)

6. R. Simha, J.A.C.S. 63, Page 1479 (1941)

7. W. I. Bengough and R. G. W. Norrish, Proceedings of the Royal Society of London, Series A 200, Page 301 (1950)

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VINYL CHLORIDE SYNTHESIS

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by

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I. Introduction

The two principle methods for producing vinyl chloride commercially in the United States have been the hydrohalogenation of acetylene and the thermal dehydrohalogenation of ethylene dichloride. General Tire uses the hydrohalogenation of acetylene route in its Ashtabula plant put on stream in 1954. The plant is presently capable of producing 30 million pounds per year of vinyl chloride monomer.

In the succeeding section, both processes will be described in detail including the sources and purification of the raw materials, conditions, catalysts and kinetics of the synthesis reaction, and industrial equipment and technique used. Emphasis will, however, be on the General Tire process. Also included will be a description of the other methods employed and suggested for industrial vinyl chloride production and the economic factors involved.

II. Industrial Production of Vinyl Chloride

A. Hydrohalogenation of Acetylene

The production of vinyl chloride from the vapor phase reaction of acetylene and hydrogen chloride was for many years the most important industrial method in the United States, Germany, and the rest of the world, as it could be easily adapted to continuous operation.

In order to have a thorough understanding of the production of vinyl chloride from acetylene and hydrogen chloride, a study of the raw materials is necessary.

1. Acetylene

The two basic industrial sources of acetylene for vinyl chloride production are from calcium carbide and natural gas or other hydrocarbons.

a. Calcium Carbide Process for Acetylene

The calcium carbide process is the classical source for acetylene. Carbide acetylene is used by General Tire for its vinyl chloride synthesis operation. One of the main reasons for the Ashtabula plant's location is the close proximity of pipeline acetylene from a generating station. A flow diagram of an acetylene generator plant is given in Figure 1. Acetylene generation is based on the following equation:[1,2]

$$CaC_2 + 2H_2O \xrightarrow[93\text{-}95\%\ \text{yield}]{8\text{-}12\ \text{psig}} CH \equiv CH + Ca(OH)_2 \quad \text{------ (I)}$$

Calcium carbide is formed from the reaction of lime and coke in an electric arc furnace.

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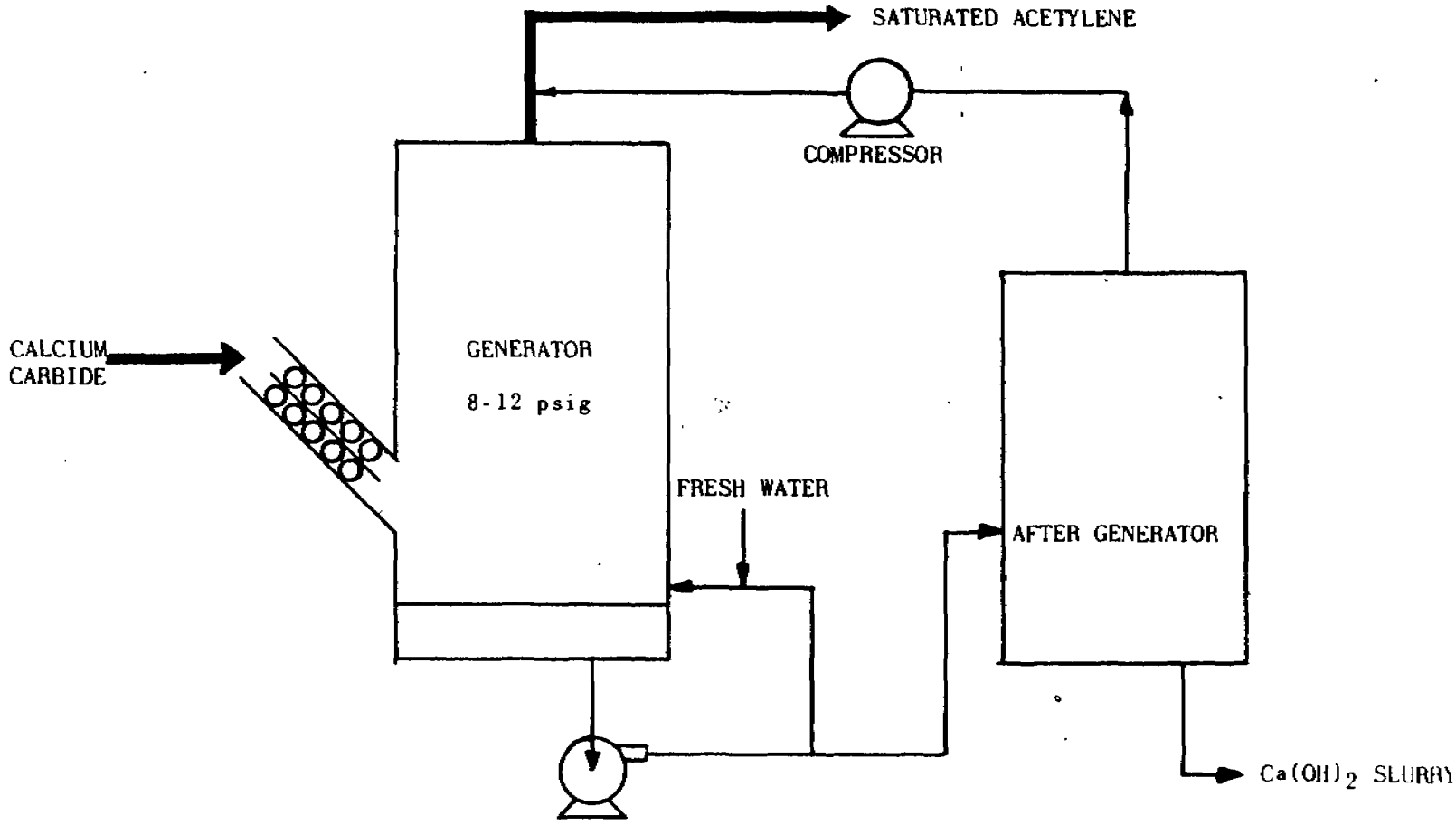

FIGURE 1. ACETYLENE FROM CALCIUM CARBIDE

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Acetylene is generated by the wet process which consists of adding calcium carbide to a relatively large quantity of water, releasing acetylene. The calcium hydrate residue is discharged from the generator in the form of a lime slurry. A variable speed screw feeder is used for the calcium carbide charging to maintain an 8-12 psig generator pressure. Temperature is controlled by the addition of fresh water. A low pressure, after-generator removes the last traces of acetylene from the lime slurry. The 99.8 per cent acetylene produced is saturated with water. The saturated acetylene gas is delivered to General Tire untreated.

b. Natural Gas and Hydrocarbon Process for Acetylene

Processes for converting hydrocarbon feeds to acetylene include electric arc, thermal cracking, and partial oxidation techniques. The classical examples of these processes are respectively the Schoch, Wulff and Sachsse processes.

The Schoch[3] and DuPont Plasma Arc Processes are electrical discharge processes that supply energy to the natural gas electrically.

The Wulff[4] process is a regenerative thermal decomposition process in which a checker brick furnace is heated to cracking temperature by combustion of a hydrocarbon gas with air. The air supply is discontinued and the gas is cracked thermally to yield acetylene, other hydrocarbons, carbon monoxide, and carbon dioxide.

The Sachsse[5] process or slight variations of the partial oxidation technique are commonly used industrially. Examples of these are the Badische Anilin & Soda-Fabrik A.G. (BASF), Montecatini, and Societe Belge del'Azote (SBA) processes. The BASF process will be used as an example.

The process is based on the following reactions:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat} \quad \text{---------- (II)}$$

$$2CH_4 \xrightarrow{2700^\circ F} C_2H_2 + 3H_2 \quad \text{---------- (III)}$$

A simplified flow diagram[6] of an industrial process is given in Figure 2.

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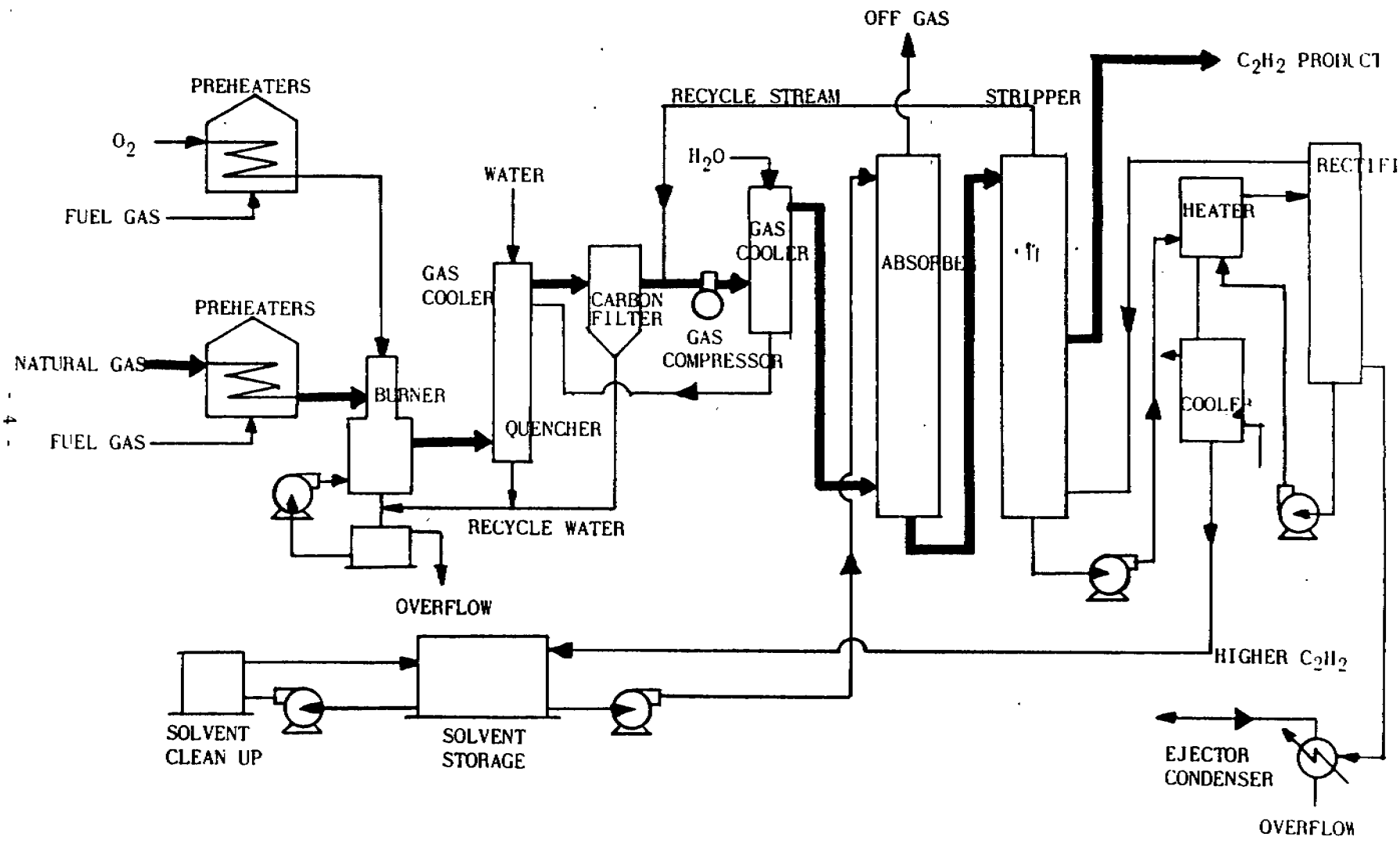

FIGURE 2. BASF PARTIAL OXIDATION ROUTE TO ACETYLENE (C_2H_2)

Natural gas (1 mole) and low purity O_2 (0.60 moles) are preheated to about 120°F and fed to a burner. Part of the methane (natural gas) is oxidized with oxygen as shown by equation II. The heat of combustion heats the gas to about 2,700°F to crack the excess methane to acetylene according to the endothermic reaction shown by equation III. The resulting cracked gas contains about 8.5 per cent C_2H_2 and is rapidly quenched to 100°F to prevent decomposition of the acetylene. The soot is filtered out and then the gases are compressed to about 160 psig and purified in an absorption-desorption operation. The off-gas from the absorber is used for heating value or synthesis gas. Acetylene is stripped from the solvent by conventional flashing and fractionation methods. Acetylene of 99 per cent purity is obtained. The overall yield of acetylene based on carbon content in the natural gas is approximately 30 per cent.

Acetylene at a considerable reduction in cost can be obtained from the hydrocarbon source. Therefore, the amount of acetylene produced by calcium carbide has decreased considerably in recent years.

c. Acetylene Impurities

Since the General Tire process uses acetylene from calcium carbide, the discussion of acetylene impurities and their effects will deal with calcium carbide derived acetylene.

Acetylene gas generated from commercial calcium carbide generally exceeds 99.5 per cent purity. The gaseous impurities present are shown in a typical analysis (dry basis) for acetylene received by General Tire:[7]

	Wt. %
C_2H_2	99.82
Total Sulfur	0.0011
H_2S	0.0001
Organic Sulfur	0.0010
Phosphorous	0.0025
Phosphine	0.0302
NH_3	0.0052
CO_2	0.0037

Other impurities in small amounts might include arsenic, phosphorous, and silicon compounds.

Since General Tire uses mercuric chloride impregnated on activated carbon as a catalyst, any impurity reacting with mercuric chloride can be significant in reducing catalyst life. Phosphine and arsine will react with mercuric chloride and reduce it to metallic mercury. Hydrogen sulfide reacts with mercuric chloride catalyst at vinyl chloride synthesis temperature to form mercuric sulfide.

Most of the sulfur present is divinyl sulfide[8] which is also a potent catalyst poison. The water present in the raw gas will react to form aldehydes as a by-product which in turn can reduce the mercuric chloride to metallic mercury.

d. Purification and Processing

General Tire's acetylene purification consists of cooling to remove water and the heat of compression followed by concentrated sulfuric acid scrubbing to remove phosphine, water, and organic sulfur, and then activated carbon filtering to remove divinyl sulfide, sulfur trioxide, and other trace contaminants. The following simplified flow diagram illustrates the General Tire acetylene purification and processing, Figure 3.

Acetylene is received from acetylene generators via pipeline. The acetylene goes through a hydraulic seal to prevent flashback and then is compressed from 6 psig to 14.5 psig in a Nash compressor which uses water as the sealing medium. The acetylene then is passed through an entrainment separator containing refrigerated water which removes a considerable amount of the water and lowers the temperature to 60°F. All incoming acetylene is metered. An accuracy of 0.7 per cent has been obtained metering the acetylene with a rotary positive displacement meter.

The acetylene is purified by passing it through two counter current, sulfuric acid scrubbers. The dilute scrubber is 24" diameter x 31' high column and is constructed of acid brick lined steel. The concentrated scrubber is a 20" diameter x 22' high column and is constructed of cast iron. Both scrubbers are packed with 2" raschig rings and the circulated acid temperature is controlled between 75-90°F by either cooling with water or heating with a water-steam mixture. Acid is changed whenever the minimum dilution of 75 per cent is reached in the dilute scrubber. Fresh acid used is 94-98 per cent sulfuric acid. The acetylene from the concentrated acid scrubber then goes through an activated carbon filter where traces of impurities, particularly the sulfides, are removed. The carbon filters are 36" diameter x 7' high and are constructed of steel. The acetylene from the carbon filter is essentially free of impurities and at a dew point of less than -40°F.

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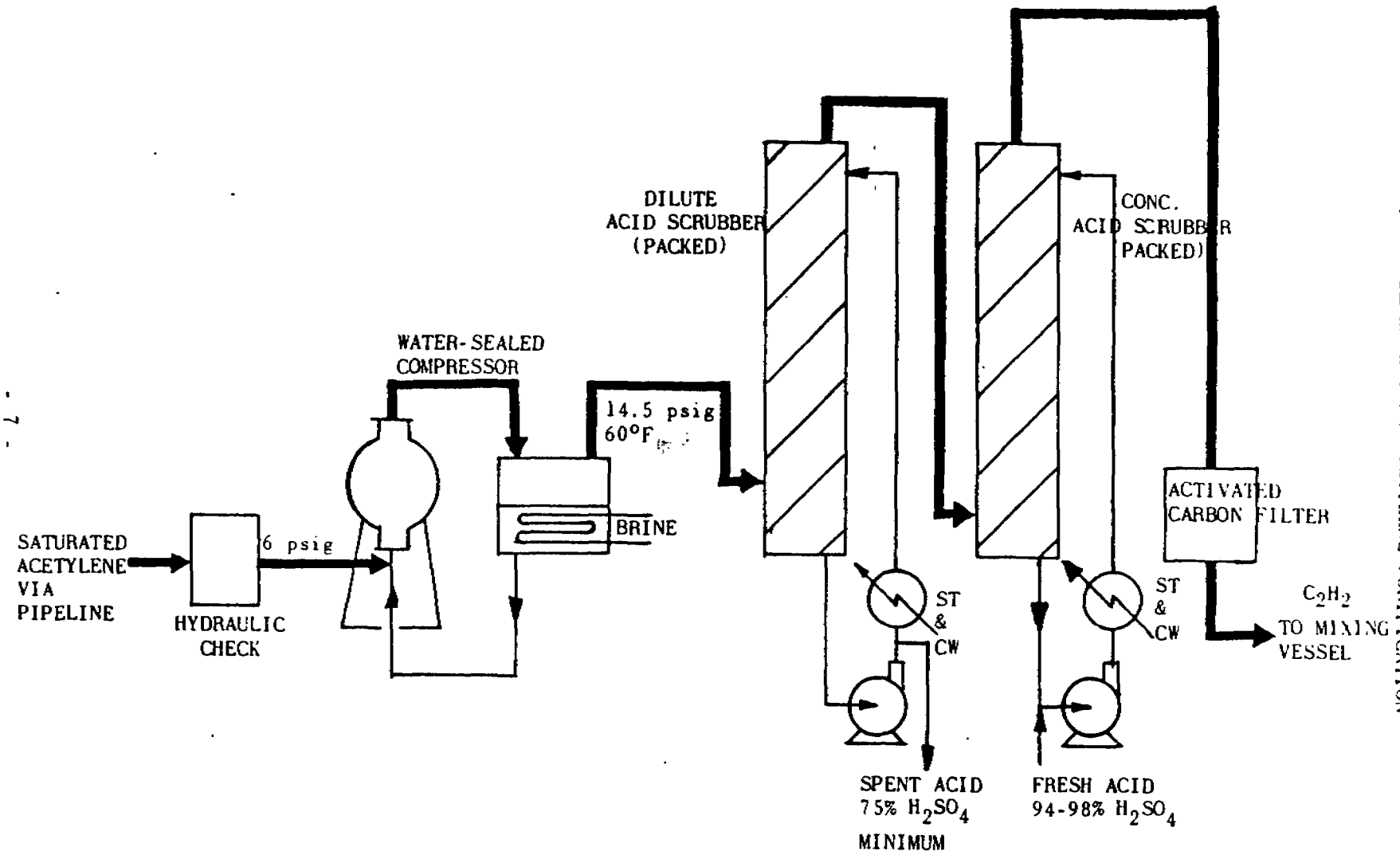

FIGURE 3. GENERAL TIRE ACETYLENE PURIFICATION

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2. Hydrogen Chloride

Hydrogen chloride can be obtained from several sources including: salt, in salt cake furnaces; by burning electrolytically-produced chlorine in excess hydrogen; and as a by-product of several industrial processes including the production of chlorinated solvents.

a. Trichloroethylene Process

General Tire receives hydrogen chloride via pipeline from local sources in Ashtabula. The hydrogen chloride is an off-gas from an organic operation, involving the production of trichloroethylene.[9] The process involves two steps given by the following equations:

$$\text{Chlorination:} \quad C_2H_2 + 2Cl_2 \xrightarrow[FeCl_3]{160\text{-}195^\circ F} CHCl_2 - CHCl_2 \text{ ------ (IV)}$$

$$\text{Dehydrohalogenation:} \quad CHCl_2 - CHCl_2 \xrightarrow{350\text{-}700^\circ F} CCl_2 = CHCl + HCl \text{ ------ (V)}$$

The process flow diagram in Figure 4 illustrates the key steps.

Acetylene is chlorinated to form tetrachloroethylene according to equation IV in a liquid phase reaction using ferric chloride catalyst at 160-195°F. After purification, the tetrachloroethylene is vaporized and dehydrohalogenated to trichloroethylene and by-product hydrogen chloride in a catalytic cracker at 350-700°F according to equation V. The relatively pure by-product HCl is separated from the trichloroethylene using a series of condensers and separators. The crude trichloroethylene is then fractionated to yield a pure trichloroethylene product. The market for the by-product hydrogen chloride is an important factor in determining the overall process economics.

b. Impurities and Effects

The impurities present in the hydrogen chloride are as given in the following average analysis:

	Vol. %
HCl	97.7
Inerts (as N_2)	0.75
Chlorinated Organics	1.50
Chlorine	Traces
Oxygen	<0.05 (by weight)

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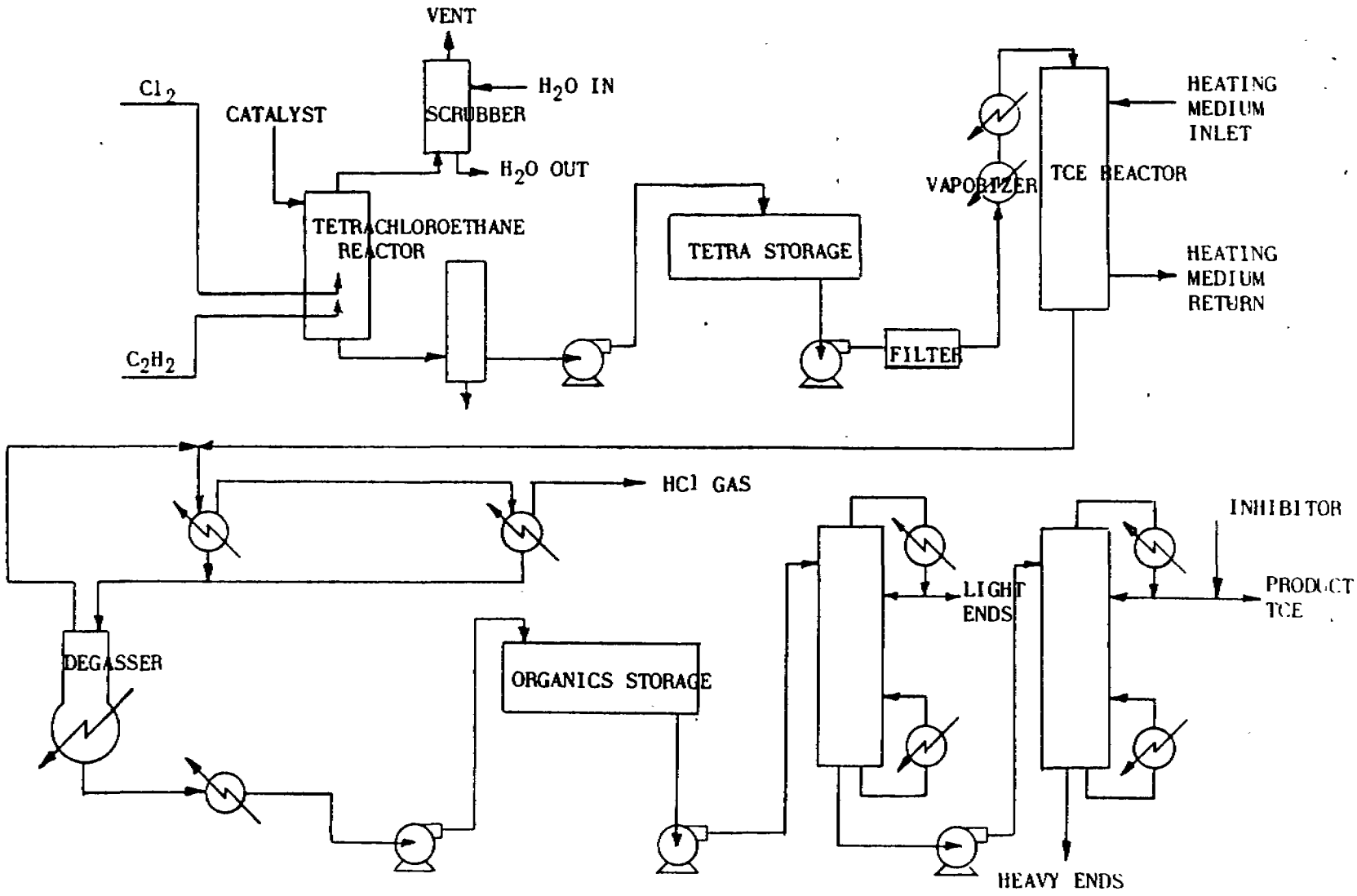

FIGURE 4. TRICHLOROETHYLENE (TCE) PROCESS[15]

The chlorinated organic impurities are present in the largest quantity and include mostly trichloroethylene with small amounts of tetrachloroethylene and dichloroethane. The chlorine and oxygen must be kept at a low level. The chlorine is a factor in by-product formation, particularly dichloroethane. The oxygen, when mixed with acetylene, is a safety hazard because of the explosive potential.

c. Purification and Processing

Refrigerated condensers are used to remove water and organic impurities before General Tire receives the hydrogen chloride. The hydrogen chloride is received by pipeline at a controlled pressure of 18" H_2O and compressed to 18 psig in a reciprocating compressor. The hydrogen chloride at 160°F is then passed through a separator tank to remove any entrained liquid before being used in the synthesis operation.

3. Vinyl Chloride Synthesis

General Tire's vinyl chloride synthesis is carried out by reacting one mole of HCl gas with one mole of acetylene at 8-10 psig and 200-280°F. The exact temperature is dependent upon the catalyst physical condition and age. The fixed bed catalyst is activated carbon impregnated with mercuric chloride.

a. Reaction

The general equation for the reaction of acetylene and hydrogen chloride in this process is:

$$C_2H_2 + HCl \xrightarrow[HgCl_2 \text{ on Act C}]{200\text{-}280^\circ F} CH_2 - CHCl \text{ (vinyl chloride)} \quad \text{---- (VI)}$$

The main by-products are trichloroethylene, dichloroethylene, and aldehydes.

b. Catalysts

Many patents and technical papers are in the literature concerning the successful use of various heavy metal salts as catalysts and many support mediums such as pumice, alumina, etc., for vinyl chloride synthesis. Mercuric chloride deposited on activated carbon support is commonly used throughout the industry.

c. Temperature

Temperature, besides being an important factor in reaction rate and conversion, also has considerable influence on the life of the catalyst. It was reported[10] that an optimum cooling medium temperature exists at various flow rates for getting the longest life from the catalyst.

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The tendency lately has been to operate at lower temperatures (200-260°F). Considerable increases in the pounds of vinyl chloride produced per pound of catalyst expended have been realized as a result of the lower operating temperatures.

d. Kinetics

Some of the latest work done on catalytic rate studies using mercuric chloride-activated carbon catalyst was done by Wesselhoft, Woods, and Smith.[11] Representing the experimental data, a rate equation was developed from the following postulates: (1) acetylene is adsorbed on the catalyst on one site; (2) hydrogen chloride and vinyl chloride are adsorbed on a different type of site; (3) the formation of vinyl chloride occurs by reaction of adsorbed acetylene and adsorbed HCl; (4) the rates of adsorption and desorption are best compared with the formation rate of vinyl chloride.

The rate equation according to Wesselhoft, et. al., is:

$$\gamma = \frac{C\, P_H\, P_A}{(1 + K_H P_H + K_{VC} P_{VC})\,(1 + K_A P_A)} \quad \text{---------- (VII)}$$

where: γ = reaction rate, lb. moles/(hr.)/(lb. of catalyst)
C = overall rate constant, lb. moles vinyl chloride/(lb. of catalyst) (hr.)
P = Partial pressure, atm
P_H = Partial pressure, atm HCl
P_A = Partial pressure, atm acetylene
P_{VC} = Partial pressure, atm vinyl chloride
K = Rate of forward and reverse reaction rate constants for adsorption reactions

The reaction rate can be related to conversion weight of catalyst and flow rate by the following equation.[12]

$$\gamma = \frac{\Delta x}{W/F} \quad \text{---------- (VIII)}$$

where: Δx = Conversion
W = Weight of catalyst, lbs.
F = Flow rate, ft.^{3}/hr.

Equation VIII can then be used to illustrate how the reactor design is affected by the kinetics. After the reaction rate has been calculated based on the desired operating conditions and the flow rate has been established, the pounds of catalyst necessary to obtain desired conversions can be calculated. The pounds of catalyst can then be changed to the length (feet) of reactor necessary for the conversion by dividing it by the pounds of catalyst per foot of reactor length. The graph in Figure 5 is a plot of conversion versus reactor length for two different temperatures and flow rates and illustrates their effect on reactor length. A reactor cross section of 13 sq. ft. is used in this calculation.

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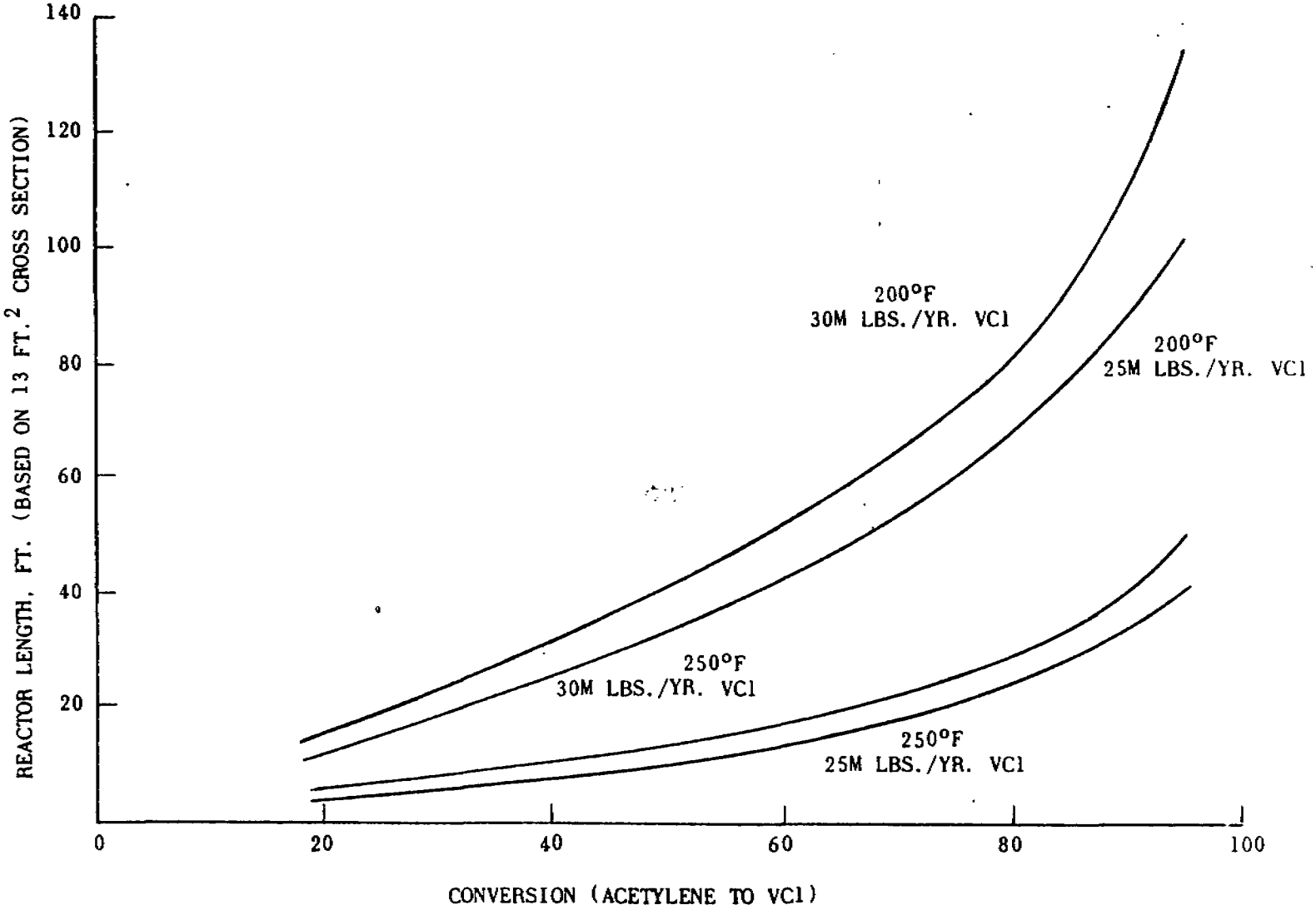

FIGURE 5. % CONVERSION VERSUS REACTOR LENGTH

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e. Heat of Reaction

The reaction of hydrogen chloride and acetylene to form vinyl chloride is strongly exothermic. Based on the latest data on the heat of formation for vinyl chloride from acetylene and HCl (8,072 cal/mole @ 25°C by Locher[13]), the estimated heat of reaction is 43,300 BTU/lb. mole monomer vinyl chloride produced at 200°F and 43,800 BTU/lb. mole monomer vinyl chloride produced at 250°F.

f. The General Tire & Rubber Company Process

Figure 6 is a simple block diagram which will aid in illustrating the overall process.

In the Reactor Section (I) the raw materials C_2H_2 and HCl are converted into vinyl chloride; in the Stripping Section (II) the unreacted HCl is removed; in the Recovery Section (III) the unreacted C_2H_2 and inerts are removed; and in the Refining Section (IV) the heavy ends and aldehydes are removed and the purified vinyl chloride is transferred to storage. The recovered acetylene from Recovery Section (III) is recycled to the Reactor Section (I). The heavy ends from Refining Section (IV) are recycled to Recovery Section (III) before storage. Small amounts of vinyl chloride are recovered from the heavy ends in the Recovery Section (III) and are recycled to Stripping Section (II). A flow diagram of General Tire's monomer synthesis and purification operation is shown in Figures 7A through 7D.

Reaction Section (I), Figure 7A

Anhydrous hydrogen chloride gas and acetylene purified and processed as described in the previous section on raw materials are metered to the process by a ratio controller.

The reactants are passed through a baffled mixing vessel and then into the top of five 16 ft. multitube reactors. The reactors can be arranged by using multiple headers to allow either combined parallel and/or series flow to obtain the best conversion and control. Normally, a 2-2-1 arrangement is used.

The reactors contain vertical steel tubes 2 in. in diameter. Activated carbon pellets impregnated with mercuric chloride catalyst are placed on the tube side and oil is circulated on the shell side, counter current to the flow of the gaseous reactants.

The oil was originally heated or cooled by shell and tube heat exchangers to maintain temperature control. However, a more efficient cooling method has been installed wherein an air-cooled fin-tube heat exchanger is used. Since the reaction is highly exothermic, the oil is usually cooled once the reaction has started. Each furnace has sufficient cooling capacity to

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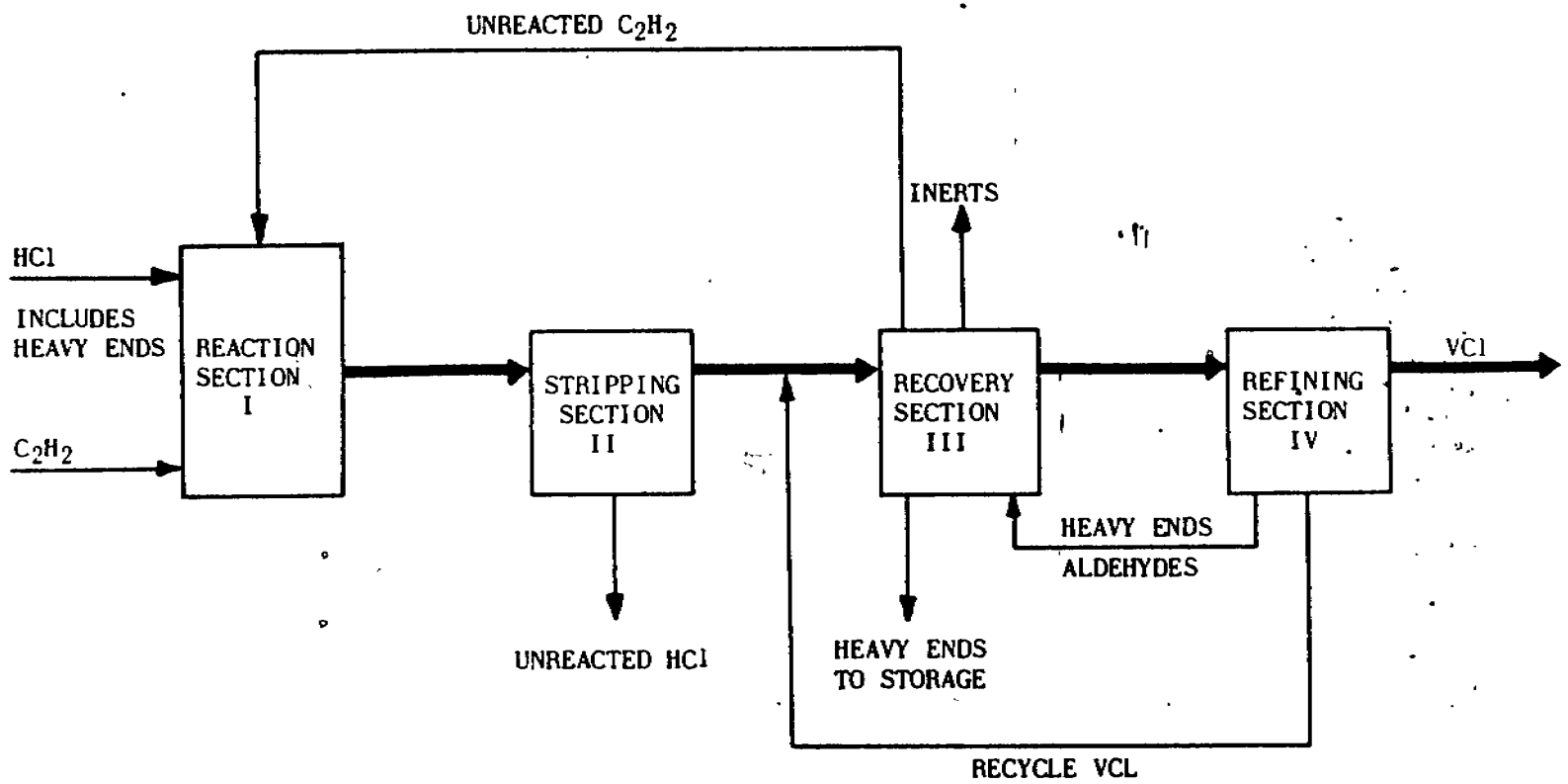
UNREACTED C_2H_2
INERTS
HCl
INCLUDES HEAVY ENDS
C_2H_2
REACTION SECTION I
STRIPPING SECTION II
RECOVERY SECTION III
REFINING SECTION IV
VCl
HEAVY ENDS
ALDEHYDES
UNREACTED HCl
HEAVY ENDS TO STORAGE
RECYCLE VCL

FIGURE 6

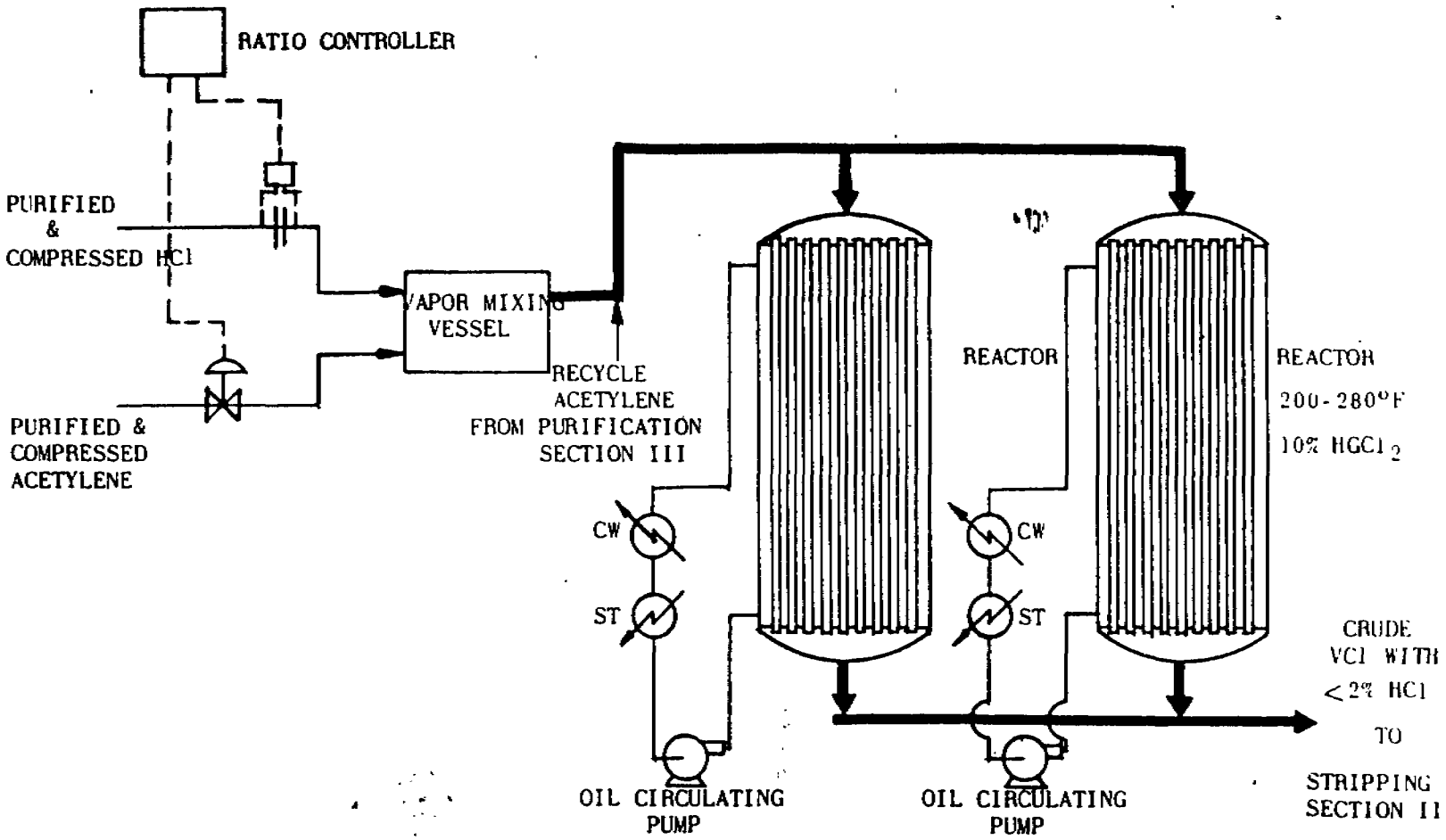

FIGURE 7A. GENERAL FLOW SYNTHESIS OPERATION - REACTION SECTION II

remove all of the heat evolved at a maximum of 50 per cent conversion based on design throughput. The temperature of the reaction is controlled between 200-260°F, increasing with the age of the catalyst. The average reactor system pressure is about 9 psig. Conversion based on HCl is 98-99 per cent. A continuous infra-red on-stream analyzer monitors the per cent HCl in the reactor outlet stream. The reactor outlet gases contain the following: Vinyl chloride, unreacted HCl, unreacted C_2H_2, inert gases, aldehydes, and chlorinated organics.

The chlorinated organics in the crude vinyl chloride include both the quantity received in the HCl feed stock and the by-product produced. About 95 per cent of the chlorinated organics are trichloroethylene.

Stripping Section (II) Figure 7B

In Stripping Section (II) the unreacted HCl is removed. Outlet gases from the reactors are fed to the bottom of a water scrubber where cooled water is circulated counter current to the gases. The column is packed with 2" Raschig rings and is brick lined steel construction. Fresh water is added to maintain a discharge concentration from the scrubber of 3-10 per cent HCl. The gas flow is then to the bottom of a second packed column through which dilute caustic (7-9 per cent NaOH) is circulated counter currently. The caustic scrubber is packed with 2" Raschig rings and is of mild steel construction. The gases leaving the caustic scrubber are essentially free of HCl. The gases pass through a suction knock-out tank and are then compressed to about 90 psig in a reciprocating compressor before further purification.

Recovery Section (III), Figure 7C

In the Recovery Section (III) the light ends, mainly unreacted C_2H_2 and inert gas are removed. The flow from the compressor goes to the stripping column overhead condenser and then to the stripping column decanter. The stripping column is 27' high and contains 20 bubble cap trays. Auxiliary equipment includes a decanter for reflux storage and water separation. Mild steel construction is used throughout. The column is operated at a pressure of 90 psig so the overhead vapor can be condensed with available cooling water.

Hot water is used in order to lower surface temperatures on the reboiler and thus minimize polymerization. The column operating conditions are maintained so that the crude vinyl chloride bottoms at 115°F are free of acetylene. The bottoms are chilled and pumped to crude vinyl chloride storage. The overheads containing all the unreacted acetylene and inerts are then processed in the acetylene recovery system.

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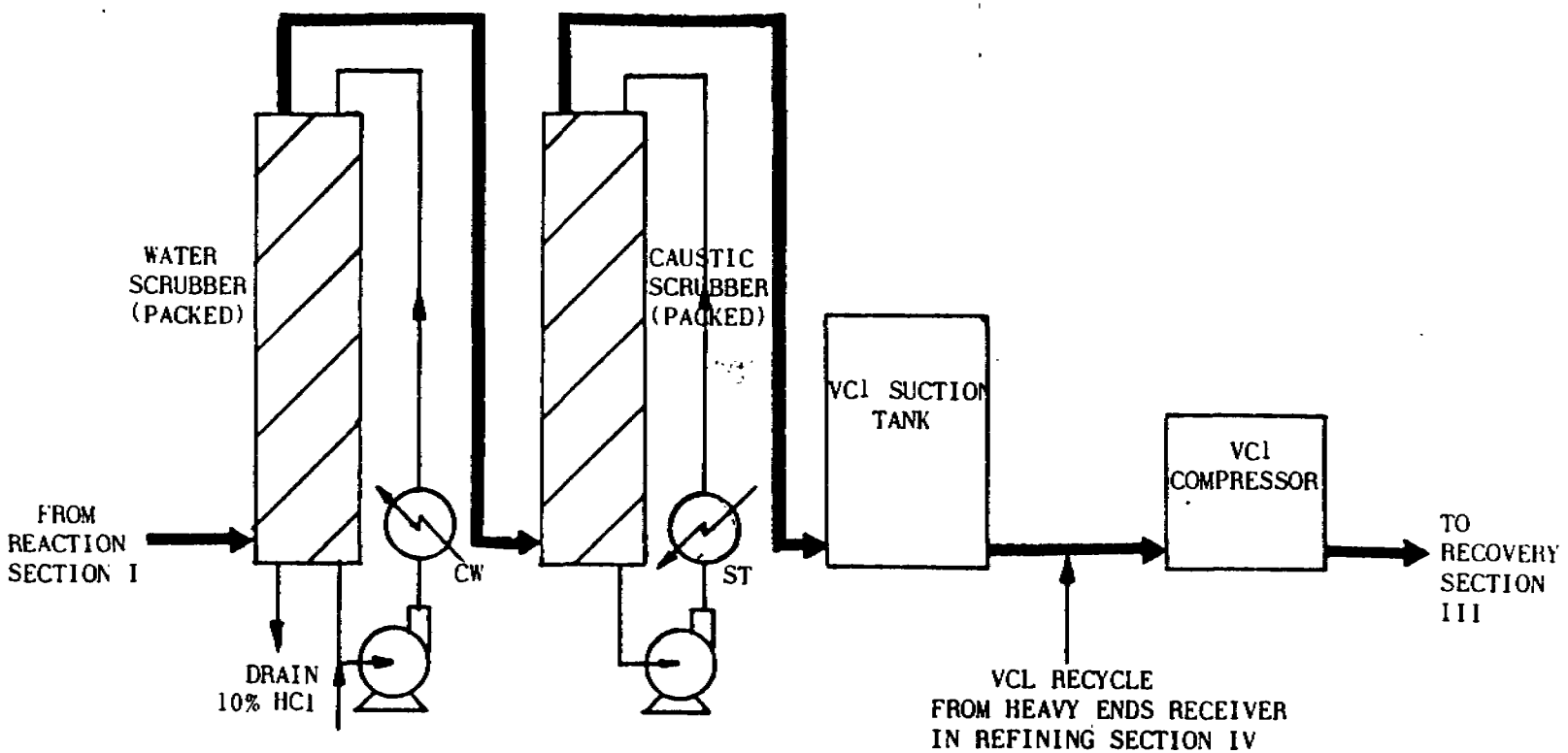

FIGURE 7B. STRIPPING SECTION (II)

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The acetylene recovery system is basically an absorption-desorption system using trichloroethylene as the recovery solvent. The absorber is a column packed with 1" saddles operating under 45 psig pressure at a temperature of about 80°F. The inerts and nonabsorbables are vented from the top of the column to the atmosphere. The vent gas is 90 per cent inerts. The trichloroethylene containing the absorbed gases is then pumped to the top of the 1" saddle packed desorber column where it is heated to about 200°F under a pressure of 18 psi. The desorbed overhead gases are first passed through a brine-cooled partial condenser to remove entrained solvent and then recycled to the inlet of the monomer reactors. The composition of this gas is 41 per cent vinyl chloride and 21 per cent C_2H_2 which represents nearly all the unreacted acetylene. The trichloroethylene from the desorber bottom is cooled and recycled to the absorber. The excess stripped solvent from the desorber is passed to a heavy ends storage tank. Solvent feed to the absorption-desorption system is from the refining column, heavy ends receiver in Refining Section (IV).

Refining Section (IV), Figure 7D

In Refining Section (IV) the chlorinated organics and aldehydes are removed from the vinyl chloride. The crude vinyl chloride is pumped from the storage tank to the 20th tray of a 30 tray, 48' high, bubble cap fractionating column. The heavy ends boil at 185-240°F compared to 8°F for vinyl chloride, at atmospheric conditions. The bubble cap column is operated under 60 psig pressure and the conditions are regulated so that the overhead pure vinyl chloride at about 95°F is essentially free of aldehydes and heavy ends. The vinyl chloride overhead is condensed and then chilled with a brine cooler and sent to horizontal stainless steel storage tanks. The top trays as well as the receiver and reflux piping are stainless steel to prevent iron contamination. The bottoms flow to a heavy ends receiver where the liquid is heated with steam to vaporize the vinyl chloride. The vinyl chloride is recycled to the suction of the vinyl chloride compressor in the Stripping Section (II). The heavy ends remaining are recycled to the acetylene recovery absorption-desorption system before being sent to storage.

General Tire specifications for vinyl chloride monomer are:

Specifications:

C_2H_2 ---------- 2 ppm max.

Moisture % by weight ---------- .01 max.

% Heavy Ends ---------- .02 max.

Aldehydes ---------- 5.0 ppm max.

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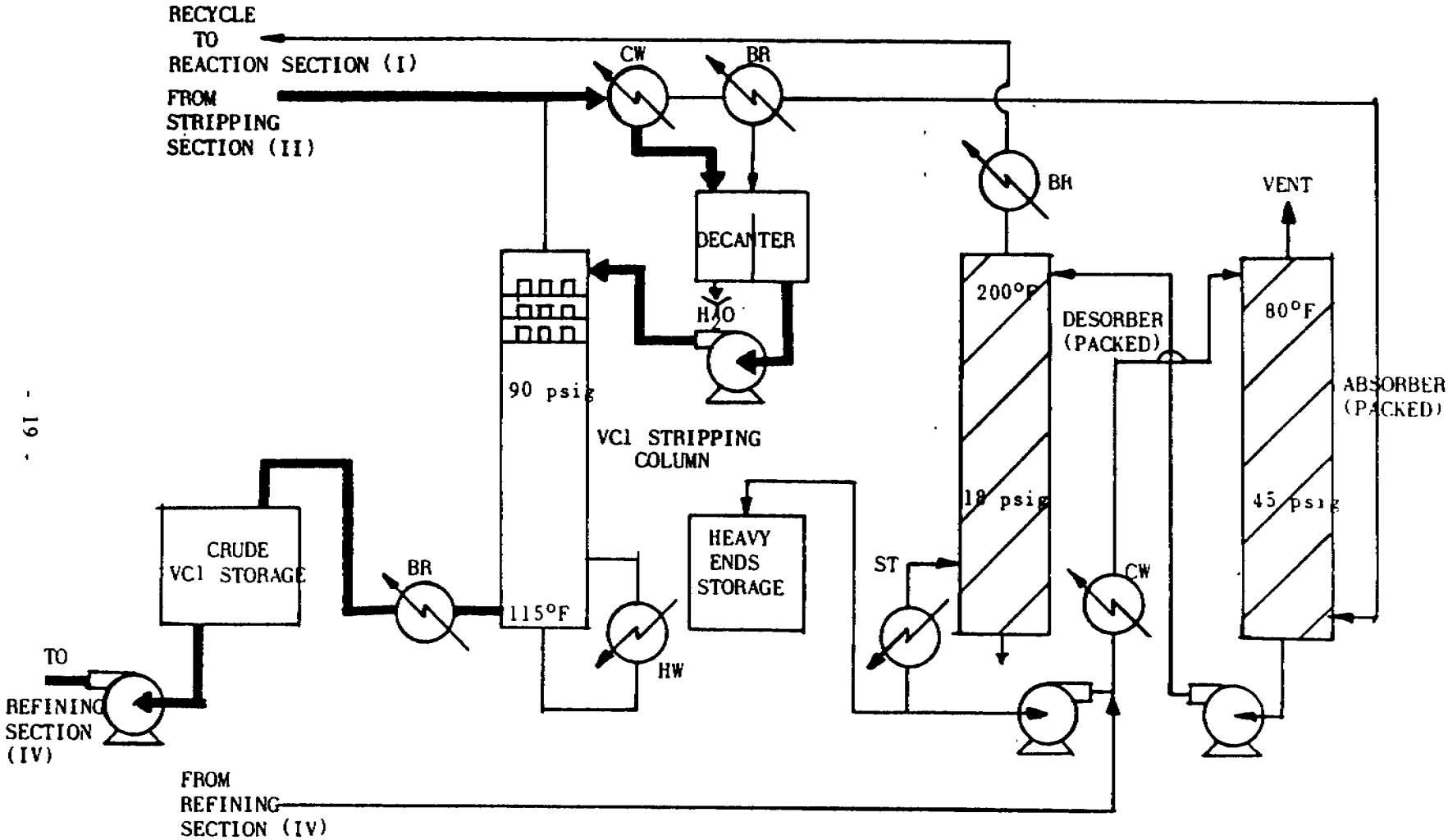

FIGURE 7C. RECOVERY SECTION (III)

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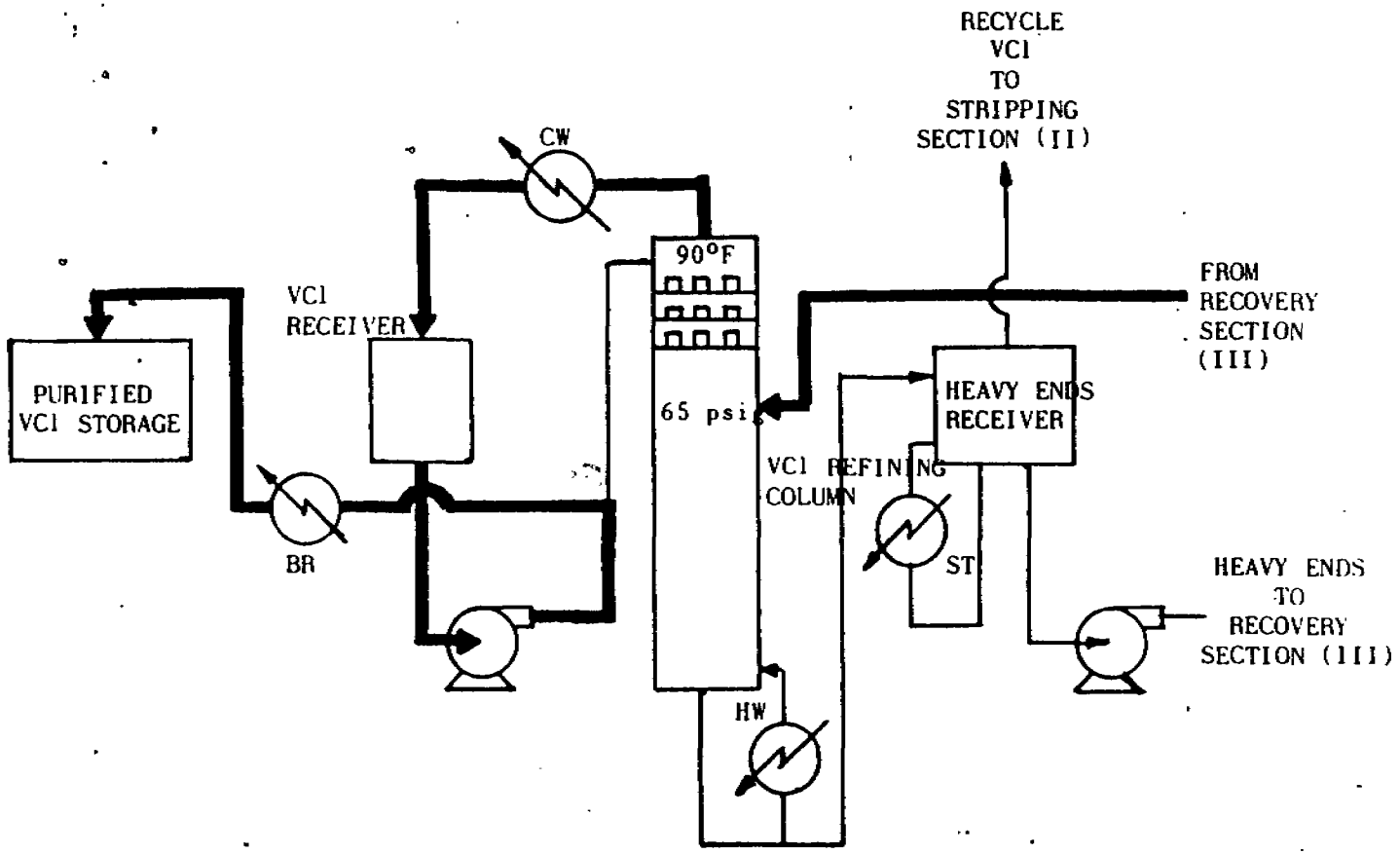

FIGURE 7D. REFINING SECTION (IV)

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Fe ----------<0.1 ppm

Acidity ---------- 5.0 ppm max.

Nonvolatile residue
(25°C) % by weight --------- .01 max.

Color ---------- Colorless

Polymerization Test ---------- Passes

Dorrell Weathering Test
Max. Temp. Differential
at .5 cc, °C ---------- 0.5

A shift sampling and test program maintaining set process specifications assures production of quality vinyl chloride monomer.

Material Balance

The following is an average material balance on vinyl chloride synthesis operation:

Overall yield based on total raw gases averages about 98 per cent.

Raw materials required for one ton of vinyl chloride:

HCl -- (1,183 lbs. HCl
(62 lbs. Heavy Ends

C_2H_2 -- 877 lbs.

Products formed:

Vinyl Chloride - 2,000 lbs.

Heavy Ends - 85 lbs. -- (62 lbs. HCl feed
(23 lbs. by-products

B. Dehydrohalogenation of Ethylene Dichloride

The dehydrohalogenation synthesis route for vinyl chloride became commercial based on the plentiful supply and low price of the basic raw material, ethylene. In order to have a thorough understanding of the vinyl chloride synthesis by this route, a study of the intermediate synthesis of ethylene dichloride is necessary. The majority of ethylene dichloride is produced commercially by the chlorination of ethylene. Recently, however, ethylene oxychlorination processes have been successfully adapted to commercial practice. The ethylene oxychorination process will be covered under the new processes section.

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1. Ethylene

The two basic raw materials used for ethylene dichloride production by direct chlorination are ethylene and chlorine. Ethylene normally is produced from the pyrolytic cracking of petroleum fractions and the economics favor large facilities. The Gulf Coast of Louisiana and Texas are favored locations for its production.

a. Petroleum Fraction Cracking Process

Almost any petroleum fraction can be cracked and fractionated to yield ethylene. The processing schemes and economics vary with each installation depending upon the feedstock, products, and by-product specifications and costs. A simplified flow diagram, Figure 8, illustrates a typical process[14] using naphtha feed.

Naphtha and steam pass through the coils in the pyrolysis furnace where cracking takes place at about 1,500°F.[15] The cracked products are quenched to 100°F prior to the purification separation. In the purification process, the product stream is passed through a fuel oil scrubber, then through a series of fractionation systems. A final low temperature fractionator separates purified ethylene from ethane.

b. Impurities

The ethylene gas usually contains diluents such as methane, ethane, and hydrogen. Some cracked petroleum fractions may contain only about 40 per cent ethylene and must be enriched by purification. Generally, ethylene of purity of 90 per cent or better is satisfactory for use in the ethylene dichloride process. The ethylene should not contain any hydrocarbon impurities heavier than propane.

c. Purification

Reported[16] ethylene enrichment and purification techniques include: A low temperature, high pressure fractionation, for example at -30°C and 200 psig, an absorption-desorption and hypersorption process using adsorption on a moving bed of activated carbon.

2. Chlorine

Electrolysis of Salt:

Nearly all chlorine is produced by the electrolysis of salt. Commercial electrolytic chlorine of 99.9 per cent purity is used by all plants as received.

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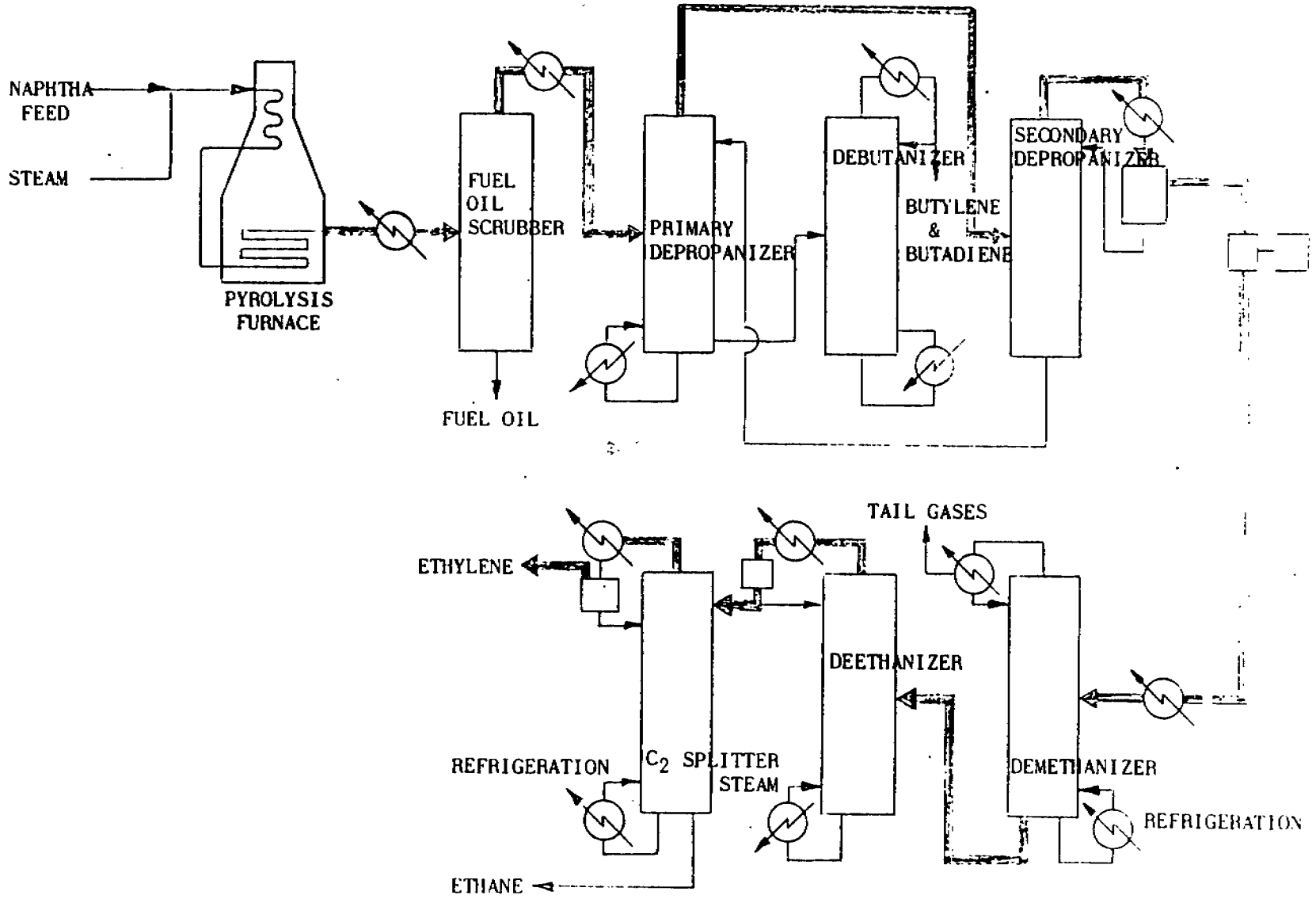

FIGURE 8. ETHYLENE FROM NAPHTHA CRACKING

3. Ethylene Dichloride Direct Chlorination Synthesis

a. Reaction

Ethylene dichloride is produced commercially by direct chlorination by both the liquid and the vapor phase chemical combination of ethylene and chlorine in the presence of a catalyst and is represented by the equation:[17]

$$CH_2 = CH_2 + Cl_2 \xrightarrow[FeCl_3]{40\text{-}80^oC} ClCH_2CH_2Cl \quad \text{----------(IX)}$$

One of the main difficulties encountered in the production of ethylene dichloride by the chlorination of ethylene is limiting the chlorination to the stage of ethylene dichloride. The by-products formed usually include hydrogen chloride, propylene dichloride, and polychloroethanes.

b. Conditions

The literature and patents contain many methods of effecting the reaction. At low temperatures (-30 to -80°C) it is possible to get substantial conversion without catalyst but it is not economical. The conditions most commonly used are temperatures between 40-80°C and a pressure between 10-20 psig in the presence of a catalyst. Higher pressures are used for dilute ethylene systems.

c. Catalyst

Numerous catalysts have been reported including iron salts, complex metallic cyanides, charcoal, aluminum oxide, etc. The liquid phase reactions have been reported more often than the vapor phase reactions using a fixed bed catalyst. The most commonly used liquid phase catalysts are ferric chloride and ethylene dibromide.

d. Heat of Reaction

The reaction is rapid and highly exothermic and consequently considerable cooling is required. The heat of reaction is 39 Kcal/mole dichloroethylene formed.[16]

e. Industrial Process

The following flow diagram,[17] Figure 9, illustrates a typical liquid phase direct chlorination process used for industrial production of ethylene dichloride: Ethylene and chlorine gas are mixed in a molar ratio of 1.05-1.10 to 1 and charged through a sparger to the reactor. The ethylene dichloride containing dissolved $FeCl_3$ catalyst is circulated at a high velocity through the reactor. External cooling is used to maintain the

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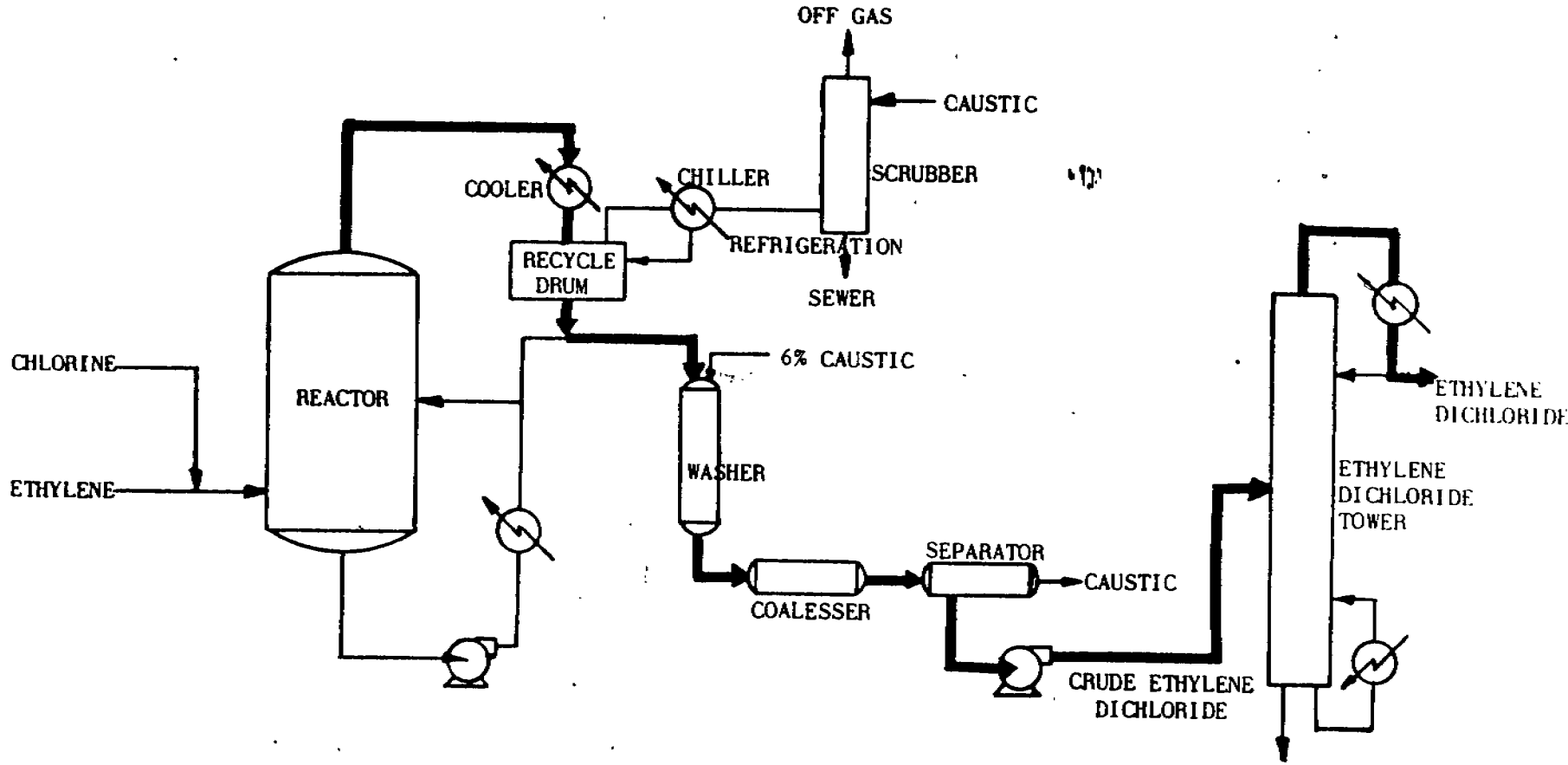

FIGURE 9. ETHYLENE DICHLORIDE PROCESS

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temperature at between 40-80°C. A pressure of 10-20 psig (sometimes higher) is maintained.

From the reaction section, the liquid and vapors are removed from the top of the reactor and are chilled with water and refrigeration to liquify the ethylene dichloride. The off-gas vapors containing hydrogen, methane, ethylene, etc., are caustic scrubbed to remove HCl. The liquid is washed with 6-8 per cent caustic in an agitated vessel and passed through a condenser to a separator tank where lower layers of crude ethylene dichloride are withdrawn. A conventional atmospheric distillation tower is used for the final purification of the ethylene dichloride. It is known that the presence of any residual $FeCl_3$ catalyst will cause decomposition and tar formation and, therefore, $FeCl_3$ must be removed prior to distillation.

Overall yields of ethylene dichloride are reported to 90-95 per cent based on chlorine.

Approximate raw materials required to produce one ton of ethylene dichloride are:

Ethylene - 630 lbs.
Chlorine - 1,600 lbs.

f. Impurities and Effects

Impurities in the ethylene dichloride can seriously affect the efficiency of pyrolysis operation for producing vinyl chloride. The presence of iron chlorides will contribute to the formation of high molecular weight tarry materials. The presence of water causes serious corrosion problems by condensing with the HCl by-product.

4. Vinyl Chloride Synthesis

a. Reaction

Commercially, ethylene dichloride is thermally pyrolyzed to yield vinyl chloride according to the following equation.[18]

$$CH_2ClCH_2Cl \xrightarrow{900\text{-}950^\circ F} CH_2 = CHCl + HCl \quad \text{---------- (X)}$$

b. Conditions and Catalysts

The main difficulty of the thermal pyrolysis is the high temperature resulting in considerable coke and tar formation causing short furnace cycle times. However, it is stated in the literature[19] that if proper operating conditions and raw material purities are strictly maintained practically theoretical yields can be obtained with no carbonaceous or high molecular weight material being formed. The thermal pyrolysis

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can be carried out in the presence of contact catalysts such as pumice, kaolin, activated carbon, etc., at lower temperatures because of improved heat transfer. Catalytic processes operating at temperatures as low as 475-500°F have been reported.

c. Heat of Reaction

The dehydrochlorination reaction is endothermic (-19 kilocalories/mole)[20] and requires heat be added to the reactor. It is estimated that for each pound of ethylene dichloride pyrolyzed, 182 BTU of heat must be added to the reaction.

d. Kinetics

The kinetics of the thermal dehydrochlorination of ethylene dichloride have been studied in considerable detail. The equations below are based on the work of Doraiswany and Pai[21] reported in 1960. The conversion to vinyl chloride can be represented by:

$$\checkmark = k\,[1 - x\,(1.33 - 5.0 \times 10^{-4}\,T)] \quad \text{---------- (XI)}$$

$$\frac{1}{S_v} = \frac{1}{k} \ln \left[\frac{1}{1 - x\,(1.33 - 5.0 \times 10^{-4}\,T)}\right] \quad \text{------ (XII)}$$

The first order rate constant (up to 80 per cent conversion):

$$k = 1.45 \times 10^{20} e^{\frac{-59,000}{RT}} \quad \text{---------- (XIII)}$$

(80 to 100 per cent conversion):

$$k = 9.8 \times 10^{7} e^{\frac{-20,000}{RT}} \quad \text{---------- (XIV)}$$

where: S_v = Space velocity, cc/hr/22.4 liters of reactor volume

$S_v = \frac{F}{V_r}$ F = Feed rate, g. moles/hr. or lb. moles/hr.
V_r = Reactor volume, 359 ft.^{3} or 22.4 liters

---------- (XV)

k = First order rate constant, liter/hr.^{2}

x = Total conversion, g. mole/g. mole feed

T = Temperature, °K

$\checkmark$ = Reaction rate, g. moles/hr./22.4 liters of reactor volume

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As reported by Bartlett and Howlett[22] the first order rate constant is independent of pressure over the range of 20-200mm and that the rate of reaction is independent of the packing.

e. Industrial Process

The simplified flow diagram reference shown in Figure 10 is based on industrial preparation. The process steps and conditions vary throughout the industry.

Reaction Section

Fresh and recycle ethylene dichloride are mixed and pumped through a desicant dryer to remove the last traces of moisture.

The dry gases are transferred to the reactor. The basic design of the reactor consists of a multiple number of stainless steel tubes. A contact catalyst packing is sometimes used. Most references list the operation of the reactor between 900-950°F and 30-50 psig. Conversion in the reactor is controlled between 50-70 per cent to limit undesirable by-product formation.

Purification Section

The gaseous, low boiling HCl, and by-products are stripped from the reaction gases leaving the reactor by quenching rapidly to 212°F in a modified absorption system by direct contact with a recycled stream of ethylene dichloride. Rapid quenching prevents secondary reactions. The HCl leaving the top of the absorber is passed through a partial condenser to remove the remaining vinyl chloride and ethylene dichloride. The HCl by-product can be used for other processes either in the anhydrous state or it can be water scrubbed and used as hydrochloric acid.

The product stream from the bottom of the HCl removal equipment is essentially HCl free and contains unreacted ethylene dichloride, vinyl chloride, and traces of high boiling liquids. The mixture goes to a vinyl chloride fractionating column operated under pressure where the product vinyl chloride is removed overhead. The bottoms contain the unreacted ethylene dichloride and high boiling liquids. Depending on the efficiency and conditions of the operation, another final purification by distillation, etc., may be necessary. Vinyl chloride of 99.9+ per cent purity is removed as overhead in the final column. The last column contacted with the vinyl chloride is constructed of stainless steel to prevent iron contamination.

Some of the unreacted ethylene dichloride bottoms serve as quenching medium and absorbing liquid in the absorption column for the HCl removal. The remainder is further refined to remove the heavy ends from the ethylene dichloride recycled to the pyrolyzer for dehydrohalogenation. Although the heavy ends are present in small quantities, their removal is essential to prevent secondary reactions which contaminate the pyrolysis

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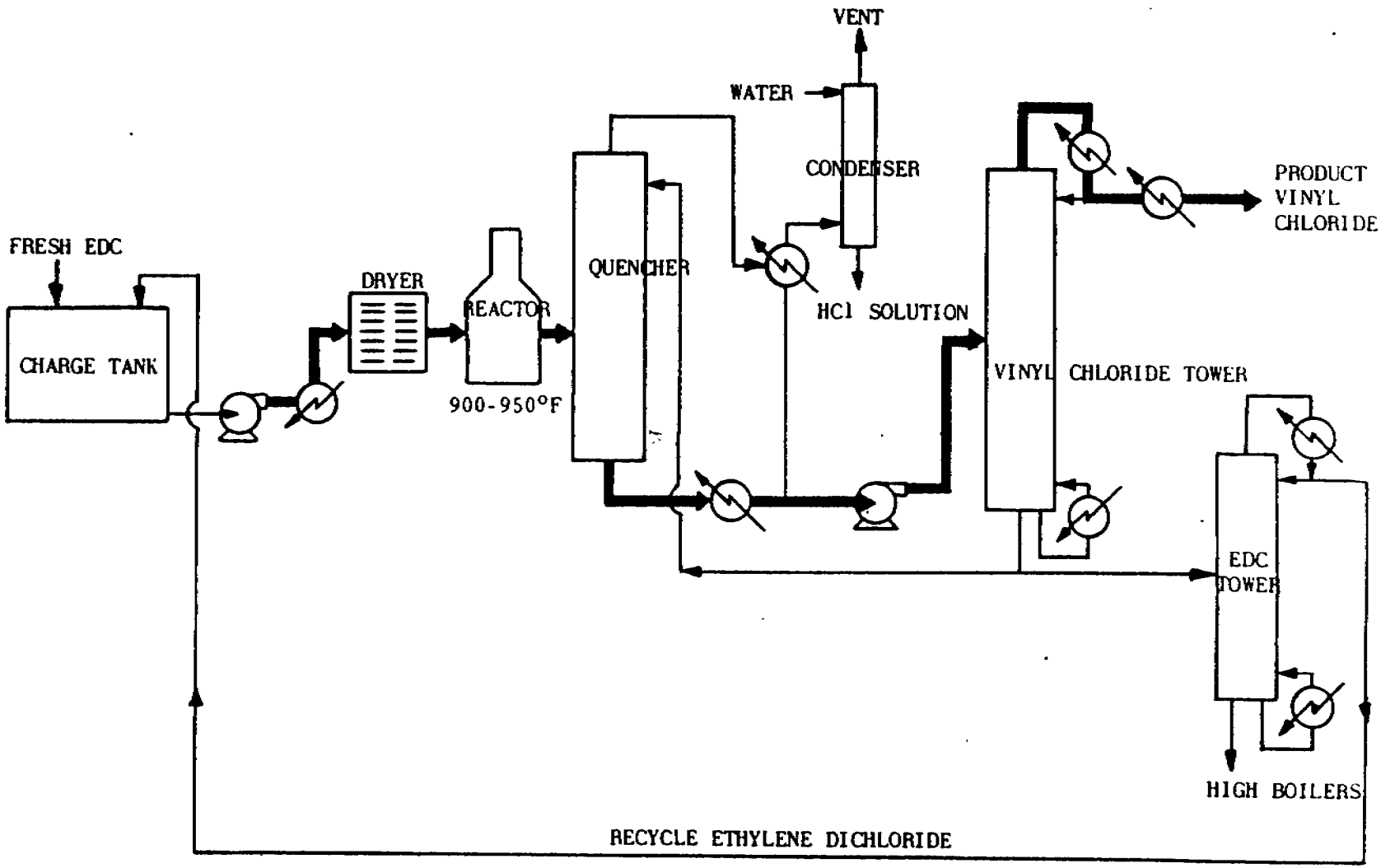

FIGURE 10. VINYL CHLORIDE FROM DEHYDROHALOGENATION OF ETHYLENE DICHLORIDE

equipment with tarry materials, etc. The ethylene dichloride refining column used operates at slight pressure with the overhead ethylene dichloride removed at about 200°F. Overall yields of 95+ per cent are reported.

C. Combined or Balanced Process

Several large producers have gone to the use of a combined or balanced process to improve the overall economics. The combined process uses the hydrogen chloride by-product from the ethylene dichloride cracking as the source of raw hydrogen chloride for the acetylene synthesis route. The two basic equations are:

$$CH_2ClCH_2Cl \xrightarrow[900\text{-}950^\circ F]{\Delta} CH_2 = CHCl + HCl \quad \text{---------- (XVI)}$$

$$HCl + C_2H_2 \xrightarrow[HgCl_2]{200\text{-}260^\circ F} CH_2 = CHCl \quad \text{---------- (XVII)}$$

A simple block flow diagram is shown in Figure 11. A detailed description of the process will not be given since the processes were covered individually in the preceding sections. The only difference is that many times the final purification is carried out in a common system. Ethylene dichloride is used to absorb the vinyl chloride from the outlet of the acetylene and hydrogen chloride reactor and is combined with the product stream from the ethylene dichloride pyrolysis.

D. Vinyl Chloride Manufacturers

The estimated capacity for vinyl chloride today in the United States is about 1,885 billion pounds per year. It is estimated that about 50-60 per cent of the vinyl chloride produced today uses acetylene as a starting material.

Much of the vinyl chloride monomer produced in the United States is captively consumed. Allied, Ethyl Corporation, and American Chemical are exclusively monomer merchants. Union Carbide, Monsanto, and Dow are producers that sell a portion of their production.

III. New Vinyl Chloride Processes

Several of the new synthesis routes are worth reviewing.

A. Vinyl Chloride from Acetylene and Ethylene Mixtures

The thermal cracking of natural gas or other hydrocarbons to produce ethylene, acetylene, and other products is commonly practices in industry. However, the cracked gases usually contain diluents as hydrogen, methane, carbon monoxide, etc., besides ethylene and

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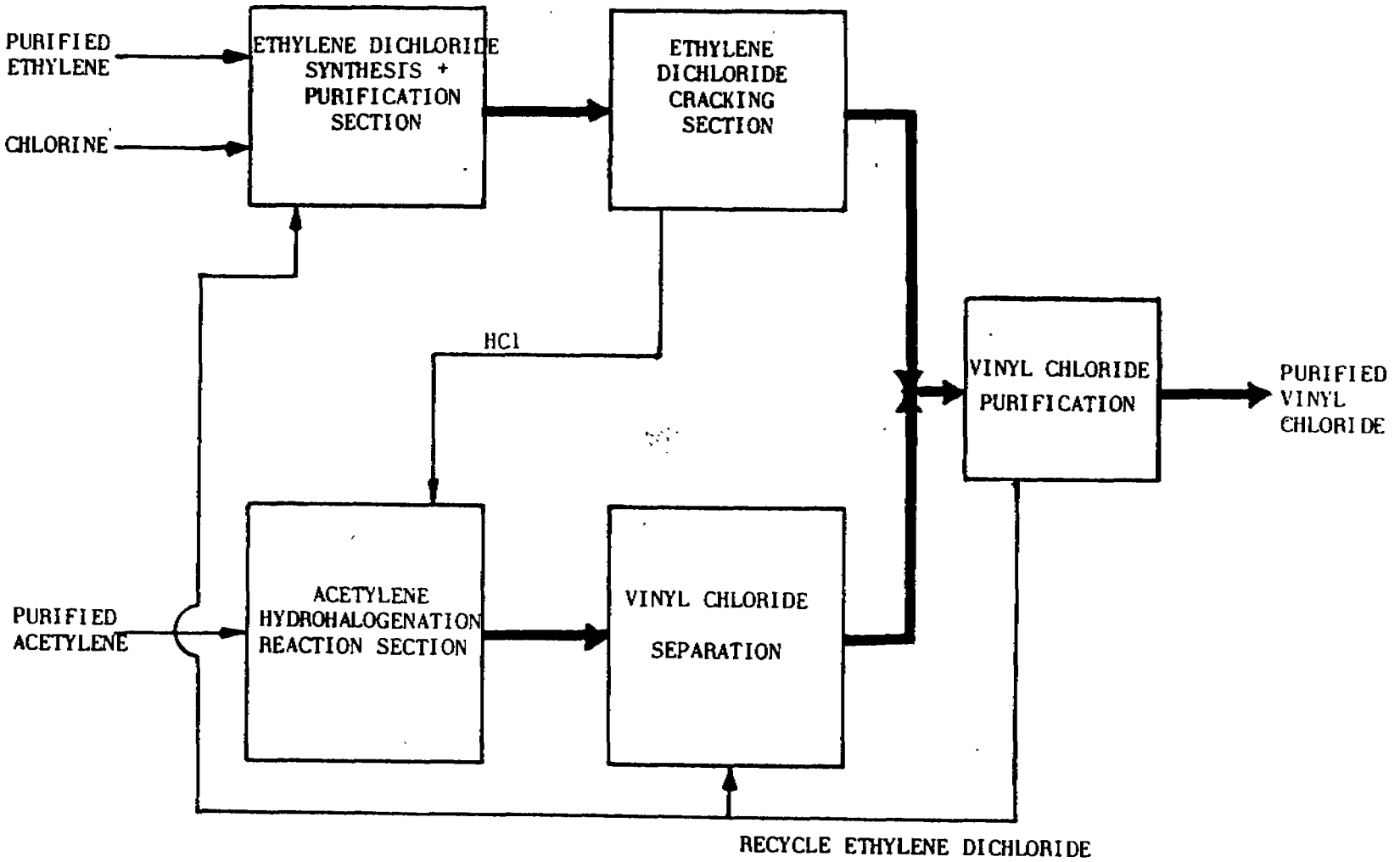

FIGURE 11. COMBINED PROCESS

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acetylene. Separation and purification of the acetylene or ethylene from the diluents is difficult and adds to the raw material costs. Use of unseparated cracked gases as a raw material has been proposed.[23, 24]

The raw materials required for the process are a source of hydrocarbons. The reaction consists of pyrolyzing the hydrocarbon source at the necessary conditions to produce a cracked gas containing about 10 per cent acetylene, 10 per cent ethylene, and 80 per cent of diluents including CO_2, CO, H_2, CH_4, etc.

The process is similar to the balanced or combined process except the two reactor systems are in series. A simplified flow diagram of a process of this type is shown in Figure 12.

In the first phase the diluted acetylene reacts with HCl and produces vinyl chloride. The ethylene behaves as an inert gas. In the second phase the ethylene is combined with chlorine to give ethylene dichloride. In the third phase the ethylene dichloride is pyrolyzed to form vinyl chloride and HCl. The HCl is recycled to the first phase.

The gases such as hydrogen, carbon monoxide, and carbon dioxide behave as inert gases and in no way affect the rate of formation of the vinyl chloride, but are beneficial in that they improve the heat transfer characteristics of the system. The diluent gases from the outlet of the ethylene dichloride cracking furnace in the third phase are water and caustic scrubbed and then used as fuel for the ethylene dichloride or naphtha cracking furnaces. Vinyl chloride produced in the first and third phases is refined in one system. The ethylene dichloride is redistilled and recycled. The vinyl chloride obtained has a purity higher than 99.9 per cent.

B. Vinyl Chloride from Dilute Acetylene Gases

The reaction mixture containing acetylene as produced by partial oxidation of natural gases rich in methane described in the earlier section on acetylene production contains approximately 10 per cent acetylene before purification. The proposed[25, 26] use of dilute acetylene gas without purification for vinyl chloride synthesis has economic advantages.

Conventional acetylene-HCl reactors described in the first half of the preceding process are applicable to dilute acetylene gases. However, operating conditions usually make it necessary to recycle the unreacted acetylene and an absorption system is essential. Suggested systems use tetrahydrofuran or trichloroethylene which are two excellent solvents for both acetylene and vinyl chloride. The main disadvantage with this process is the necessity of handling large volumes of diluent gases.

C. Vinyl Chloride by Oxychlorination Techniques

Oxychlorination is generating considerable interest among chemical processors and engineering firms for the production of vinyl chloride. The low price of raw material ethylene, the availability of HCl and the overall balance obtained are the main reasons for the interest.

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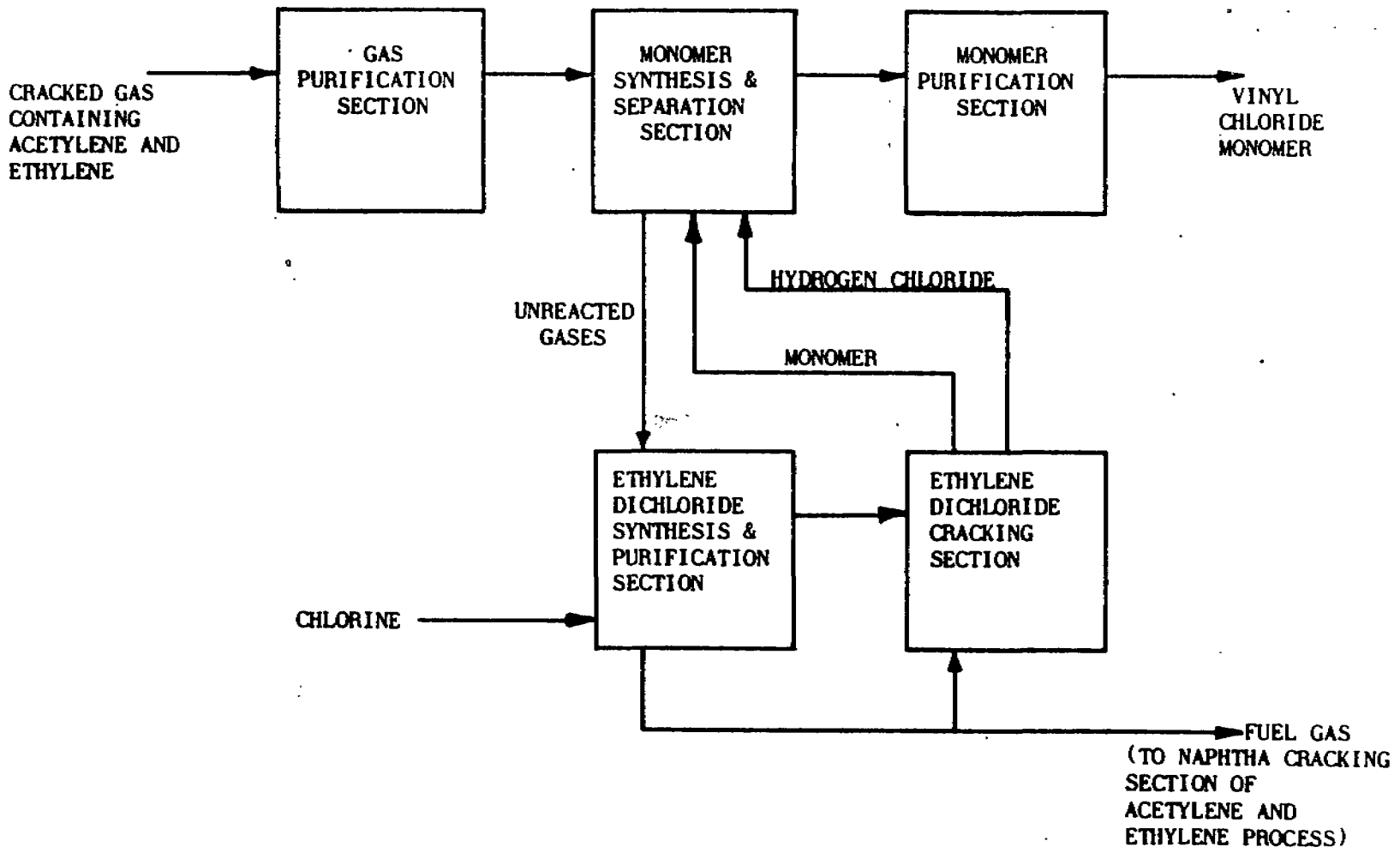

FIGURE 12. DILUTE GAS VCl PROCESS

Three methods of using oxychlorination techniques for vinyl chloride synthesis have been extensively investigated.

1. Dehydrochlorination Using Ethylene Dichloride Produced by Oxychlorination

Using oxychlorination for the synthesis of the vinyl chloride intermediate ethylene dichloride is growing in importance commercially. Three large producers of ethylene dichloride, Dow, Monsanto, and Goodrich Chemical[27] are using oxychlorination for ethylene dichloride production. French Solvay recently revealed[27] a 330 million pounds per year vinyl chloride venture using the oxychlorination technique. The process is based on the equation:[28]

$$2HCl + \tfrac{1}{2}O_2 + Cl_2 + 2C_2H_4 \longrightarrow 2\ C_2H_4Cl_2 + H_2O \text{ ---------- (XVIII)}$$

Most companies will not give details of the processes but information can be obtained from the patent[29] literature. Copper chloride catalyst is stated in most patents. There is considerable variation in types of additives and supports used to prevent catalyst bed hot spots and volatilization of the copper chloride. One company recommends alkali metal salt (KCl) and copper chloride impregnated on silica gel support. Both fluidized and fixed bed oxychlorination reactors operating at temperatures of 485-570°F are reported used. Corrosion is a problem at the higher reaction temperature. Ethylene dichloride yields of 95% or better are reported. The ethylene dichloride is then pyrolyzed by conventional methods and the hydrogen chloride recycled to the ethylene dichloride synthesis.

2. Dehydrohalogenation Route with Modified Deacon Process

Oxychlorination can also be used to utilize the by-product HCl from ethylene dichloride cracking. The HCl is oxidized to chlorine using a modified Deacon process represented by the equation:[29, 30]

$$2HCl + \tfrac{1}{2}O_2 \longrightarrow Cl_2 + H_2O \text{ ---------- (IXX)}$$

The HCl is oxidized to chlorine in a unit completely separate from the vinyl chloride monomer operations. The chlorine can then be used for the conventional ethylene chlorination synthesis. In one proposed industrial process the gaseous HCl from the vinyl chloride plant is mixed with air and passed through a fluidized catalyst bed consisting of a mixture of copper and other chloride catalysts. The reaction temperature is 630-800°F. The reacted effluents are then dryed to remove the water vapor. Although the effluent composition depends on the HCl feed, a typical composition by weight is 48 per cent chlorine, 48 per cent nitrogen, and 4 per cent oxygen and is suitable for use in the ethylene dichloride plant. The HCl conversion to chlorine is essentially complete.

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3. Oxychorination of Ethylene

Another reported method promising a balanced route to vinyl chloride is the direct oxychlorination of ethylene based on the following equation:[31]

$$\tfrac{1}{2}O_2 + Cl_2 + 2\ C_2H_4 \longrightarrow 2\ C_2H_3Cl + H_2O \text{ ---------- (XX)}$$

In this process the raw materials are oxygen, chlorine, and ethylene. The hydrogen chloride liberated from the ethylene dichloride cracking is oxychlorinated to chlorine to react with additional ethylene. Although the route eliminates one step from the conventional two-step ethylene dehydrohalogenation route, there is a difference in temperatures for oxychlorination of ethylene dichloride over conventional catalysts (570°F) and the cracking of ethylene dichloride (850-950°F). Therefore, the efficiency and yield are affected by the high operating temperatures required. One reported[31] solution is to operate under vacuum and ultraviolet light where temperatures can be reduced. Using this method yields of over 95 per cent are obtained at a pressure of 7 psia.

IV. Economics and the Future

Market competition stimulated by over capacity has caused the selling price of vinyl chloride to drop considerably the last 5 years. The price has dropped from $.115/lb. to $.08/lb.[32] and is almost sure to drop more in the future. This has stimulated the need to reduce overall raw material and production costs by either improving the economics of existing processes or developing new processes.

The production of vinyl chloride by the acetylene halohydrogenation route was hindered for many years by the high price of the basic raw material acetylene obtained from calcium carbide. More emphasis was given to the ethylene dichloride route favored by the low price and plentiful supply of ethylene. Petrochemical acetylene produced at a considerably lower price by partial oxidation techniques again stimulated interest in the acetylene route. Three companies, Diamond Alkali, Monochem, and Tenneco have recently constructed vinyl chloride production plants that use petrochemical acetylene as the basic raw material. The plants have a combined capacity of about 450,000,000 pounds per year. Carbide acetylene is not now considered a building block of the future in the vinyl chloride industry since the cost of producing it even in a fully depreciated electrofurnace cannot compare to the potentially lower cost of petrochemical acetylene. However, it should be noted that several of the petrochemical acetylene plants have encountered unexpected difficulties that have added to operating costs.

Advantages of the simple acetylene-HCl additive route for producing vinyl chloride are that the initial capital investment for a plant is modest. Therefore, the size of the plant is not as much of an economic factor. The reaction is a straight forward high yield reaction with no major by-product problems. Manufacturing costs are also moderate. The one disadvantage is the cost of the raw material acetylene. An economical acetylene-HCl process has been proposed that uses the dilute petrochemical cracked gas containing 10 mole per cent acetylene gas before purification. This would result in

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a still greater reduction in raw material costs per pound of vinyl chloride produced than by using purified petrochemical acetylene. However, using the diluted acetylene stream necessitates the handling of extremely large volumes of gases in the product plant. This factor will, therefore, have an influence on the economics by increasing the equipment size and manufacturing costs, thus adding to the cost of vinyl chloride produced and initial capital plant costs.

The low price and plentiful supply of ethylene compared to calcium carbide acetylene was the main factor for the switch to the ethylene dichloride dehydrohalogenation route particularly in the 1950's. Ethylene today has a "list price" of about $.045/lb.[32] One disadvantage of the ethylene process is that the equipment required for producing and purifying the intermediate ethylene dichloride as well as the ethylene make initial capital investment costs high. Therefore, a large plant is necessary for economic operation. However, the main disadvantage of the process is that half the chlorine is lost in by-product HCl which has to be marketed or used.

Finding a market for by-product HCl is becoming a difficult problem since there is far more by-product HCl produced from chlorination and other processing plants than is required. Production of linear alkylates for the new soft detergents could potentially dump another 200 million pounds of HCl on the market. The cost of the chlorine lost in the HCl plus the cost of the neutralization when no market is available, is a heavy charge against the vinyl chloride produced by the ethylene route.

The combined or parallel mixed route using two separate systems has been adopted by several large companies to improve the economics by using the by-product HCl from the ethylene route in an acetylene-HCl synthesis system. There is then no loss of HCl and half the acetylene is replaced by lower priced ethylene. The disadvantages are that two reactor systems are needed and two separate hydrocarbon feed streams have to be prepared increasing manufacturing costs and capital investment costs which make large operations necessary economically.

Among the newer techniques for improving the economics, a series mixed route has been proposed where a mixed stream of ethylene and acetylene from a naphtha pyrolysis plant is used. In Japan, Kurhea is building a 110 million pounds per year plant based on this process. The advantage is that the extra cost of separation of ethylene and acetylene is eliminated. Although the process has definite economic advantages over the other routes because of the low raw material costs, it still has the disadvantage that two reactor systems are necessary, thus making manufacturing costs and initial capital investment high.

A more direct approach is in the proposed direct oxychlorination of ethylene to vinyl chloride using oxygen, ethylene, and chlorine as raw materials. The low basic raw material costs per pound of vinyl chloride produced and the overall material balance obtained are definite advantages. The main factors influencing the economics are the questionable product yield and the high capital cost of the plant. The necessity of adding oxygen to the process and the corrosion problems involved in handling water vapor add to the capital cost. However, this process has a lot of promise for the future.

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The two step oxychlorination of ethylene to ethylene dichloride and pyrolysis of the ethylene dichloride to vinyl chloride is one of the more popular recent proposed methods of producing low cost monomer. The by-product HCl from the ethylene dichloride pyrolysis is used with oxygen, ethylene, and chlorine in the ethylene dichloride synthesis to give the plant overall product balance. The raw material costs are also reduced considerably in this process. High product yields are reported. The disadvantages of all oxychlorination methods are the necessity of adding oxygen and the potential corrosion problems from handling water vapor in the presence of HCl.

Another proposed solution to the HCl by-product problem is to oxidize the HCl economically back to chlorine using the modified Deacon process. The chlorine is then recycled and used in the ethylene chlorination. It is reported[33] that including plant depreciation and manufacturing costs, chlorine can be recovered in a process unit at half the market price of chlorine. This process has the advantage of being used separately in conjunction with present vinyl chloride industrial processes by the ethylene route.

Although raw materials are a major factor in any decision to build a plant, other factors must be taken into account including the size of the plant, location of the plant, distance to the markets, and availability or marketability of by-product HCl. An economic comparison of two processes is shown in Figure 13.

The choice of a process route for any particular company depends somewhat on its own particular circumstances. A company desiring low volume vinyl chloride and having available dump or by-product HCl and moderately priced acetylene could conceivably build a plant using the HCl-acetylene route at a low capital investment cost. However, a company desiring to produce large quantities of vinyl chloride for marketing, say 200-300,000,000 pounds per year, must take all economic aspects into account.

The most promising processes for large plants in the near future are the petrochemical mixed ethylene and acetylene process, and the ethylene processes incorporating oxychlorination including (1) the two-step process where ethylene is oxychlorinated to ethylene dichloride and the ethylene dichloride is pyrolyzed and (2) the ethylene dehydrohalogenation plant where a separate modified Deacon process is used for converting HCl to chlorine. Large plants using petrochemical acetylene as a raw material could have a bright future if operating and manufactured cost can be reduced. Also, in the future, the direct oxychlorination of ethylene to vinyl chloride has considerable potential as a very economical route to vinyl chloride.

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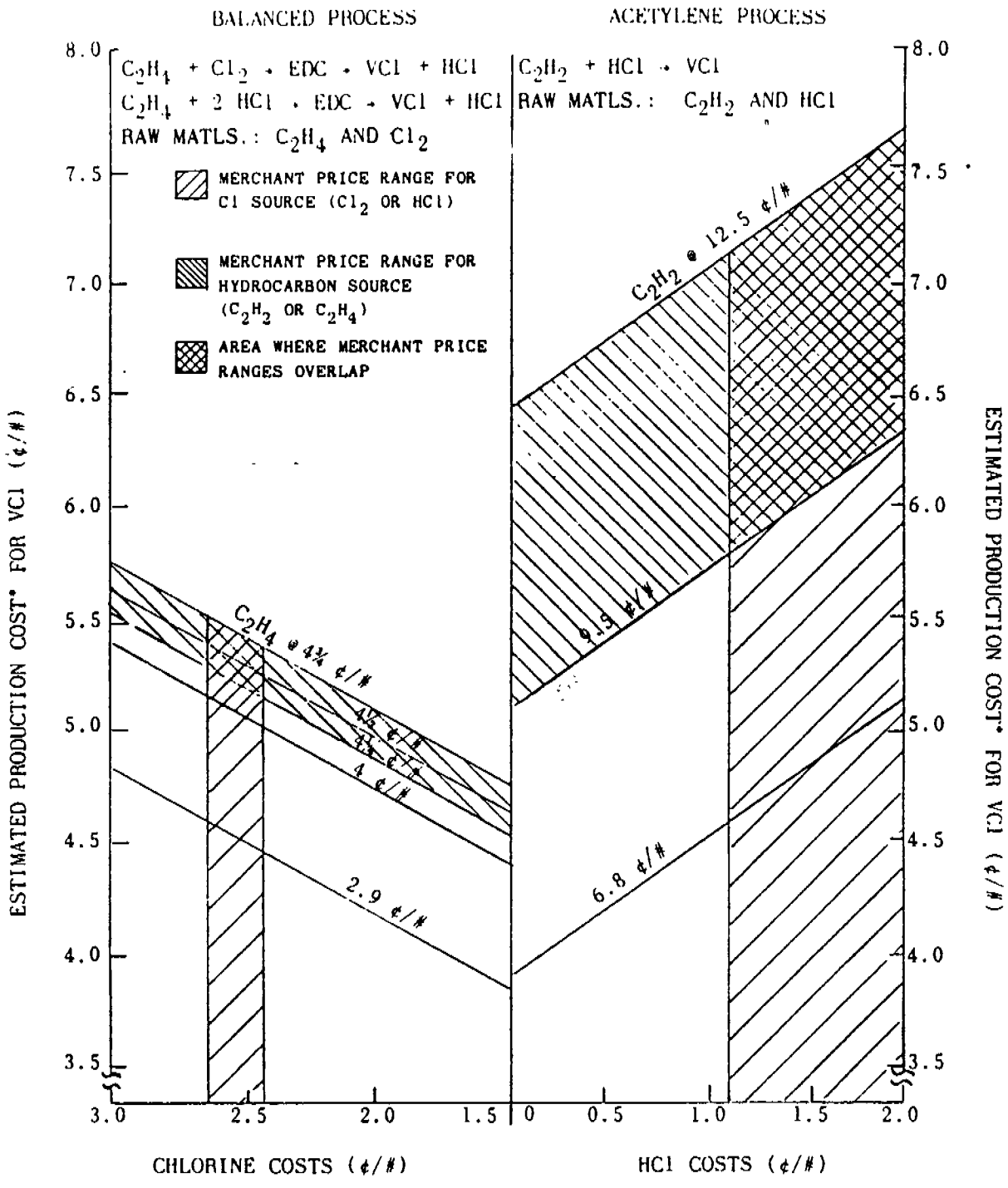
FIGURE 13.27 VCl COSTS: BALANCED OXYCHLORINATION VS. ACETYLENE



*IN A 100 MILLION LBS./YEAR VCl PLANT, THIS COST WOULD NOT INCLUDE SUCH ITEMS AS SELLING AND ADMINISTRATIVE OR RESEARCH AND DEVELOPMENT COSTS.

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"The General Tire Suspension Process" will be concerned with the [illegible] method of 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
Elvanol 50-42 (polyvinyl alcohol)	0.1

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.

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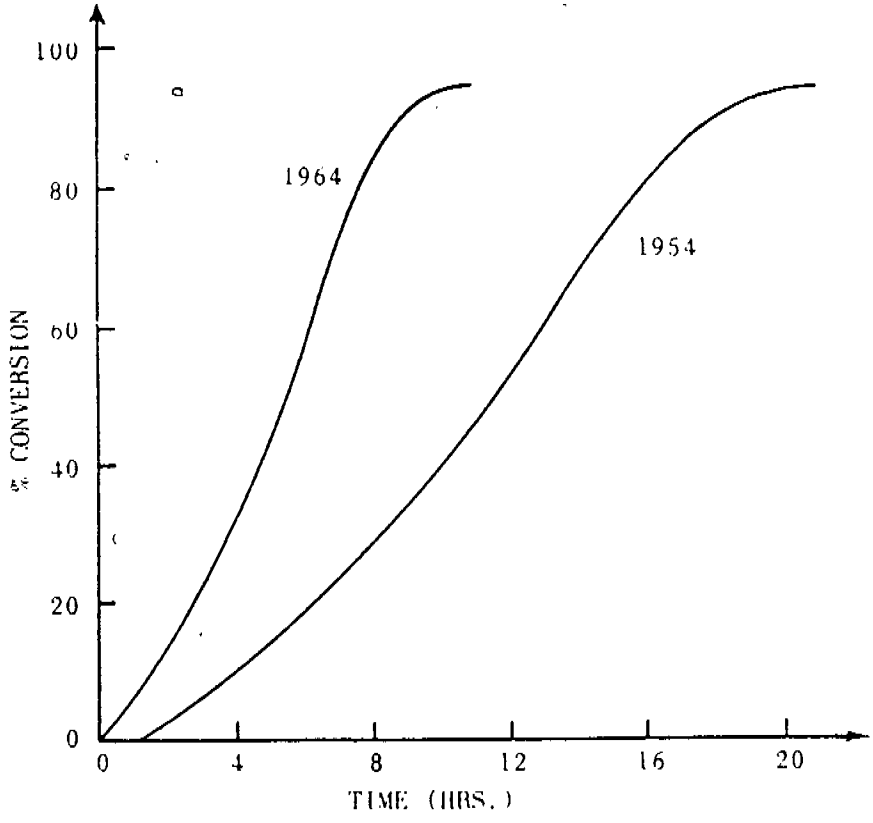
C. [illegible]

The objective of the technical program at Natrium 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



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[illegible] period, is one in which the reaction is inhibited. [illegible] arises from the presence of very small traces of impurities. [illegible] combine with active centers of polymerization or with the initiator.

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

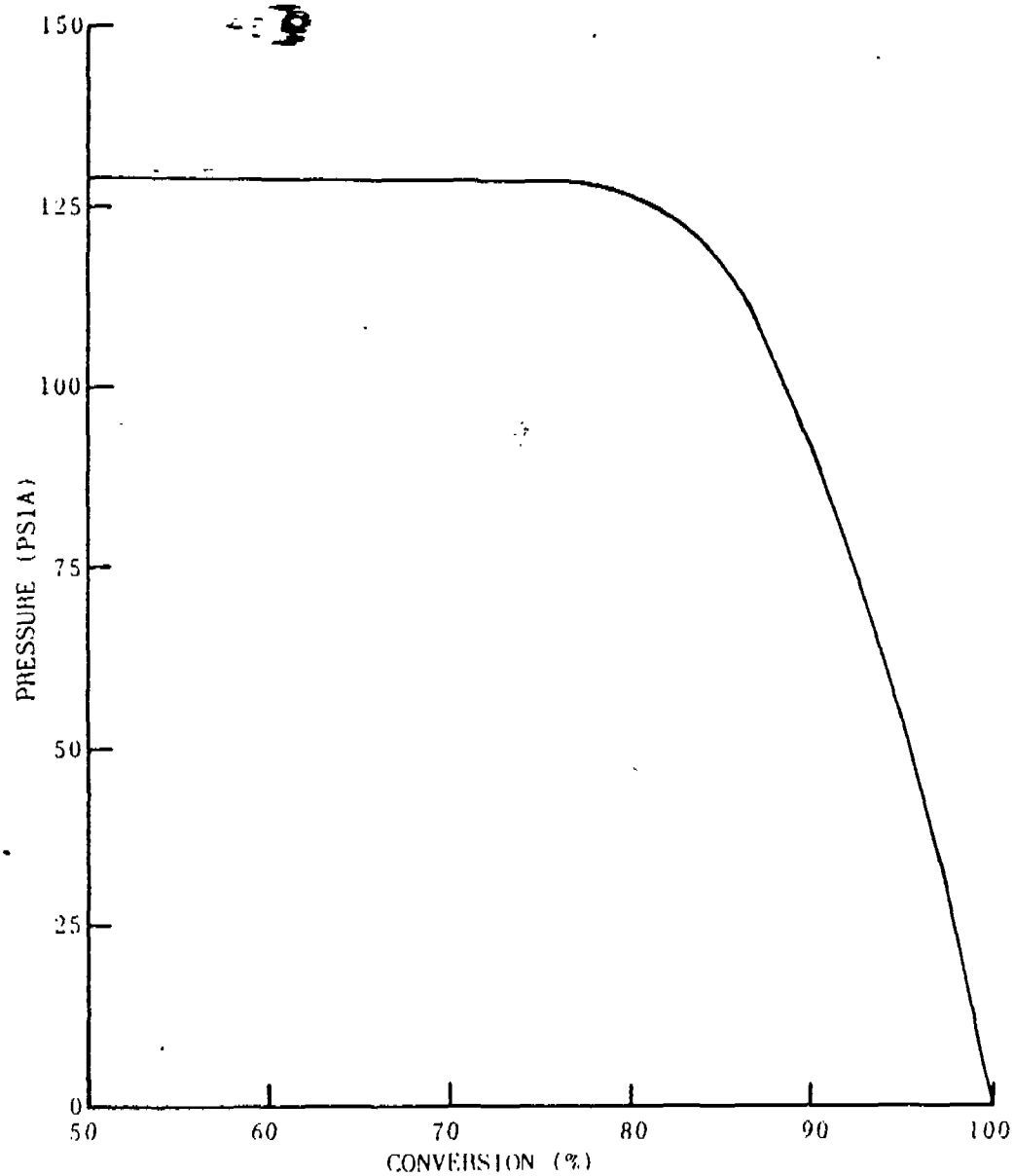

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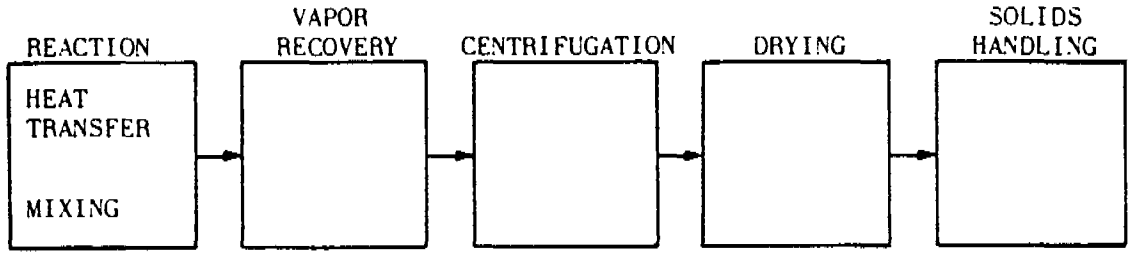
Figure 2 shows that there is a useful relationship between pressure and extent of conversion in the material from 70 to 90% conversion. Below a 70% conversion the rate of reaction can be roughly estimated by the temperature differential between the batch and the jacket cooling water. This temperature 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.

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A [illegible] polymerization process to [illegible] only three reactors but takes advantage of maximum conversion rates to almost double the output of batch-wise 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.

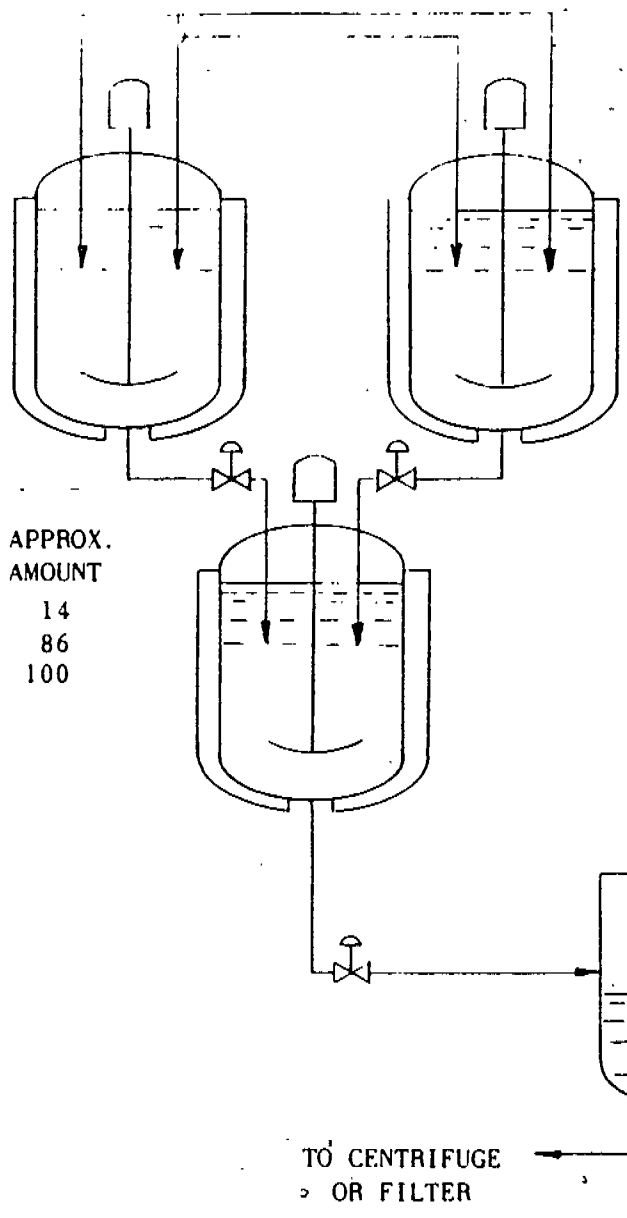
The batch is then dropped to one of three agitated dump tanks. In the dump tank the unreacted monomer is stripped from the polymer slurry (75% water and 25% PVC) through a water sealed vacuum pump and is returned to the monomer area for purification and reuse. The stripped slurry is pumped to slurry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

GENC 000455

MONOMER
WATER
(PLUS CATALYST)
AND COLLOID)

	APPROX. AMOUNT
MONOMER	30
POLYMER	70
WATER	100
T 131°F	
P 150 PSIG	



	APPROX. AMOUNT
MONOMER	30
POLYMER	70
WATER	100
T 131°F	
P 150 PSIG	

	APPROX. AMOUNT
MONOMER	14
POLYMER	86
WATER	100
T 131°F	
P 45 PSIG	

TO RECOVERY

FLASH CHAMBER

TO CENTRIFUGE
OR FILTER

II. 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

GENC 000457

[illegible] identical for [illegible] available. [illegible] based on plant experience, can be [illegible]

Table [illegible]

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.

GEMC 000458

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

$$Q = \rho V \Delta H \times \text{wt. \% reacting per unit time} \quad \text{---------- (II)}$$

$$= 7.88 \frac{\#\ \text{mix}}{\text{gal.}} \times V \times 650 \frac{\text{BTU}}{\#\ \text{VCl}} \times 0.1\text{b} \frac{1}{\text{hr.}} \times \frac{100\ \#\ \text{VCl}}{282\ \#\ \text{Mix}}$$

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

Heat Transferred Through the Reactor Walls

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

Equating

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

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

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).

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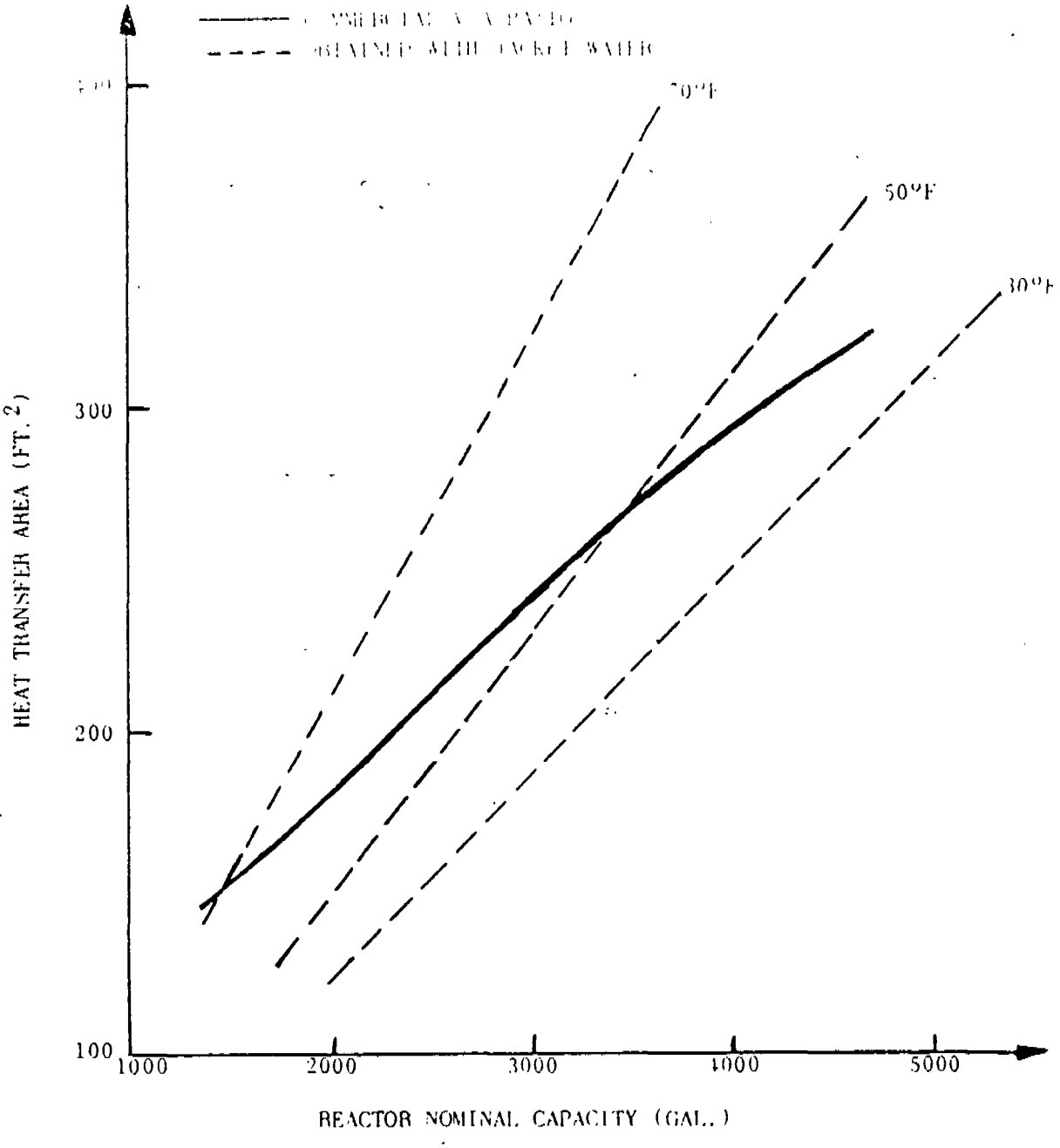

The 70°F water from a cooling tower will not maintain control over the batch if the only heat transfer surface available is the jacket wall. Accordingly, methods for extending the heat transfer area have been investigated. These take the form of external heat exchangers through which the slurry is recirculated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

GENC 000460

[illegible] 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.

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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.

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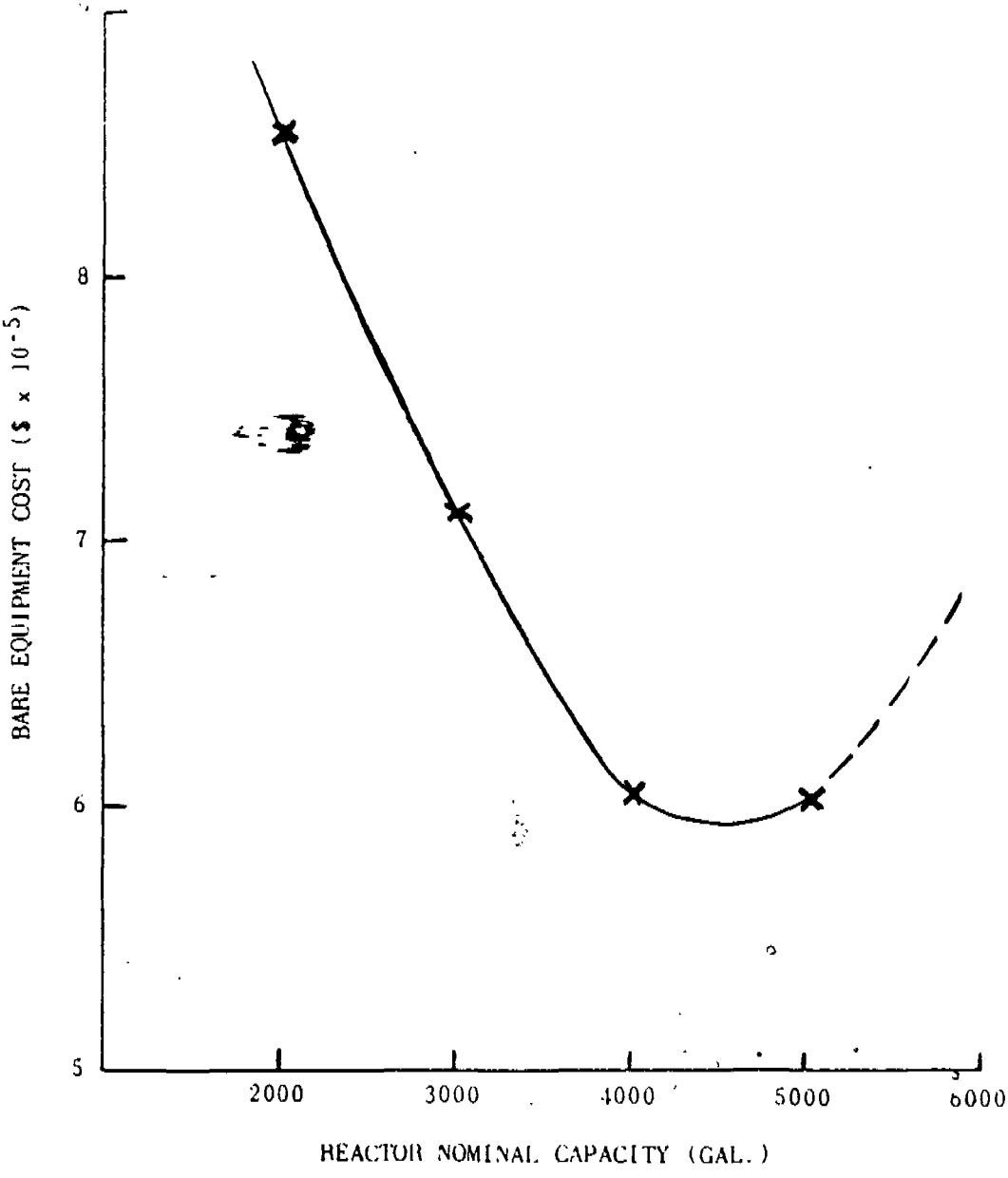


2. Ashtabula Design

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

BENC 000433

[illegible] depending on the product [illegible] 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:

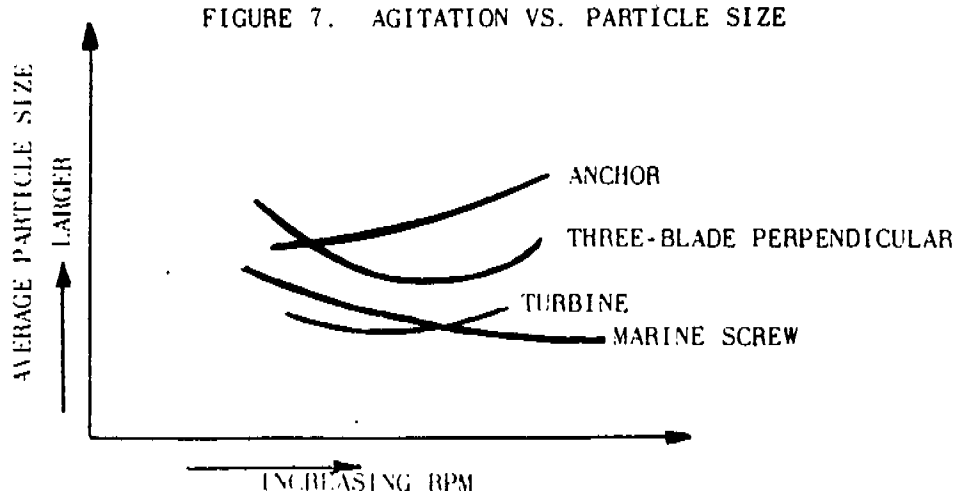
a. Agitator speed.
b. Impeller size and design.
c. Number of baffles and their design.
d. Material of construction.

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



GEMC 3[illegible]

[illegible] the marine screw agitator and particle size [illegible] increase 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

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[illegible] 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.

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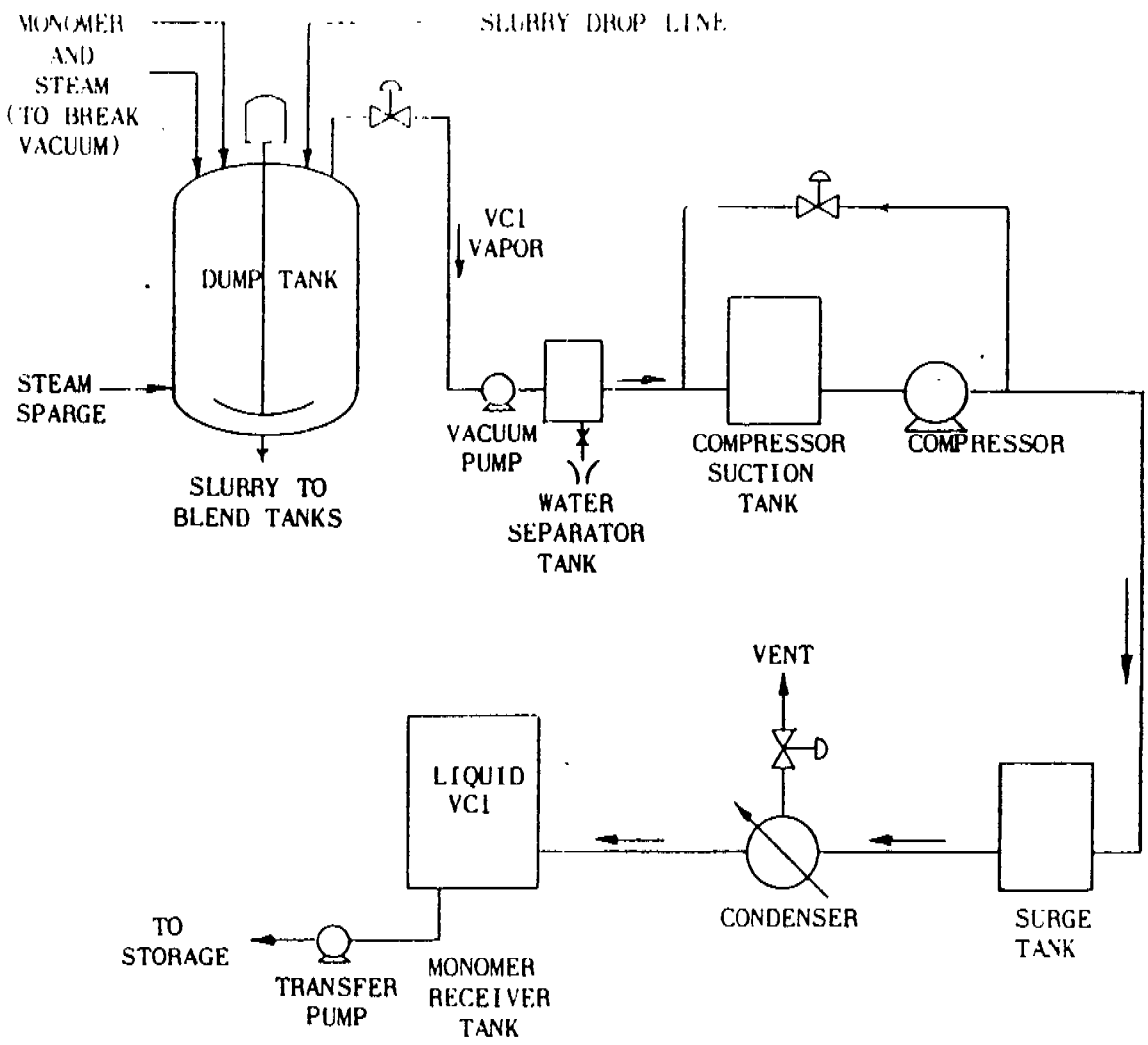
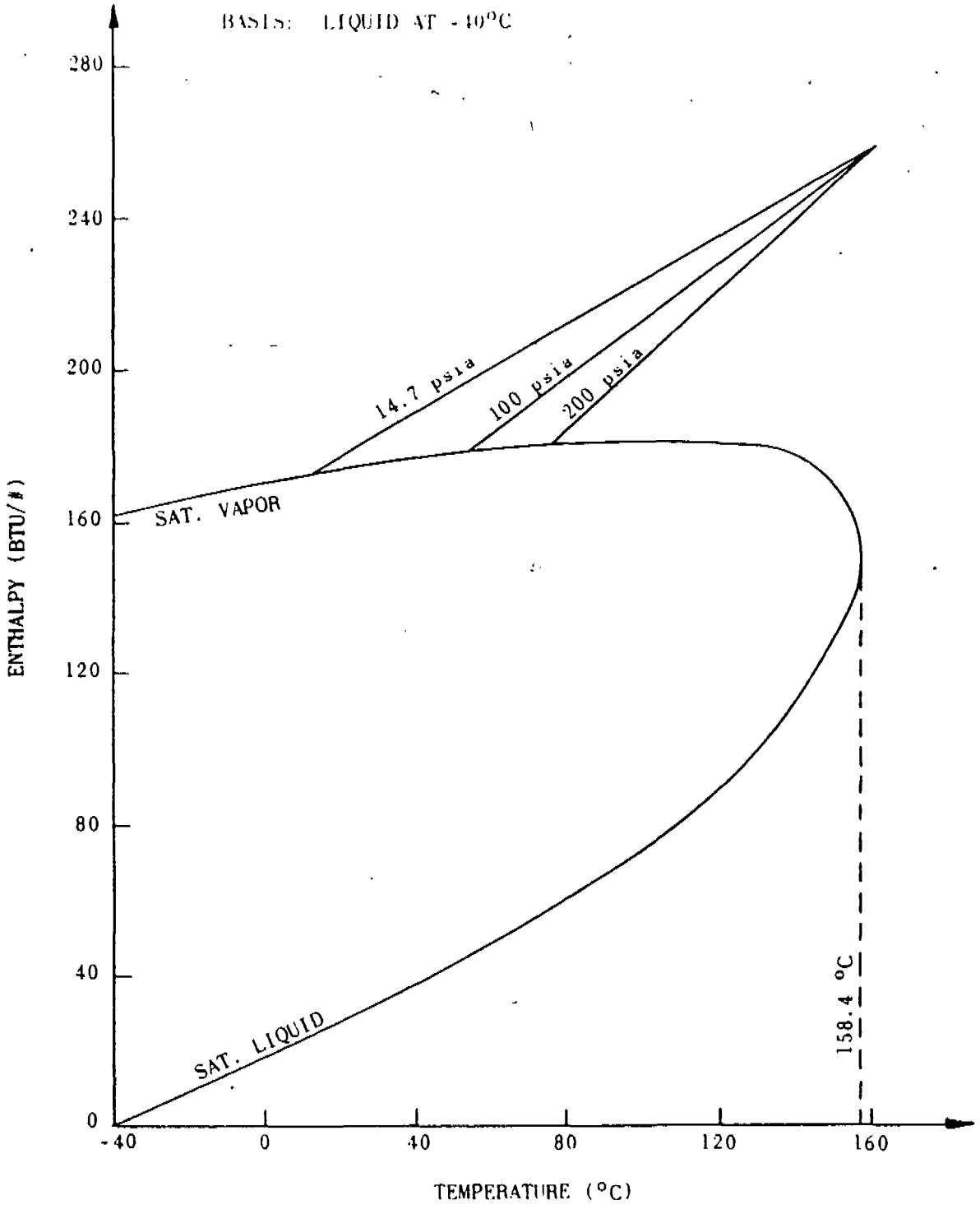

MONOMER
AND
STEAM
(TO BREAK
VACUUM)
SLURRY DROP LINE
DUMP TANK
VCI
VAPOR
STEAM
SPARGE
SLURRY TO
BLEND TANKS
VACUUM
PUMP
WATER
SEPARATOR
TANK
COMPRESSOR
SUCTION
TANK
COMPRESSOR
VENT
LIQUID
VCI
CONDENSER
SURGE
TANK
TO
STORAGE
TRANSFER
PUMP
MONOMER
RECEIVER
TANK

GEHC 000467

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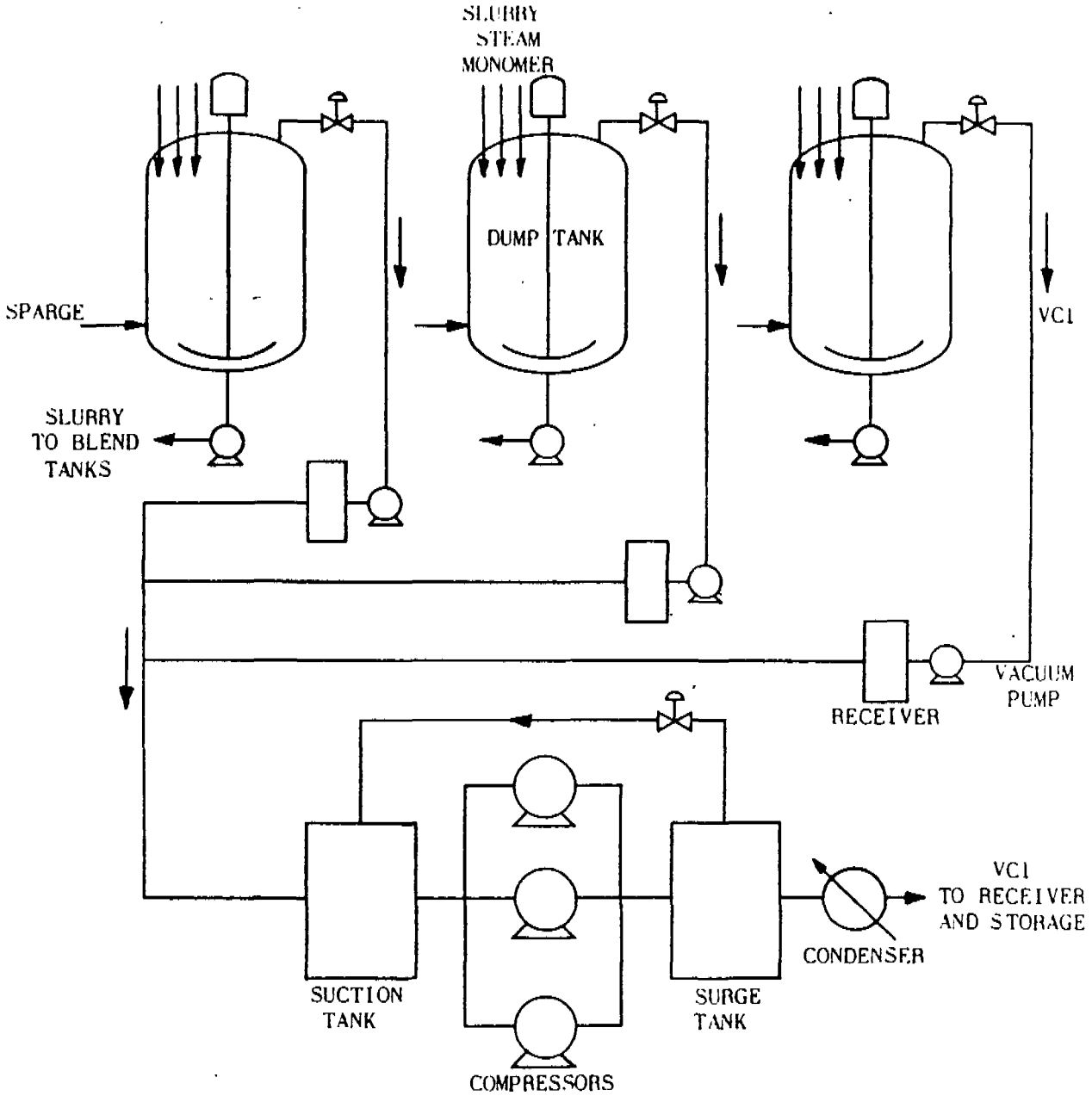
The Ashtabula recovery system consists of three dump tanks [illegible] 7,000 gal. and one of 5,000 gal. capacity. Each has a suction pump and recovery compressor feeding a common recovery condenser. The system is given in Figure 10.

FIGURE 10. ASHTABULA RECOVERY SYSTEM



GENC 000469

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

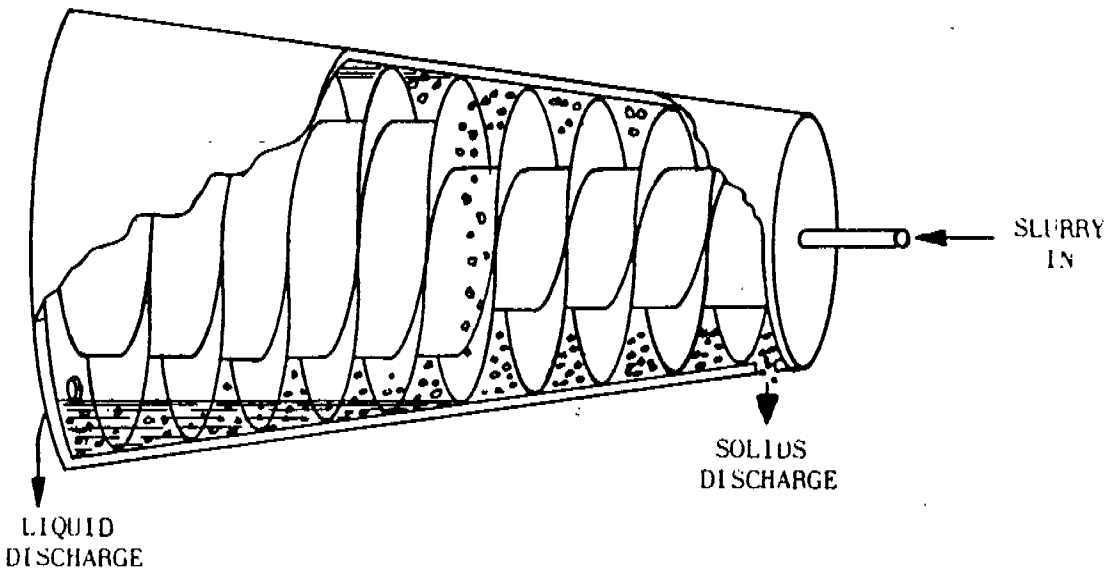
The slurry storage tanks ("blend" tanks) of the original Ashtabula design consisted of three 15,000 gal. 304 stainless steel tanks. Continuous agitation is provided to prevent phase separation. The transfer lines are constantly recirculated to prevent line plugging and to further increase the blending 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.

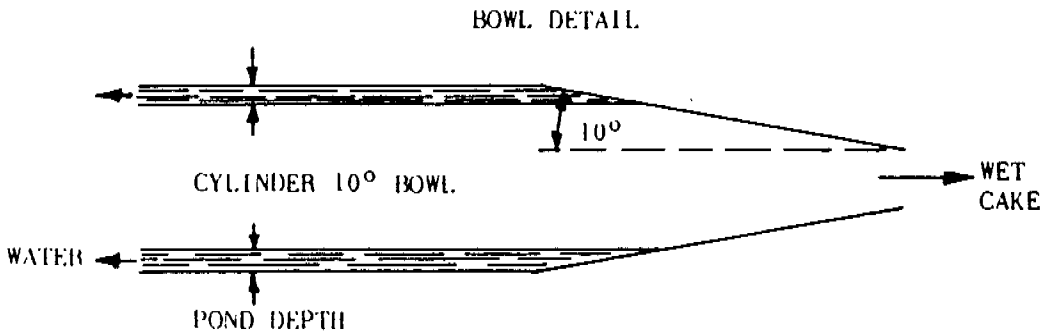
GENC 000470

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





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[illegible]

[illegible] The [illegible] rotates in the [illegible] 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

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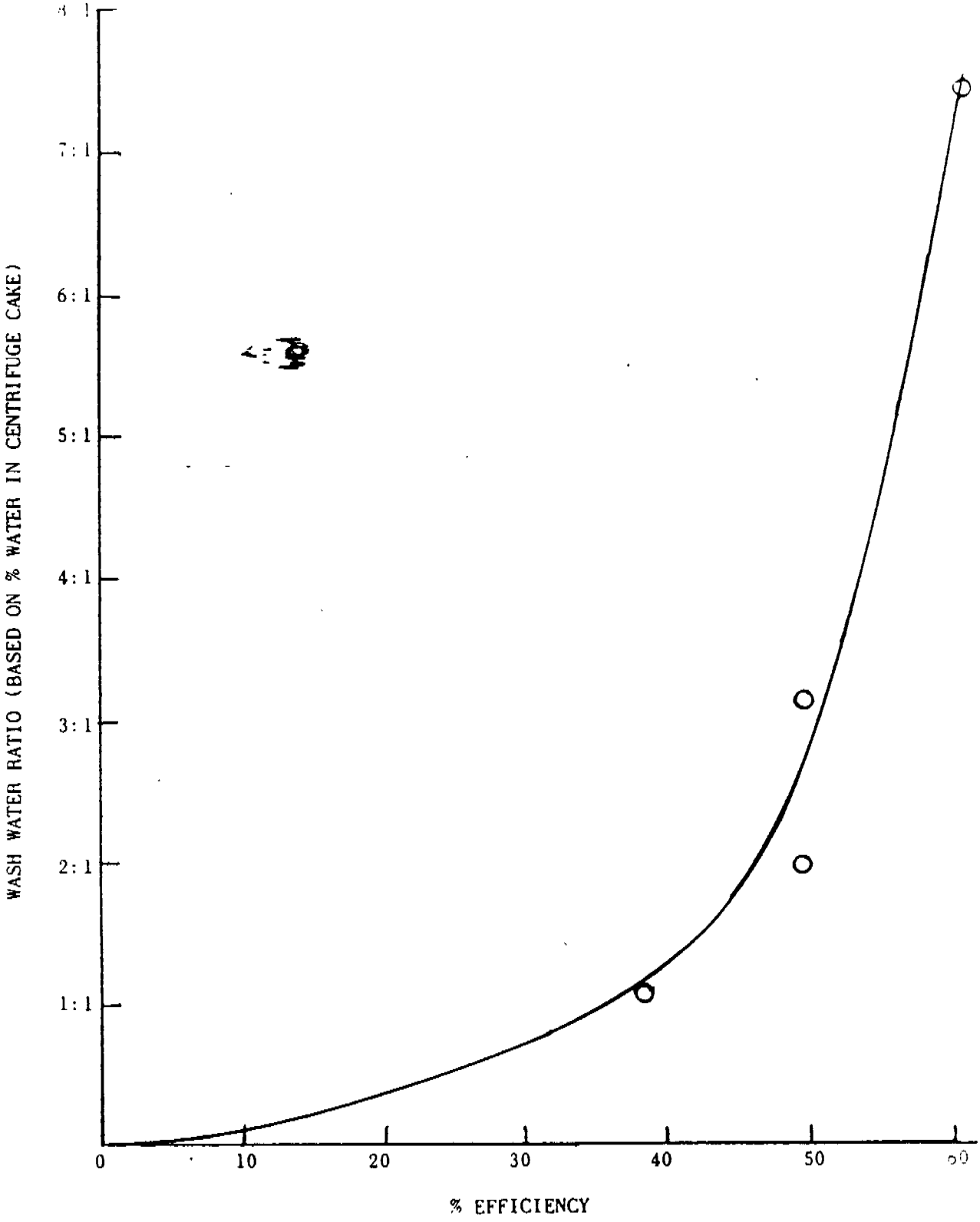
WASH WATER RATIO (BASED ON % WATER IN CENTRIFUGE CAKE)
7:1
6:1
5:1
4:1
3:1
2:1
1:1
0
10
20
30
40
50
% EFFICIENCY

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to heat as contained. The two types in use for PVC are rotary and flash. The rotary dryer is used by General Tire.

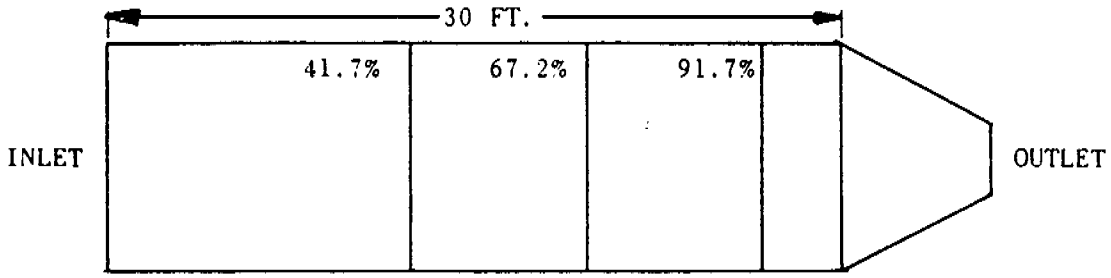
2. Ashtabula Design

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 x 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.				

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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}°F

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

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

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

Evaluation of Equation VII

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

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.

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

$q_p = 1,400 \times 0.25 \times (107-120) + 1,400 \times 1.000 \times (107-120)$

$q_p = -3.23 \times 10^4$ BTU

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

$q_v = 1.13 \times 10^6$ BTU

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

$q_s = 3.15 \times 10^4$ BTU

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

Ignoring the last term:

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

$q_t = 1.13 \times 10^6$ 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

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

$= 151°F$

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

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

$= 49°F$

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$$\frac{1}{(\Delta t)_m} = \frac{1.23 \times 10^{-3}}{1.13 \times 10^{6} \times 151} + \frac{1.13 \times 10^{6}}{1.13 \times 10^{6} \times 106} + \frac{1.13 \times 10^{6}}{1.13 \times 10^{6} \times 151}$$

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

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

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.

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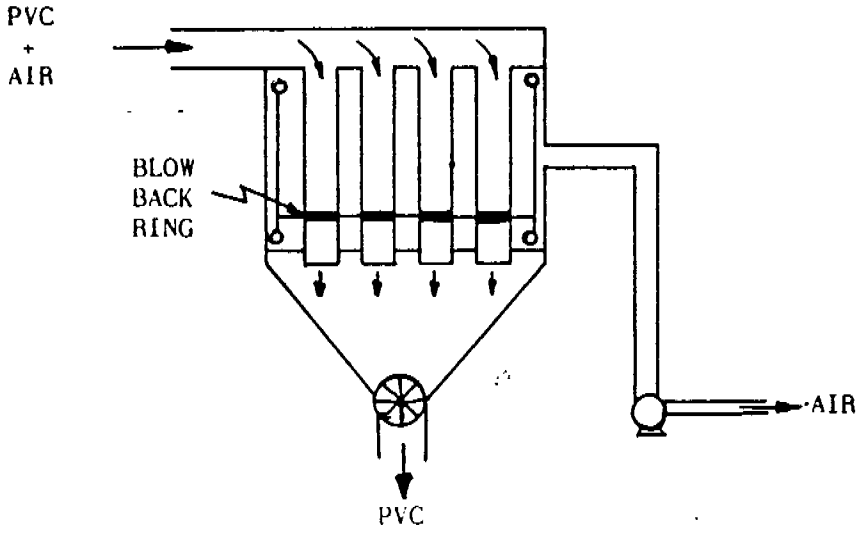
[illegible] of bag filters, [illegible] or a combination of cyclone and cloth filters. The primary design criteria is overall collection efficiency. Even the loss of one-tenth of one per cent of the product in a 75 million pound plant represents a loss of $12,000 per year. The various methods of recovery 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

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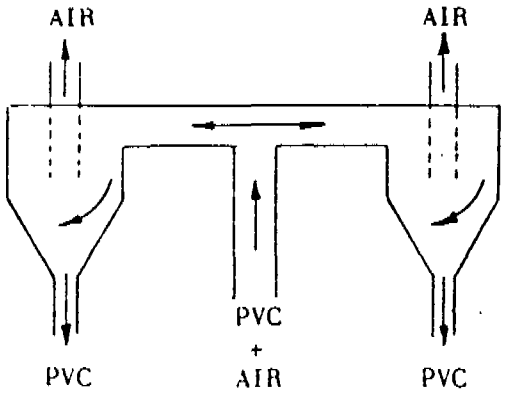
bags will cause fluffy powdering PVC to drop off. The product garnered in this manner is primarily "fines" (smaller than 270 mesh) and is designated as off-specification material. This method is not successful indefinitely and bag replacement is frequent. Continual wear on the cloth from the mechanical 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 inaide. 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.

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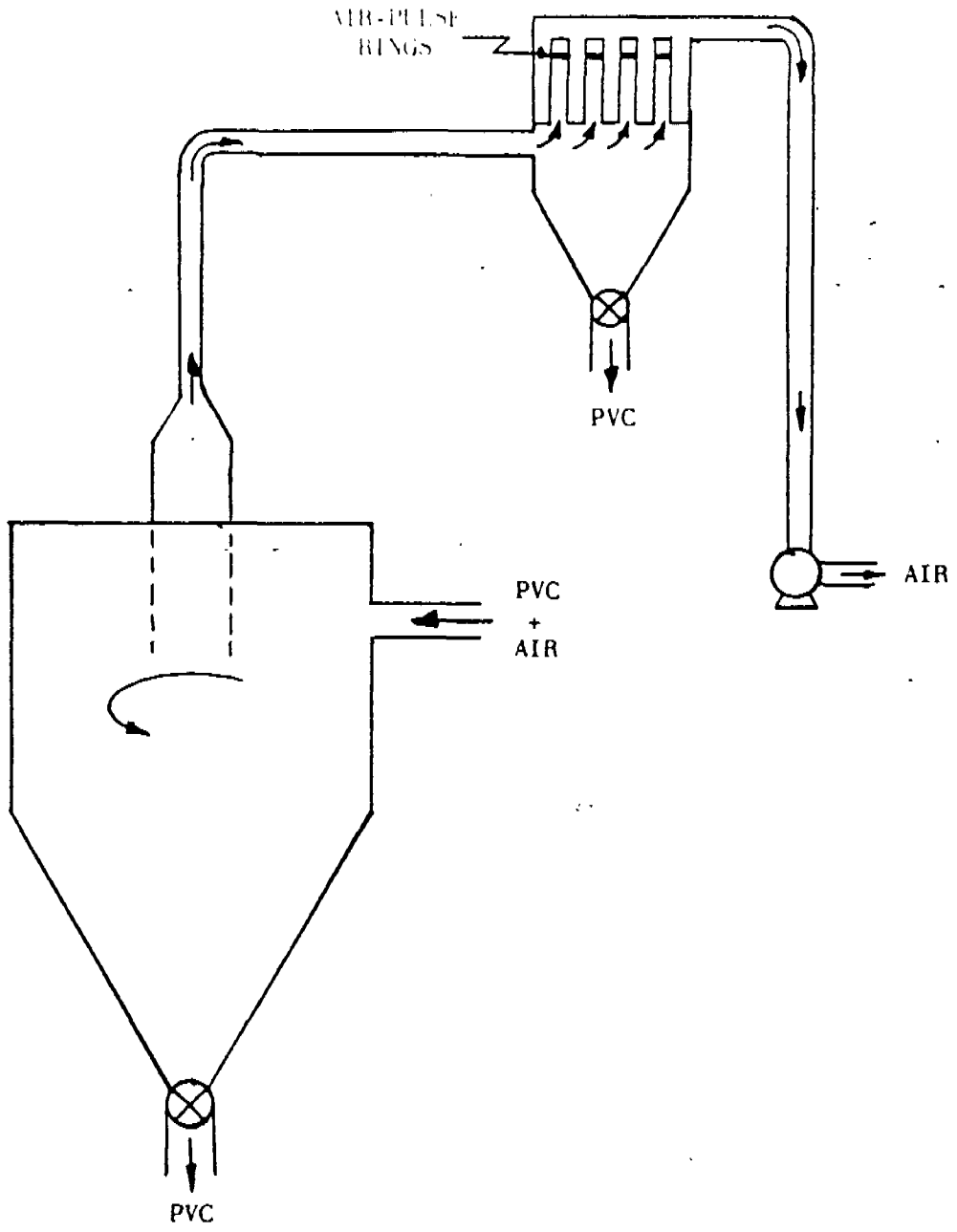

2. Ashtabula Design

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.

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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.

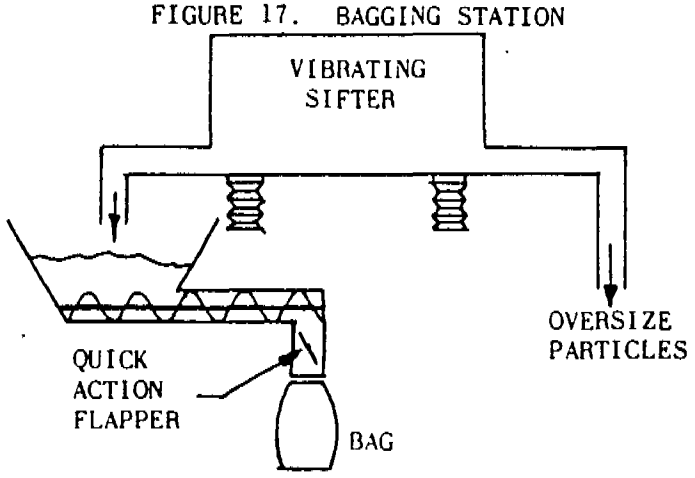
I. Dry Polymer Handling

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



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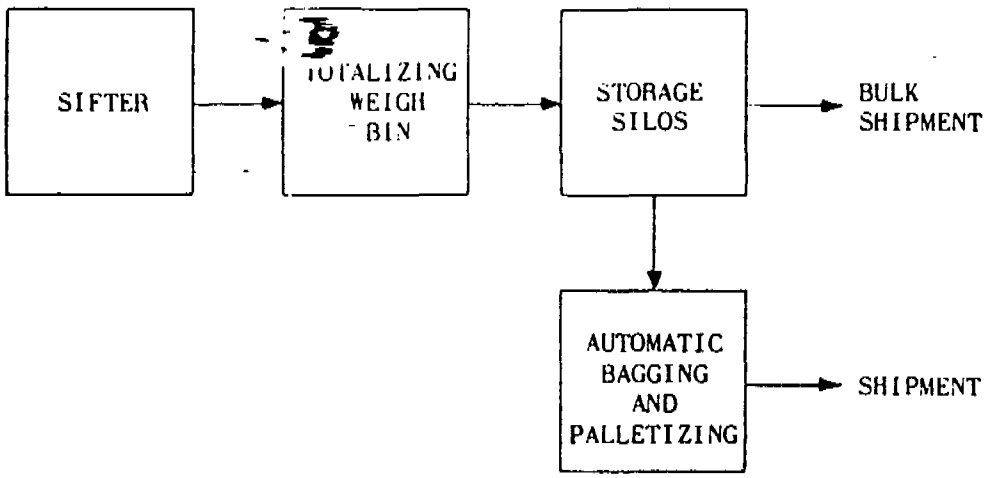
Dry product is discharged from the sifter into a hopper fitted with a bagging machine. The new bulk handling methods utilizing pneumatic conveying have changed this procedure radically. PVC fluidized with small quantities of air can be moved rapidly to and from storage. Automated bagging stations operating 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.

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[illegible] 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

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[illegible] 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

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to 1952 to an estimated 50 million pounds this year with a total 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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1. B. Goldberg, [illegible], D. Van Nostrand Company, Inc., New York, 1953

2. U. S. Patent 3,125,553, March 17, 1964

3. C. H. Chilton, Cost Engineering in the Process Industries, McGraw-Hill Book Company, Inc., New York, 1960

4. H. C. Bauman, Fundamentals of Cost Engineering in the Chemical Industry, Reinhold Publishing Corp., New York, 1964

5. R. L. Bates, P. L. Fondy, R. R. Corpstein, "An Examination of Some Geometric Parameters of Impeller Power," Presentation at Mixing Symposium, Chicago Meeting A.I.Ch.E., December 3, 1962

6. J. H. Rushton, Chemical Engineering Progress, Vol. 47, 485 (1951)

7. Friedman and Marshall, Chemical Engineering Progress, Vol 45, 482 (1949)

8. E. D. Ayers and A. W. Rhodes, Chemical Engineering, September 16, 1963, p. 157

GEHC 000487

PVC FABRICATION AND APPLICATIONS

by

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J. M. Gyenge was graduated from Baldwin Wallace College in 1943 with a Bachelor of Science degree in Chemistry. He has done graduate work at Akron University in polymer chemistry. From 1946 to 1956, he was a development chemist at the Akron Government Development Laboratories of Rubber Reserve. In The General Tire & Rubber Company's Chemical Division he has served as both Technical Service Representative and as Sales Development Engineer. He was appointed to his present position, Manager, Technical Service, in 1959. Mr. Gyenge is a member of the American Chemical Society.

George Hackim was graduated from the University of Akron in 1947 with the degree of Bachelor of Science in Chemistry. First employed by the Sun Rubber Company, he came to The General Tire & Rubber Company in 1948 in the production training program. From a first assignment in Research, he was transferred to the Chemical Division in 1950 as Manager of Technical Service and later became Sales Manager. In the newly formed Chemical Plastics Division he was: Assistant Director of Sales, 1962; General Sales Manager, 1963; and has been Vice President-Industrial Sales since early 1964. Mr. Hackim is a member of the American Chemical Society, the Society of the Plastics Industry, and is former chairman of the Akron Rubber Group.

Albert J. Hanley is Section Head of Plastic Evaluation and Application for The General Tire & Rubber Company. Graduated in 1920 from Massachusetts Institute of Technology with a Bachelor of Science degree in Chemical Engineering, he went on to serve as head of the chemistry department at Mount Saint Mary's College, Maryland, until 1926. He became, in turn, chief chemist at Textileather and Technical Director for Respro, Inc., plastics manufacturers, until these firms were absorbed by the parent company in 1955. At that time he became Group Head of Plastic Evaluation and Application until appointed to his present post in 1962. Mr. Hanley is a member of the American Chemical Society, the Society of Plastics Engineers, and the Society of Plastics Industries.

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I. Introduction

The previous papers have described how polyvinyl chloride is obtained as a granular powder. In this state, PVC has very limited use and the conversion of PVC into commercial products depends upon its modification through compounding.

The many compositions obtainable from PVC are highly adaptable to a number of operations which convert the materials into usable products. Most PVC products are obtained by calendering, extrusion, and coating techniques. Other conversion methods such as blow molding, compression molding, injection molding, and fluidized bed are used to a lesser degree.

The molecular weight of the resin, compounding, processing, and finishing all contribute to the performance and appearance of the final product. The great variety of end uses for PVC make it one of America's most thriving and expanding industries. PVC, more than any other polymer, is synonomous with versatility.

II. End Use Applications

In 1962, PVC became the world's first billion pound plastic. Figure 1 shows the sales volumes of the various classifications of vinyl for 1962 and 1963. It can be seen from the curves that calendering and extrusion captures the bulk of the market. Poundage for 1963 was greater than in 1962 in every classification except miscellaneous, and the total increase for the one year period is 18%. Indications are that 1964 will show a similar increase over 1963 and PVC seems headed toward a two billion pound market in the near future.

As PVC has grown in volume, the price has dropped accordingly, further accelerating the plastics industry's interest in the material. The current low price of 16¢/lb. contributes toward making PVC one of the first materials considered when production of a new plastic article is being planned. Though the 1.40 specific gravity of the unplasticized resin is relatively high, the pound-volume costs of the plasticized compounds are much more favorable.

This poundage is not consumed as a single product or application. PVC has widespread utility in products ranging in stiffness from rigid sheet for construction applications to flexible film for food wrapping. This extreme difference in end product application is possible because the basic vinyl polymer can be solvated by plasticizers over a range of concentrations.

All of these PVC compounds are thermoplastic in character and acquire at some critical elevated temperature a rubber-like consistency. Therefore, it is not surprising that in the early days plasticized vinyl compounds were converted or formed to shape on equipment found in the rubber industry. Experience soon demonstrated that calendering, tubing, extruding, and pressing machines for rubber were inefficient for making quality vinyl products. These same types of converting machines were modified in basic engineering design, temperature range, and automatic control in order to manufacture vinyl end-products to extremely close dimensional tolerances.

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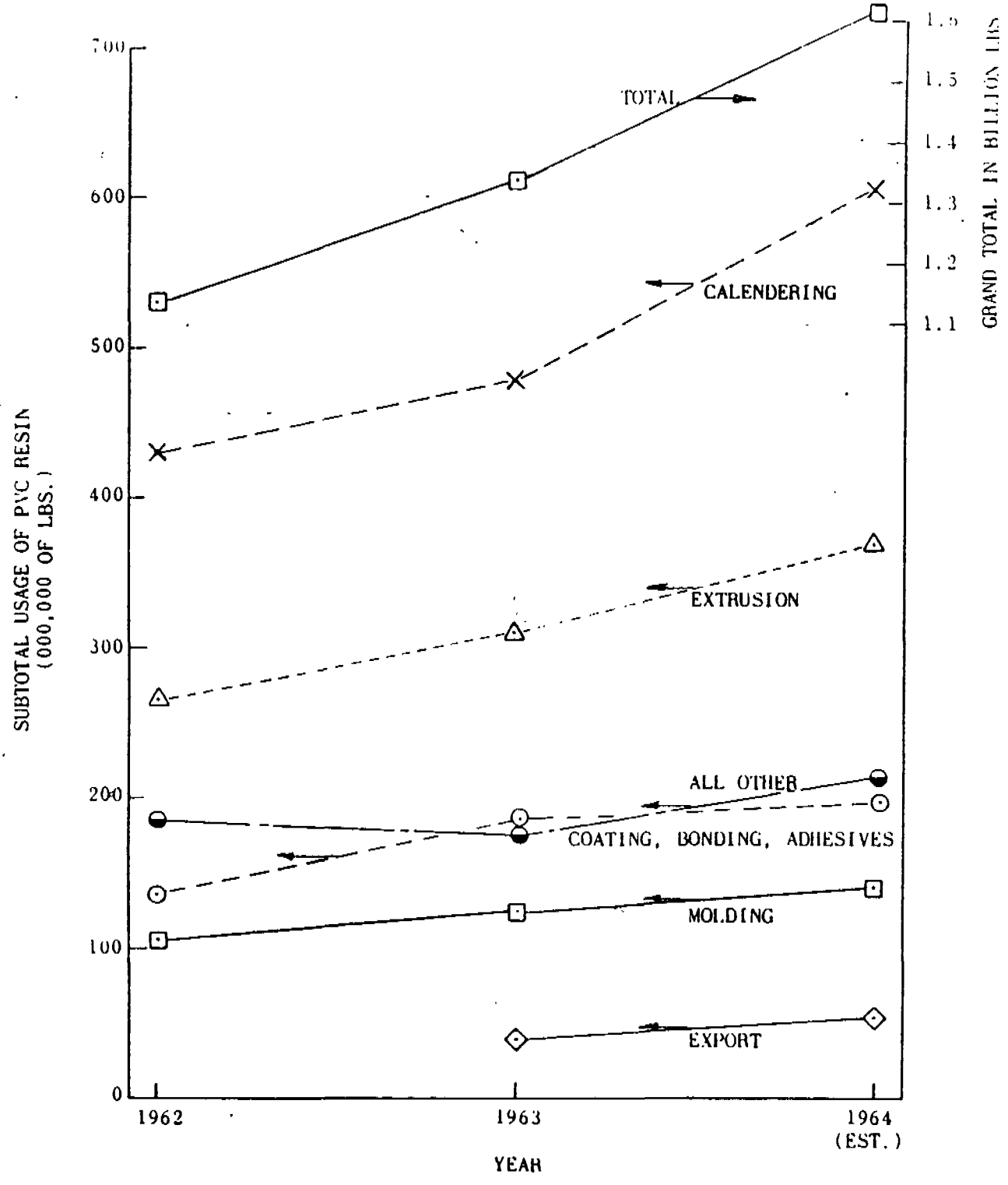
FIGURE 1. YEARLY CONSUMPTION OF PVC RESIN



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As mentioned earlier, the basic polyvinyl chloride can be polymerized by suspension, emulsion, or solution techniques. For the purposes of this paper, the emphasis will be placed on the suspension type of resin.

PVC polymer can be made in a wide range of chain lengths or molecular weights. For control and identification purposes, the molecular weight is characterized by the polymer's intrinsic viscosity in a solvent solution. The higher molecular weight polymers possess higher tensile strength and hardness, better resistance to flow at elevated temperatures, and improved solvent resistance, when compared to their lower molecular weight homologs.

Table 1

Effect of Molecular Weight on PVC Properties

Resin	Vygen 85	Vygen 105	Vygen 110	Vygen 120
Molecular Weight*	74,000	83,000	93,000	107,000
Intrinsic Viscosity	.80	.93	1.03	1.18
Tensile Strength, psi**	2160	2490	2730	2890
Ultimate Elongation, %**	230	300	340	350
Tensile Stress at 100% Elongation, psi**	1290	1400	1420	1460
Shore A Hardness,				
0 Sec.	91	91	91	92
10 Sec.	80	80	81	82
Formulation	Resin - 100 parts			
	DOP - 50 parts			
	Ba-Cd Stabilizer - 2 parts			

* D. J. Mead and R. M. Fuoss, J. American Chemical Society, 64, 277, (1942)
** ASTM D-412-61T

In a typical formulation using 50 parts of dioctyl phthalate (DOP) plasticizer per hundred parts of resin and resins of differing intrinsic viscosity ranging from 0.80 to 1.18, it can be seen that the tensile strength, elongation at break, and Shore A hardness increase with increasing molecular weight. Figures 2 and 3 show these points graphically.

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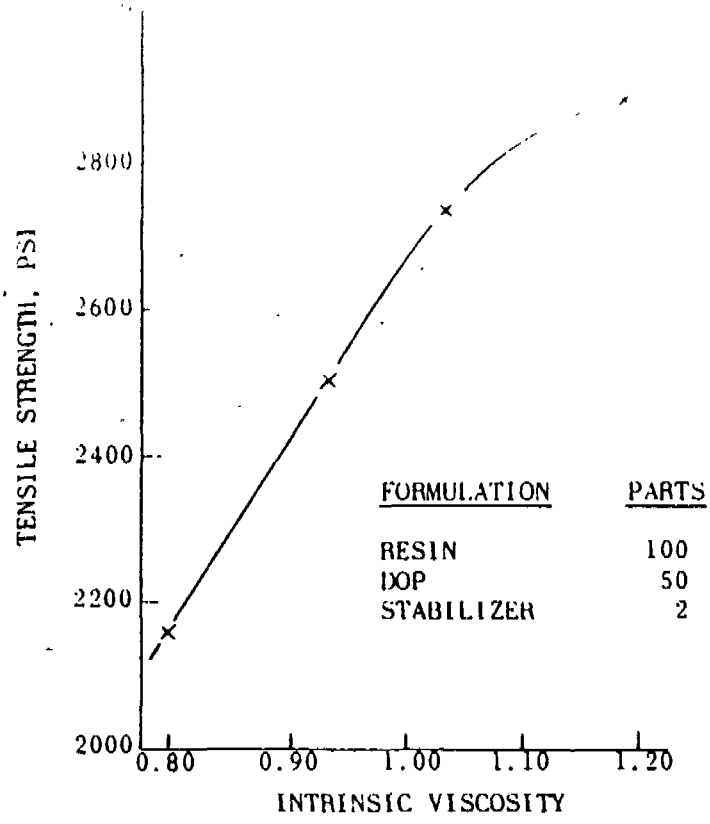
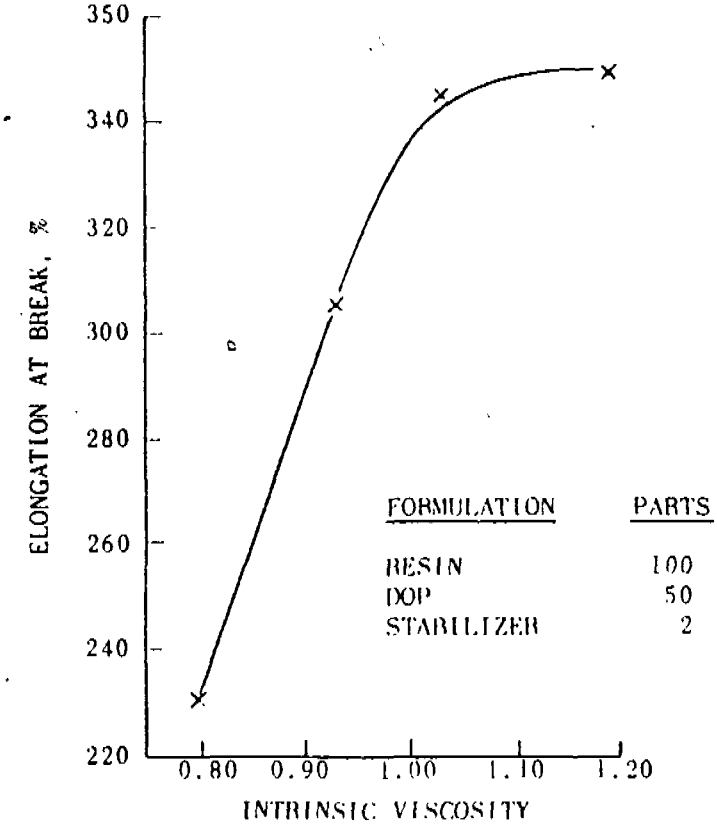


FIGURE 3. EFFECT OF MOLECULAR WEIGHT ON ELONGATION



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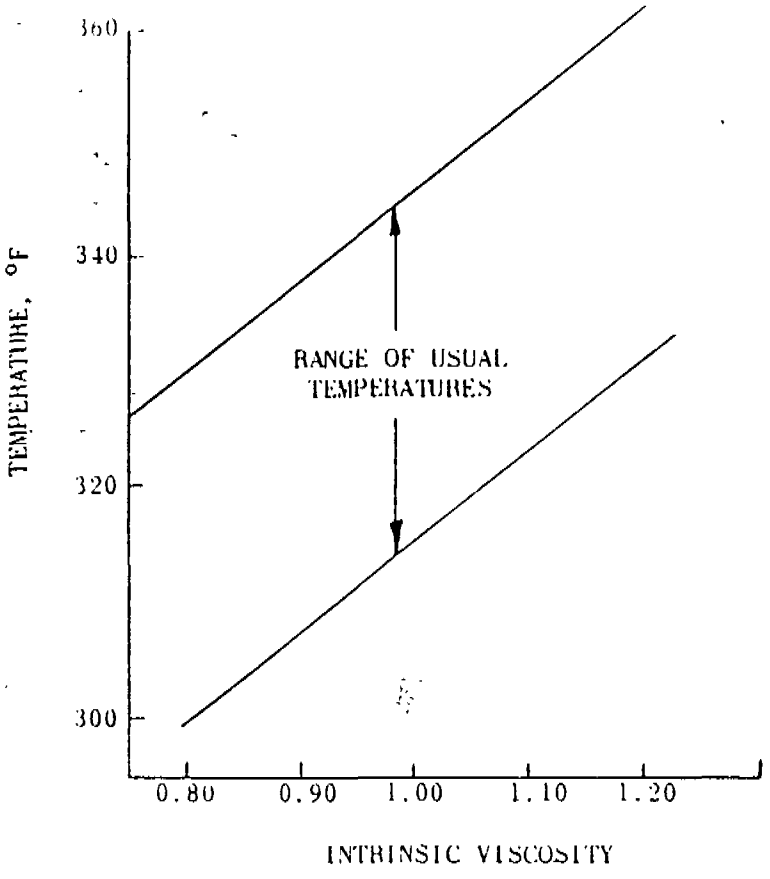
[illegible] shown in Figure 4.

FIGURE 4. EFFECT OF MOLECULAR WEIGHT ON CALENDERING TEMPERATURE



Higher processing temperatures tend to create resin instability problems if the processing cycle is of long duration. A compromise must often be made between the molecular weight resin selected and the processing technique.

The higher molecular weight resins are used in extrusions of flexible tubing, welting, electrical components, garden hose, and calendered film which require short dwell times at the elevated processing temperatures. Intermediate molecular weight resins are used in film and sheet, coated fabrics and rigid applications. Low molecular weight resins are used in fluidized bed coatings, phonograph records and injection molded parts.

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IV. [illegible] to Product

A. Compounding

1. Stabilization

Very few polymers inherently possess outstanding heat or light resistance on long term exposure, and polyvinyl chloride is no exception. The science of PVC degradation is well established and, although complicated, is known to involve the loss of a chlorine and a hydrogen atom from adjacent carbon atoms on the backbone chain. Strong alkali promotes this loss of hydrogen chloride. A slightly alkaline metallic salt will act as an acid acceptor and prevent further generation of HCl along the polymer chain. Lead salts such as basic lead carbonate or lead silicate were the earliest stabilizers used in polyvinyl chloride. Lead stabilizers are still used in electrical insulation where the service specifications require up to a 105°C temperature rating.

Organo-tin compounds such as dibutyl tin dilaurate or tin maleate are liquid at processing temperatures and can be dispersed through the PVC compound more readily than solid metallic salts. They also protect the polymer by saturating the double bond created wherever HCl is lost in the first stage of decomposition.

A major advance in stabilization was the discovery that organo-cadmium compounds are synergized in their stabilizing action by companion barium organic compounds. These systems are readily dispersed and have limited solubility in plasticized PVC compounds and make possible haze-free products of good clarity and color.

2. Plasticization

It was stated previously that polyvinyl chloride resins are capable of being compounded into a wide variety of products having different degrees of flexibility and hardness. This great versatility is possible because of the softening action of plasticizers on the hard horny resin. In general, the degree of softness of the compound will be in direct proportion to the plasticizer-resin ratio. By varying this ratio, a wide range of PVC properties can be achieved.

The chemical function of a plasticizer is dependent upon the presence of polar groups in its molecular structure. This polarity allows the plasticizer molecules to be inserted between PVC resin molecules, neutralizing the Van der Waal or secondary valence bonds. This weakening of the Van der Waal forces creates localized flexible areas intermingled with resin strength areas. The combination results in a strong, yet pliable, polymer.

There is evidence that the plasticizer swells the amorphous regions and that the small regions of crystallites are unattacked or unaffected by the plasticizer. This situation is unique to polyvinyl

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[illegible] being weak, [illegible] have good abrasion resistan[illegible]

Commercial products of satisfactory durability require that the solvent or plasticizing agent have long term permanence. The plasticizer should be at least as permanent as the properly stabilized resin. To be permanent, the plasticizer must either be a true solvent or be associated with a true solvent for the PVC resin. The plasticizer must resist oxidation both during processing and during long term in-use aging for periods up to five or more years. Its affinity to the resin must be greater than to foreign substances which would normally contact the PVC product in service. For upholstery, these substances would include resistance to wicking into clothing, dust or dirt, and soapy water washing. It must have a very low volatility to eliminate evaporation. It should be odorless and colorless in order to have widespread utility. When the material in question meets these specifications to a practical degree, it becomes known as a primary PVC plasticizer.

Ordinarily, a plasticizer will be a high molecular weight ester formed by the reaction of an aliphatic alcohol of eight to twelve carbon chain length with an acid which may be either phthalic, azelaic, adipic, or sebacic. Polymeric forms of esters are usually in the 2000-5000 molecular weight range. These plasticizers are used where special permanence is required.

Plasticizers are commonly liquids with viscosities which may be as low as a light oil or as thick as honey. They vary widely in their efficiency in flexibilizing the PVC resin and the particular properties contributed to the PVC product. For this reason, it is common practice to blend a mixture of plasticizers to obtain a compromise of their individual assets and defects. It is this type of blending that makes vinyl products so versatile.

Figures 5, 6, and 7 show the effect of DOP plasticizer (di-octyl phthalate) concentration on the tensile strength, elongation, and Shore A Hardness of a Vygen 120 formulation.

Where exceptional permanence or dimensional stability is demanded, chemically bound copolymers and physical polymer blends provide the answer. Nitrile rubber (butadiene/acrylonitrile) can be used, although its poor color limits it to dark colored applications. Other polymers used for modification are chlorinated polyethylene, acrylics, and acrylonitrile-butadiene-styrene (ABS) resins.

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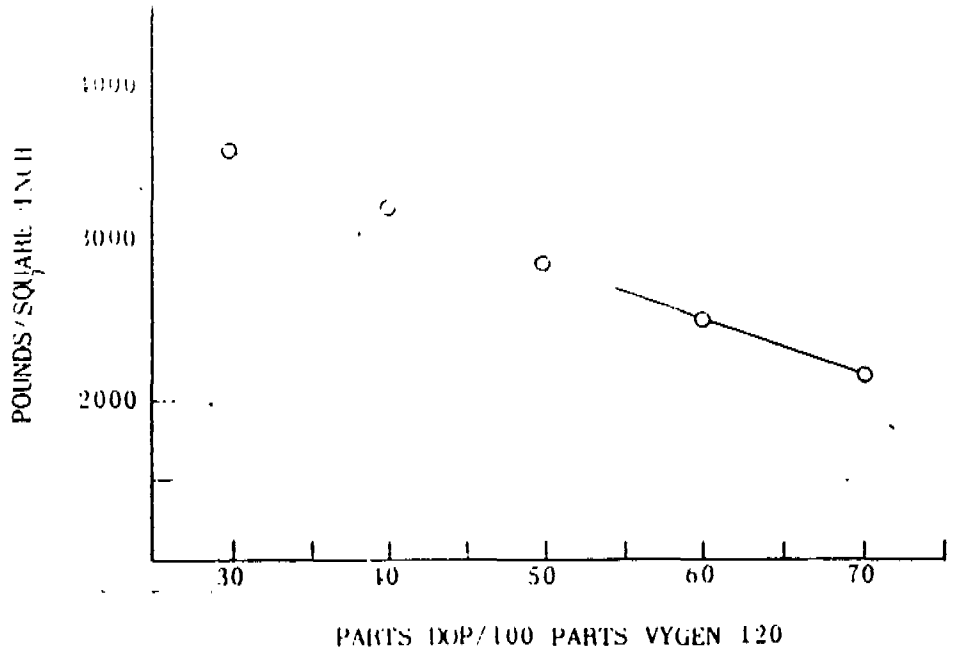
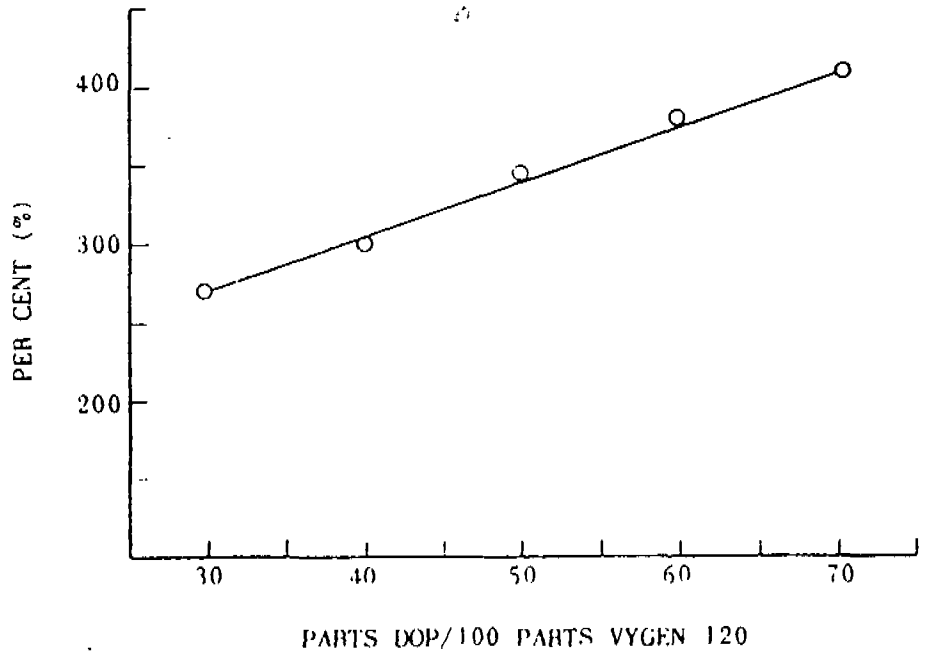


FIGURE 6. EFFECT OF DOP LEVEL ON ELONGATION



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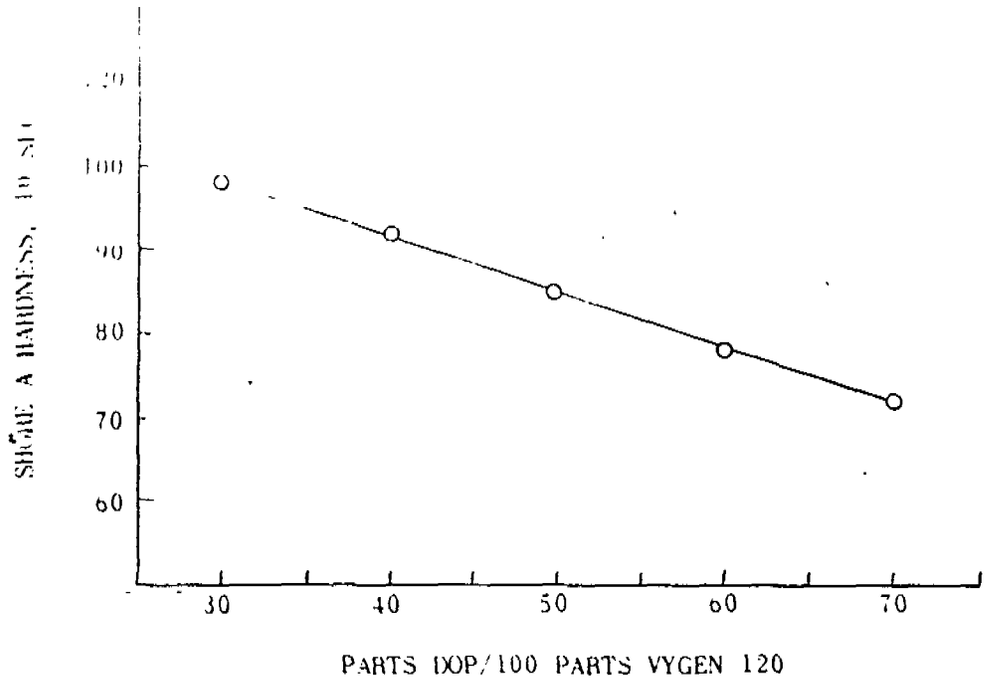

3. Lubrication

Vinyl is processed and formed by metallic parts which may be a set of rolls, a forming die, a mold, or some other device. During this processing, the vinyl must adhere to the metal so that the plastic draws in, fills, and flows with the forming surfaces. However, this adhesion must not be great enough to cause distortion when the article is removed from these metal surfaces. Adequate parting is obtained by including in the compound trace quantities of lubricants that act as metal release agents. The release agents are soluble to only a limited degree in the vinyl compound at the processing temperatures. Thus, minute particles of the release agent are deposited on the hot metal surfaces and form a semi-continuous coating. Excessive quantities of the release agent should be avoided to prevent exudation on the finished PVC surface. Exudation of lubricant appears after processing and is not only unsightly, but can interfere with the application of decorative finishes or subsequent dielectric heat sealing. Stearic acid is a common release agent, but metallic stearates, waxes, or polyethylene have been used. Proper technology in the use of lubricants is an important factor in successful production of vinyl products.

4. Pigmentation

The growing use of PVC has been due in part to the color possibilities of the plastic.

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[illegible] and [illegible] upholstery [illegible] to the [illegible] colors to match or contrast with any [illegible]. PVC sheeting having superior durability is produced in colors and textures which offer unlimited creative styling possibilities to the designer. The pigments used must be acid resistant, stable to the processing temperatures up to 400°F, nonmigratory, and light stable. The pigments are dispersed to a fine particle size by grinding in a three-roll paint mill with part of the plasticizer. Satisfactory pigments include titanium dioxide, phthalocyanine blues and greens, and high tint carbon blacks.

Fillers are often used for cost reduction. Finely divided calcium carbonate is most often used, but clay, asbestos, and other fillers are common. Certain electrical properties are improved through the use of fillers. Flame resistance is bolstered through the incorporation of [illegible]timony trioxide and phosphate plasticizers. Electrical properties are improved with the addition of calcined clay.

B. Processes and Fabrication

1. Dryblending

A PVC compound initially is a heterogeneous mixture of the many components. The major ingredients are a PVC resin powder and a liquid plasticizer which must solvate the resin. The solvation rate of this type of system is time and temperature dependent. The most economical method of solvating the resin is through the use of inexpensive mixing equipment with large capacities. Thus, large stainless steel chambers jacketed for heating are used to churn, tumble, or agitate three to five thousand pounds of the compound. At this stage, only the colorant is omitted. The temperature is maintained at 180° to 200°F for about an hour. This equipment is often a ribbon blender.

2. Banburying

Part of the presolvated resin-plasticizer masterbatch from the preblender, together with the pigment paste, is fused into a homogeneous mass in an intensive shear internal mixer such as a Banbury. This machine consists of a two cylindered stator containing two powered rotors. Their operation is such that the plastic compound is sheared against and around the stator's surfaces. The stators and/or the rotors are heated to raise the temperature of the vinyl compound to its fusing temperature between 300-350°F. A plunger retains the compound within the chambers and a sliding door in the bottom of the chambers allows the fused homogeneous compound to be discharged. The capacity of production size Banburys for the vinyl industry varies from a 110 to a 600 lb. batch delivered on five minute cycles.

3. Milling

Normally, a Banbury batch is delivered to one or more 60" to 90" wide two-roll mills designed for high temperature operation. The

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[illegible] shipped in a high speed Banbury [illegible] plastic to a controlled temperature and, therefore, a [illegible] plastic consistency, and able to deliver the plastic in a ribbon of predetermined width and gauge of thickness. This ribbon stock can be fed directly to a calender or an extruder in practically an ideal plastic state, or it may be partially cooled and fed to a dicer or pelletizer to make a reserve compound inventory for future processing.

4. Calendering

A large percentage of the above mill-prepared vinyl plastic compound is fed to a calender which converts the crudely shaped ribbon into continuous lengths of film, sheeting, or coating for a substrate (i.e., woven cloth, knit fabrics, or paper, etc.) of surprising accurate widths and thicknesses. For example, a modern plastic calender is capable of delivering a 0.0018" gauge film with a maximum variation in gauge of ± 0.0001". Normally, film of this gauge can be more economically produced by extrusion, since a two million dollar calender train must have a high poundage output to justify its capital investment.

A modern calender engineered for handling plastics has four cast chilled iron rolls mounted in a Z type frame so that the influences of forces on any one roll can affect only one adjacent roll. A roll with a working face of 66" width will be from 20" to 24" in diameter while a 96" width roll face will have from 30" to 36" in diameter.

This calender will be automated both to control the gauge of the film and also to emboss, cool, and deliver the film to the packaging unit. These devices and their controls in the calender train represent an investment of a million dollars. The output production of a calender is dependent upon the gauge of the plastic delivered and generally falls in the range of 2000 to 3000 lbs. per hour for a 66" width machine.

The ordinary plastic calender produces film between 0.003" and 0.005" gauges to be used for raincoats, shower or window curtains, aprons, baby pants, food covers, and similar articles. Film between 0.005" and 0.010" gauges is used for inflatable toys, air mattresses, industrial protective covering, and electrical tape. Sheeting between 0.016" and 0.022" is used for novelty purposes such as ladies handbags, belts, wallets, and briefcases. All of these gauges are used for coating fabrics or paper that are widely used in upholstery, rainwear, apparel, boat decking, shoe trimmings, book covers, and many other uses.

Table 2 shows a typical formulation for a General Purpose Film.

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Typical PVC Formulation

General Purpose Film

		Parts
Resin:	Vygen 110	100.00
Plasticizers:	DOP	37.00
	Cresyl diphenyl phosphate	8.00
	Monomeric epoxy plasticizer	5.00
Processing aid:	Stearic acid	0.25
Stabilizer:	Ba-Cd	2.00

5. Extrusion

A second method for shaping a molten plastic into a desired shape is with an extruder. This device consists of a smooth bore cylinder with a close fitting worm screw rotating inside the cylinder. PVC compound as cold pellets, cold dry blended powder, or hot mill ribbon is fed to the extruder. It is homogeneously mixed and brought to its proper working viscosity for ultimate forming by the mechanical energy of the screw and the heat provided by the controlled temperature cylinder or barrel. The changed pitch of the screw at its end alters the screw's function from masticating and mixing to that of a positive displacement pump. The orifice or die mounted at the head of the screw is similar in shape to the desired product. The shaped extrudate is drawn in a measured degree from the die to the cooling medium, usually water. The die must be designed in such a fashion as to compensate for the change in dimensions and shape that this pull or draft exerts on the hot extrudate.

The extruder can form flat film, sheeting, and coated products similar to the products of a calender and, in addition, make hollow articles and complex shapes impossible to obtain from a calender. It is considerably less costly to install, but has only a small fraction of the capacity of a calender.

Film as thin as ¼ mil can be extruded by the blown film technique. A tube with a wall thickness of 0.012" is extruded. As the tube of hot plastic issues from the extruder, air is introduced inside the tube in sufficient quantity to expand the plastic to a 72" diameter cylinder. This simultaneously widens the film and reduces the gauge of the wall thickness. The percentage gauge tolerance of this film is far greater than the ± 5% allowable for calendered film, but it is adequate for film used in packaging applications.

An alternate procedure to blown film is the use of a slit die with dimensions approximately equal to that of the film desired. This die requires a high degree of engineering sophistication to produce uniform flow of the PVC plastic across wide widths and especially to prevent any sectional areas in the flow of the PVC plastic that are slow moving or "dead." This latter condition can lead to

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[illegible] die extrusion is true plastic forming. The films produced are conform to close tolerances in gage not possible with blown film. Lamination of the hot film directly to a preheated substrate such as a fabric or paper is possible with slit die extrusion. Milk carton paper is often coated in this manner.

The extruder is used for making film, monofilament strips, rods, tubing, hose and profile shapes such as refrigerator gasketing. Table 3 shows a typical PVC refrigerator gasket compound.

Table 3

Extruded Refrigerator Gasket

		Parts
Resin:	Vygen 120	100.00
Plasticizers:	Polymeric epoxy plasticizer	10.00
	Polymeric plasticizer	80.00
Filler:	Calcium carbonate	25.00
Stabilizer:	Ba-Cd	1.50
Processing aid:	Lubricant	0.25

The extruder is the universal device used for PVC coating of electrical wire. In this latter application, the copper wire is preheated, passed through a cross head on the extruder and carefully centered in a circular stream of extruding plastic so that an even coating surrounds the wire. The wire is pulled at a constant rate of speed and actually aids the production rate of the extruder in assisting the flow of the plastic. A cross head is a device for changing the flow of the plastic to a right angle with its normal flow.

The capacity of an extruder is rated by the diameter of its cylinder. Extruders are available in a range from 1½" to 12" with the 2½", 4½", and 6" the most popular sizes. Their output capacities are about 175, 500, and 1000 pounds per hour, respectively. The technology of the action of various thermoplastic materials during extrusion has received intensive study during the past five years and many plastics have had their behaviour reduced to mathematical terms. For example, screw design has been keyed to specific thermoplastic compositions and the proper ratio of the length of the screw to its diameter (L/D) has been established. Plastic extruders normally have an L/D of at least 20/1 and often are 30/1.

As in the case of calendering, the process of cooling the extrudate and handling during postforming are highly developed operations which affect the surface characteristics, clarity, flatness, shape, and gauge of the product.

a. Rigid Vinyl

Rigid PVC contains only a small amount of plasticizer or none at all. Two types of rigid PVC are available. Type 1 possesses

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[illegible] distortion, and weather resistance. Type 2 has [illegible] electrical and physical properties but has better impact resistance, up to 20 times that of Type 1. The impact strength provided by the inclusion of nitrile rubbers or modifying resins, along with stabilizers, fillers, and additives. Fabrication of Type 2 is easier and surface defects are less of a problem. Types 1 and 2 PVC are used in electrical conduit, pipe, construction panels, tank linings, valves and skylights, and many other rigid applications. Table 4 shows the effect of molecular weight and resin modifier on the physical properties of rigid PVC. The use of the ABS resin provides a substantial increase in impact resistance.

Table 4

Effect of Molecular Weight and Modifying Resin on Rigid PVC Properties

Resin	Intrinsic Viscosity	1	2	3	4	5
Vygen 65	0.70	100	-	-	-	-
Vygen 85	0.80	-	100	-	70	-
Vygen 120	1.18	-	-	100	-	70
ABS*	-	-	-	-	30	30
Properties						
Tensile Strength, psi		7,750	7,775	7,850	6,150	6,250
Flexural Strength, psi		11,750	12,000	12,500	9,225	9,600
Flexural Modulus, psi		4.2×10^5	4.2×10^5	4.4×10^5	3.3×10^5	3.6×10^5
Notched Izod @ 77°F, ft. lb./in.		0.44	0.50	0.80	14.0	18.0
Heat Distortion @ 264 psi, °C						
10 mil deflection		69	69	75	66	72
60 mil deflection		75	76	80	74	78
Rockwell "R" Hardness		115	115	116	107	108

* Acrylonitrile-Butadiene-Styrene resin

b. Vinyl Foam

Vinyl foam may be prepared from suspension resin by extrusion. Nitrogen compounds which decompose under heat are used to provide the gas needed for expansion. The decomposition temperature is adjustable by a post expansion technique. In this process, the material is extruded at a temperature below the blowing agent decomposition temperature; subsequent expansion

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[illegible] densities of seven pounds per cubic foot by [illegible].

High density (40 lb. cu. ft. and higher) closed cell foam is to be produced by direct extrusion and blowing of the compound within the barrel of the extruder. Expansion occurs upon the emergence of the compound from the extruder head.

Closed cell vinyl foams are also made from blends of vinyl and nitrile rubber. The proper relationship must be maintained between the cure of the nitrile and the decomposition of the blowing agent, since the curing nitrile supports the cellular matrix. Too rapid a cure leads to ruptured cells; too slow a cure results in lost gas, giving high densities. Proper balancing of the system gives densities as low as four to six pounds per cubic foot.

6. Blow Molding

Blow molding is a well-accepted process for the production of plastic bottles especially, but the use of vinyl in this process in the U.S.A. has not reached the volume which it enjoys in Europe. The slower growth of blown PVC bottles in this country has been due to a lack of stabilizers which will permit clarity of the finished bottle and still pass the toxicity requirements of the Food and Drug Administration.

Blown PVC bottles do show superior properties to polyethylene types. In addition to high clarity and good oil resistance, PVC bottles have 1/10 the oxygen permeability of similar PE bottles. Due to the high rigidity of PVC, thinner walls can be used.

An extruder is the source of the prepared hot plastic compound for blow molding. In this process a cylinder of hot plastic falls in a vertical position below the extruder head and between the opening of a split mold. The split mold closes to pinch the ends of the plastic, making a sealed tube. A hypodermic needle penetrates the interior of the sealed tube, and pressurized air is injected to expand the sealed tube until it fills the mold cavity. The cold or relatively cold mold converts the plastic to its hardened condition in a few seconds. The mold opens and discharges the molded object, and the cycle repeats itself automatically. The formed object may be a waste basket, an automobile arm rest, or a part of a toy doll, although PVC bottles have one of the most interesting possibilities for future markets. This is an intricate art requiring extremely accurate control of the temperature (i.e., viscosity) of the PVC compound.

Clarity is achieved through proper compounding and is based mainly on the stabilizer used, although the chilling rate of the hot article, particularly bottles, is also important. A rapid chill usually improves the clarity. Some degree of clarity is lost due to the increased molecular weight needed for impact strength.

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[illegible] processing temperatures.

Stabilizers and those FDA are primarily zinc and calcium types. However, these materials give less protection at processing temperatures than the barium-cadmium and tin types. The success of PVC blow molding in Europe is due to the use of di-octyl tin compounds, which are as yet unacceptable in this country.

As more acceptable stabilizers are developed, a large market will be created for PVC bottles where other thermoplastics are unacceptable. The future should see PVC bottles used to package gasoline, motor and mineral oils, polishes and insecticides, cosmetics, perfumes, disinfectants, detergents, foods, and soft drinks.

7. Compression Molding

The molders of phonograph player records consume large tonnage of vinyl compounds for compression molding of their disks. They use a low molecular weight homopolymer or copolymer resin for this purpose and the application is a specialized industry. Clear rigid sheeting as windows for instrument panels, flexible clear sheeting as rear windows in automobiles and novelty applications, are also press molded.

8. Injection Molding

PVC compounds are used to a limited extent in injection molded parts. The rotating plasticating screw plunger type of machine is definitely preferred in processing vinyl.

9. Fluidized Bed Coatings

The fluidized bed coating technique is excellent for coating intricate metallic parts. This can be done with a powder blend containing all plasticizers, pigments, and stabilizers. The more popular and successful method is to fuse the powder blend and to then pulverize it into a fine powder.

The coating technique is to heat the part to be coated to a temperature in excess of 450°F. The heated part is then suspended in an environment of the powdered resin blend which is fluidized with a stream of air. The thickness of the fused layers can be controlled very accurately. Repeated dippings can build up thick and uniform coatings.

10. Contour Forming

Irregular formed parts, such as automotive crash pads, are usually made from flat sheets which are postformed to the desired shape. The most common procedure is to use the vacuum forming system.

In this technique the flat sheeting is softened by radiant heat to the forming temperature. The preheated sheet is then placed over

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a female mold, a vacuum is drawn to evacuate the atmospheric air pressure causes the vinyl sheeting to flow and fill the contours of the mold. Since the mold is cold, the vinyl sheet loses its heat rapidly and can be lifted from the mold a minute or two later.

An alternative type of molding to vacuum forming uses air pressure to distort the hot vinyl sheeting into a female mold providing it is equipped with holes for the escape of air entrapped in the molds. The use of matched male and female molds results in products with the closest dimensional tolerance.

II. Assembly of PVC Products

PVC products are readily cut to size in multiple layers by the commonly employed motor driven circular knives or by cutting with pattern shaped dies.

Dielectric heat sealing is often used to seal PVC films and flexible sheets. In the process, the PVC to be joined is placed between two electrode sealing bars which transmit a high frequency current to the PVC and exert the required pressure on it. Heat provided by friction from shifting of the polar chains within the material causes the films to flow together and seal. The resultant seams have bond strengths equal to the strength of the goods.

The use of recommended solvent cements to make assemblies is as satisfactory as dielectric sealing and are used for large objects such as in tent-making or swimming pools. Fabric backed or supported PVC products are sewn with thread as in upholstery assembly.

C. Decorative Effects

A high percentage of vinyl resin products are consumer items and dependent upon their attractive surface appearance and style to sell. These effects are obtained by either embossing or printing the colored surface, or both.

1. Embossing

Embossing of the plastic is achieved using steel rolls engraved with impressions that will give a pleasing appearance. These rolls are mounted over rubber backup rolls in the calender or extruder train as close to the forming orifice as possible. At this location, the plastic sheet is in its ideal rheological condition to form into and permanently retain the configuration of the delicate engraving pattern of the embossing roll.

2. Printing

The majority of automotive upholstery is currently finished in metallic effects across the entire surface. These chrome tones cannot be obtained directly from the calender since the aluminum flake does not have an opportunity to "leaf" as it does in a highly

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[illegible] a rotogravure print [illegible] the fabric is subsequently [illegible] flow of solvent.

Design print falls into two classes. There are the delicate and subtle shadings associated with high grade leather effects and the gaudy and often multi-color effects of houseware and apparel materials. These are also applied on rotogravure print machines equipped with print rolls having the appropriate design engraved into their surface. At times, print machines must have up to eight stations applying different colors which print in register to make a flower reproduction.

D. Mixing and Processing of Plastisol Resins

So far we have discussed how PVC suspension produced resins are compounded and processed. Plastisol resins are handled and processed in an entirely different manner. Plastisol compounds are made so that when the resin is blended with a liquid plasticizer, the mixture is in the form of a fluid.

Plastisol resins are often termed "stir-in resins," for a common method of blending a plastisol resin formulation is the use of a simple agitator. Hi-shear mixers are quite common, although practically any method by which the resin can be dispersed uniformly in the plasticizer and/or solvents is acceptable.

In the blending process, the liquids in a formulation are charged to a vessel and agitated until mixed. Then the plastisol resin and other powders are added gradually under agitation until all materials are charged and a uniform liquid, called a "plastisol," is produced. When organic solvents are included in the formulation, the liquid is termed an "organosol." The solvents are used as viscosity reducing agents. The rheology of these liquid systems is quite critical, since they are processed by methods where the flowability must be closely controlled. Plastisols are used in the following ways:

1. Dip Coating

A widely used process is dip coating. In this process, an article, such as a wire dish drainer, is dipped into the plastisol and removed. The coating is then fused onto the dipped article in forced draft ovens. When an organosol is used, the heating of the article must be carried out in two stages. The first stage consists of evaporation of the solvent under low heat; the second stage consists of fusion of the vinyl. In this way, surface imperfections due to boiling solvent during fusion are eliminated. Usually, a solvent recovery system is installed in plants using organosols for reasons of economy. In a variation of this process, cotton gloves on metal hands are dip coated in order to impart chemical protection and solvent resistance to work gloves. Articles too large for dip coating may be sprayed with plastisol and subsequently fused.

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2. Slush Molding

Slush molding is, in a sense, the reverse process of dip coating. In this process the plastisol is poured into a heated mold. The pot is then inverted and only a coating of the gelled vinyl remains in the mold. Fusion and stripping of the article from the mold complete the process. Boots are made by such a technique. The main restriction of slush molding is that the article must have at least one sizeable opening to the interior to permit filling and emptying the mold of plastisol.

3. Rotational Molding

Rotational molding is much like slush molding, except that there need be no opening in the article for the introduction of plastisol. It is used for complex shapes like dolls' heads, arms, etc. It is also used for play balls, footballs, and basketballs. In the technique, a quantity of plastisol is poured into a mold, the mold is closed and rotated in three dimensions while heat is used to fuse the formulation inside. Temperatures must be controlled so as to permit even fusion and uniform flow characteristics.

4. PVC Foams

PVC foams are easily prepared from plastisols. Either a chemical which decomposes under heat or a mechanical entrapment of gas may be used. The plastisol is often laid down as a thin coating over another vinyl layer which may or may not be fused. When blown, the combination is effectively used as an insulating material resembling leather for use in outerwear. The areas of cushioning and insulating are more often captured by urethanes or polystyrenes.

GENC 000510

[illegible], [illegible], [illegible], New York, 1956

2. Schildknecht, Calvin Everett, Vinyl Polymers, Wiley and Sons, New York, 1952

3. Bernhardt, Ernest C., Processing of Plastic Materials, Reinhold, New York, 1959

4. Cope, Dwight, Plastic Materials, Goodheart-Wilcox Co., Chicago, 1956

5. Esterez, J. M. J. and Powell, D. C., Manipulation of Thermoplastic Sheet, Rod and Tube, Iliffe & Sons Ltd., London, 1960

6. Simonds, Herbert Rumsey, Source Book of the New Plastics, Reinhold, New York, 1959

7. Frados, Joel (Editor), Modern Plastics Encyclopedia for 1964, Vol. 41/ No. 1A, Hildreth Press, Inc., Bristol, Connecticut, 1963

8. SPI Plastics Engineering Handbook, 1960

GENC 000511

1. Faith, Keyes, Clark, Industrial Chemistry (New York: John Wiley & Sons, Inc., 1950), pp. 34-37

2. Personal Communication, Union Carbide, Ashtabula, Ohio

3. Schoch, E. P., "Acetylene from Hydrocarbons," University of Texas Publication, No. 5011 (June 1950), pp. 34-41

4. Bixler, G. and C. W. Coberly, Industrial & Engineering Chemistry, Vol. 45, No. 12 (December 1953), pp. 2596-2606

5. Ibid 1, pp. 37-39

6. "Petrochemical Handbook," Petroleum Refiner, Vol. 38, No. 11 (1959), p. 202

7. Union Carbide Acetylene Analysis

8. Kennedy and Holm, "Divinylsulphide in Commercial Acetylene," Canadian Chemistry & Process Industries (October 1959)

9. Ibid 6, p. 298

10. Monsanto U. S. Patent 757,661 (1954)

11. Wesselhoft, Woods, Smith, "Vinyl Chloride from Acetylene and Hydrogen Chloride: Catalytic Rate Studies," A.I.Ch.E. Journal, Vol. 5. (September 1959), pp. 361-366

12. Frescoln, The Production of Vinyl Chloride in a Fluidized Catalyst Bed, Ph. D. Thesis, Case Institute of Technology (1951)

13. Locher, Trans. Faraday Society, Vol. 58 (1962)

14. Ibid. 6, p. 238

15. Ibid. 1, p. 367-368

16. LaChimica e L'Industria 33 (1951), pp. 613-619

17. "Petrochemical Handbook," Petroleum Refiner, Vol. 34, No. 12 (1955), p. 1960

18. Ibid 15

19. "Industrial Vinyl Chloride," The Chemical Age, (December 1951), pp. 801-803

20. Ibid 15

21. Doraiswany, L. K. P. H. Brohme, M. V. Pai, and S. Chidambarum, "A Study of the Kinetics and Thermodynamics of a Reaction Producing Vinyl Chloride," J. Chem. & Engineering Data (New York: Reinhold Publishing Company, 1962)

22. Barton and Howlett, J. Chem. Soc. (1949), p. 155

BENC 002513

23. "Petrochemical Handbook," Petroleum Refiner, Vol. 42, No. 11, [illegible], pp. 239-240

24. Belgium Patent 598,251, Societe Belge De L'Azote et des Products Chimiques du Marly (1960)

25. Chemical Week, (March 18, 1961), p. 41

26. "Vinyl Chloride from Dilute Acetylene Gases," Industrial & Engineering Chemistry (April 1954), p. 633

27. "Oxychlorination," Chemical Week (August 22, 1964), p. 94

28. "HCl: PPG Finds Possible Way Out of By-Product Glut," Oil, Paint, & Drug Reporter (September 24, 1962)

29. Ibid 27, p. 99

30. "A Package Deal for Making Vinyl Chloride," European Chemical News (March 20, 1964), p. 29-31

31. Ibid 27

32. Oil, Paint, & Drug Reporter (August 10, 1964), p. 24

33. Ibid 30

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GENERAL TIRE
SUSPENSION PROCESS

THE GENERAL TIRE SUSPENSION PROCESS

by

D. J. CLARK
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GENC 000515

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.