

A CRITICAL REVIEW OF METHODS
FOR CONTROLLING EMISSIONS OF VINYL
CHLORIDE INTO THE WORKPLACE AND COMMUNITY

A Thesis submitted to the
Division of Graduate Studies
of the University of Cincinnati
in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in the Department of Environmental Health
of the College of Medicine

1976

by

Thomas E. Kupferer
B.S. ChE. University of Louisville, 1971

CTL030574

ACKNOWLEDGEMENTS

The following work would not have been possible if it were not for the timely and unselfish assistance which this writer received from many individuals and organizations. Special thanks are due my advisor, Mr. Lawrence J. Schafer, whose guidance, assistance and friendship have been of constant benefit in the course of my studies. This author also wishes to express deep appreciation to the B. F. Goodrich Chemical Company and its employees, especially Mr. Ken Pember, Mr. James D. Fannin, Mr. Ronald L. Martin, Mr. Daniel P. Anderson, and Mr. William C. O'Brien. This organization and these men, accorded me the great service of spending many man-hours candidly discussing the vinyl chloride problem and providing a first-hand view of control techniques in use in the industrial environment. Special thanks are also due the Air Products and Chemicals Company and their representative, Mr. Thomas W. Herbig, for providing a complete file on their training and control program. The author would also like to take this opportunity to express appreciation for assistance in locating information to Mr. Loren Anderson and Dr. Martha Radike of the Kettering Laboratory, Captain Phil Brown of the U. S. Air Force, Mr. Clifford Shotwell, Mr. Bob Hughes and Mr. Jay Jones of the U. S. National Institute for

CTL030575

ACKNOWLEDGEMENTS (continued)

Occupational Safety and Health, and Mr. John Knight of the U. S. Environmental Protection Agency. Acknowledgement is also paid to the Air Force Institute of Technology whose sponsorship has made my studies possible. Finally, the greatest appreciation goes to my wife, Sylvia, for having constantly provided support and encouragement throughout this entire project.

CTL030576

TABLE OF CONTENTS

<u>Chapter</u>	<u>Title</u>	<u>Page</u>
I	INTRODUCTION	1
	A. Background of the Vinyl Chloride Problem	1
	B. Brief History of Vinyl Chloride	4
	C. Methods of Production of Vinyl Chloride	6
	D. Methods of Production of Polyvinyl Chloride	15
	E. Health Effects of Vinyl Chloride	28
II.	METHODS OF CONTROL IN THE WORKPLACE	34
	A. Previous Control Practices and Exposures	34
	B. Methods of Control in the Vinyl Chloride Monomer Industry	38
	C. Methods of Control in the Polyvinyl Chloride Industry	67
	D. Methods of Control in Polyvinyl Chloride Fabrication	76
III.	ENVIRONMENTAL CONTROLS	83
	A. Concern for Possible Effects on The Community	83
	B. EPA Surveys for Vinyl Chloride in the Vicinity of Plants	85
	C. Methods for Abating Emissions	93
IV.	SUMMARY	107
	A. Review of the Current State-of-the-Art for Vinyl Chloride Control	107
	B. Review of the Effectiveness of Controls	112

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
1.	Properties of Vinyl Chloride	7
2.	Vinyl Chloride Production Processes	8
3.	Polyvinyl Chloride Production Processes	18
4.	Signs and Symptoms of Vinyl Chloride Disease in a 1972 Survey of 70 Patients	31
5.	Respiratory Protection Requirements	45
6.	Respirator Cartridge Test Data for 50 ppm Vinyl Chloride	46
7.	Respirator Canister Test Data for 100 ppm Vinyl Chloride	47
8.	Effects of Aspiration and Air Stripping in Reducing Vinyl Chloride Residuals	80
9.	Results of Grab Samples Taken by the EPA Near Vinyl Chloride Plants	87
10.	Results of Integrated Samples Taken by the EPA Near Vinyl Chloride Plants	91

CTL030578

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1.	Simplified Flow Sheet for Production of Vinyl Chloride from Acetylene and Hydrogen Chloride	10
2.	Simplified Flow Sheet for Production of Vinyl Chloride by Direct Chlorination of Ethylene with Dehydrochlorination	11
3.	Simplified Flow Sheet for Production of Vinyl Chloride by Oxychlorination of Ethylene with Air Followed by Dehydrochlorination	14
4.	Simplified Flow Sheet for Production of Vinyl Chloride by Oxychlorination of Ethylene with Oxygen Followed by Dehydrochlorination	16
5.	Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Suspension Process	20
6.	Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Emulsion Process	23
7.	Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Bulk Process	25
8.	Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Solution Process	27
9.	Closed Loop Sampling System	52
10.	Closed System for Tank Car Loading	54
11.	Equipment Maintenance Clearing System	55
12.	Tapered-thread Pipe Joints	57
13.	Examples of Flanged Pipe Joints	58
14.	Chempumps Canned-Motor Pump	60

CTL030579

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Title</u>	<u>Page</u>
15.	Standard Single Mechanical Seal for a Rotating Shaft	61
16.	Typical Double Mechanical Seal for a Rotating Shaft	62
17.	Typical Diaphragm Valve	64
18.	Layout and Sampling System for Polymerization Plant	69
19.	GAF Solvent Reactor Cleaning System	74
20.	Exhaust Hood for Blender as Recommended by Tribukh	78
21.	Aspiration System for Dry Blender	79
22.	Typical Improved Stripping Process Parameters	98
23.	Effects of Increased Temperature in Stripping of Polyvinyl Chloride Resin	99
24.	Simplified Flow Sheet for Activated Carbon Adsorption System	101
25.	Solvent Absorption System for Vinyl Chloride Control	103
26.	Refrigerated Vent System for Vinyl Chloride Control	106

CTL030580

CHAPTER I

INTRODUCTION

My purpose in the following pages is to review the technology available for the control of vinyl chloride, as it relates to preventing hazards in the environment of both the workplace and the community. I will first review the processes involving vinyl chloride, then briefly describe its hazards, and finally discuss, in detail, the methods and equipment used for its effective control. This first section will acquaint, or reacquaint, the reader with the vinyl chloride industry and with the vinyl chloride problem. It will also serve the reader as a ready reference for processes and items of equipment discussed in the main sections of this work.

A. BACKGROUND OF THE VINYL CHLORIDE PROBLEM:

In the past two decades, vinyl chloride has become one of the world's most economically significant chemicals. Although it is used in its pure form, its polymer, polyvinyl chloride, is one of the most important of all plastics. This polymer may be fabricated into sheets, extruded, molded, vacuum formed, or used as a coating. In short, it can be fabricated in any way applicable to thermoplastics. In

CTL030581

addition, it has excellent properties for resisting attack by many chemicals and has good electrical resistance. Also, it may be processed for a wide range of rigidities and strengths. Its uses vary tremendously, with the polymer being used for such diverse applications as clothing, floor tile, shoes, pipes, building materials, wire insulation, paints and coatings, unbreakable bottles, credit cards, phonograph records, upholstery and automobile tops.(73) Vinyl chloride may also be polymerized with other materials such as vinyl acetate or vinyl ether, or vinylidene chloride to form plastics with even more varied properties.(29)

The monomer's only commercial use which directly reached the public was as a propellant in aerosol cans.

One can then see that since the major portion of vinyl chloride monomer is consumed in producing the polymer, the main exposure has been an industrial one, where for many years, vinyl chloride was thought to present no serious hazard other than that of fire or explosion. In fact, it was even briefly tried as an anesthetic. As it came into general industrial use in the nineteen-fifties, more of its chronic effects became known, and hygienists began to recognize that there were certain characteristic chronic effects. Studies concerning these effects in the early seventies yielded the first hints of vinyl chloride

carcinogenicity. It was not until early 1974, the B. F. Goodrich Chemical Company announced that the health and safety personnel at their Louisville, Kentucky polyvinyl chloride plant had determined that it was probable that a rare form of liver cancer seen in several workers at the plant might be related to vinyl chloride exposure. Within a very short time, a European group which was a following-up to the earlier studies suggesting carcinogenicity, released some of its preliminary data which showed a relationship in laboratory animals between cancer incidence and vinyl chloride exposure. These test animals developed a variety of cancers, which included the type of liver cancer seen in the Louisville polymerization workers.

These revelations set off a whole series of regulatory and investigative actions, leading to an emergency temporary standard of one tenth of the previous standard for human exposure, and later to another even more drastic lowering of the allowable exposures. As a result, industry has been faced with a standard that is, in effect, three orders of magnitude lower than it was only two years ago. In addition, new environmental regulations for controlling emissions have been proposed, and, in all likelihood, will soon be adopted. This has placed a great demand on emission control technology in an industry where process losses were previously acceptable

CTL030583

at levels as high as six percent.

B. BRIEF HISTORY OF VINYL CHLORIDE:

Vinyl chloride is not a new chemical by any means, having been first synthesized and reported by Regnault in 1833. He also observed the polymer during the same time period, but did not fully recognize its character. It was not until 1911, however, that a process of commercial potential was discovered, when Klatte and Roulette developed a method of synthesizing vinyl chloride from acetylene and hydrogen chloride on a mercuric chloride catalyst. The first commercial plant was completed in the United States in 1928, followed some five years later by another small operation in Germany. Still, there was no significant interest in vinyl chloride until World War II created a pressing need for substitutes for natural rubber. By 1950, world-wide vinyl chloride production had not yet reached two million tons per year. Between 1950 and 1960, demands began to grow very rapidly as more and more practical applications were discovered, with the result that production increased four-fold by 1960. (28,43) United States production for 1973 was 2.6 million tons of vinyl chloride and 2.3 million tons of polyvinyl chloride and copolymers. The average annual increase in production from 1968 through 1973 was fourteen percent, and this growth rate is not expected to slacken more than

CTL030584

moderately over the next four years. The only brake on further increases has been a short supply of the petroleum-based raw material, ethylene, and uncertainty over new federal regulations. In the United States in 1973 there were fifteen vinyl chloride plants with 1000 to 1500 employees, and thirty-seven polymerization plants with about 5000 employees. As of that time, new plants and expansions of older ones were being constructed to add another 1.378 billion pounds per year to the United States' vinyl chloride capacity. In addition to these, there were about 7500 plants performing fabrication of the polymer, employing about 350,000 workers.(73) Figures for the summer of 1975 confirm that this growth rate has continued in spite of the new regulatory requirements, with U.S. vinyl chloride capacity at 3.42 million tons per year and polymer capacity up to 3.03 million tons per year (about 27 pounds per capita per year).(74) It has been estimated that between 1,700,000 and 2,200,000 jobs ultimately depend upon the vinyl chloride/polyvinyl chloride industry when one considers those employed in using fabricated materials such as automobile upholstery and some construction items.(76)

With this background on the significance of vinyl chloride and polyvinyl chloride, it can be seen why the discovery of its carcinogenicity caused such concern. The population of

CTL030585

industrial workers is large, and since the polymer is a part of almost every American's daily life, essentially all persons are exposed to the polymer at least to some minute degree. Further, vinyl chloride is a chemical of vital economic importance, which has a profound impact on the nation's way of life. The consequences of the illness which it causes are very grave, yet the importance of the continued production of the chemical is also tremendous. Thus, clearly, it is indicated that the problem must be solved such that production may continue while the potential for harm to workers and the community is eliminated. The chemical and physical properties are listed in Table I.

C. METHODS OF PRODUCTION OF VINYL CHLORIDE:

There are currently four processes used in the United States for the synthesis of vinyl chloride monomer. These are shown in Table II.

Hydrochlorination of Acetylene: This is the oldest of the commercial methods for preparing vinyl chloride, and until rather recently it was the primary production route in the United States. (21,28) The economics of this process are inferior to those based on ethylene and it has thus lost favor in industry. As of August, 1975, the Environmental Protection Agency reported that the last of these plants was shut down. (74,76) The basic reaction is that of acetylene and hydrogen chloride:

CTL030586

TABLE I

PROPERTIES OF VINYL CHLORIDE (27,28,29,34,74)

SYNONYMS: Chloroethylene, Monochloroethylene, Chloro-
ethene, VC, VCM

FORMULA: CH_2CHCl molecular weight = 62.5

STRUCTURE:
$$\begin{array}{cc} \text{H} & \text{H} \\ & \text{C} = \text{C} \\ \text{H} & \text{Cl} \end{array}$$

BOILING POINT: -13.37° at 760 mm Hg

SPECIFIC GRAVITY: 0.99 at -25°C

DENSITY: 2.55 grams/liter at 25°C and 760 mm Hg

VAPOR PRESSURE: $10\text{ mm Hg @ } -87.5^\circ\text{C}$
 $100\text{ mm Hg @ } -55.8^\circ\text{C}$
 $692\text{ mm Hg @ } -15.8^\circ\text{C}$
 $2660\text{ mm Hg @ } +25.0^\circ\text{C}$

SOLUBILITY: Slightly soluble in water (0.11%)
Soluble in alcohols and mineral oil
Very soluble in ether or carbon tetrachloride
Solubility of water in vinyl chloride is 0.03%

HAZARD DATA: Flashpoint = -108°F (Cleveland open cup)
Auto ignition temperature = 472°C
Lower explosive limit = 1.2% by volume in air
Upper explosive limit = 22% by volume in air

CONVERSION FACTORS: At 25°C and 760 mm Hg

$1\text{ ppm} = 0.00256\text{ mg/l} = 2.56\text{ mg/m}^3$
 $1\text{ mg/l} = 391\text{ ppm}$
 $1\text{ mg/m}^3 = 0.391\text{ ppm}$

PHYSICAL APPEARANCE: Colorless, in either gaseous or
liquid form

ODOR: Usually described as sweet or pleasant, sometimes
as etherical. Those familiar with odor may first
detect it at 1200 to 2000 ppm.

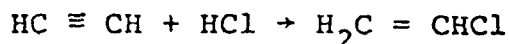
CTL030587

TABLE II

VINYL CHLORIDE PRODUCTION PROCESSES (12,74,76)

<u>Process</u>	<u>Number of Plants (1975)</u>	<u>Percent of 1975 Capacity</u>
1. Hydrochlorination of acetylene	2	8
2. Chlorination-Oxychlorination of ethylene with air with dehydrochlorination	10	77.5
3. Chlorination-Oxychlorination of ethylene with oxygen with dehydrochlorination	1	4.5
4. Direct chlorination of ethylene with dehydrochlorination	3	10

CTL030588

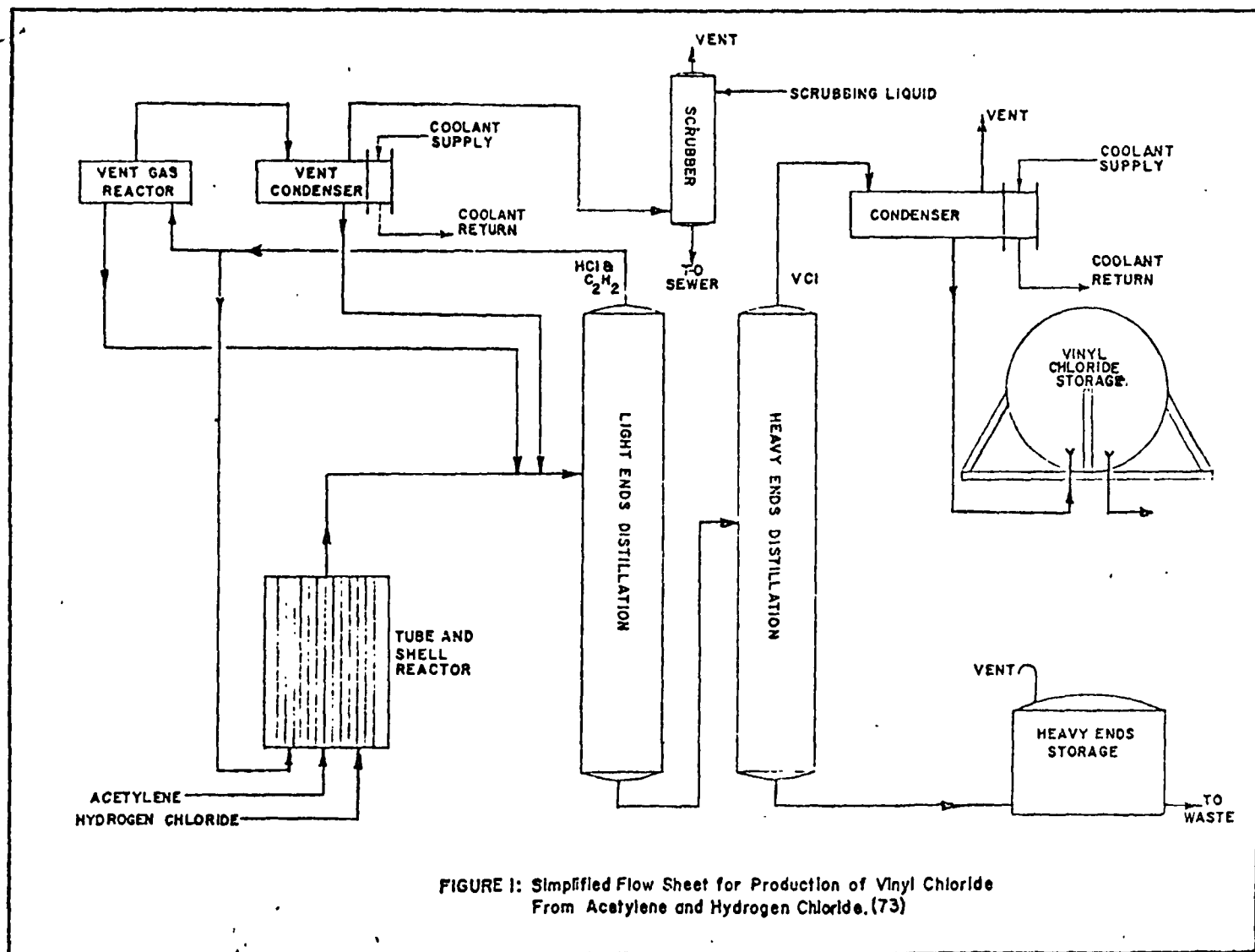


A schematic representation of the process is shown in Figure 1. The hydrogen chloride and acetylene are dried and introduced into a bed of activated carbon upon which a catalyst (traditionally mercuric chloride) is absorbed. The reactants are then passed through a two stage distillation process. In the first stage the lower boiling point impurities (mostly acetylene and hydrogen chloride) are allowed to boil off, while in the second, the vinyl chloride goes overhead leaving the higher boiling point impurities (mostly ethylidene chloride and aldehydes). The yield is very high, and the separation clean enough to yield vinyl chloride at better than 99% purity. (21,28,76)

Dehydrochlorination of 1,2 Dichloroethane (Ethylene

Dichloride or EDC: There are three different processes used which depend on the process of dehydrochlorination of ethylene dichloride to produce vinyl chloride. These vary only in the use made of the hydrogen chloride which is formed during cracking, and how, if at all, it is returned to the process.

The simplest process is direct chlorination of ethylene, followed by dehydrochlorination (cracking), which is schematically represented in Figure 2. In this process, the

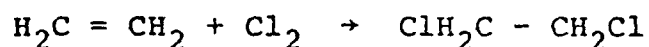


10

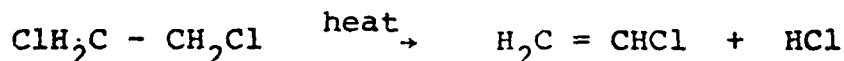
The flow sheet illustrates the production of vinyl chloride. It begins with the 'TO RECOVERY SYSTEM' input, which feeds into the 'EDC RECYCLE' loop. Ethylene and Chlorine enter the 'REACTOR'. The output goes to 'CRUDE STORAGE', then through 'PRIMARY STRIPPER' and 'SECONDARY STRIPPER' columns. The 'WASH WATER STRIPPER' is also shown. The main process continues through 'LIGHT ENDS COLUMN' and 'FINISHING COLUMN'. A 'CONDENSER' and 'EDC STORAGE' unit are involved, with 'EDC SALES' as an output. The 'BOILER' and 'CRACKER' are part of the dehydrochlorination stage. The 'PARTIAL CONDENSER' and 'QUENCH COLUMN' follow. The final products are 'LIGHT ENDS COLUMN' and 'HEAVY ENDS COLUMN', with 'FINISHED VINYL CHLORIDE STORAGE' at the bottom right. A 'TAR' unit is shown for waste handling. The diagram includes various pumps, valves, and heat exchangers throughout the process.

FIGURE 2: Simplified Flow Sheet for the Production of Vinyl Chloride by Direct Chlorination of Ethylene. Followed by Dehydrochlorination. (73)

basic materials are chlorine and ethylene. These are fed into the reactor where they are contacted with either iron chloride or calcium chloride catalyst. The following reaction then occurs:



This reaction is normally run at about 125°C at seven to ten atmospheres, yielding nearly theoretical conversions. Following the ethylene dichloride synthesis, the product is washed twice with water in counter-current columns, then distilled in two successive columns to separate the low and high boiling impurities. The purified ethylene dichloride is then fed to a cracking furnace where it is contacted with pumice or charcoal catalyst at about fifty pounds pressure and 480 to 510°C. About 94 to 97% of the ethylene dichloride is thus converted to vinyl chloride in each pass by the following reaction:

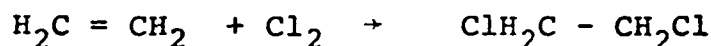
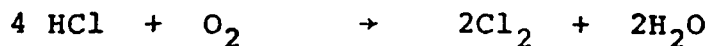


The reactor products stream is introduced into a distillation column where it is quenched with liquid ethylene dichloride, which separates the components with the vinyl chloride and the hydrogen chloride going overhead. The bottoms are then chilled, and either returned to the quenching column, or recycled back to the start of the process or to the initial

CTL030592

distillation step. This step, while essential from the engineering standpoint, does present the unfortunate consequence of introducing vinyl chloride into the process streams even at the earliest stages. The distillate is then charged to a second column where the vinyl chloride is separated with the bottoms, while the hydrochloric acid goes overhead. In the direct chlorination process, this acid is not reintroduced into the process, and is considered a by-product. The final step in the process, then, is to distill the vinyl chloride stream in a final column in which the nearly pure vinyl chloride goes overhead, with the higher boiling impurities being removed in the bottoms. (1,2,7,12, 28,76)

The most common process used in the United States is the chlorination-oxychlorination of ethylene with air, followed by dehydrochlorination, as shown schematically in Figure 3. The main difference between this procedure and the direct chlorination procedure is that the hydrogen chloride from the cracking process is reacted with air and ethylene in the presence of a ferric chloride catalyst to yield additional ethylene dichloride by the following reactions:



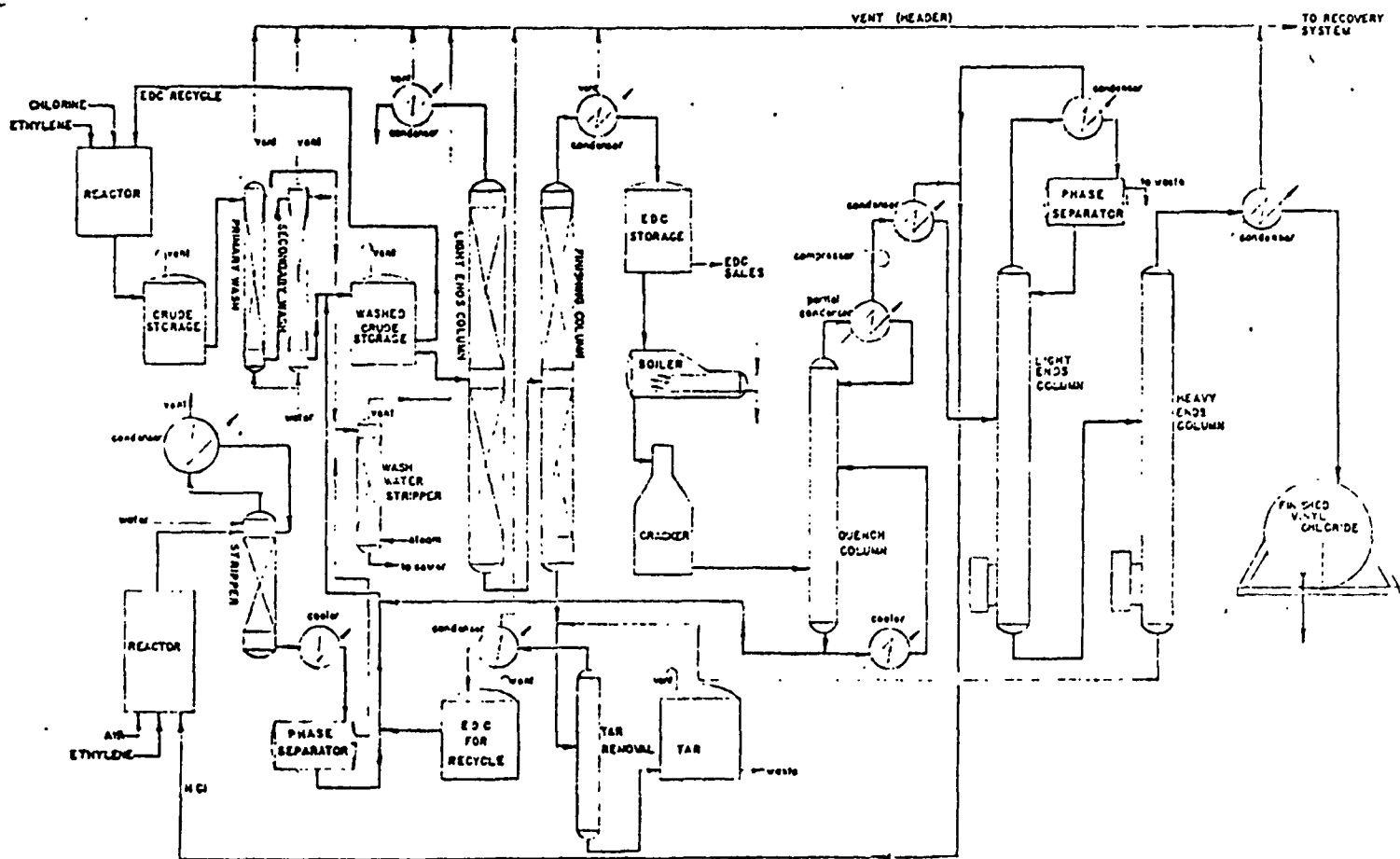


FIGURE 3: Simplified Flow Sheet for the Production of Vinyl Chloride by Oxychlorination of Ethylene with Air, Followed by Dehydrochlorination (73).

The product stream from this reaction is washed in a counter-current column, with hot water, after which the water and the ethylene dichloride are separated by virtue of their being essentially insoluble in one another. The ethylene dichloride stream from this process is then combined with that from a simultaneous direct chlorination process. The ethylene dichloride is then processed as in the direct chlorination process, except that the hydrogen chloride formed in the cracking process is returned to the oxychlorination reactor. (1,2,7,12)

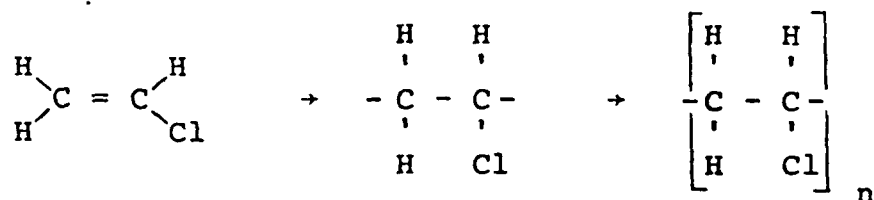
One manufacturer is currently using a modified oxychlorination process in which oxygen is used in place of air, as shown schematically in Figure 4. The process after that point is essentially the same as for oxychlorination of ethylene with air. (12) The primary advantages of this process are the tremendous reduction of the gas stream leaving the reactor and the reduction of subsequent processing requirements for separating the inert components such as nitrogen which would be present if air were used. This also results in decreased emissions from the oxychlorination reactor and provides a vent stream which is combustible without supplementary fuel. (74,75)

D. METHODS OF PRODUCTION OF POLYVINYL CHLORIDE:

The vast majority, over 97%, of the vinyl chloride produced

has been polymerized to make polyvinyl chloride or one of its copolymers.(73) Since the banning of the use of vinyl chloride as an aerosol propellant, it is likely that even this high percentage will increase, as this will leave only uses as a pharmaceutical base and as a chemical intermediate in trichloroethane and pesticide production as significant uses of the monomer.(76) Currently four basic processes are in use in the United States for the production of polyvinyl chloride, as shown in Table III.

The reaction in all processes is similar, with the basic mechanism being the joining of the monomer molecules through cleavage of the double bond, as shown:



The reaction, its kinetics, and its endpoints have been well characterized,(11) but are not relevant to this discussion. The vinyl chloride may also be combined with another monomer to produce copolymers. An example of one of the more common of these is its copolymer with vinylidene chloride, which is formed as follows:

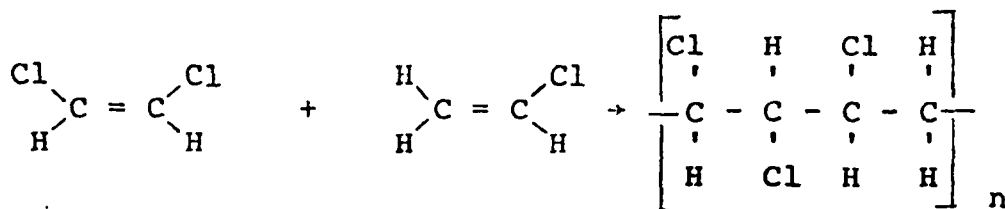


TABLE III

POLYVINYL CHLORIDE PRODUCTION PROCESSES (12)

1973

<u>Process</u>	<u>Number of Plants</u>	<u>Percent of Total</u>
Suspension	34	78
Dispersion (emulsion)	11	12
Bulk	3	6
Solution	3	4

CTL030598

The typical polyvinyl chloride process is of a batch type and the plant will normally include the following operations:

(3,4,5,12)

1. Receiving and storage of vinyl chloride monomer.
2. Polymerization to polyvinyl chloride
3. Stripping of the product stream and recovery of the unreacted monomer, slurry handling.
4. Centrifugation of filtration of the slurry.
5. Drying of the polymer.
6. Pneumatic conveying, and storage of the product.
7. Packaging and shipping.
8. Blending.
9. Waste treatment.

The mostly widely used polymerization process in the United States is the suspension process, which is shown schematically in Figure 5. The first step in the reaction is to introduce water, vinyl chloride, initiator, suspending agent, and buffering agent into the reactor, which is normally a glass-lined agitated vessel of from 2000 to 6000 gallon capacity. The ratios used are generally on the order of two parts water per one of monomer (with a range of 1.5:1 to 4:1), which would be varied according to the polymer qualities desired. The initiators are usually organic peroxides such as dibenzoyl peroxide, acetyl benzoyl peroxide, or dibutyl

CT1030600

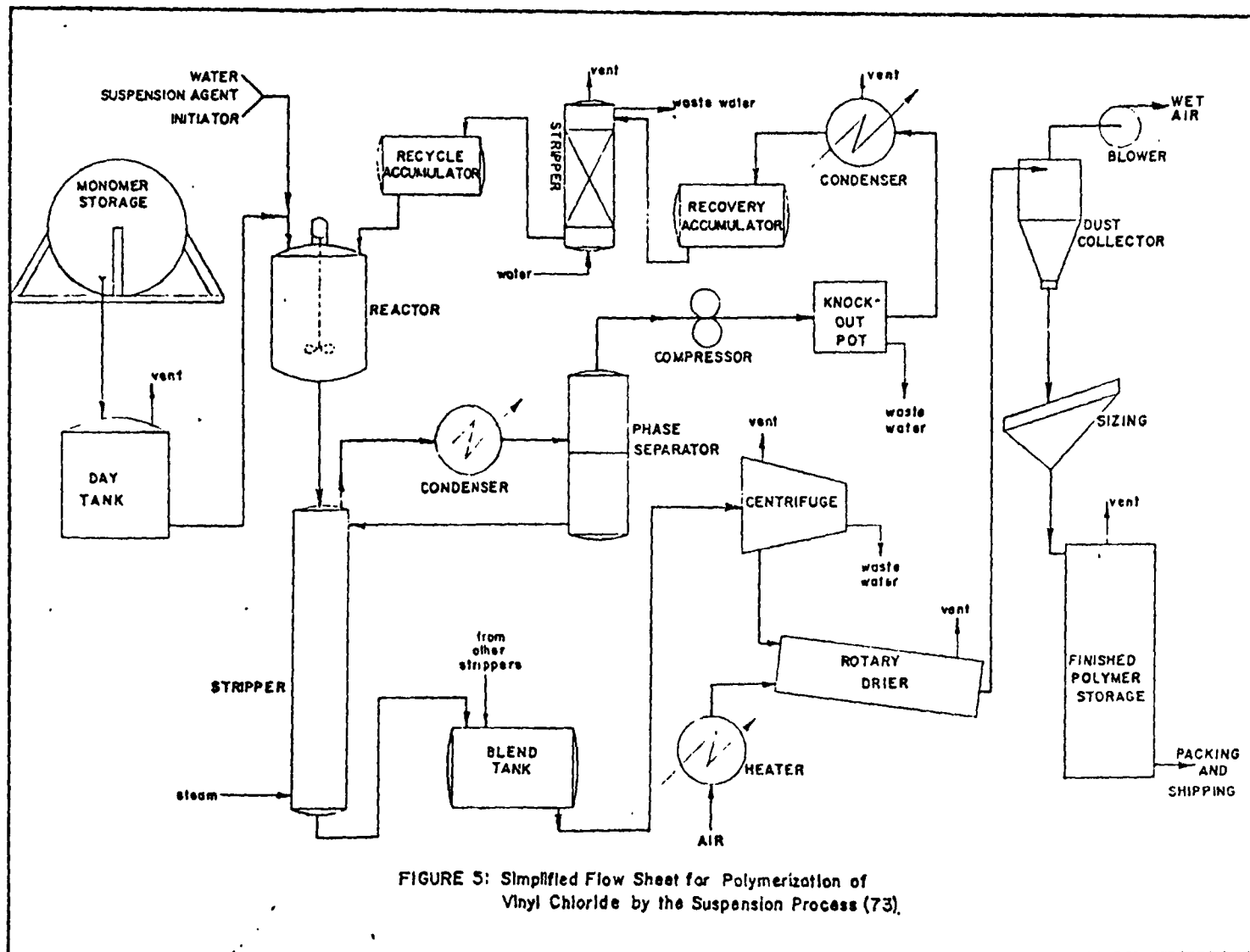


FIGURE 5: Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Suspension Process (73).

peroxide, and are added at about 0.03 to 0.2 pounds per hundred pounds of vinyl chloride. The suspending agent acts to stabilize the suspension, and is usually polyvinyl alcohol added at about 0.005 to 0.5 pounds per hundred pounds of vinyl chloride. As the reactants are introduced into the reactor, they are vigorously agitated to create a very fine suspension of vinyl chloride droplets. The reactor is controlled at between 35 and 50°C by passing cooling water through its integral cooling jacket. Once initiated, the reaction is self-catalyzing and is allowed to run to about 90% of completion.

At this point the batch is discharged from the reactor to a stripper or dump tank and is there stripped of unreacted vinyl chloride monomer by application of vacuum or injection of steam. These monomer vapors are carried, along with any noncondensable gases to a monomer recovery system. This system uses chillers and compressors to recover the unreacted monomer, but must be routinely vented to release any buildup of the noncondensable gases.(76) After stripping, the polymer suspension is discharged to a blend tank where several batches may be accumulated and mixed. The slurry is centrifuged, and then dried, usually by a rotary drier using heated air. The dried polymer is then screened for sizing and sent to be stored or packaged.(3,11,12)

CTL030601

The second most widely used polymerization process in this country is the dispersion (emulsion) process, a schematic of which is shown in Figure 6. This process is similar to the suspension process, except that the vinyl chloride is dispersed in the water in a non-settling emulsion, stabilized by surface active agents.

Another difference is that the initiators are dissolved in the water phase, whereas in the suspension process, they are dissolved in the vinyl chloride phase. The emulsifiers usually preferred are alkyl sulfates, alkane sulfonates, or fatty acid soaps. These are added at just above a critical concentration at which the emulsifiers form microscopic sized agglomerates called micelles. The reaction is triggered by initiators in the aqueous phase, usually peroxides or peroxydisulfates. The free radical so created migrates to the micelles where the polymer molecule begins to grow. At about one to two percent conversion of the vinyl chloride charge, the micelles disappear as the emulsifier is all used at the surface of the growing polymer particles. At about 60 percent conversion, essentially all the monomer is in the polyvinyl chloride. The batch is discharged to a spray drier when the solids content reaches about 50 to 55 percent. The water and unreacted monomer are removed in the drier. The polyvinyl chloride so produced as a high molecular weight

CTL030602

CTL030603

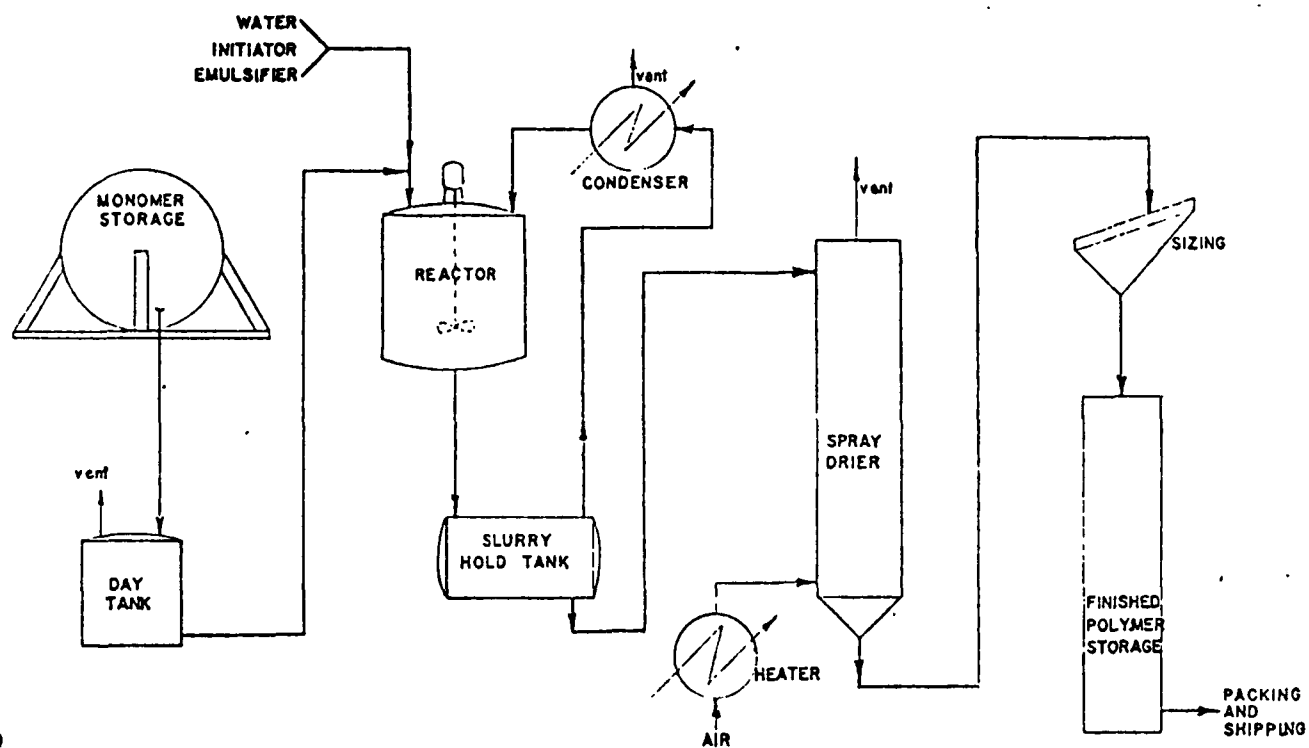


FIGURE 6: Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Dispersion (Emulsion) Process (73).

and small particle size (50 to 150 microns). (5,11,12)

The next most important, and the newest, process in this country is the bulk (Pechiney-St. Gobain) process. This process is considered desirable because there are no foreign substances such as emulsifiers or water added to the process which must be either removed at some stage, or left as contaminants in the final product. The process was only recently made practical by the introduction of a prepolymerizer as shown in the schematic in Figure 7. The first step in the process is to introduce monomer into the prepolymerizer with very small quantities of initiator (usually about 0.02 pounds of azo-bis-isobutyronitrile and 0.00005 pounds of di-isopropyl percarbonate per one hundred pounds of vinyl chloride). This is agitated for about three hours at 40 to 70°C, with cooling being provided mainly through the vaporization of unreacted monomer. At about seven to ten percent conversion, this charge is transferred to the main reactor (or autoclave) where it is slowly agitated for ten to fifteen more hours at about 50°C. The reaction is one of heterogeneous phases, since the polymer is insoluble in the monomer, and, in fact, the reaction mass is basically a powder after about twenty percent conversion. Since the reaction is strongly exothermic, cooling is provided to the reactor jacket, the agitator shaft, and by a reflux condenser. Once initiated,

CTL030604

CTLO30605

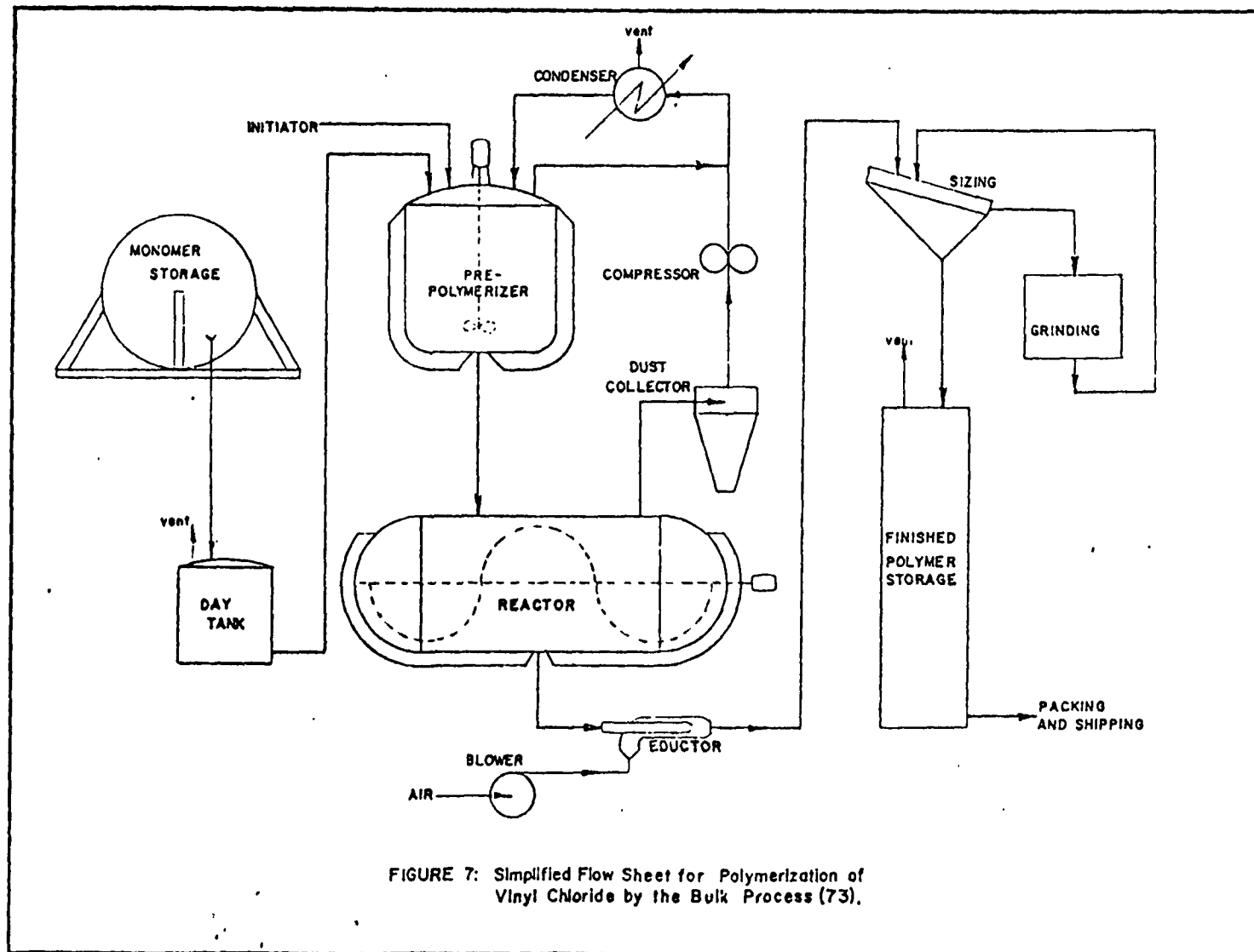


FIGURE 7: Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Bulk Process (73).

the reaction is self-catalyzing, and the rate of reaction increases with increasing percentages of polymer. The reaction is halted at about 90% conversion by vacuum stripping the unreacted monomer directly from the autoclave. The product is then drawn out of the reactor by an air eductor and air conveyed to processing and storage. (5,7,11,12)

The final process used for polymerization of vinyl chloride in the United States is the solution process, which is shown schematically in Figure 8. In this process, the vinyl chloride monomer is dissolved in a solvent such as n-butane, cyclohexane, tetrahydrofuran or 1,2 dichloroethane. As the polymerization proceeds, the polymer precipitates, but is held in a slurry by agitation. The slurry is discharged to a steam stripper from which the unreacted vinyl chloride is returned to the reactor. The polymer and solvent are blended with other batches then centrifuged and dried in a manner similar to the suspension process. The product so produced has very few impurities and is characterized by a low molecular weight. (5,7,11,12)

There is a wide variety in the details of equipment and exposures, even for plants using the same type process for production. Variations which especially affect the work environment are those such as the age of the equipment and the quality of housekeeping and maintenance. One serious

CTL030606

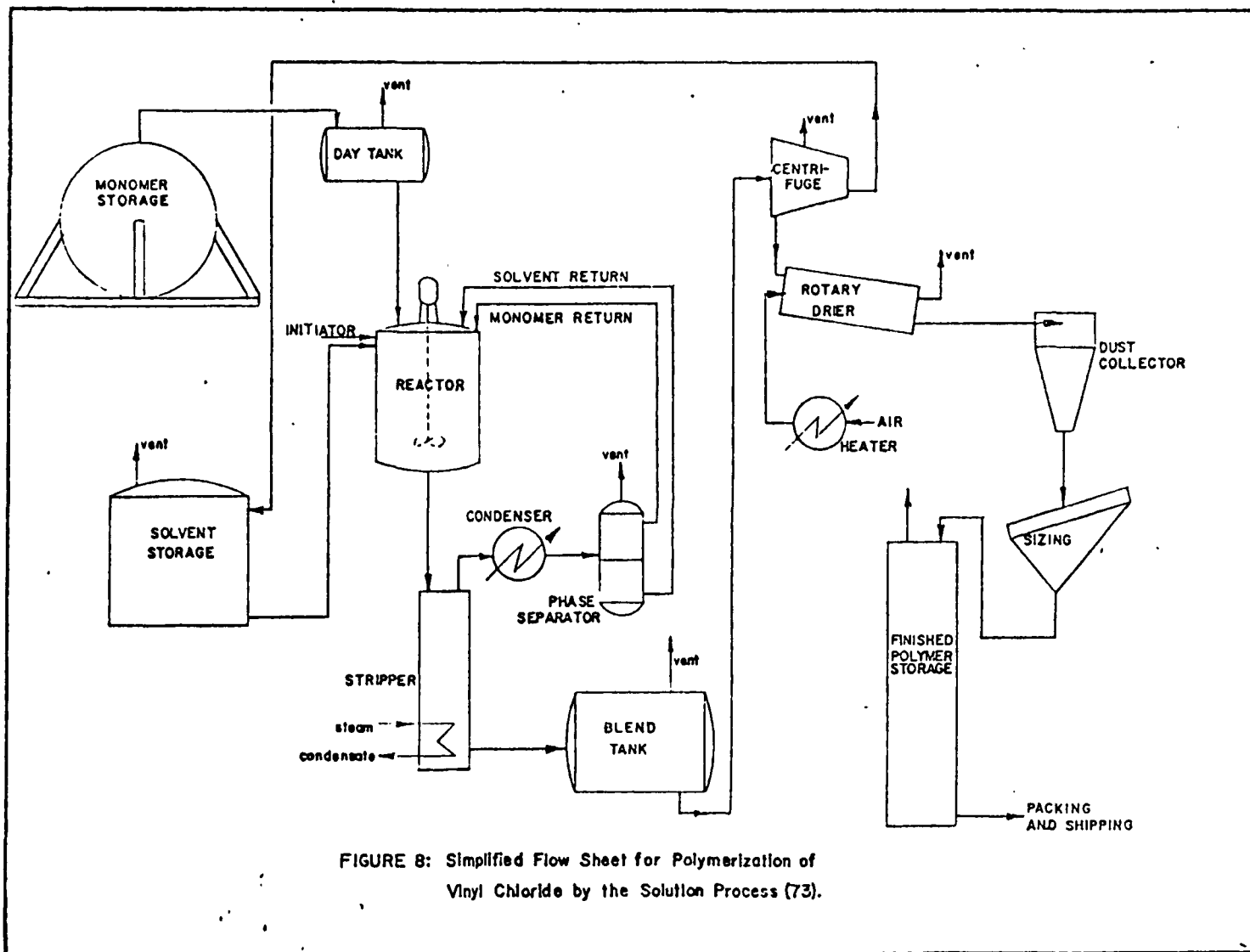


FIGURE 8: Simplified Flow Sheet for Polymerization of Vinyl Chloride by the Solution Process (73).

problem in all of these polymerization processes is the buildup of polymer on the reactor walls, which necessitates the periodic cleaning which has historically resulted in the most serious worker exposures. No continuous process of the classic type has been developed for the polymerization of vinyl chloride with the main deterrent being the long residence time required for the reaction.

E. HEALTH EFFECTS OF VINYL CHLORIDE:

The vinyl chloride problem has been a very emotionally charged issue since the announcement of its implication as a carcinogen in January, 1974, and it is likely to remain so for some time yet to come. One of the major reasons for this reaction has been that for many years, toxicologists had not related any serious health threat to occupational vinyl chloride exposure. Much has been said about how new chemicals should be pre-tested before being used or produced on any large scale.(42) However, it is important to note that vinyl chloride has been known as a commercial product for over forty years, and had been examined for health effects for many years by various researchers, and was repeatedly certified as having a very low hazard except for fire and explosion potential.

Early research centered mainly on central nervous system effects, since vinyl chloride has obvious effects on that

system in acute exposures. In fact, vinyl chloride was proposed and studied for use as a general anesthetic during the 1930's and 1940's. These early studies concluded that the primary effect was acute central nervous system depression, and that essentially no chronic effects were found. (43,55) In 1949 one researcher in the U.S.S.R. did find certain chronic changes including "more-or-less profound hepatitis" in some vinyl chloride fabrication workers, but he attributed the changes to the plasticizers which were being added to the polymer. (72)

In the late 1950's and the early 1960's, researchers began to become aware that vinyl chloride did indeed have chronic effects. Some of the problems noted were circulatory disorders, skin problems, liver damage, and a peculiar skeletal defect known as acroosteolysis. One of the earliest of these problems to be noted was angioneurosis, an irregularity of the circulatory and nervous systems of the extremities. (23) These symptoms are generally referred to as Reynaud's syndrome, and involve spastic behavior of the arterial system which results in numbness and pallor or cyanosis of the fingers or toes. (78) This is apparently related to a characteristic deformation of the terminal digits of the fingers, in the form of pseudo-clubbing and acroosteolysis. Acroosteolysis in vinyl chloride workers

was first observed as a resorption of bone in the terminal digits of the fingers, with the pseudo-clubbing, and a deformation of the nails. This defect has been epidemiologically related to high exposures especially as in reactor cleaning. (16,37,67,78) Table IV gives a summary of the signs and symptoms found in a survey of seventy patients from a German study (78) which more-or-less illustrate the effects of chronic vinyl chloride poisoning, or what has become known as "Vinyl Chloride Disease".

Another more serious aspect of chronic vinyl chloride exposure began to emerge during this same period, that is, chronic liver injury. The injury is characterized by portal fibrosis, a nodular surface on the liver, enlargement of the liver, and elevated hepatic venous pressure. The injury is apparently either very slow healing, or does not heal. (28) Unfortunately, no completely reliable screening test has been determined as a means of ascertaining if injury is being done, or if it already exists in such cases. (80)

The most significant development in vinyl chloride toxicology was first suggested when one researcher announced that he had observed an increase in cancer incidence in animals exposed to 30,000 parts per million for four hours per day, five days a week, for ten to twelve months. The tumors observed did not, however, include angiosarcoma. (40) However,

CTL030610

TABLE IV

SIGNS AND SYMPTOMS OF VINYL CHLORIDE DISEASE

IN A 1972 SURVEY OF 70 PATIENTS (67)

<u>Sign or Symptom</u>	<u>Number of Patients</u>	<u>Percent of Patients</u>
Upper abdominal complaints	42	60
Tiredness	27	39
Frequent dizziness	26	37
Numbness or tingling of fingers and toes	22	31
Increased perspiration	19	27
Sensation of coldness in fingers and toes	18	26
Pain in the joints	17	24
Impotency.	13	19
Head pain	9	13
Pain in the calves	9	13
Low platelet count	57	81
Increased BSP retention time	45	67
Enlarged Spleen	39	57
Reticulocytosis	24	41
Increased SGOT, SGPT, AP or SP	10	14
Scleredema-like skin changes	8	11
Varices of the esophagus or fundus	8	11
Acroosteolysis	6	9
Raynaud's syndrome	6	9
Low white cell count	5	7

CTL030611

in December 1973, angiosarcoma was diagnosed as the cause of death in a vinyl chloride worker in Louisville, Kentucky. This represented the third such case of this rare cancer at the same plant, and thus the possibility of an occupationally related cancer was announced. Resulting epidemiological data established that while the expected death rate for angiosarcoma of the liver in the general population was about 0.0014 cases per 100,000 persons, thirteen cases of it had been found among vinyl chloride workers, who number less than 20,000. The incidence was thus about 400 times that of the general population.(30) These announcements also prompted the release of some preliminary data by Maltoni which showed angiosarcoma, and other cancers being related to vinyl chloride exposure in several laboratory animals. Maltoni has since found some increases in tumor incidence down to exposure levels as low as 50 parts per million.(40,41) More recent epidemiological research has indicated that there may indeed be other carcinomas occurring at greater than expected rates among vinyl chloride workers.(70)

Other current subjects of interest which are at present unresolved are the potentials for mutagenesis and teratogenesis. A preliminary report of a teratogenicity test done on rabbits, rats, and mice did not show any such effect.(65) Testing for mutagenicity in bacteriological systems has shown

CTL030612

some possibility that there may be some mutagenetic potential, but no definitive results are yet available.(60)

Thus, as research has progressed, and the number of persons exposed has increased, vinyl chloride has been found to be anything but the innocuous compound that it was first thought to be. The one undetermined fact that can be expected to continue to cause controversy is at what level risk is incurred. This has not been experimentally determined, and, in all likelihood, cannot be reliably measured.(63)

CTL030613

CHAPTER II

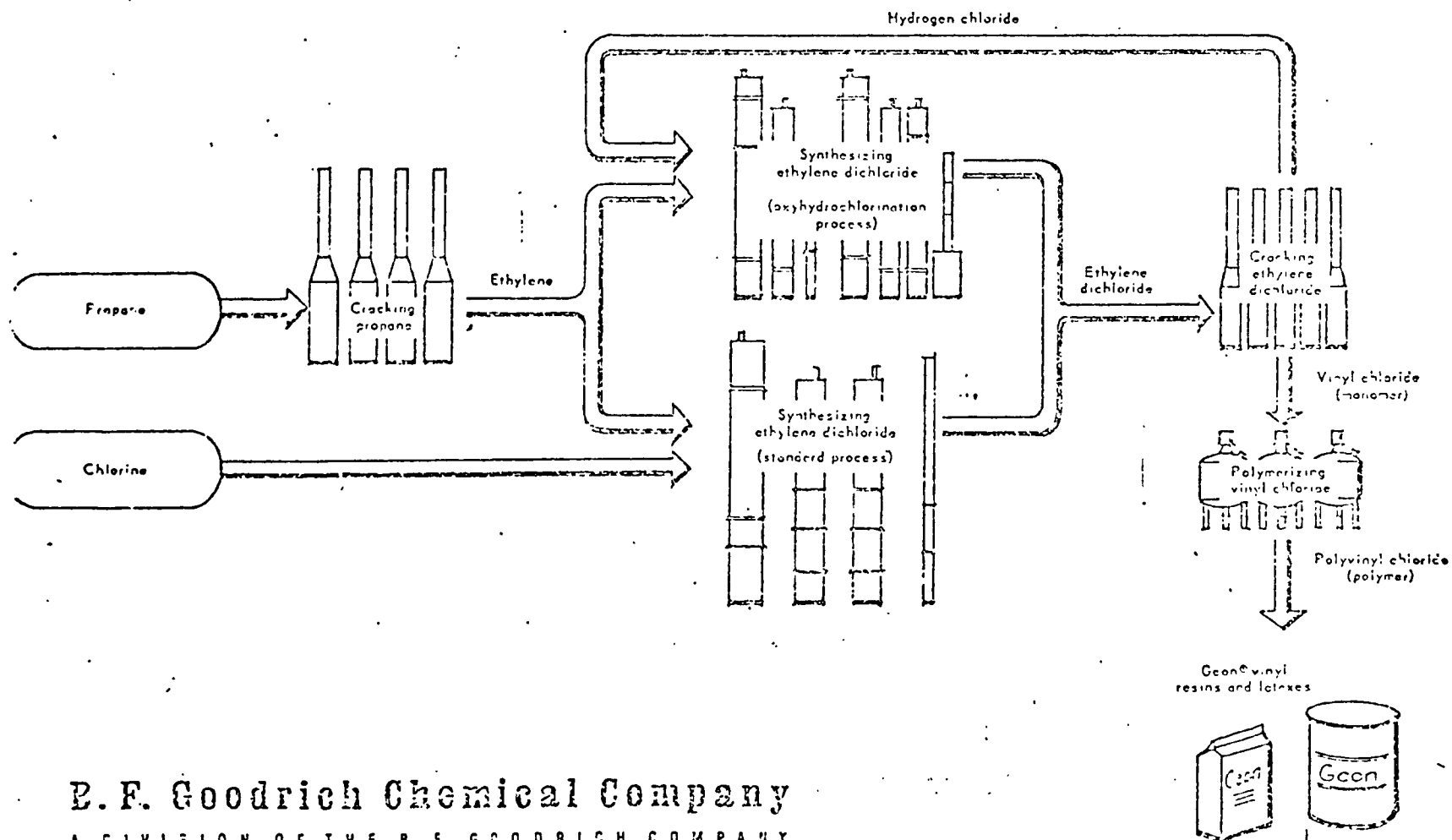
METHODS OF CONTROL IN THE WORKPLACE

A. PREVIOUS CONTROL PRACTICES AND EXPOSURES:

In the past, relatively little attention was given to control of vinyl chloride in the workplace, since the toxicologic data of the time indicated that there was little hazard. As mentioned earlier in this paper, the first to actually observe the chronic effects were the Soviet researchers Tribukh, Tikhomiroun, and Levin. In their 1949 survey of a vinyl chloride fabrication plant they observed exposures from 1 to 470 parts per million of chlorinated hydrocarbons in various work areas, however, they attributed the health effects which they observed to the plasticizers which were being added instead of the residual monomer being released from the heated polymer.(72) In the United States, the earliest apparent efforts to determine exposures were those done by Dow Chemical, who started routine monitoring in about 1950. At that time, analytical techniques did not differentiate between vinyl chloride and other chlorinated hydrocarbons, such as vinylidene chloride. Prior to 1960, exposures were generally fairly high, but mostly below a time-weighted average of 500 parts per million. However, exposures as high as 4000 parts per million were measured under

CTL030614

THE CHEMISTRY OF GEON® VINYL



E. F. Goodrich Chemical Company

A DIVISION OF THE E. F. GOODRICH COMPANY

CTL030862

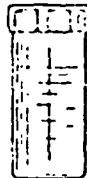
CONVERSION OF GEON POLYMERS TO GEON PLASTICS

PRIMARY INGREDIENTS

GEON POLYMERS—THE SAMPLE MAY BE CONSIDERED AS REPRESENTATIVE OF GEON POLYMER MATERIALS WHETHER THEY ARE IN THE FORM OF STANDARD RESIN ATLY LATER, OR PASTE RESIN. ALL REQUIRE THE SAME BASIC INGREDIENTS ALTHOUGH COMPOUNDING TECHNIQUES MAY VARY.



PLASTICIZERS—HIGH BOILING ORGANIC LIQUIDS WHICH DISSOLVE GEON POLYMERS AT ELEVATED TEMPERATURES. MOST TO THE POLYMER THEY ARE THE MOST IMPORTANT INGREDIENTS. MANY PROPERTIES OF THE COMPOUND ARE DEPENDENT UPON THEM. THE AMOUNTS USED DETERMINE THE SOFTNESS AND FLEXIBILITY.



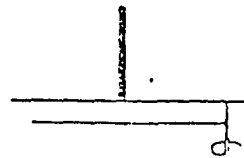
PIGMENTS—FINELY DIVIDED COLORED POWDERS CAREFULLY SELECTED TO IMPART SPECIAL PROPERTIES TO GEON PLASTICS, e.g. COLOR, HARDNESS, ETC. FILLS AND LUBRICANTS ARE ALSO CONSIDERED AS PIGMENTS.



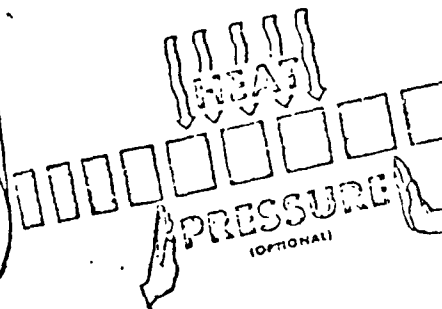
STABILIZER—THIS INGREDIENT PROTECTS THE STABILITY OF GEON PLASTICS TO ELEVATED TEMPERATURES AND SUNLIGHT.



THE INGREDIENTS ARE FIRST BLENDED TOGETHER. APPLICATION OF HEAT AND PRESSURE SUPPLIED DURING PROCESSING FUSE AND KNIT THE MIXTURE INTO A HOMOGENEOUS MASS OR SHAPE. THE NEED FOR PRESSURE IS USUALLY DETERMINED BY THE PHYSICAL FORM OF THE GEON POLYMER AND METHOD OF PROCESSING.



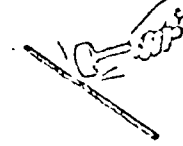
BLENDED
INGREDIENTS



HEAT

PRESSURE
(OPTIONAL)

RIGID COMPOUNDS



THESE ARE STRONG RIGID PLASTICS OF USUAL IMPACT STRENGTH. SOME GEON POLYMERS REQUIRE NO PLASTICIZER, OTHERS USE VERY SMALL QUANTITIES FOR RIGID COMPOUNDS.

ELASTOMERIC COMPOUNDS

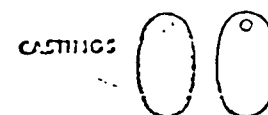
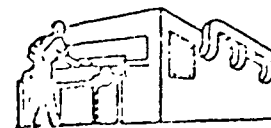
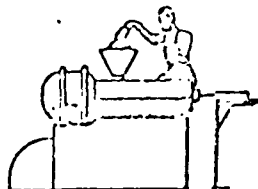
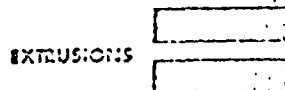
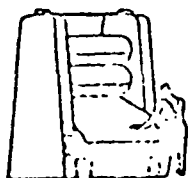
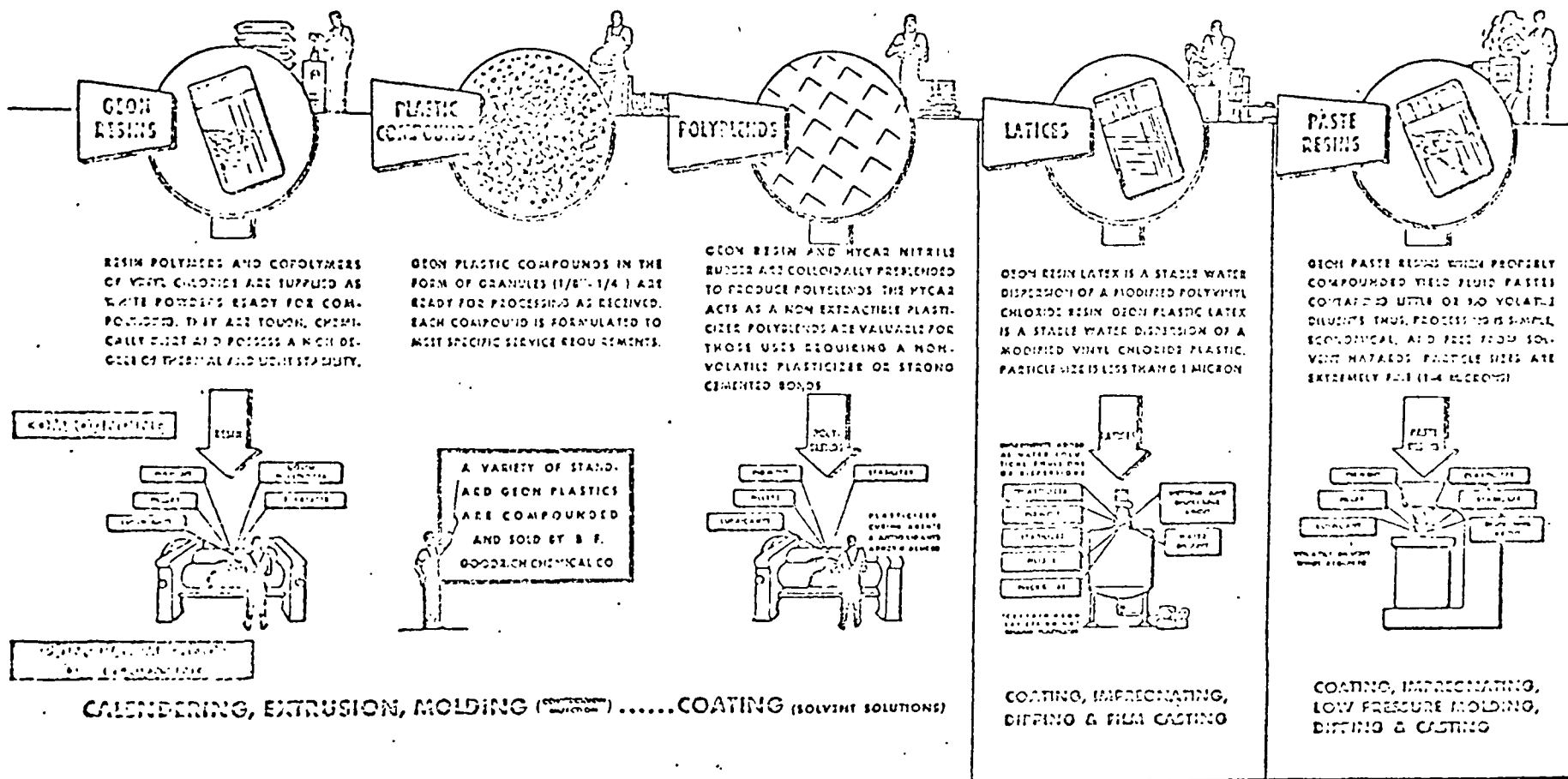


EXTRACTS THE PLASTICIZER CONTENT TO MODERATE AMOUNTS. THESE SOFTER ELASTIC MATERIALS BECAUSE OF THEIR FLEXIBILITY COUPLED WITH EXCELLENT PHYSICAL, CHEMICAL AND ELECTRICAL PROPERTIES THEY OFFER A COMBINATION OF PROPERTIES NOT OBTAINABLE FROM ANY OTHER MATERIAL.

GEON
VINYL
COMPOUNDS

GEON PLASTICS ARE THERMOPLASTIC. AT ELEVATED TEMPERATURES THEY SOFTEN AND ARE EASILY FORMED OR RECESSED. ON COOLING THEY HARDEN AND ASSUME THEIR NORMAL FORM. THIS IS A CYCLE OF SOFTENING AND HARDENING THAT IS REPEATED WITHOUT APPRECIABLE CHANGE IN THE MATERIAL. WITH PLASTICS ARE PRODUCED IN VARIOUS FORMS OF THERMOPLASTICITY.

THE GEON FAMILY OF VINYL



THE PROCESS OF SYNTHESIS

COPOLYMERIZATION

