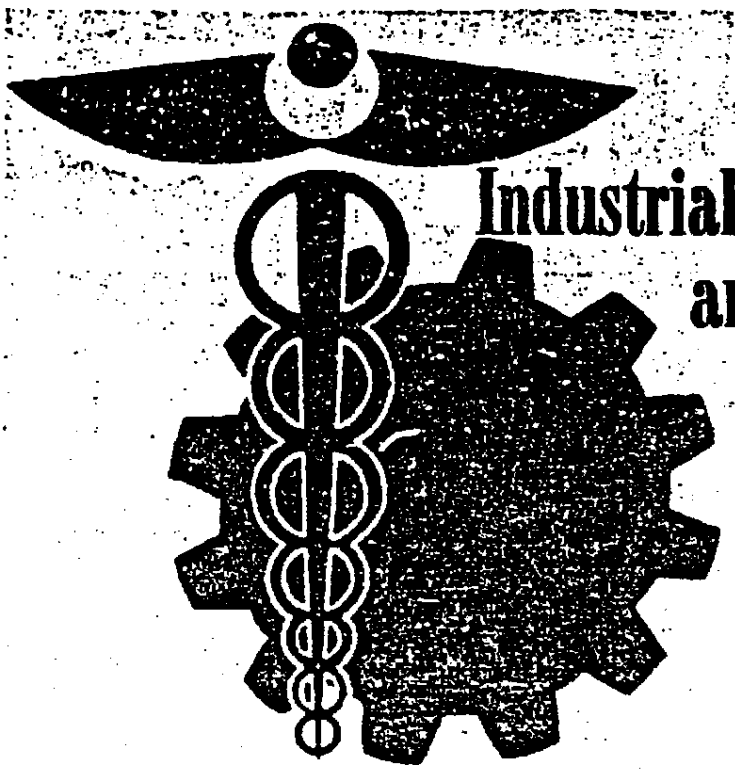

Industrial Analytical Chemists and OSHA Regulations for Vinyl Chloride

S. P. Levine, K. G. Hebel, J. Bolton, Jr., and R. E. Kugel

Stauffer Chemical Co., Eastern Research Labs, Dobbs Ferry, N.Y. 10522

In 1971 the newly created Occupational Safety and Health Administration (OSHA) with the advice of its technical arm, the National Institute for Occupational Safety and Health (NIOSH), adopted a 500 parts-per-million (ppm) by volume permissible level for worker exposure to vinyl chloride monomer gas (VCM). In 1974 a review of this standard was prompted by reports of several deaths from a rare form of liver cancer called angiosarcoma among polyvinyl chloride (PVC) plant employees. This suggested a possible relationship to PVC production. Animal studies and epidemiological surveys indicated that exposure to VCM might be a causative agent involved in the development of angiosarcoma in humans (*1*). These facts led OSHA to issue in April 1974 a temporary emergency standard of a 50-ppm ceiling exposure. This standard also provided for regular monitoring of the work space by personnel monitoring systems able to assay 5-ppm VCM with a relative precision of ±20% (average for a 10-min air sample). This was to have a profound effect on the vinyl chloride and the polyvinyl chloride industries which employ approximately 360,000 workers in over 7,500 plants.

Following public hearings, OSHA published a final standard for VCM in October 1974 (Figure 1) (*2, 3*). However, the emergency temporary standard remained in effect until April 1, 1975. The final standard sets a maximum permissible level of 1 ppm for an 8-hr time-weighted average exposure. A ceiling limit of not more than 5-ppm VCM over a 15-min period has also been set. In addition, an action level of 0.5 ppm was set up; exposures above the action level require periodic monitoring, medical examinations, and training (*4*).

The emergency and the final standards called for vastly different approaches from an industrial hygiene point of view. Under the temporary standard, a survey was made to determine areas of emission, and only "grab" sampling was performed. It was only necessary to ensure that work areas did not exceed 50 ppm of VCM in the air. This sampling approach was changed with the advent of the permanent standard. Now areas must be regulated by both the ceiling (maximum) value and by the time-weighted average exposures of workers in those areas. These requirements call for classifying the areas and types of jobs in plants and for monitoring the actual exposures of workers over a typical workday. The combined sampling and analytical methods used have to be capable of determining VCM down to the 0.25-ppm level with a precision at the 95% confidence limit of ±50%.

Analytical Approach

To aid industry in monitoring programs designed to comply with this standard, NIOSH published a preliminary procedure for VCM sampling and analysis that was classified as "operational, but not thoroughly characterized" (*5*). This method calls for collection of VCM in glass adsorption tubes containing one of the specific NIOSH-approved lots of activated charcoal. Air from the breathing zone of the worker is drawn through the adsorption tube with the aid of a small low-flow battery-operated pump. After sample collection is completed, the tube is capped and sent to the laboratory for analysis. VCM is desorbed from the charcoal with CS_2, and the resulting solution is injected into a gas chromatograph (GC) for analysis. Separation of VCM from other components is performed with an SE-30 column. Since NIOSH realized that this procedure had not yet been thoroughly characterized, the final standard allowed this method or any equivalent method to be used.

Preliminary testing by our laboratory, as well as by others, indicated that

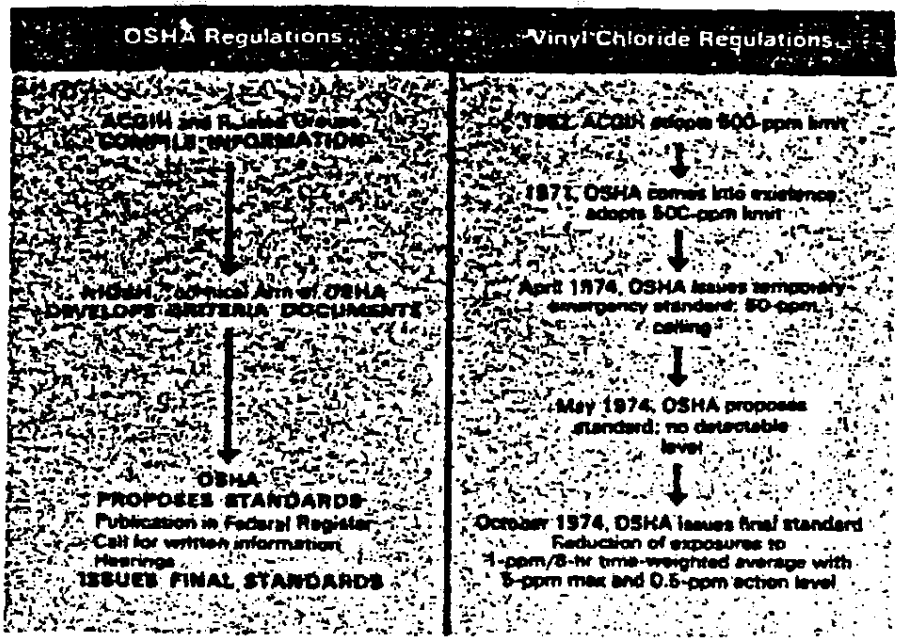

Figure 1. Genesis of OSHA regulations

ACGIH = American Conference of Government Industrial Hygienists. NIOSH = National Institute of Occupational Safety and Health. OSHA = Occupational Safety and Health Administration

there were some disadvantages with the recommended method. These were: poor storage stability of VCM on the charcoal tubes, lot-to-lot variations in charcoal, low and variable desorption efficiency of VCM with CS_2, the inadequacy of the SE-30 column to resolve VCM from other components (of the plant air) and/or CS_2 impurities, and the toxicity and flammability of CS_2. In addition, the volatility of CS_2 made it difficult to prepare stable standard solutions of VCM in CS_2.

Because of these problems, our laboratory, the Analytical Section of Stauffer Chemical Co.'s Eastern Research Center, sought to develop an improved method capable of VCM personnel monitoring for Stauffer Chemical Co.'s PVC resin and fabricating plants. In addition to the requirements set forth by OSHA, we had several other considerations to include when deciding which analytical approach to use:

- The sampling device had to be capable of storing VCM with no losses for periods of up to one week to permit shipping of samples from several plant locations to a central laboratory for analysis.
- The GC column must cleanly resolve VCM from interfering substances that might be found in plants employing VCM or VCM-containing materials used in a wide variety of synthetic and/or fabricating formulations.
- The analytical procedure should exceed in both accuracy and precision the stated OSHA requirements so that the number of personnel monitoring samples could be minimized. This requirement, plus a well-designed sampling program, was needed to ensure the validity of the resulting VCM exposure data, because the variations due to personnel, work shift, process, and even day of the week are not always controllable.
- Due to the effective date of the standard (January 1, 1975, delayed to April 1, 1975, by court order) and the time required to train personnel, strict time limits were imposed on the analytical method development stage of this project. This timing precluded the use of semiautomated VCM analysis systems that have since appeared on the market. Although many of these commercial systems are perfectly satisfactory, their precision, reliability, and delivery date were all unknown at the time that the VCM personnel monitoring surveys were started by Stauffer Chemical Co.

In an industrial environment, method development frequently involves more method adaptation than actual invention. The development and adaptation problems for this project involved two categories, the sampling system and the analysis system.

Sampling System

We have investigated the utility of two types of personnel sampling systems for organic gases. The first involves concentrating the sample in an adsorbent tube, such as that used in the NIOSH procedure. Although certain drawbacks have been noted in the NIOSH procedure, variations of adsorbent tube design, adsorbent, and/or VCM desorption techniques have been applied successfully by several groups. These variations involve the use of modified reusable charcoal tubes, heat desorption devices, head space analyzers, and desorption with CS_2 at Dry Ice temperatures. Advantages of the adsorbent tube approach are the small size of the sampling apparatus and the fact that large volumes of air can be drawn through the tube, thereby concentrating the VCM by several orders of magnitude. A drawback in the heat desorption and head space analysis procedures (which are applied to the adsorbent tubes) is that gas chromatographic analysis can be performed only once; repetitions are not possible since the sample is either totally consumed in a single determination or its concentration has been substantially changed. The use of Dry Ice baths to minimize losses of VCM and/or CS_2 during desorption from charcoal tubes was developed by Dow Chemical Co. (*6*). This procedure is a variation of the NIOSH-developed method and has been tested by our

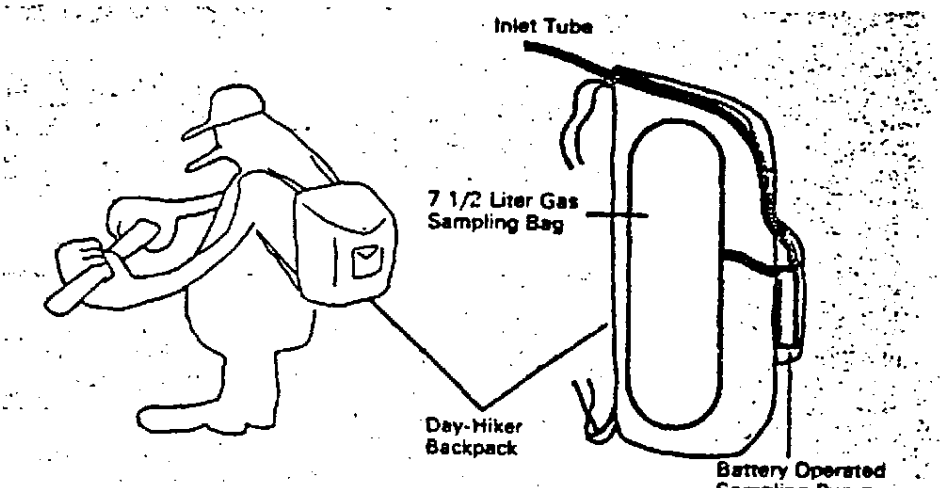

Figure 2. Vinyl chloride personnel sampling unit

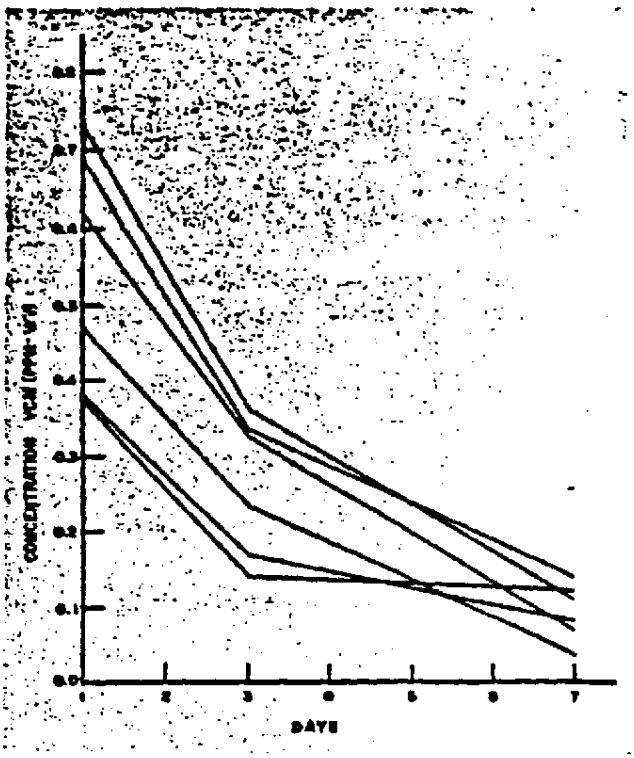

Figure 3. Loss of vinyl chloride gas from Teflon gas sampling bags

laboratory. Although somewhat time-consuming, it is more reliable than the original NIOSH procedure.

A second basic sampling procedure involves the collection and storage of the sample gases without concentration. The method of choice for personnel monitoring involves the use of gas sampling bags. A battery-operated pump is used to draw air from around the worker's breathing zone and exhaust it into the bag. The contents of the bag are then analyzed directly by gas chromatography or any other suitable analytical technique. The pump and the bag are placed in a small day-hike backpack which is then worn by the worker for a complete workshift (Figure 2).

Gas sampling bags are commercially available and are usually fitted with a metal twist-lock valve, although some are also equipped with a permanent or replaceable septum or with a filling snout. Although the storage stabilities of a wide variety of volatile materials in these bags have been summarized in the literature (*7–11*), none of these reports has dealt with 0.2–1.0 ppm concentrations of VCM in air. Therefore, the storage stability, memory effect (from previous samples), and losses of VCM in two commercially available gas sampling bags were studied. In addition, the precision and accuracy of the total sampling system (pump, bag, and tubing) were defined. Chosen for this study were a Teflon bag equipped with a replaceable septum and a twist-lock valve and an aluminized Scotchpak three-layer bag equipped with a valve.

Figure 3 shows the loss of VCM from Teflon bags to be in the range of 20% per day. It was not determined whether this loss resulted from the permeability of Teflon or from mechanical problems. There is really little need for a septum on a gas sampling bag since maximum GC precision can more easily be achieved by using gas sampling valve injection rather than gas syringe injection techniques.

Figure 4 illustrates the storage stability of VCM in aluminized Scotchpak bags. There is no detectable loss of VCM for a period of one week over the concentration range of 0.1–1.1 ppm VCM in air. Because of the possibility of leaks in gas sampling bags, it is recommended that they should be leak tested with clean compressed air for a period of several hours before use or reuse. In actual field use, we find about a 10% "mortality" rate for aluminized Scotchpak bags when they are used repeatedly.

All further studies were carried out on only the aluminized Scotchpak bags. Bags experimentally filled with between 1.0 and 10 ppm VCM had no detectable amount (<0.03 ppm) of VCM remaining after two repetitions of vacuum pumping of the bags and refilling with compressed air. It is, therefore, our practice to perform three pump-and-fill cleaning cycles before each reuse of a sampling bag.

The performance of the entire sampling and analytical system was checked by pumping 1.0 ppm of VCM in air from a full gas sampling bag through connecting tubing and a sampling pump into a second bag which had been evacuated prior to the experiment. The lengths of Teflon-lined neoprene tubing used and the pump were the same as would be used in the field. This was a simulation of the

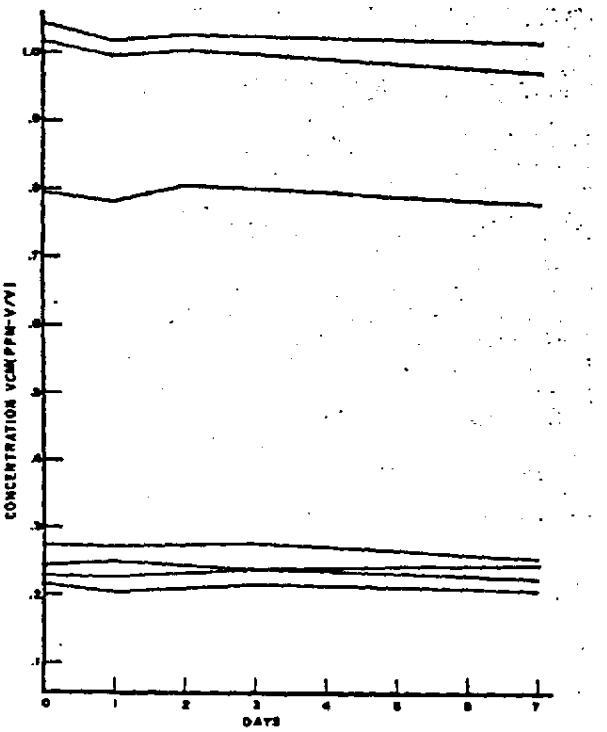

Figure 4. Stability of vinyl chloride gas in aluminized Scotchpak gas sampling bags

losses that could be expected under actual use conditions. The data showed a mean recovery of 96–97% of the VCM.

Analytical System

Because of the inadequacy of the NIOSH-recommended SE-30 gas chromatographic column, we have chosen to use a Durapak (Carbowax 400 on Porasil) packing. The use of Durapak requires a low inlet pressure which results in only minor baseline disruption during sample injection with the gas-injection valve. Sample loops of up to 5.0 ml can be used without significant loss of resolution. We have found nominal analysis times of between 3 and 5 min to yield more than adequate resolution and results with relative precisions (95% confidence level, single injection) of ±3% at the 1.0-ppm level and ±11% at the 0.25-ppm level. Since the precision increases as 1/square root of the number of injections, we routinely inject each sample two or more times. This system can detect less than 0.03-ppm concentrations of VCM in air.

Several valving configurations have been developed by other laboratories which incorporate the function of column backflush and injection, and cut-and-backflush and injection in a single automated valve. These valves minimize the time necessary to clean the GC column of constituents from the air sample having longer retention times than VCM. A cut-and-backflush system presently in use by many laboratories incorporates a precolumn of Durapak (*n*-octane on Porasil) with porous polymer and a short analytical column of porous polymer. An automated 10-port valve is used (*12*).

In conclusion, the industries which use VCM for resin production and PVC for fabrication of finished vinyl products were faced with developing, field proving, and installing a complete VCM personnel monitor system in a short time. Sampling and analysis guidelines supplied by NIOSH were not adequate for the goals of our program, thus necessitating extensive method adaptation and development. The method outlined above represents a viable analytical approach for an industrial setting.

The long-range goal for determining worker exposure to VCM must be, however, the utilization of continuous monitors. These VCM monitors must have the capability of correlating variable ambient air VCM concentrations with the results of corresponding personnel monitoring samples.

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CONFIDENTIAL

TENTATIVE PROCESS FOR VYSET RE (VINYL CHLORIDE, ETHYL-β-HYDROXYETHYL FUMARATE, ISOBUTYLENE TERPOLYMER)

VOLUME I - TENTATIVE PROCESS

TENTATIVE PROCESS No. 1595 — March, 1964

Authors: B. T. Janker
D. Carter
L. J. Breuklander

Chemists: R. Z. Greenley
H. P. Holladay
R. J. Slocombe
S. C. Yang

Chemical Engineers: L. J. Breuklander
D. Carter
E. C. Dybdal
B. T. Janker

Approved by: R. W. Schuler

Job No. 9388

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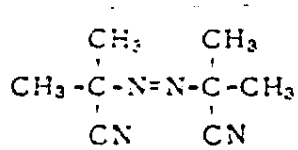
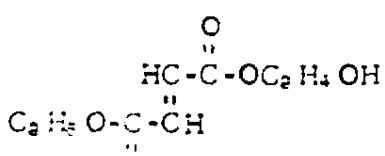
CHEMICAL ABBREVIATIONS

1. AZBN (Azo-bis-isobutyronitrile)



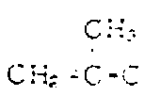
(m.w. = 164)

2. EHF (Ethyl-2-hydroxyethyl fumarate)



(m.w. = 188)

3. IB (Isobutylene)



(m.w. = 56)

4. VC' (Vinyl chloride)

(m.w. = 62.5)

I. INTRODUCTION

VYSET RE is a low molecular weight terpolymer of vinyl chloride (VCl), ethyl-β-hydroxyethyl fumarate (EHF) and isobutylene (IB). The end use for this polymer is thermosetting metal surface coatings. The resin was invented in the Central Research Department Polymer Research Section (1, 2).

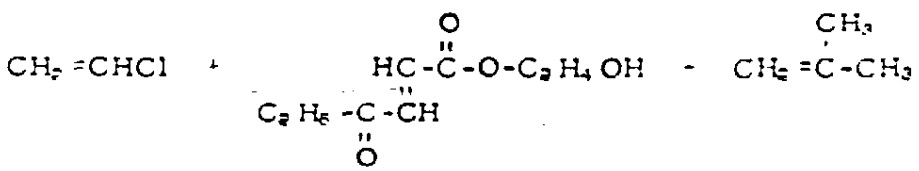
VYSET RE films on metal have substantially better impact resistance and adhesion than existing surface coating products such as acrylics and melamine-alkyds. Wilson (3) has concluded as a result of a market survey that at 40-45¢/lb VYSET RE can compete successfully with these products in spray and dip coatings and in the rapidly expanding coil coating* field. It has been shown by Dybdal (4) that VYSET RE can be sold in the 40-45¢/lb range and earn 20% return after taxes.

A tentative process for VYSET RE synthesis was developed during 1962-63 at the Central Research Department. The tentative process is described in this report. The report is published in two volumes. Volume I presents the tentative process proper, and contains the information normally required by design and manufacturing functions. Volume II is an experimental supplement which gives the details of all experimental work performed in the course of developing the process.

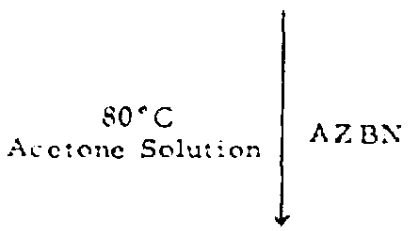
A tentative process for the synthesis of EHF monomer has been published separately (5).

* The term applied to coating long strips of metal sheet prior to fabrication. The sheet is subsequently fabricated into useful shapes and does not require repainting.

II. CHEMISTRY



VCl EHF IB



VCl/EHF/IB terpolymer

III. SYNOPSIS OF PROCESS

VCl, EHF, IB, and AZBN-acetone solution are continuously pumped to a continuous stirred tank polymerization reactor operated at 80°C and 120 psig pressure. Heat of polymerization is removed from the reactor by transfer to the jacket. Polymer solution consisting of about 30% VCl/EHF/IB terpolymer, 30% acetone, 39% monomeric VCl and IB and 1% monomeric EHF is continuously withdrawn from the reactor.

The monomeric VCl and IB are distilled from the reactor effluent in a sieve tray stripping column, condensed, and recycled to the reactor. Open superheated acetone vapor is used to operate the stripping column. Paraplex G-62 stabilizer is mixed with the polymer solution effluent from the bottom of the stripping column.

The polymer is precipitated from the stripped polymer solution by mixing with water in a tank with specially designed high intensity agitation.

The polymer slurry from the precipitation operation is filtered and washed with water on a rotary vacuum filter. The wash filtrate is used in the precipitation operation. The filtrate is distilled to recover acetone, which is recycled to the polymerization reactor and to the stripping column.

The wet filter cake produced on the rotary vacuum filter is dried in an air convection oven and packaged in polyethylene-lined Leverpaks for shipment.

IV. BILL OF MATERIALS

The following raw materials are required to make 100 lbs of finished goods:

Vinyl chloride	74.3 lb
Ethyl-β-hydroxyethyl fumarate	22.2 lb
Isobutylene	4.2 lb
Azo-bis-isobutyronitrile	1.0 lb
Acetone	5.3 lb
Paraplex G-62	0.5 lb
City water	2120.0 lb

V. RAW MATERIALS

A. ACETONE

Source: Enjay Chemical Co., 60 West 49th St., New York 20, N. Y.

Grade: Commercial grade.

Comment:

1. Enjay commercial grade acetone is made by isopropanol dehydrogenation. Acetone made by other processes should not be used without laboratory investigation.

2. Baker and Adamson A. C. S. grade acetone was used in the early pilot plant work. The performance of the Enjay acetone was in all respects equivalent to the A. C. S. grade acetone.

B. AZO-BIS-ISOBUTYRONITRILE

Source: E. I. du Pont de Nemours & Co., Industrial and Biochemicals Dept., Wilmington 28, Del.

Grade: Commercial

Alternate Source:
Eastman Organic Chemicals. Distillation Products Industries, Rochester 3, N. Y.

Comment:

1. The du Pont Company are the assignors of U. S. patents 2,471,959 and 2,500,023 which relate to the use of azo-bis-isobutyronitrile in polymer manufacture. Their current practice is to grant a license to use these patents to all applicants for a royalty fixed at 10¢/lb catalyst. It is their current practice to require customers to execute a license agreement before they will sell azo-bis-isobutyronitrile in greater than development quantities.

C. ETHYL-β-HYDROXYETHYL FUMARATE

Source: Monsanto Chemical Co., Plastics Division, Springfield, Mass.

Grade: Ethyl-β-hydroxyethyl fumarate monomer prepared according to the methods of CRD Tentative Process Report 1577 (5).

Specifications:

Ethyl-β-hydroxyethyl fumarate	> 75%
Hydroxyl content	> 7.8%
Acidity	< 0.01 meq/ml
Glycol difumarate	< 5%
Ethyl-β-hydroxyethoxyethyl fumarate	< 11%
Color	light amber

D. ISOBUTYLENE

Source: Petro-Tex Chemical Corp., P.O. Box 2584, Houston, Texas.

Grade: 99% isobutylene.

Specifications:

Isobutylene	99% min.
Butanes	0.5% max.
Butylenes (other than IB)	0.8% max.
Propane and propylene	0.05% max.
Sulfur	10 ppm max.
Water	100 ppm max.

Alternate Sources:

Phillips Petroleum Co., Special Products Division, Bartlesville, Oklahoma.

Enjay Chemical Co., 60 West 49th St., New York 20, N.Y.

Comment:

1. All research work was done with Phillips material distributed by the Matheson Co. The specifications for the products of the other manufacturers are comparable to Phillips.

2. Monsanto Chemical Co. Hydrocarbons Division have a process stream at the Chocolate Bayou plant from which isobutylene may be extracted. Isobutylene may become available from this source in the future.

E. PARAPLEX G-62

Source: Rohm and Haas, Inc., Philadelphia, Pa.

F. WATER

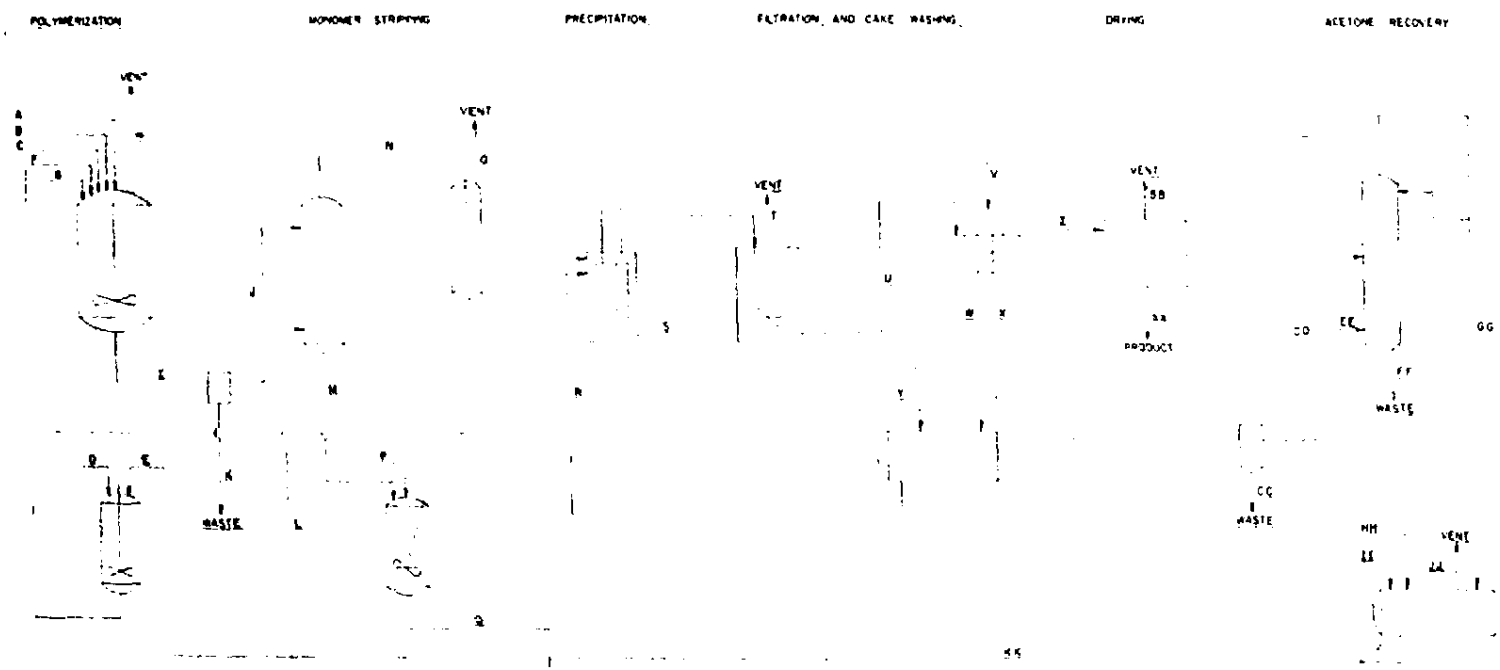
Source: Springfield, Mass., municipal water supply.

Comment:

1. The performance of Springfield municipal water was equivalent to that of deionized water in the pilot plant.

VI. MATERIAL BALANCE

Figure 1 is a material balance for the VYSET RE process.



VYSET RE PILOT PLANT MATERIAL BALANCE (LB/HR)

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	BB	CC	DD	EE	FF	GG	HH	II	JJ	KK
VCL	9519						9073	TRACE	947	947			74	9073	TRACE		74		74																		
EMF		481							481	481			481				141	04	43		45		04	71		70	69	01		71		71						
EB			341				695	TRACE	701	701			06	695	TRACE		06		06	06																		
INITIATOR				73		73			16	16			16				18		6		16					6	6	TRACE									
ACETONE					306	306	3652	TRACE	5738	5738		4880	7986	3652	TRACE		7986	430	8386		8386		400	7826		40	01	159		826		235	7591	395		TRACE	7986
WATER					62	62	10		72	72		120	182	10			82	87088	87169		87268	45036	44632	50432	12454	7270	73	7197		50402	4064	46431	153	01	26		82
POLYMER									7307	7307	TRACE		7307				7307		7307	TRACE	7307					7307	7254	75	TRACE								
VAMAC G-612																37	37		37		37					37	37	TRACE									
NITROGEN								10																													
TOTAL	9519	481	341	73	368	5241	13430	10	2442	2442	0	5000	15712	13430	0	37	5748	87490	75332	80	175869	45036	45036	68299	12454	4860	7430	7430	0	58293	4064	64667	7745	396	26	0	888

MONSANTO CHEMICAL COMPANY

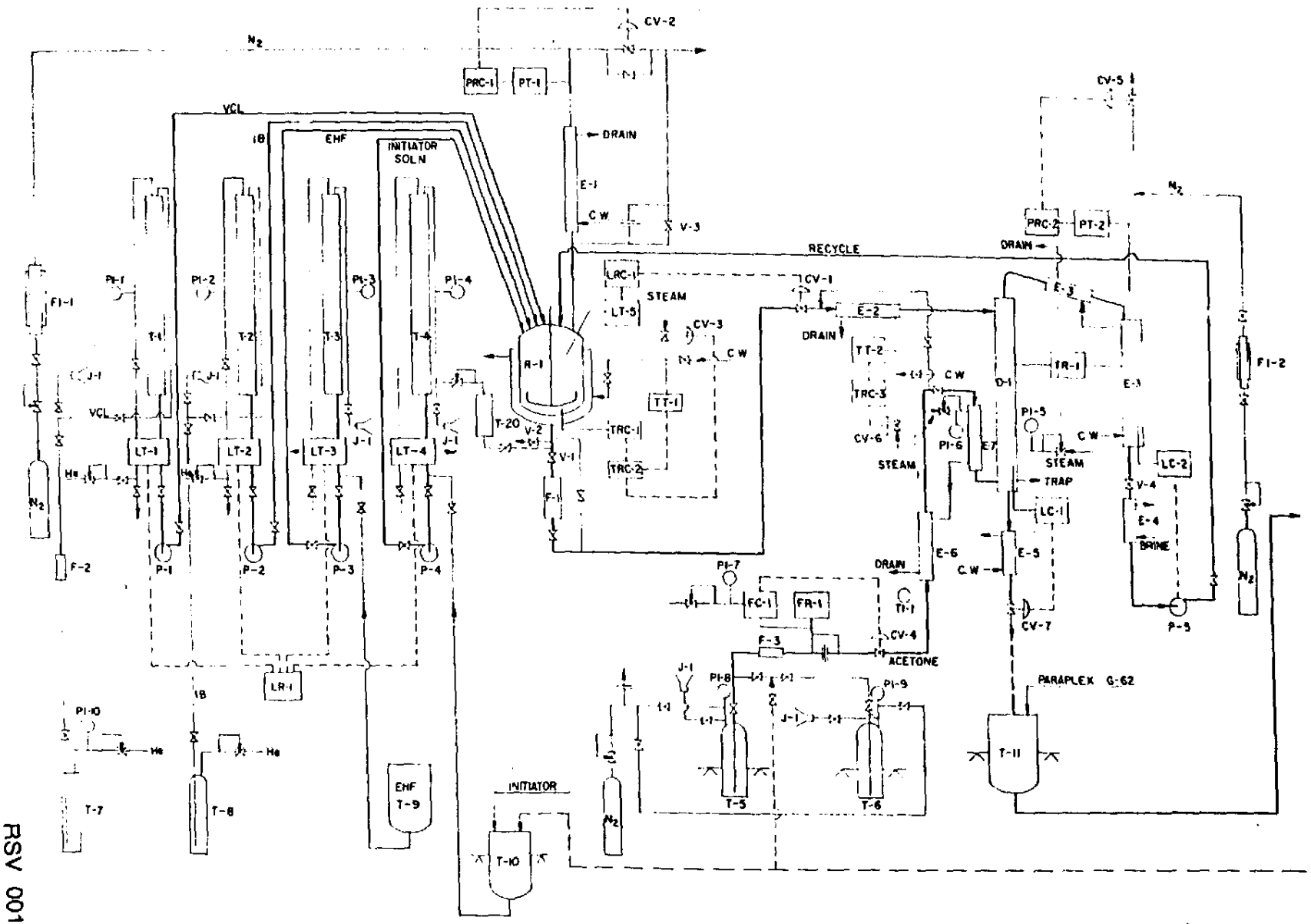
VII. FLOW SHEET AND EQUIPMENT DESCRIPTIONS

Figures 2 and 3 are process flow sheets. Table I is an equipment list for the polymerization pilot plant.

Table I

Equipment List - Polymerization Pilot Plant

CV-1	Control valve - reactor effluent flow
CV-2	Control valve - reactor inerts bleed
CV-3	Control valve - reactor jacket water temperature
CV-4	Control valve - stripping acetone flow
CV-5	Control valve - recycle system nitrogen bleed
CV-6	Control valve - stripper preheat water temperature
CV-7	Control valve - polymer solution takeoff
CV-8	Control valve - acetone column bottom pressure
D-1	Monomer stripper
D-2	Acetone column
E-1	Reactor reflux condenser
E-2	Stripper feed preheater
E-3	Recycle condenser and collector
E-4	Recycle subcooler
E-5	Product cooler
E-6	Stripping acetone vaporizer
E-7	Stripping acetone superheater
E-8	Acetone column feed heater
E-9	Reflux head
E-10	Acetone column bottoms cooler
F-1	Reactor effluent filter
F-2	VCl monomer filter
F-3	Stripping acetone filter
F-4	Water filter
F-5	Rotary vacuum filter
F-6	Acetone column primary filter
F-7	Acetone column secondary filter
F-8	Recycle acetone filter
FI-1	Nitrogen bleed rotameter (reactor)
FI-2	Nitrogen bleed rotameter (recycle system)
FI-3	Precipitant rotameter
FI-4	Wash water feed rotameter
FI-5	Acetone column feed rotameter



RSV 0017305

	MONSANTO CHEMICAL COMPANY	
	FIGURE 2 FLOW SHEET POLYMERIZATION & MONOMER STRIPPING	

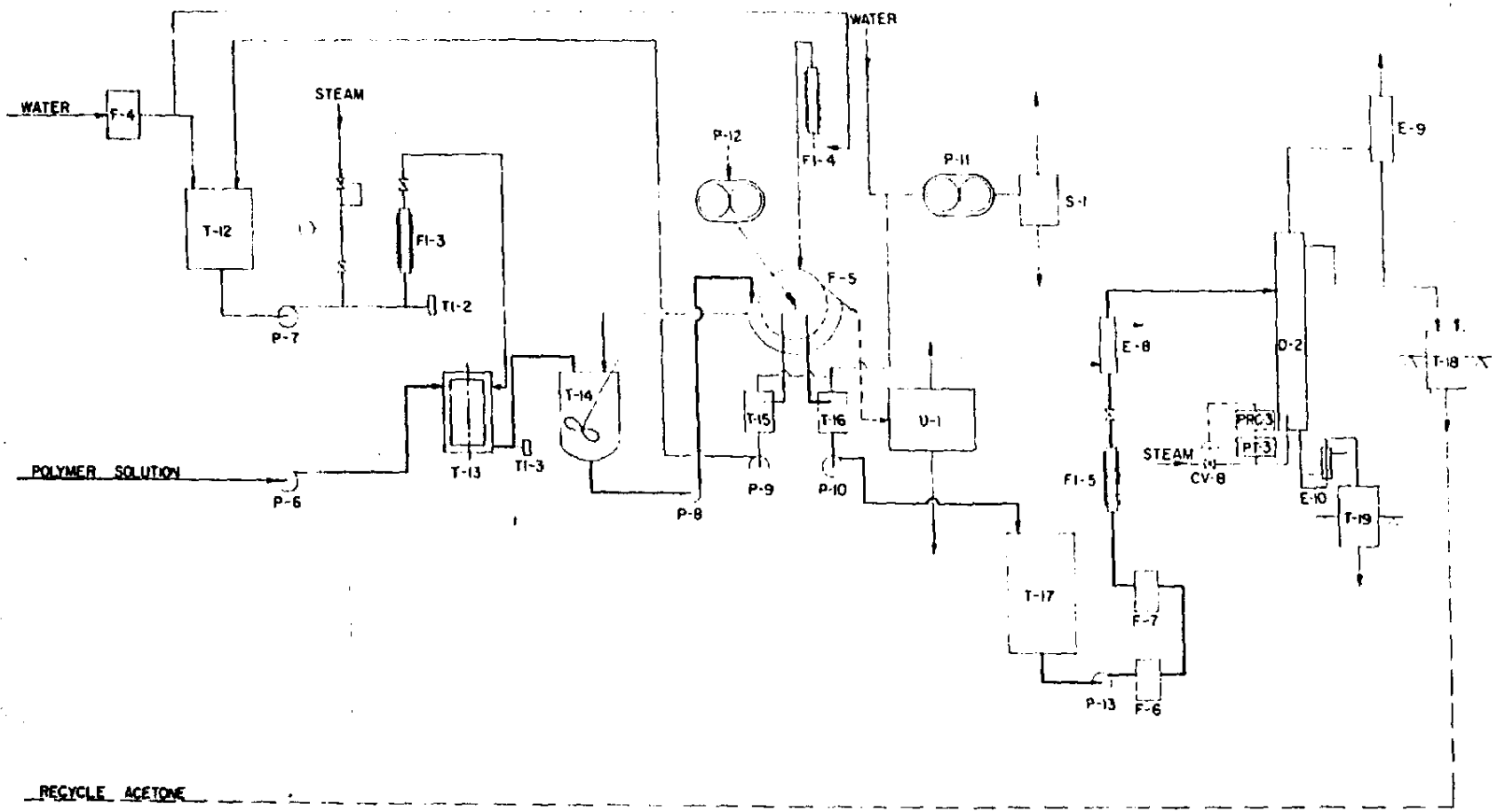


FIGURE 3

DRAWN	MONSANTO CHEMICAL COMPANY	PROJ. NO.
CHECKED	800 N. LINDBERGH BLVD. ST. LOUIS, MO. 63166	LOCATION
DATE	FLOW SHEET - PRECIPITATION, FILTRATION, DRYING AND ACETONE RECOVERY	DIVISION
SCALE		DWG. NO.

J-1	Feed system ejector
LC-1	Monomer stripper liquid level control
LC-2	Recycle collector liquid level control
LR-1	Feed system level recorder
LRC-1	Reactor level recorder controller
LT-1	VCl level transmitter
LT-2	IB level transmitter
LT-3	EHF level transmitter
LT-4	Initiator solution level transmitter
LT-5	Reactor level transmitter
P-1	VCl feed pump
P-2	IB feed pump
P-3	EHF feed pump
P-4	Initiator solution feed pump
P-5	Recycle pump
P-6	Polymer solution pump
P-7	Precipitant pump
P-8	Polymer slurry pump
P-9	Wash filtrate pump
P-10	Filtrate pump
P-11	Vacuum pump
P-12	Blower
P-13	Acetone column feed pump
PI-1	VCl standpipe pressure indicator
PI-2	IB standpipe pressure indicator
PI-3	EHF standpipe vacuum indicator
PI-4	Initiator solution standpipe vacuum indicator
PI-5	Stripper steam trace pressure indicator
PI-6	Steam pressure indicator stripping acetone system
PI-7	Flow control pressure indicator
PI-8	Pressure indicator stripping acetone tank, Item T-5
PI-9	Pressure indicator stripping acetone tank, Item T-6
PI-10	Pressure indicator VCl storage system
PI-11	Pressure indicator steam
PI-12	Pressure indicator acetone column feed
PRC-1	Reactor pressure recorder controller
PRC-2	Recycle system pressure recorder controller
PRC-3	Acetone column bottom pressure recorder controller
PT-1	Reactor pressure transmitter
PT-2	Recycle system pressure transmitter
PT-3	Acetone column bottom pressure transmitter
R-1	Polymerization reactor
S-1	Discharge snubber
T-1	VCl metering standpipe
T-2	IB metering standpipe
T-3	EHF metering standpipe

T-4	Initiator solution metering standpipe
T-5	Stripping acetone storage tank
T-6	Stripping acetone storage tank
T-7	VCl monomer storage tank
T-8	IB monomer storage tank
T-9	EHF monomer storage tank
T-10	Initiator solution tank
T-11	Polymer solution tank
T-12	Precipitant feed tank
T-13	SRC disintegrator
T-14	Slurry hold tank
T-15	Wash filtrate receiver
T-16	Filtrate receiver
T-17	Filtrate storage tank
T-18	Distillate receiver
T-19	Bottoms receiver -
T-20	Initiator injection tube
TI-1	Temperature indicator, acetone vaporizer steam supply
TI-2	Precipitant feed temperature indicator
TI-3	Disintegrator temperature indicator
TI-4	Acetone column feed temperature indicator
TR-1	Temperature recorder recycle system
TRC-1	Reactor temperature recorder controller
TRC-2	Reactor jacket temperature recorder controller
TRC-3	Feed preheater jacket temperature recorder controller
TT-1	Temperature transmitter reactor jacket
TT-2	Temperature transmitter feed preheater
U-1	Tray dryer

ITEM CV-1 CONTROL VALVE - REACTOR EFFLUENT FLOW

Function: To control reactor effluent flow to stripper (D-1).

Description: Research Control minim flow valve, Trim M

Mat'l of Const: Body and trim, stainless steel

Comment: 1. See comment, Item LRC-1.

ITEM CV-2 CONTROL VALVE - REACTOR INERTS BLEED

Function: To control nitrogen bleed inerts from polymerization reactor (R-1).

Description: Research Control minim flow valve, Trim P-1

Mat'l of Const: Body and trim, stainless steel

Comment: 1. See comment, Item PRC-1.

ITEM CV-3 CONTROL VALVE - REACTOR JACKET WATER TEMPERATURE

Function:	To control steam addition to polymerization reactor (R-1) jacket tempered water system.
Description:	Research Control minim flow valve, Trim D.
Mat'l of Const:	Body and trim, stainless steel.
Comment:	1. See comment, Item TRC-2.

ITEM CV-4 CONTROL VALVE - STRIPPING ACETONE FLOW

Function:	To control stripping acetone flow to acetone vaporizer (E-6).
Description:	Research Control minim flow valve, Trim P-1.
Mat'l of Const:	Body and trim, stainless steel.
Comment:	1. See comment, Item FC-1.

ITEM CV-5 CONTROL VALVE - RECYCLE SYSTEM NITROGEN BLEED

Function:	To control inerts bleed from recycle system.
Description:	Research Control minim flow valve, Trim L.
Mat'l of Const:	Body and trim, stainless steel.
Comment:	1. See comment, Item PRC-2.

ITEM CV-6 CONTROL VALVE - STRIPPER PREHEAT WATER TEMPERATURE

Function:	To control steam addition to the hot water system for the stripper feed preheater (E-2).
Description:	Research Control minim flow valve, Trim N.
Mat'l of Const:	Body and trim, stainless steel.
Comment:	1. See comment, Item TRC-3.

ITEM CV-7 CONTROL VALVE - POLYMER SOLUTION TAKEOFF

Function:	To control flow of polymer solution from the stripper (D-1) bottom.
Description:	Research Control minim flow valve, Trim O.

Mat'l of Const: Body and trim, stainless steel.

Comment: 1. See comment, Item LC-1.

ITEM CV-8 CONTROL VALVE - ACETONE COLUMN BOTTOM PRESSURE

Function: To control flow of steam to the acetone column (D-2) bottom.

Description: Research Controls minim flow valve, Trim O.

Mat'l of Const: Body and trim, stainless steel.

Comment: See comment, Item PRC-3.

ITEM D-1 MONOMER STRIPPER

Function: To remove unreacted IB and VCl from the reactor (R-1) effluent stream.

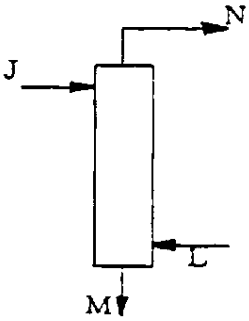
Description: Precision Distillation Apparatus Co., 2 in. dia. Oldershaw column with 5 sieve trays.

Mat'l of Const: Stainless steel.

Services: Steam.

Comment: 1. Details of the monomer stripper are given in Figure 4.

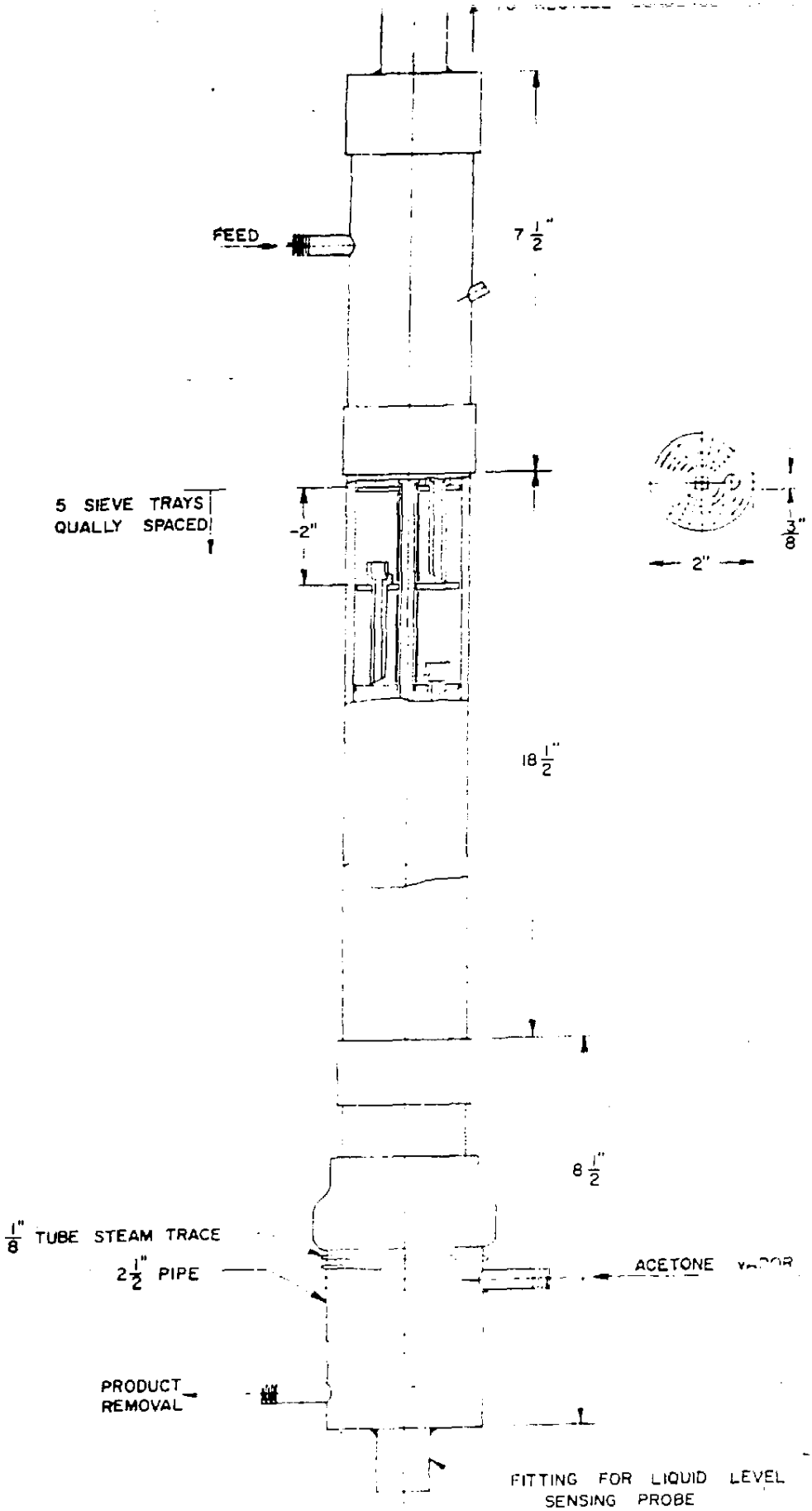
2. Material balance and typical operating conditions:



	Feeds (g/hr) Nonvolatiles	VCl-IB	Acetone	Temp. (°C)	Pressure (psig)
J	744.8	[illegible]	675.8	53	21
L	-	-	488.0	118	21
M	744.8	8.0	798.6	85	21
N	-	[illegible]	365.2	55	21

3. Heat Balance:

A completely valid heat balance cannot be given, because the relative proportions of vapor and liquid in the monomer stripper feed stream J are unknown. The heat balance given below is based on pilot plant operations, using the proportion of vapor and liquid computed by the methods described in Section IX-B-2.



FITTING FOR LIQUID LEVEL SENSING PROBE

DRAWN	MONSANTO CHEMICAL COMPANY
CHECKED	800 N LINDBERGH BLVD ST LOUIS 66 MO
DATE	FIGURE 4. MONOMER STRIPPING COLUMN
SCALE	
DIVISION	LOCATION
DWG NO.	PROJ NO

RSV 0017311

This heat balance should be used in design with full awareness of its limitations.

Basis: One hour's feed.

Reference: Liquids at feed temperature (53°C) zero enthalpy.

Thermodynamic properties (at 35 psia):

a. VCl (6)

Latent heat of vaporization	ΔH_v = 70.1 cal/g
Specific heat of vapor	C_{p_v} = 0.227 cal/g°C
Specific heat of liquid	C_{p_l} = 0.27 cal/g°C

b. Acetone (7, 8)

Latent heat of vaporization	ΔH_v = 96.8 cal/g
Specific heat of vapor (50°C)	C_{p_v} = 0.36 cal/g°C
(118°C)	C_{p_v} = 0.40 cal/g°C
Specific heat of liquid	C_{p_l} = 0.57 cal/g°C

c. Polymer (9)

Specific heat of liquid	C_{p_l} = 0.25 cal/g°C

	J		L		M		N	
	Flow g/hr	Enthalpy cal/hr	Flow g/hr	Enthalpy cal/hr	Flow g/hr	Enthalpy cal/hr	Flow g/hr	Enthalpy cal/hr
VCl - IB (vapor)	848.6	59,487	-	-	-	-	976.8	68,900
VCl - IB (liquid)	136.2	0	-	-	8.4	73	-	-
Acetone (vapor)	271.1	26,242	488.0	53,518	-	-	365.2	35,647
Acetone (liquid)	404.7	0	-	-	798.6	14,500	-	-
Polymer (liquid)	744.8		-	-	744.8	5,958	-	-
Total cal/hr		85,729		53,518		20,500		104,550
Btu/hr		340.1		81.7		414.9		212.3

Radiation losses in the column J - L - M - N = 55.8 Btu/hr

4. The vapor-liquid equilibria necessary for making rigorous theoretical stage calculations are not available. Approximate calculations have been made considering the binary system VCl-acetone. These calculations are given in detail in Section IX-B.

5. The viscosity of 50 weight percent polymer solution at 50°C is about 130 cp. A plant stripping column should be designed to handle a liquid phase of this viscosity.

6. An entrainment disengaging space is required at the top of the column. Vapor velocity in this space should not exceed 0.1 ft/sec. The use of a wire mesh demister at the top of the column is not recommended because of possible plugging problems. There was little entrainment in the pilot plant column.

7. Control of the stripping column operation is discussed in detail in Section IX-B-3.

ITEM D-2 ACETONE COLUMN

Function: To recover acetone from rotary vacuum filter (F-5) filtrate accumulated in filtrate storage tank (T-17).

Description: Rectifying section - 1 in. ID , 10-tray Oldershaw sieve tray column.
Stripping section - 1-7/8 in. ID , x 24 in. column packed with Goodloe wire mesh packing.

Mat'l of Const: Rectifying section - Pyrex glass.
Stripping section - Pyrex glass with stainless steel packing.

Comment:

1. The acetone column was operated with open steam to avoid a reboiler fouling problem.

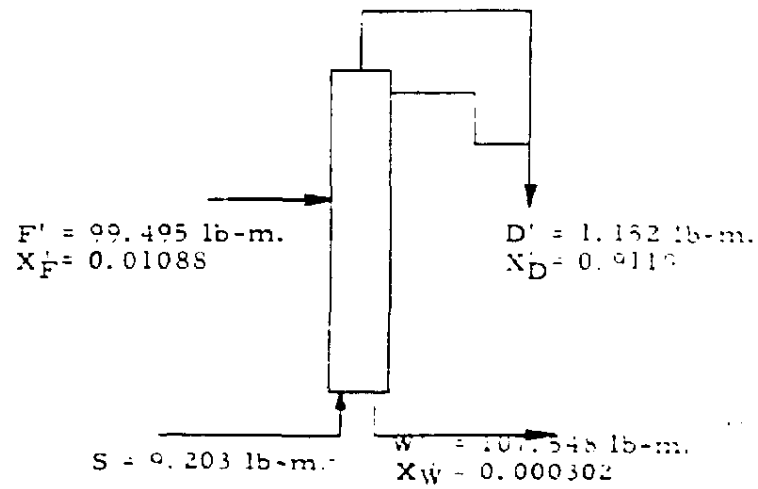
2. Calculation of the number of theoretical stages required for the separation is properly done by the modified latent heat of vaporization method (*10*).

3. Latent heats of vaporization at 56.1°C (acetone boiling point).
   Water: 18,327 Btu/lb-m.
   Acetone: 12,492 Btu/lb-m.

   Modified molecular weight acetone = $\left(\frac{18,327}{12,492}\right)(58.1) = 85.2$

4. Material balance for modified molecular weights.

   Basis: 100 lb-m feed actual
   Reflux ratio 2



Note: Primed symbols refer to modified molecular quantities. The X's are modified mole fractions of acetone.

5. Figure 5 is a McCabe-Thiele diagram for the actual pilot plant column. Figure 6 is a plot for the low concentration region. The material balance in Figure 5 is for actual pilot plant operation and uses a more dilute feed shown in Figure 1. The plots show five stripping and seven rectifying theoretical stages.

6. The design of a distillation column for recovering acetone from dilute aqueous solution is considered in detail in Section IX-F. Provision must be made for the very high liquid rates in the stripping section.

ITEM E-1 REACTOR REFLUX CONDENSER

Function: To condense VCl and IB vapors from reactor R-1.

Description: 3 ft length of jacketed 1 in. schedule 40 pipe.

Mat'l of Const: Stainless steel.

Services: Cooling water.

Comment:

1. This condenser was not actually used in any of the pilot plant polymerization runs. The reactor (R-1) temperature was controlled by adjusting the temperature of the water in the reactor jacket.

2. The condenser was used when the reactor was cleaned with refluxing solvent.

ITEM E-2 STRIPPER FEED PREHEATER

Function: To preheat monomer stripper (D-1) feed.

Description: 2 ft length of jacketed $\frac{3}{4}$ in. schedule 40 pipe.

Mat'l of Const: Stainless steel.

Services: Hot water.

Comment:

1. The inlet temperature of the stripper feed preheater was measured at 30°C. This temperature reflects the radiation losses from the reactor effluent flowing through the effluent filter (F-1) and the effluent line leading to the flow control valve (CV-1).

2. A heat balance for the stripper feed preheater is dependent on the inlet temperature which in plant operation would be expected to be considerably higher than 30°C because of smaller radiation losses. The plant heat balance should be based on consideration of expected radiation losses.

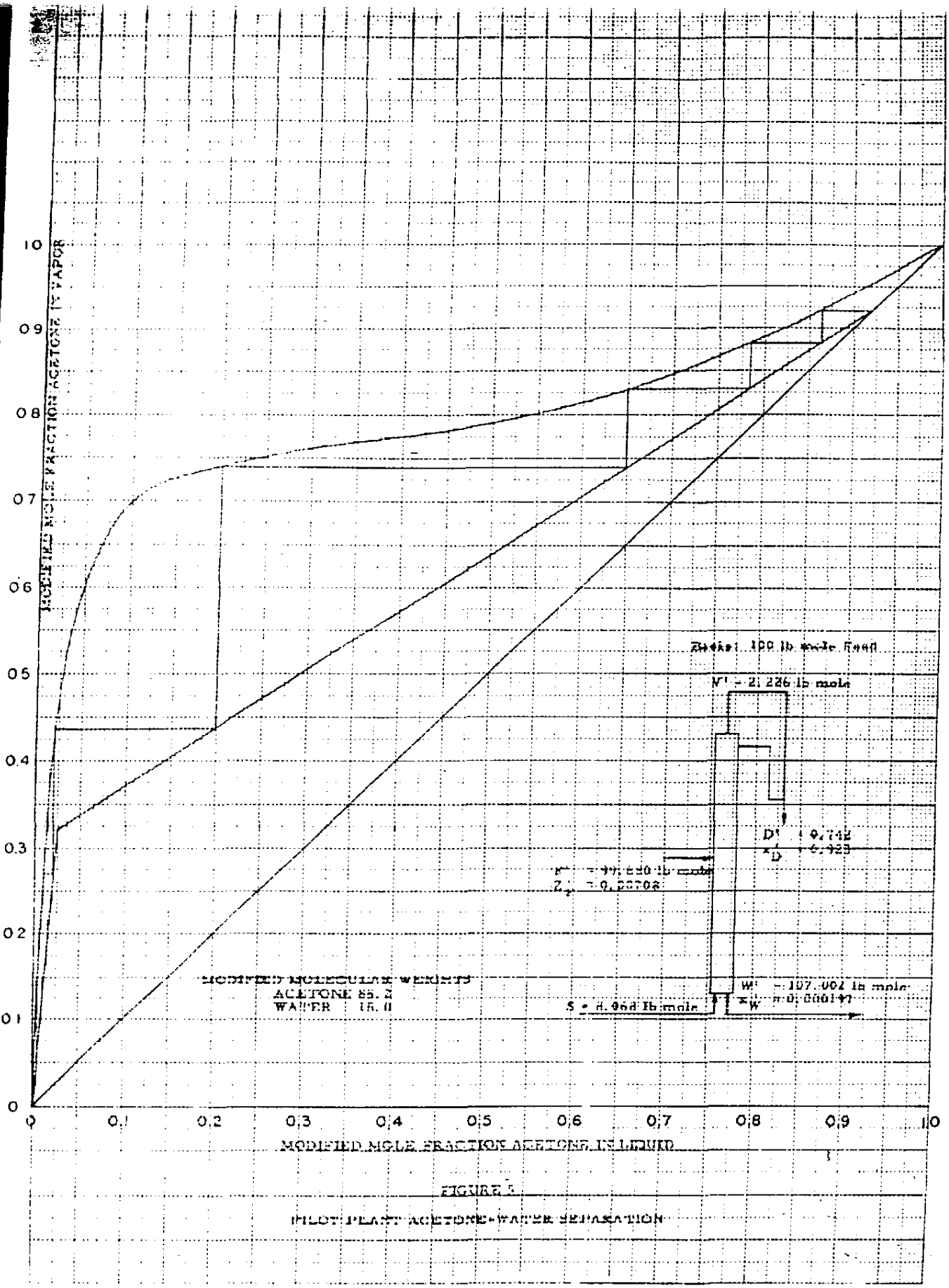


FIGURE 5

PILOT PLANT ACETONE-WATER RELAXATION

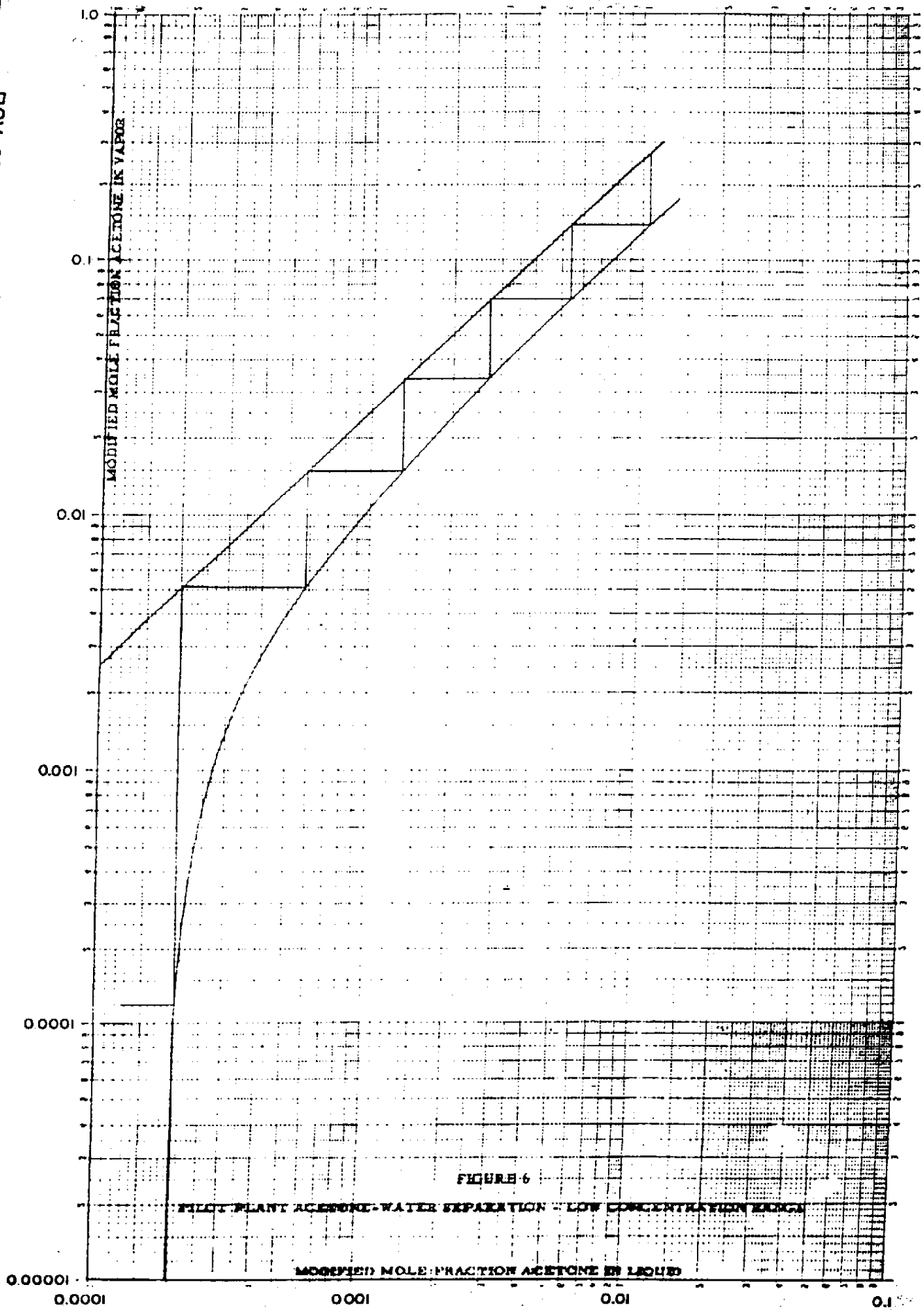


FIGURE 6

PILOT PLANT ACETONE-WATER SEPARATION - LOW CONCENTRATION RANGE

ITEM E-3 RECYCLE CONDENSER AND COLLECTOR

Function: To condense and collect the recycle vapors from the stripper (D-1).

Description: Young Radiator Co. heat exchanger Model 202Y followed by a 3 ft length of jacketed 2½ in. schedule 40 pipe.

Mat'l of Const: Stainless steel.

Services: Cooling water.

Comment:

1. The condenser sloped downward from the stripper (D-1) to the vertical collector. The feed line extended 24 inches into the collector. Top of the collector served as an inerts separator. In a plant installation the condenser should be operated vertically with the vapor inlet at the top to give a subcooled feed for the recycle pump (P-5).

2. The sensing probe of the liquid level controller (LC-2) extended 6 inches through the bottom of the collector.

3. A drain port was provided for draining the collector to waste in the case of entrainment of polymer from the stripping column (D-1).

4. The maximum temperature at which the recycle vapors will condense at 35 psia is 22.5°C.

5. Heat balance: (Basis liquid condensate at zero enthalpy. See Item D-1, Stream N.)

Enthalpy condensate	0
Enthalpy feed	414.9 Btu/hr
Heat duty	- 414.9 Btu/hr
	- 140.4 Btu/lb vapor

ITEM E-4 RECYCLE SUBCOOLER

Function: To subcool condensed recycle vapors from the recycle condenser and collector (E-3).

Description: 1½ ft length of jacketed ¾ in. schedule 40 pipe inside a 24 x 6 x 7¾ in. sheet metal brine bath.

Mat'l of Const: Stainless steel.

Services: Refrigerated brine.

Comment:

1. The purpose of E-4 was to subcool the recycle stream to prevent flashing across the suction check valves of the recycle pump (P-5).

2. The bath was designed to accommodate and cool the remote pump head of pump (P-5) utilizing available refrigeration.

3. In the plant use of an adequate head between the recycle collector (E-3) and recycle pump (P-5) will prevent flashing across the check valves. For a mixture of 70% VCl and 30% acetone at 60°F the head should be calculated on the basis of 2.6 ft of head per psi pressure drop across the suction valve. With this arrangement no recycle subcooler will be required.

4. In pilot plant operations, a small amount of ice which fouled the check valves of the recycle pump (P-5) formed when the brine in the recycle subcooler was operated below -5°C.

ITEM E-5 PRODUCT COOLER

Function: To cool the polymer solution effluent from the bottom of the monomer stripper (D-1).

Description: ¼-in.OD 20-ft coiled tube in 2-in.schedule 40 pipe.

Mat'l of Const: Stainless steel.

Services: Cooling water.

Comment:

1. The product cooler was used to cool the polymer solution below its normal boiling point (58.8°C) to prevent flashing of acetone during letdown to atmospheric pressure.

2. Heat Duty.
The heat capacities are (8, 9)

Polymer C_p = 0.25 cal/g°C
Acetone C_p = 0.357 cal/g°C at 50°C
C_p = 0.378 cal/g°C at 85°C

To cool 47.3% polymer solution from 85 to 58°C, assuming negligible heat of mixing (basis 1.0 g)

$\Delta H = -0.473\ (0.25)(85-50) - 0.523\ (0.367)(85-50)$
$\Delta H = -10.85$ cal/g
$\Delta H = -20.1$ Btu/lb polymer solution

ITEM E-6 STRIPPING ACETONE VAPORIZER

Function: To vaporize the acetone fed to the bottom of the stripper (D-1).

Description: Jacketed coiled tube 3/8 in.OD. Mean coil diameter 2½ in. 23 ft long. Total length of heat exchanger 2½ ft.

Mat'l of Const: Stainless steel.

Services: 120 psig steam.

Comment:

1. Heat duty (basis: 1.0 g). See Item D-1 for thermodynamic properties.
   Sensible heat duty liquid acetone (85-30) 0.57 = 31.4 cal/g
   Heat of vaporization = 96.8 cal/g
   ΔH_v = 128.2 cal/g = 231 Btu/lb.

2. Steam pressure in the jacket was regulated.

ITEM E-7 STRIPPING ACETONE SUPERHEATER

Function: To superheat the acetone feed to the bottom of the monomer stripper (D-1).

Description: 3-ft length of jacketed $\frac{1}{2}$-in.OD tubing.

Mat'l of Const: Stainless steel.

Services: 120 psig steam.

Comment:

1. The steam supply to heat exchangers (E-7) and (E-6) is connected in series with (E-7) leading (E-6). Temperature control is effected through steam pressure regulation.

2. Heat Duty.
   Sensible heat duty acetone vapor
   ΔH_s = (118-85) 0.39 = 12.9 cal/g = 23.2 Btu/lb.

ITEM E-8 ACETONE COLUMN FEED HEATER

Function: To heat feed to the acetone column (D-2).

Description: 12 mm dia x 30-in.glass tube wound with nichrome heating wire.

Mat'l of Const: Pyrex glass.

Services: 110 v electricity.

Comment:

1. The temperature of the heater effluent was controlled by manual adjustment of a variable transformer in the heater power supply.

2. Heat Duty:
   Inlet temperature 20°C.
   Outlet temperature 36°C.
   Specific heat of mixture = 0.98 Btu/lb-°F.
   Heat duty = (0.98)(36-20)(1.8) = 28.2 Btu/lb.

3. This heater would not be required in a plant, since use of cold feed to the acetone column (D-2) is desirable to minimize the number of theoretical stages required.

ITEM E-9 REFLUX HEAD

Function: To condense vapor from acetone column (D-2) and split distillate and reflux.

Description: Swinging funnel type glass reflux head.

Mat'l of Const: Pyrex glass.

Services: Cooling water
110 v a-c electricity.

Comment:

1. The reflux ratio to the acetone column was controlled by a Flexopulse timer in the power supply to a solenoid-operated valve in the reflux head.

2. Heat Duty:
ΔH_v = 225 Btu/lb vapor condensed at reflux ratio 2.
Heat duty = (3)(225) ▫ 675 Btu/lb distillate.

3. For plant application, a cooler for the distillate might be required to keep the distillate receiver (T-18) from running hot. Hot acetone may not be used to dissolve initiator because of the explosion hazard.

ITEM E-10 ACETONE COLUMN BOTTOMS COOLER

Function: To cool acetone column (D-2) bottoms.

Description: 20 mm dia x 10-in.glass tube with water jacket.

Mat'l of Const: Pyrex glass.

Services: Cooling water.

Comment:

1. This stream need be cooled only if value can be recovered from the sensible heat,or if discharge of hot water into the plant sewers is prohibited.

ITEM F-1 REACTOR EFFLUENT FILTER

Function: To filter reactor (R-1) effluent to remove polymer "grit".

Description: Cuno "Micro-Klean" fiber cartridge filter Model 1H1 with filter cartridge 2278-33 (5 μ).

Mat'l of Const: Filter housing - stainless steel
Filter cartridge - cellulose fiber.

Comment:
1. This cartridge filter is in general use in the paint and varnish industry where filtration is required after formulation.
2. A similar filter cartridge made of wool fibers (Cuno 2278-C1) should not be used because it discolors polymer solution.

ITEM F-2 VCl-MONOMER FILTER

Function: To filter VCl monomer charged to VCl metering standpipe (T-1).

Description: Hoke 540 series 50 micron filter.

Mat'l of Const: Body - stainless steel.
Gasket - Teflon.

ITEM F-3 STRIPPING ACETONE FILTER

Function: To filter stripping acetone upstream of stripping acetone flow controller (FC-1).

Description: Hoke 540 series 50 micron filter.

Mat'l of Const: Body - stainless steel.
Gasket - Teflon.

ITEM F-4 WATER FILTER

Function: To filter water feed to the disintegrator (T-13) and the rotary vacuum filter (F-5).

Description: Cuno "Micro-Klean" fiber cartridge filter Model C1AG with 5 μ cartridge.

Mat'l of Const: Filter housing - stainless steel.
Filter cartridge - cellulose.

Comment:
1. Used to filter rust particles from water supply.

ITEM F-5 ROTARY VACUUM FILTER

Function:	To filter and wash precipitated polymer accumulated in slurry hold tank (T-14).
Description:	Eimco Corp. drum type laboratory filter station 18 in. dia x 12 in. face.
Mat'l of Const:	All wetted parts stainless steel.
Services:	220 V, 3-phase electricity. Seal water for vacuum pump Item P-11.

Comment:

1. The laboratory filter station consisted of the following components:
   a. Filter drum: 18 in. dia x 12 in. wide.
   b. Filter medium: Cotton filter cloth on 4 x 4 wire mesh support.
   c. Drum drive: ½ hp variable speed (0.1-1 rpm).
   d. Agitator: Two steel arcs for swing type agitation. During operation it was found that filter cake formation on the drum was improved with a more vigorously agitated polymer slurry. A small air-driven laboratory mixer was employed for agitation of the slurry in the filter tank.
   e. Vacuum pump, Item P-11.
   f. Blower, Item P-12.
   g. Filtrate pumps, Items P-9 and P-10.
   h. Filtrate receivers, Items T-15 and T-16.

ITEM F-6 ACETONE COLUMN PRIMARY FILTER

Function:	To remove polymer solids from acetone column (D-2) feed.
Description:	Enzinger (Duriron Co., Dayton, Ohio) Laboratory vertical leaf pressure filter. The filter had 3 leaves, one with two 4-1/8" x 8-1/2" and two with two 2-1/8" x 8-1/2" filtering surfaces. The leaves were dressed with cloth bags sewn over them.

Mat'l of Const: Filter - type 316 stainless steel.
Gaskets - Buna-N.
Cloth - polypropylene style B-3407 (National Filter Media Corporation).

Comment:

1. The size of filter required for the plant will depend on the amount of solids passed by the rotary vacuum filter (F-5). An undetected cloth failure on the rotary vacuum filter could produce a very large surge of solids into the acetone. This did not occur in the pilot plant, but in extended plant operation an occasional mishap of this type would be inevitable. Plant designs should be developed to deal with this situation.

2. In the pilot plant an average cake of about 1/64" polymer was developed upon filtering 910 kg of acetone column feed. The material was mostly, but not entirely soluble in acetone.

3. A small amount of polymer was found on the leaves, inside the filter bags. This was mostly, but not entirely soluble in cold acetone. A Sparkler-type filter, which has easily cleaned internals, is recommended over the pressure leaf type filter for this service.

ITEM F-7 ACETONE COLUMN SECONDARY FILTER

Function: To remove fines passing the acetone column primary filter (F-6) from the acetone column (D-2) feed.

Description: Cuno model 1C1AG Micro-Klean filter with 2215-B element (Cuno Engineering Co., Meridan, Conn.).

Mat'l of Const: Body - die-cast aluminum.
Element - cellulose.

Comment:

1. The very small amount of material collected in this filter from 910 kg of acetone column feed appeared roughly equal to that deposited in the acetone column (D-2). For this reason, inclusion of the secondary filter in plant design appears justified. Another advantage is that it will prevent a large amount of polymer from entering the column in the event of a failure in the acetone column primary filter (F-5).

ITEM F-8 RECYCLE ACETONE FILTER

Function: To filter recycle acetone downstream of the distillate receiver (T-18).

Description:	**Cuno Model 1C1AG Micro-Klean filter with 2215-B element.**
Mat'l of Const:	**Body - die-cast aluminum.** **Element - cellulose.**

ITEM FC-1 STRIPPING ACETONE FLOW CONTROLLER

Function:	To sense and control flow of liquid stripping acetone to the acetone vaporizer (E-6).
Description:	Foxboro model M /59 flow controller mounted on Foxboro model 13A d/p cell with 0.020-inch integral orifice.
Mat'l of Const:	Body - stainless steel. Gaskets - Teflon.
Services:	Instrument air.
Comment:	1. Controller set point signal was indicated by PI-7. Flow was recorded on FR-1. The output signal was applied to CV-4.

ITEM FI-1 NITROGEN FEED ROTAMETER (REACTOR)

Function:	To indicate N_2 flow to the reactor (R-1). This nitrogen provided a N_2 pad over the reactor charge.
Description:	Fischer and Porter 1700 series rotameter with 02F-1/8-16-5/70 tube and 1/8-in.sapphire ball float.
Mat'l of Const:	Tube - glass. Body - stainless steel. Gaskets - neoprene.
Comment:	1. When the reactor (R-1) was operated at autogeneous pressure, this rotameter was needed only for purging during start-up.

ITEM FI-2 NITROGEN FEED ROTAMETER (RECYCLE SYSTEM)

Function:	To indicate N_2 flow to the recycle condenser (E-3).
Description:	Fischer and Porter 2700 series rotameter with FP-1/16-20-G-5/81 tube and 1/16-in.sapphire ball float.
Mat'l of Const:	Tube - glass. Body - stainless steel. O-Ring - Buna-N.

ITEM FI-3 PRECIPITANT ROTAMETER

Function:	To indicate flow of precipitant to first stage of SRC disintegrator (T-13).
Description:	Fischer and Porter 700 series rotameter with B-4-21-10/27 tube and special float.
Mat'l of Const:	Tube - glass. Body - stainless steel. Gaskets - neoprene.

ITEM FI-4 FILTER CAKE WASH ROTAMETER

Function:	To indicate flow of wash water to rotary vacuum filter (F-5).
Description:	Fischer and Porter 700 series rotameter with B-4-21-10/27 tube and special float.
Mat'l of Const:	Tube - glass. Body - stainless steel. Gaskets - neoprene.

ITEM FI-5 ACETONE COLUMN FEED ROTAMETER

Function:	To indicate flow of acetone filtrate feed to acetone column (D-2).
Description:	Fischer and Porter 2700 series rotameter with 2F tube and ¾-in.ball float.
Mat'l of Const:	Body - stainless steel. Tube - glass. Float - stainless steel. Gaskets - Viton.

ITEM FR-1 STRIPPING ACETONE FLOW RECORDER

Function:	To record stripping acetone flow to acetone vaporizer (E-6).
Description:	Foxboro universal case pneumatic recording receiver.
Comment:	1. See comment, Item FC-1, for details of application.

ITEM J-1 FEED SYSTEM EJECTOR

Function:	To evacuate all feed system components requiring charging by vacuum (T-3, T-4, T-5, and T-6).
Description:	Worthington 2½ cpa steam ejector with 9-in.barometric condenser used at atmospheric pressure.
Mat'l of Const:	Porcelain.
Services:	100 psig steam, water to condense plume.

ITEM LC-1 MONOMER STRIPPER LIQUID LEVEL CONTROL

Function:	To control product withdrawal rate through liquid level control in the bottom of the monomer stripper.
Description:	Robertshaw Fulton model 305-A3-N1 Level-Tek liquid level control operating a Skinner X-5 three-way solenoid valve through an Agastat 22QT time delay relay.
Mat'l of Const:	Sensing probe - Teflon covered, in stainless steel mounting gland.
Services:	110 V, 1-phase electricity. Instrument air.
Comment:	1. The 110 V output of the liquid level control relay was converted to a 3-15 psi off-on air signal utilizing the three-way solenoid valve. 2. The Agastat time delay relay was included in the system to prevent too rapid cycling of the solenoid valve.

ITEM LC-2 RECYCLE COLLECTOR LIQUID LEVEL CONTROL

Function:	To control the operation of the recycle pump (P-5) through liquid level control in the recycle collector (E-3).
Description:	Robertshaw Fulton model 305-A3-N1 Level-Tek liquid level control operating the recycle pump (P-5) through an Agastat 22QT time delay relay.
Mat'l of Const:	Sensing probe - Teflon covered, in stainless steel mounting gland.
Services:	110 V, 1-phase electricity.
Comment:	1. The Agastat time delay relay was included in the system to prevent too rapid cycling of the recycle pump.

ITEM LR-1 FEED SYSTEM LEVEL RECORDER

Function:	To record the signals from the feed metering standpipe level transmitters (LT-1, LT-2, LT-3 and LT-4).
Description:	Minneapolis-Honeywell Brown 6-point strip-chart recorder; 0-10 mv range.
Services:	110 V electricity.
Comment:	1. The signals recorded indicate the liquid level in the standpipes (LT-1, LT-2, LT-3 and LT-4). 2. The instrument included a device for marking the chart at half-hour intervals.

ITEM LRC-1 REACTOR LEVEL RECORDER CONTROLLER

Function:	To record and control the reactor (R-1) liquid level by setting the control valve reactor effluent flow (CV-1).
Description:	Bristol series 532 recording pneumatic controller with 5-8 psig input span.
Services:	Instrument air.
Comment:	1. For proper operation of the stripping column (D-1), the flow of reactor effluent to the stripper must be controlled by a flow controller cascaded with the output of the reactor level controller (LRC-1). See Discussion, Section IX.-A-3-C. 2. See comment, Item LT-5.

ITEM LT-1 VCl LEVEL TRANSMITTER

Function:	To transmit VCl level in VCl metering standpipe (T-1) to feed system level recorder (LR-1).
Description:	Foxboro model 613 electronic d/p cell transmitter.
Mat'l of Const:	Body - stainless steel.
Services:	110 V electricity.

ITEM LT-2 IB LEVEL TRANSMITTER

Function:	To transmit IB level in IB metering standpipe (T-2) to feed system level recorder (LR-1).

Description:	Foxboro model 613 electronic d/p cell transmitter.
Mat'l of Const:	Body - stainless steel.
Services:	110 V electricity.

ITEM LT-3 EHF LEVEL TRANSMITTER

Function:	To transmit EHF level in EHF metering standpipe (T-3) to feed system level recorder (LR-1).
Description:	Foxboro model 613 electronic d/p cell transmitter.
Mat'l of Const:	Body - stainless steel.
Services:	110 V electricity.

ITEM LT-4 INITIATOR SOLUTION LEVEL TRANSMITTER

Function:	To transmit initiator solution level in initiator solution metering standpipe (T-4) to feed system level recorder (LR-1).
Description:	Foxboro model 613 electronic d/p cell transmitter.
Mat'l of Const:	Body - stainless steel.
Services:	110 V electricity.

ITEM LT-5 REACTOR LEVEL TRANSMITTER

Function:	To sense and transmit reactor (R-1) level to reactor level recorder controller (LRC-1).
Description:	A device for measuring the force exerted on a paddle attached to the end of a lever by the swirling motion of liquid in the reactor and transmitting a pneumatic signal proportional to this force.
Mat'l of Const:	Paddle and lever assembly - stainless steel.
Services:	Instrument air.
Comment:	1. Details of the instrument are given in the Central Research Department Analytical Devices Laboratory Drawing G-6272. The device consisted essentially of a lever extending into the reactor (R-1) through a top nozzle, a paddle at the end of the lever which was

partially immersed in the process fluid, a bellows seal on the lever at the nozzle, a fulcrum just above the nozzle and a Tate Emery DA-60 pneumatic load cell above the fulcrum for measuring the force exerted on the paddle by the swirling liquid.

2. In operation the force exerted on the paddle was proportional to the depth of immersion of the paddle in the reactor charge. As the level rose, the signal transmitted by the load cell increased; as it fell, the signal decreased.

3. A new design for a level transmitter employing the principle of measuring the force exerted on a partially immersed paddle by a swirling liquid has been prepared. In this design the measuring head of a Foxboro Type 18A target flow transmitter is used to sense the force on a lever extending into a stirred reactor. The Foxboro transmitter contains sensing device, fulcrum and seal. Its use offers the advantage of substantial mechanical simplicity.

4. The calibration of this device was checked periodically by opening the outlet of an inverted dip tube which extended into the reactor from the top and terminated at the desired reactor operating level.

ITEM P-1 VCl MONOMER FEED PUMP

Function: To pump and meter VCl monomer feed to the reactor (R-1).

Description:
a) For flow rates above 800 g/hr - Lapp Pulsafeeder type CPS-1 positive displacement diaphragm pump.

b) For flow rates below 800 g/hr - Lapp Pulsafeeder type LS-20 positive displacement diaphragm pump.

Matl of Const: Reagent head - stainless steel.
Diaphragm, CPS-1 - stainless steel.
LS-20 - Kel-F.

Services: 110 V, 1-phase electricity.

Comments:
1. The check valves on the larger pump type CPS-1 were unsatisfactory for VCl service and were supplemented with Hoke series 570 check valves at both suction and discharge locations.

2. The feed rates of all Lapp pumps were monitored continuously during runs and the pump settings were adjusted at half-hour intervals to maintain desired feed rates. This was done because the volumetric efficiencies of the diaphragm pumps, particularly when operated below 50% of rated capacity, were poor and exhibited pronounced sensitivity to fluctuations in suction pressure. A complete charge of a standpipe would increase the suction pressure 2-3 psi with a concurrent increase of flow rate of about 10%. In the case of the volatile feed streams fluctuations in the static pressure controllers caused considerable drift in pump feed rates (as much as 20%). Through continued monitoring the feed rates were generally maintained within ± 2% of the total feed.

ITEM P-2 IB MONOMER FEED PUMP

Function:	To pump and meter IB monomer feed to the reactor (R-1).
Description:	Lapp Pulsafeeder type LS-10 positive displacement diaphragm pump with 4:1 gear reduction in the motor drive.
Mat'l of Const:	Reagent head - stainless steel, Diaphragm - Kel-F.
Services:	110 V, 1-phase electricity.
Comment:	1. See comment, Item P-1.

ITEM P-3 EHF MONOMER FEED PUMP

Function:	To pump and meter EHF monomer feed to the reactor (R-1).
Description:	Lapp Pulsafeeder type LS-20 positive displacement diaphragm pump.
Mat'l of Const:	Reagent head - stainless steel. Diaphragm - Kel-F.
Services:	110 V, 1-phase electricity.
Comment:	1. See comment, Item P-1.

ITEM P-4 INITIATOR SOLUTION FEED PUMP

Function:	To pump and meter initiator solution feed to the reactor (R-1).
Description:	Same as Item P-3.

Comment: 1. See comment, Item P-1.

ITEM P-5 RECYCLE PUMP

Function:	To pump condensate from recycle collector (E-3) to reactor (R-1).
Description:	Lapp Pulsafeeder type LS-3 positive displacement diaphragm pump with remote head.
Mat'l of Const:	Reagent head - stainless steel. Diaphragm - stainless steel.
Services:	110 V, 1-phase electricity.
Comment:	1. See comment, Item E-4.

ITEM P-6 POLYMER SOLUTION PUMP

Function:	To pump and meter polymer solution feed to SRC Disintegrator (T-13).
Description:	Viking model C54G pump with Vickers variable speed drive.
Mat'l of Const:	All iron.
Services:	220 V, 3-phase electricity.

ITEM P-7 PRECIPITANT PUMP

Function:	To pump precipitant (water) from precipitant feed tank (T-12) to SRC Disintegrator (T-13).
Description:	Eastern model D-11 centrifugal pump.
Mat'l of Const:	Body and impeller - stainless steel. Seal gaskets - Teflon.
Services:	110 V, 1-phase electricity.

ITEM P-8 POLYMER SLURRY PUMP

Function:	To transfer polymer slurry from slurry hold tank (T-14) to rotary vacuum filter (F-5).
Description:	Eastern model D-11 pump with mechanical seal.

Mat'l of Const:	Body and impeller - 316 stainless steel. Seal gaskets - Teflon.
Services:	110 V, 1-phase electricity.

ITEM P-9 WASH FILTRATE PUMP

Function:	To transfer wash filtrate from wash filtrate receiver (T-15) to precipitant feed tank (T-12).
Description:	Worthington Worthite model 1-CNG-64 centrifugal pump.
Mat'l of Const:	Stainless steel.
Comment:	1. A check valve is required in the pump discharge line to preserve vacuum in the filter system. 2. This pump is part of the rotary vacuum filter (F-5).

ITEM P-10 FILTRATE PUMP

Function:	To transfer filtrate from filtrate receiver (T-16) to filtrate hold tank (T-17).
Description:	Worthington Worthite model 1-CNG-64 centrifugal pump.
Mat'l of Const:	Stainless steel.
Comment:	1. See comment, Item P-9.

ITEM P-11 VACUUM PUMP

Function:	To maintain vacuum in the rotary vacuum filter (F-5).
Description:	Nash rotary wet pump model MD-573.
Mat'l of Const:	Unknown.
Comment:	1. The vacuum pump is part of the rotary vacuum filter (F-5).

ITEM P-12 BLOWER

Function:	To supply air for blowing filter cake from filter cloth on the rotary vacuum filter (F-5).
Description:	Roots-Connersville model 22-AF low-pressure blower.

Mat'l of Const:	Unknown.
Comment:	1. The blower is part of the rotary vacuum filter (F-5).

ITEM P-13 ACETONE COLUMN FEED PUMP

Function:	To pump feed to acetone column (D-2) from filtrate storage tank (T-17).
Description:	Eastern Industries model D-11 centrifugal pump.
Mat'l of Const:	Body and impeller - stainless steel. Seal gaskets - Teflon.
Services:	110 V, 1-phase electricity.
Comment:	1. A steel pump may be used in this service.

ITEM PI-1 VCl STANDPIPE PRESSURE INDICATOR

Function:	To indicate pressure in VCl metering standpipe (T-1).
Description:	Ashcroft 30-0-150 compound pressure gage.
Mat'l of Const:	Steel.

ITEM PI-2 IB STANDPIPE PRESSURE INDICATOR

Function:	To indicate pressure in IB metering standpipe (T-2).
Description:	Ashcroft 30-0-150 compound pressure gage.
Mat'l of Const:	Steel.

ITEM PI-3 EHF STANDPIPE VACUUM INDICATOR

Function:	To indicate vacuum in EHF metering standpipe (T-3) during charging operation.
Description:	Ashcroft 0-30-in vacuum gage.
Mat'l of Const:	Steel.

ITEM PI-4 INITIATOR SOLUTION STANDPIPE VACUUM INDICATOR

Function:	To indicate vacuum in initiator solution standpipe (T-4) during charging operation.
Description:	Ashcroft 0-30 in vacuum gage.
Mat'l of Const:	Steel.

ITEM PI-5 STRIPPER TRACE STEAM PRESSURE INDICATOR

Function:	To indicate steam pressure on trace line on the exterior surface of the bottom section of the monomer stripper (D-1).
Description:	Ashcroft 0-100 psi pressure gage.
Mat'l of Const:	Brass.

ITEM PI-6 STEAM PRESSURE INDICATOR STRIPPING ACETONE SYSTEM

Function:	To indicate steam pressure of steam supply to stripping acetone vaporizer (E-6) and superheater (E-7).
Description:	Ashcroft 0-200 psi pressure gage.
Mat'l of Const:	Brass.

ITEM PI-7 FLOW CONTROL PRESSURE INDICATOR

Function:	To indicate set point signal to stripping acetone flow controller (FC-1).
Description:	Foxboro small case indicating gage model B5084, 3-15 psi.
Mat'l of Const:	Steel.

ITEMS PI-8 AND PI-9 STRIPPING ACETONE TANK PRESSURE INDICATOR

Function:	To indicate pressure in the stripping acetone storage tanks (T-5) and (T-6).
Description:	Ashcroft 0-100 psi pressure gage.
Mat'l of Const:	Brass.

ITEM PI-10 VCl STORAGE TANK PRESSURE INDICATOR

Function: To indicate transfer pressure in the VCl monomer storage tank (T-7).

Description: Ashcroft 0-300 psi pressure gage.

Mat'l of Const: Steel.

ITEM PI-11 STEAM PRESSURE INDICATOR

Function: To indicate steam pressure in steam line to steam-water mixer used to heat precipitant feed to SRC Disintegrator (T-13).

Description: Ashcroft gage 0-200 psi.

Mat'l of Const: Stainless steel tube.

ITEM PI-12 PRESSURE INDICATOR ACETONE COLUMN FEED

Function: To indicate pressure in acetone column (D-2) feed system.

Description: Ashcroft 0-15 psig gage.

Mat'l of Const: Steel.

Comment: 1. The pressure in the feed system was controlled by recycling part of the output of the acetone column feed pump (P-13) to the filtrate storage tank (T-17) on manual control.

ITEM PRC-1 REACTOR PRESSURE RECORDER CONTROLLER

Function: To record and control pressure in reactor (R-1).

Description: Foxboro model M40 recorder controller.

Services: Instrument air.

Comment: 1. Pressure control was effected through inerts bleed through control valve (CV-2).

ITEM PRC-2 RECYCLE SYSTEM PRESSURE RECORDER CONTROLLER

Function: To record and control pressure in the recycle system.

Description:	Foxboro model M54 Consotrol receiver recorder with integrally mounted M58 controller.
Services:	110 V electricity. Instrument air.
Comment:	1. Pressure control was effected through inerts bleed through control valve (CV-5).

ITEM PRC-3 ACETONE COLUMN BOTTOM PRESSURE CONTROLLER

Function:	To control pressure drop across acetone column (D-2) as indicated by acetone column bottom pressure transmitter (PT-3) by controlling flow of open steam to the column bottom.
Description:	Foxboro M-40 pneumatic recording controller with proportional and reset control actions.
Services:	Instrument air.
Comment:	1. Acetone column bottom pressure control valve (CV-8) was set by this controller.

ITEM PT-1 REACTOR PRESSURE TRANSMITTER

Function:	To transmit reactor (R-1) pressure to reactor pressure recorder controller (PRC-1).
Description:	Foxboro model 45 indicating pressure transmitter, 0-350 psi.
Matl of Const:	Sensing element - stainless steel.
Services:	Instrument air.

ITEM PT-2 RECYCLE SYSTEM PRESSURE TRANSMITTER

Function:	To transmit recycle collector (E-3) pressure to recycle system pressure recorder controller (PRC-2).
Description:	Foxboro model 45 indicating pressure transmitter, 0-75 psig range.
Matl of Const:	Sensing element, stainless steel.
Services:	Instrument air.

ITEM PT-3 ACETONE COLUMN BOTTOM PRESSURE TRANSMITTER

Function: To sense pressure in steam line leading to bottom of acetone column (D-2).

Description: Taylor pneumatic differential pressure transmitter 0-40 in H_2O range.

Mat'l of Const: Stainless steel.

Comment:

1. The high-pressure tap of the transmitter was connected to the steam line leading to the column bottom. The low-pressure tap was open to the atmosphere.

2. See comment, Item PRC-3.

ITEM R-1 POLYMERIZATION REACTOR

Function: Reactor for solution polymerization of VCl, EHF and IB.

Description: Glascote type LR-2 2-gallon jacketed glass-lined laboratory reactor with agitator.

Mat'l of Const:
Vessel - glass-lined steel.
Flanges - stainless steel.
Gaskets - Teflon envelope.
Safety head - nickel.

Services:
Jacket - hot water.
Drive - 220 V, 3-phase electricity.

Comment:

1. Reactor was rated for 500 psig internal working pressure. The safety head was rated to burst at 305 psig.

2. Reactor agitator: Two-bladed anchor type, glass coated, to fit 1¼ in. rotary mechanical seal.

   Agitator drive: Single speed belt driven 345 rpm.

   Rotary mechanical seal: Durametallic type consisting of 1¼ in. rotary double dura-seal assembly and unitized seal oil circulating and cooling system Dura-pressure unit G-5-100. The seal oil pressure was set at 30 psi above reactor operating pressure. Seal oil SAE #10.

3. Reactor nozzles:
   Head:
   Agitator shaft - 1¼ in.
   Vent assembly - 1 in.
   Feed inlet - 1 in.
   Bottom:
   Product removal - 2 in.

Vent Assembly:

One in. stainless steel flange containing a 1 in. schedule 40 vent line which was connected to the reflux condenser and from which a 1 in. schedule 40 pipe was branched to the safety head and the manual vent valve. Contained within the vent line were a ¼ in. stainless steel tube recycle line which extended 6 in. below the flange face of the nozzle and a ¼ in. stainless steel dip tube, the immersion length of which provided a reference for the reactor volume.

Feed Inlet:

The mounting plate for the reactor level transmitter (LT-5) acted as a flange containing four 1/8 in. stainless steel feed inlet tubes which extended 2½ in. below the mounting plate face without interfering with the motion of the liquid level sensing lever (LT-5).

Bottom:

Two in. stainless steel flange containing a ½ in. product drain flush with flange face, a ¼ in. tube thermowell extending 3 in. above the flange face and a ¼ in. sample port extending 2 in. above the flange face.

4. Heat Release:

The standard heat of polymerization for vinyl chloride estimated by Roberts (11) is -17 kcal/g-mole (liquid-liquid). This estimate is taken as the heat of reaction for VCl/EHF/IB terpolymer at 80°C in the absence of better data.

For reaction at 80°C with the feed and recycle input streams at 20°C, the enthalpy of the feed relative to liquid at 80°C per hour is:

VCl	(1459.2)	(0.27) (20-80)	= -23639 cal/hr
EHF	(165.1)	(0.56) (20-80)	= - 5481 cal/hr
IB	(100.6)	(0.62) (20-80)	= - 3742 cal/hr
Acetone	(675.8)	(0.57) (20-80)	= -23112 cal/hr
H_2O	(7.2)	(1.00) (20-80)	= - 432 cal/hr
AZBN	(7.3)	(0.50) (20-80)	= - 219 cal/hr
			-56625 cal/hr

Moles polymer/hr = 10.056 g.mole/hr.

Heat release = (17,000) (10.058) - 56625
= (170986 - 56625 = 114361 cal/hr
= 114361/730.7 = 156.5 cal/g polymer
= 282 Btu/lb polymer

ITEM S-1 DISCHARGE SNUBBER

Function:	To separate seal water from exhaust products of blower (P-12).
Description:	Burgess STC-1 snubber.
Mat'l of Const:	Unknown.
Comment:	1. The discharge snubber was part of rotary vacuum filter (F-5).-

ITEM T-1 VCl METERING STANDPIPE

Function:	To store VCl under helium pressure for continuous feed to reactor (R-1).
Description:	7 ft length 3 in. schedule 40 seamless pipe mounted vertically.
Mat'l of Const:	Stainless steel.
Services:	100 psig helium, vacuum.
Comment:	1. Helium pressure was adjusted to 15 psi above the vapor pressure of VCl at ambient temperature.

ITEM T-2 IB METERING STANDPIPE

Function:	To store IB under helium pressure for continuous feed to reactor (R-1).
Description:	7 ft length 3/4 in. schedule 40 seamless pipe mounted vertically.
Mat'l of Const:	Stainless steel.
Services:	100 psig helium, vacuum.
Comment:	1. Helium pressure was adjusted to 15 psi above the vapor pressure of IB at ambient temperature.

ITEM T-3 EHF METERING STANDPIPE

Function:	To store EHF for continuous feed to reactor (R-1).
Description:	7 ft length 3/4 in. schedule 40 seamless pipe mounted vertically.
Mat'l of Const:	Stainless steel.
Services:	Vacuum.
Comment:	Standpipe was charged by applying 10 in. Hg vacuum.

ITEM T-4 INITIATOR SOLUTION METERING STORAGE STANDPIPE

Function:	To store initiator solution for continuous feed to reactor (R-1).
Description:	7 ft length 2 in. schedule 40 seamless pipe.
Mat'l of Const:	Stainless steel.
Services:	Vacuum.
Comment:	1. Standpipe was charged by applying 10 in. Hg vacuum.

ITEMS T-5 AND T-6 STRIPPING ACETONE STORAGE TANK

Function:	To store under nitrogen pressure stripping acetone for continuous feed to monomer stripper (D-1).
Description:	2000 cu. in. Air Force surplus oxygen tank mounted vertically on platform scales.
Mat'l of Const:	Stainless steel.
Services:	50 psig nitrogen, vacuum.
Comment:	1. Nitrogen supply line was equipped with 50 psig pressure relief valve. 2. Tanks were charged by applying vacuum.

ITEM T-7 VCl MONOMER STORAGE TANK

Function:	To store under helium pressure VCl monomer for transfer to VCl monomer metering standpipe (T-1).

Description: Size 1A cylinder with full-length dip tube.

Mat'l of Const: Carbon steel.

Services: 100 psig helium.

Comment: 1. The tank was equipped with a 200 psig pressure relief valve.

ITEM T-8 IB MONOMER STORAGE TANK

Function: To store under helium pressure IB monomer for transfer to IB monomer metering standpipe (T-2).

Description: Size 2 cylinder with full-length dip tube.

Mat'l of Const: Carbon steel.

Services: 100 psig helium.

Comment: The cylinder shut-off valve was equipped with a 1400 psi bursting disc.

ITEM T-9 EHF MONOMER STORAGE TANK

Function: To store EHF monomer for transfer to EHF monomer metering standpipe (T-3).

Description: 2 liter burette.

Mat'l of Const: Glass.

ITEM T-10 INITIATOR SOLUTION TANK

Function: To prepare and store initiator solution fed to the initiator solution metering standpipe (T-4).

Description: 1 gallon jug.

Mat'l of Const: Glass.

Comment: 1. The preparation of large quantities of initiator solution should be carried out observing the following precautions:

a. The concentration of azo-bis-isobutyronitrile in acetone should never exceed 4%, i.e., the azo-initiator should be added to the bulk of acetone in an agitated vessel.

b. Avoid mixing and storage facilities which would permit accumulation of nondissolved initiator.

c. Avoid exposure of initiator solution to temperatures in excess of 35°C.

d. Details of hazards involved in handling initiator are given in Section XII-A-5.

ITEM T-11 POLYMER SOLUTION TANK

Function: To collect polymer solution effluent from monomer stripper (D-1), stabilize with Paraplex G-62, and store for feed to disintegrator (T-13).

Description: 1 gallon jug.

Mat'l of Const: Glass.

Comment: 1. In the plant the stabilizer should be metered to the polymer solution in an agitated vessel. Paraplex G-62 can be handled in a metering pump without dilution.

ITEM T-12 PRECIPITANT FEED TANK

Function: To store precipitant for feed to SRC disintegrator (T-13).

Description: 55 gallon drum.

Mat'l of Const: Phenolic lined steel drum.

ITEM T-13 SRC DISINTEGRATOR

Function: To precipitate acetone-polymer solution stored in polymer solution tank (T-11) by mixing with water from precipitant feed tank (T-12).

Description: Four inch ID x 8 inch cylindrical tank with special high intensity agitators.

Mat'l of Const: Tanks and agitators - stainless steel.
Packing - Teflon impregnated asbestos.

Services: 220 V, 3-phase electricity.

Comment: 1. The design of this equipment is closely held proprietary information of Shawinigan Resins Corp. Details of the pilot plant SRC disintegrator are given in Shawinigan Resins Corp. drawing RD 497.

ITEM T-14 SLURRY HOLD TANK

Function:	To collect and store slurry from the SRC disintegrator (T-13) for feeding to the rotary vacuum filter (F-5).
Description:	20 gallon polyethylene garbage can.
Mat'l of Const:	Polyethylene.
Comment:	1. In a plant operation this tank will pose a substantial fire and explosion hazard because of the small amounts of VCl and IB which may be evolved there. Two solutions are possible -- blanket the tank with inert gas, or maintain a heavy stream of air through it to dilute the VCl and IB.

ITEM T-15 WASH FILTRATE RECEIVER

Function:	To collect and store wash filtrate for feeding to the precipitant feed tank (T-12).
Description:	10 in. dia x 20 in. receiver.
Mat'l of Const:	Stainless steel.
Comment:	1. This receiver was part of the rotary vacuum filter (F-5).

ITEM T-16 FILTRATE RECEIVER

Function:	To collect and store filtrate for feeding to the acetone recovery system.
Description:	10 in. dia x 20 in. receiver.
Mat'l of Const:	Stainless steel.
Comment:	1. This receiver was part of the rotary vacuum filter (F-5).

ITEM T-17 FILTRATE STORAGE TANK

Function:	To accumulate filtrate from the rotary vacuum filter (F-5) for feeding to the acetone column (D-2).
Description:	55 gallon drum.
Mat'l of Const:	Polyethylene-lined steel.

Comment:

1. **This tank should be equipped with a suitable flame arrestor in the vent.**
2. **This tank was located on platform scales.**

ITEM T-18 DISTILLATE RECEIVER

Function: To collect and weigh distillate from acetone column (D-2).

Description: 1 gallon jug.

Mat'l of Const: Glass.

Comment:

1. Steel or stainless steel can be used in plant operations. Stainless is recommended to prevent contamination of acetone by rust.
2. In a plant application this tank should be equipped with a suitable flame arrestor in the vent.
3. This tank was located on platform scales.
4. For plant application, a day tank equipped with gage glass is recommended.
5. For plant application, a product cooler between the reflux head (E-9) and the distillate receiver may be required. Hot acetone may not be used to prepare initiator solution in initiator solution tank (T-10) because of the explosion hazard.

ITEM T-19 BOTTOMS RECEIVER

Function: To collect and weigh bottoms from acetone column (D-2).

Description: 5 gallon can.

Mat'l of Const: Steel.

Comment:

1. This tank was located on platform scales.
2. This tank will not be needed in a plant. The bottoms may be cooled by mixing with cold water and sent to the waste disposal or sewer system.

ITEM T-20 INITIATOR INJECTION TUBE

Function: To store the initial charge of AZBN-solution for transfer to the reactor (R-1) under helium pressure.

Description:	2 ft length of 1½ in. schedule 40 pipe.
Mat'l of Const:	Stainless steel.
Services:	300 psig helium.
Comment:	1. The contents of the initiator injection tube were transferred to the reactor through the sampling manifold (Figure 14).

ITEM TI-1 TEMPERATURE INDICATOR ACETONE VAPORIZER STEAM SUPPLY

Function:	To indicate steam temperature in the jacket of the acetone vaporizer (E-6).
Description:	Ashcroft dial thermometer 0-300°C.
Mat'l of Const:	Stainless steel.

ITEM TI-2 PRECIPITANT FEED TEMPERATURE INDICATOR

Function:	To monitor precipitant feed temperature to SRC Disintegrator (T-13).
Description:	Ashcroft dial thermometer 0-100°C.
Mat'l of Const:	Stainless steel stem.

ITEM TI-3 DISINTEGRATOR TEMPERATURE INDICATOR

Function:	To monitor disintegrator (T-13) temperature.
Description:	Thermometer.
Mat'l of Const:	Glass.
Comment:	1. Used in exit line to indicate slurry temperature. Preferred location for sensor would be inside disintegrator near slurry exit. Should be a temperature controller to regulate steam flow to precipitant feed. See Section IX-C.

ITEM TI-4 ACETONE COLUMN FEED TEMPERATURE INDICATOR

Function:	To indicate temperature of acetone column (D-2) feed.
Description:	Minneapolis-Honeywell copper-constantan potentiometric temperature indicator, range 0°-200°C.

ITEM TR-1 TEMPERATURE RECORDER RECYCLE SYSTEM

Function: To indicate and record temperatures at various points in the recycle system.

Description: Minneapolis-Honeywell 12-point copper-constantan 0-200°C strip-chart recorder.

Services: 110 V electricity.

ITEM TRC-1 REACTOR TEMPERATURE RECORDER CONTROLLER

Function: To record and control temperature in reactor (R-1).

Description: Foxboro Dynalog recorder controller M/40 integral plus derivative control mode.

Services: Instrument air, 110 V electricity.

Comment: 1. The controller output was used as set point signal for reactor jacket temperature recorder controller (TRC-2).

ITEM TRC-2 REACTOR JACKET TEMPERATURE RECORDER CONTROLLER

Function: To record and control temperature in the reactor (R-1) jacket.

Description: Foxboro type M/40 Stabilog recorder controller.

Services: Instrument air.

Comment: 1. See comment, Item TRC-1.

ITEM TRC-3 FEED PREHEATER JACKET TEMPERATURE RECORDER CONTROLLER

Function: To record and control water jacket temperature in the feed preheater (E-2).

Description: Foxboro type M/40 Stabilog recorder controller.

Services: Instrument air.

ITEM TT-1 TEMPERATURE TRANSMITTER, REACTOR JACKET

Function: To sense and transmit reactor jacket water temperature to reactor jacket temperature recorder controller (TRC-2).

Description:	Foxboro type 12A pneumatic temperature transmitter.
Services:	Instrument air.

ITEM TT-2 TEMPERATURE TRANSMITTER FEED PREHEATER

Function:	To sense and transmit feed preheater (E-2) water temperature to feed preheater jacket temperature recorder controller (TRC-3).
Description:	Foxboro type 12A pneumatic temperature transmitter.
Services:	Instrument air.

ITEM U-1 TRAY DRYER

Function:	To dry filter cake from rotary vacuum filter (F-5).
Description:	Proctor and Schwartz 10-tray dryer.
Mat'l of Const:	Trays - stainless steel.
Services:	220 V, 3-phase electricity, 100 psi steam.
Comment:	1. The drying tray arrangement in the oven was changed to hold 20 trays 20 x 29.75 in. 2. Filter cake was deposited 3/4 in. thick on drying trays. 3. Operating temperature 50°C. 4. Average drying time 15 to 20 hours. 5. Charge of oven 32 lb dry polymer. 6. To prevent dusting the fan speed of the dryer was reduced from 1169 rpm to 681 rpm.

VIII. OPERATING PROCEDURE

A. PRELIMINARIES TO REACTOR OPERATION

1. Reactor

a. Turn on cooling water to reactor (R-1) seal oil circulating system. Turn on seal oil circulating pump and reactor agitator.

b. Bring the reactor pressure to 160 psig by feeding nitrogen through nitrogen feed rotameter (FI-1). Pressure check reactor for 15 minutes and find and repair leaks if necessary. While the reactor is at 160 psig pressure, zero the reactor level transmitter (LT-5) and check the reactor thermocouple for continuity.

c. Vent the reactor (R-1) to 2 psig through the reactor vent valve (V-3). Close the reactor vent valve.

d. Open the reactor drain valve (V-3) and start nitrogen purge to reactor at the rate of 60 std cu ft/hr. After 30 std cu ft of nitrogen have been fed, close the reactor drain valve without interrupting the nitrogen feed and bring the reactor to operating pressure. When the reactor is at operating pressure, reduce the nitrogen feed to 1.5 std cu ft/hr and put the reactor pressure controller (PRC-1) in operation.

e. Turn on water to the reactor reflux condenser (E-1).

f. Fill the reactor effluent filter (F-1) with acetone and close the reactor effluent valves (V-1 and V-2).

2. Feed System

a. Energize the electronic feed system level transmitters (LT-1, LT-2, LT-3 and LT-4) and the feed system level recorder (LR-1). Check the zero and span of each instrument. Span is checked by applying gas pressure to the high pressure side of the standpipe.

b. Purify VCl monomer if VCl of satisfactory purity is not available. *

*Clean, uninhibited VCl will presumably be available in a plant. Purification is discussed in Section IX-J.

c. **Prepare the initial charge and the feed solution of AZBN in acetone. The initial charge solution consists of 6.0 g AZBN in 150 g acetone. The feed solution consists of 25.6 g AZBN in 2474.4 g acetone. CAUTION: ADD AZBN TO SOLVENT. DO NOT EXCEED 4% AZBN CONCENTRATION.**

d. Evacuate all standpipes (T-1, T-2, T-3 and T-4) and charge with VCl, IB, EHF and pure acetone, respectively. The volatile monomers VCl and IB are pressured in from the storage tanks (T-7 and T-8) by helium pressure. The EHF and acetone are drawn into the standpipes from the storage tanks (T-9 and T-10) by vacuum.

e. Pressure the VCl and IB standpipes to 20 psi above the monomer vapor pressures with helium. Vent the EHF and acetone standpipes to atmospheric pressure.

f. Fill the initiator injection tube (T-20) with the initial AZBN-acetone solution (6.0 g AZBN in 150 g acetone) and connect the tube to the bottom of the reactor by way of the bottom sample connection.

3. Recycle System

a. Pressure check the recycle system at 50 psig.

b. Energize the monomer stripper liquid level control (LC-1) and the recycle collector liquid level control (LC-2). De-energize the recycle pump relay in LC-2 until recycle operation commences.

c. Prepare stabilizer solution (7.4 weight percent Paraplex G-62 in acetone).

d. Charge the stripping acetone storage tanks (T-5 and T-6) and pressurize with 50 psig nitrogen.

e. Bleed acetone through the stripping acetone flow controller (FC-1) and check zero adjustment.

f. Set recycle system pressure controller (PRC-2) at 21 psig.

B. REACTOR START-UP AND FORWARD FEED OPERATION

During this operation the reactor (R-1) is operated without recycle. The unreacted VCl and IB monomer in the reactor effluent is stripped from the polymer solution in the monomer stripper (D-1) and wasted.

1. Pump the following initial charge as indicated by the standpipe levels to the reactor.

VCl	2040 g (Standpipe T-1)
IB	193 g (Standpipe T-2)
EHF	57 g (Standpipe T-3)
Acetone	3330 g (Standpipe T-4)

During this time, adjust the pumps to the rates required for forward feed conditions.

VCl	1430 g/hr (Pump P-1)
IB	94 g/hr (Pump P-2)
EHF	165.1 g/hr (Pump P-3)
Acetone	713 g/hr (Pump P-4)

The pumping rate checks should be made with feed and suction pressures leveled out at operating conditions.

2. Drain remaining pure acetone from initiator solution metering standpipe (T-4) and fill with feed solution (25.6 g AZBN in 2474.4 g acetone). Refill all other standpipes. VCl and IB standpipes are refilled at their operating pressures (20 psig above vapor pressures of the monomers).

3. Heat the reactor (R-1) charge to operating temperature (60°C) by applying hot water to the reactor jacket. The temperature of the water is controlled by the reactor temperature control system (TRC-1, TRC-2). To avoid excessive overshoot of the charge temperature, limit the output of the reactor jacket temperature controller to 95°C during the heat-up period.

4. When the reactor (R-1) temperature has leveled out at 60°C, pressurize the initiator injection tube (T-20) to 300 psig with helium and blow the AZBN-acetone solution into the reactor. The recorded run time is started at the instant the AZBN-acetone solution is in. This is indicated by a rise in the reactor pressure.

5. Start all reactor feed pumps (P-1, P-2, P-3, and P-4) operating at the rates indicated in Section VIII-B-1.

6. Set the control point of the reactor level controller (LRC-1) to the operating level. Open the manual reactor effluent line valve (V-1).

7. As soon as reactor effluent flow starts, turn on acetone feed to bottom of the monomer stripper (D-1). Turn on steam to stripping acetone vaporizer (E-6) and stripping acetone superheater (E-7). Turn on hot water to stripper feed preheater (E-2). Adjust the monomer stripper to operate under the following conditions:

Stripper feed preheater (E-2)	53°C
Stripper bottom (D-1)	85°C
Stripper head (D-1)	55°C
Acetone vapor to stripper (E-7)	115°C
Stripping acetone flow (FR-1)	500 g/hr

During this feed forward period the vapor from the monomer stripper is vented to waste by the recycle system pressure controller (PRC-2). The cooling water is turned off the recycle collector and condenser (E-3) during this period. Some liquid may accumulate in the collector during this period which must be drained to waste.

t the monomer stripper liquid level controller (LC-1) to withdraw ripped polymer solution from the bottom of the monomer stripper)-1). Mix stabilizer solution (7.4 weight percent Paraplex G-62 in etone) with the stripped polymer solution at the rate of 50 ml/hr.

emove the initiator injection tube (T-20) from the sampling manifold and nnect the conversion (nonvolatiles) sampling system (Section XIII-A).

etermine conversion (nonvolatiles) by the method described in ction XIII-A at one-hour intervals starting one hour after the run was arted.

ecord all operating data at hourly intervals starting 30 minutes after the art of the reaction.

eck feed pump rates and adjust pump settings as required at half-hour tervals.

eady state is reached when the three successive hourly determinations nonvolatiles differ by no more than $\pm$ 1%. This normally requires 6-8 urs. If the steady-state condition, when reached, differs from 30% non-latiles by more than $\pm$ 1 unit, adjust the AZBN concentration in the AZBN-itiator feed solution according to the formula

$$\left(\frac{\text{New AZBN}}{\text{Concentration}}\right) = \left(\frac{\text{Present AZBN}}{\text{Concentration}}\right) \times \left(\frac{30}{\text{observed \% nonvolatiles}}\right)$$

ontinue operation until a new steady state at 30 $\pm$ 1% is reached.

EACTOR RECYCLE OPERATION

he reactor (R-1) reaches steady-state operation with nonvolatiles content %, recycle operation is started.

repare a solution of 58.7 g AZBN in 2441.3 g acetone. This initiator olution is to be used during recycle operation. If a change has been made AZBN during the forward feed operation to attain 30 $\pm$ 1% solids in the fluent, a proportional change should be made in the AZBN content of this olution.

urn on cooling water to the recycle condenser and collector (E-3). Turn refrigerated brine to recycle subcooler (E-4). *

nergize the recycle collector liquid level control (LC-2) and turn on the ecycle pump (P-5). If the level control and recycle pump operate

* recycle subcooler will not be required in plant operation if sufficient head is provided for the recycle pump (P-5).

roperly, stop the pump.* Drain the initiator solution metering standpipe
T-4) and charge with the solution of 58.7 g AZBN in 2441.3 g acetone.

hange the reactor (R-1) feeds to following rates:

VCl	511.9 g/hr	(Pump P-1)
IB	31.1 g/hr	(Pump P-2)
EHF	165.1 g/hr	(Pump P-3)
Initiator solution	316.8 g/hr	(Pump P-4)

nmediately start the recycle pump (P-5).

perate the recycle system under the following conditions:

Stripper feed preheater	(E-2)	53°C
Stripper bottom	(D-1)	85°C
Stripper head	(D-1)	55°C
Vapor to stripper	(E-7)	118°C
Stripping acetone flow	(FR-1)	500 g/hr
Recycle condenser water	(E-3)	< 22.5°C
Recycle subcooler brine	(E-4)	10°-20°C
Stripper head pressure	(PRC-2)	21 psig

t hourly intervals determine nonvolatiles in reactor charge (Section III-A), VCl, IB and acetone in reactor charge (Section XIII-B) and VCl ontent of stripped polymer solution (Section XIII-D). Adjust AZBN oncentration in initiator solution feed as required to maintain non-olatiles at 30 ± 1%. Adjust IB feed as required to maintain VCl/IB eight ratio at 13. Adjust stripper feed preheater temperature and cetone vapor temperature as required to maintain acetone stripper ottoms flow at 1571 ± 30 g/hr and VCl content at less than 1% (wt).

djust VCl feed to maintain 40.8% free VCl + IB in reactor.

REACTOR SHUTDOWN

hut off all feeds and apply cold water to the reactor (R-1) jacket.

hut off recycle pump (P-5) and operate monomer stripper (D-1) a. ... orward feed operation (Section VIII-B-7).

During the last few minutes of recycle operation note the average output f the reactor level controller (LRC-1). When the feeds and recycle ump are shut off, put the reactor level controller on manual and adjust

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e pilot plant the recycle stream was pumped to a tared cylinder for a hour period to see that all equipment was operating properly and that e were no leaks in the recycle system. This can probably be dispensed in a plant if a good pressure test of the recycle system is made before t-up.

the output to this average reading. Continue operation of the stripping column until all material in the reactor has been stripped.

4. Shut down and drain the stripping column. Vent the reactor.

5. Fill the reactor (R-1) with two gallons acetone and reflux for 45 minutes with the stirrer running. Drain the reactor hot through the monomer stripper (D-1) and mix with a large amount of water in the SRC disintegrator (T-13). Drain the acetone-water solution to waste.

6. Shut off reactor agitator and seal oil system pump and cooling water supply. Shut off water to reactor reflux condenser (E-1).

7. Remove filter cartridge from reactor effluent filter (F-1), clean filter and replace cartridge.

8. Drain and vent feed system standpipe (T-1, T-2, T-3 and T-4). Shut manual valves in the reactor feed lines. Rinse EHF metering standpipe (T-3) and initiator metering standpipe (T-4) with acetone.

9. Shut off brine system and nitrogen, helium, vinyl chloride and acetone supply lines.

10. Shut off steam and cooling water supplies to the recycle system (D-1, E-5, E-6, E-7, E-8 and E-9).

11. Drain the stripping column (D-1). Fill column with acetone, allow to soak 30 minutes and drain acetone to waste.

E. PRECIPITATION

1. Turn on water sprays to cool SRC disintegrator (T-13) packing glands.

2. Turn on the precipitant feed pump (P-7) and adjust the precipitant rate to 460 lb/hr as indicated by precipitant rotameter (FI-3).

3. Expel the air trapped above the outlet nozzle of the SRC disintegrator (T-13) by placing a hand over the slurry discharge to force air out through the agitator packing glands.

4. Adjust the precipitant temperature to 25°C as indicated by precipitant feed temperature indicator (TI-2). *

5. Turn on agitator in slurry hold tank (T-14).

*If lower bulk density product is desired, the precipitant temperature should be lower. See Section IX-C.

6. Turn on SRC disintegrator (T-13) agitator drive. Adjust tip speed of beaters (agitators) to 1600 ft/min.

7. Start polymer solution feed from polymer solution tank (T-11) to SRC disintegrator (T-13). Adjust speed of polymer solution pump (P-6) to feed polymer solution at the rate of 46 lb/hr.

8. Start filtration (Section VIII-F) as soon as polymer slurry reaches slurry hold tank (T-14).

9. When polymer solution feed is exhausted, flush polymer solution feed pump (P-6) with acetone and turn off.

10. Allow SRC disintegrator (T-13) to run until effluent is clear. Then turn off agitator and precipitant feed.

11. Filter all slurry in the slurry hold tank (T-14) and shut off agitator.

12. Shut down filtration.

F. FILTRATION AND CAKE WASHING

1. Start feed of polymer slurry by polymer slurry pump (P-8) from slurry hold tank (T-14) to rotary vacuum filter (F-5).

2. Start agitator in slurry tank of rotary vacuum filter (F-5).

3. When the level of polymer slurry has reached the overflow level, start rotation of rotary vacuum filter (F-5). Turn on vacuum to filter drum and adjust wash water to 6 lb water/lb dry polymer as indicated by the wash water feed rotameter (FI-4). Simultaneously start the vacuum pump (P-11) and the blower (P-12). The doctor knife should be 1/8 inch from the surface of the filter.

4. Start the wash filtrate pump (P-9) and the filtrate pump (P-11).

5. Adjust the rotation of the rotary vacuum filter (F-5) to a rate which matches the rate of slurry production by the SRC disintegrator (T-13).

6. Add water to the precipitant feed tank (T-12) as necessary to supplement the supply of wash filtrate used as precipitant.

7. To shut down the rotary vacuum filter (F-5), turn off the polymer slurry pump (P-8) and continue operation of the filter until cake formation ceases. Shut down the wash filtrate pump (P-9), the filtrate pump (P-10), the vacuum pump (P-11) and the blower (P-12). Turn off the wash water feed.

8. Drain the residual slurry into the slurry hold tank (T-14).

9. Wash the rotary vacuum filter (F-5) down with a hose. Turn off the drum rotation.

G. DRYING

1. Clean all dust and foreign particles from the tray dryer (U-1) tray compartment, trays and plenum chamber with a vacuum cleaner.

2. Charge dryer trays with filter cake to a depth of 3/4 inch. Break up any filter cake lumps. Place trays in dryer.

3. Start up tray dryer and operate at 50°C. Check trays periodically for lumps and break up any lumps which may form.

4. After 15 hours determine moisture content of polymer (Section XIII-J). If moisture content is below 1%, terminate drying and discharge product to polyethylene-lined Leverpaks. If moisture content is above 1%, continue drying until an analysis shows it to be below 1%.

H. ACETONE DISTILLATION

1. Set reflux head (E-9) for total reflux and turn on cooling water.

2. Turn on cooling water to acetone column bottoms cooler (E-10).

3. Turn on acetone column feed pump (P-13) and adjust by-pass so that feed pressure is 5 psig.

4. Start filtrate feed to acetone column (D-2) at the desired rate, 12.5 kg/hr.

5. Turn on open steam to bottom of acetone column and set the acetone column bottom pressure controller to maintain 5 in. H_2O g pressure at the column bottom.

6. When the acetone column head temperature is at 56°C or less and the feed tray temperature is 72°C, start distillate takeoff to distillate receiver at reflux ratio 2.

7. Adjust acetone column feed as required to maintain feed tray temperature at 71°-73°C. Increasing the feed rate lowers the feed tray temperature.

8. When feed is exhausted, immediately set reflux head for total reflux and turn off acetone column feed pump. Turn off open steam feed and allow column to drain. Turn off cooling water. *

9. Examine feed filters (F-6 and F-7) and discharge cake if necessary.

*If a fresh supply of filtrate for distillation is anticipated, the column may be left on total reflux indefinitely.

IX. DISCUSSION

A. POLYMERIZATION

The polymerization reactor (R-1) is an overflow, or continuous stirred tank reactor. VCl, EHF, IB and AZBN-initiator solution are continuously pumped to the reactor by metering pumps. In normal (recycle) operation the condensed vapors from the monomer stripper (D-1) are also continuously pumped to the reactor. A solution of polymer, unreacted monomer and acetone is continuously withdrawn from the reactor.

1. Reactor Operating Conditions

An extensive synthesis and evaluation program has shown that VCl/EHF/IB terpolymer containing 42.5% wt chlorine and 1.65% wt hydroxyl and having a Gardner viscosity* of Z-Z2 (specific viscosity 0.240**) is required for surface-coating applications. This corresponds to a monomer content of 75% VCl, 20.6% EHF*** and by difference 4.4% IB.(2).

To produce polymer of this type in the continuous reactor it has been found experimentally that the following physical limitations apply:

a. The total concentration of free monomer must not be less than 38% wt in order to achieve reasonable polymerization rates. Under these conditions the polymerization rate is approximately 6.0 lb/hr ft^3 of reactor. The AZBN initiator consumption is about 0.01 lb/lb polymer made.

b. The solvent content of the reactor effluent must be no less than 0.75 lb/lb polymer and preferably should be 1.0 lb/lb polymer in order to have fluid solutions. This establishes the known feasible upper operating limit at about 35% nonvolatiles in the reactor. The operating level for design and research purposes is taken at 30%.

c. Reactor holdup must be no less than 2.10 hrs. Below this value the initiator consumption increases sharply (in excess of 100%) yielding polymer with undesirably low molecular weight.

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*The viscosity of a solution of 25% MIBK, 25% xylene and 50% polymer measured at 25°C.

**1% polymer in cyclohexanone at 25°C.

***For EHF monomer containing 5.0% OH.

d. EHF monomer is by far the most reactive of the monomers in the system. Figure 7 shows the relative weight proportions of the free monomers to produce polymers having the desired 75.0% VCl, 20.6% EHF and 4.4% IB composition. The low concentration of EHF monomer is important in that no recycle of EHF monomer from the reactor effluent to the reactor is required.

e. Molecular weight of the product is established primarily by chain transfer. This is clear from the fact that about 10 moles of polymer are produced per equivalent of initiator decomposed. Isobutylene is an active (but not the only) chain transfer agent present. Fine control of the molecular weight of the polymer can be maintained by adjusting the free isobutylene concentration in the reactor. In the pilot plant isobutylene was fed to maintain the ratio of VCl/IB at 13.1.

f. The operating temperature in the reactor must be maintained at 80°C. The operating pressure of the reactor must not be less than the autogeneous pressure of the reaction mixture (about 120 psig).

2. Control of Polymerization Reaction

In the pilot plant the reactor temperature, pressure and liquid level were automatically controlled. The makeup feed streams were metered by manually reset diaphragm metering pumps. Analytical methods were available for monitoring the nonvolatiles content and the VCl, EHF, IB and acetone contents of the reactor charge.

In all operations the temperature, pressure and liquid level were set to predetermined levels and maintained constant. The feed streams were manipulated to obtain the desired nonvolatiles, product composition and product viscosity.

Two modes of operation must be considered -- the feed forward mode in which all unreacted monomer is wasted, and the recycle mode in which the vapor from the monomer stripper (D-1) is condensed and immediately recycled to the reactor.

In the feed forward mode the monomer feeds are calculated to give, for a set conversion, the proper amount and proportion of free monomers in the reactor to produce the desired product. The concentration of nonvolatiles in the reactor effluent (conversion - residual EHF) is controlled by adjustment of the AZBN (initiator) concentration in the AZBN-acetone solution feed. It is not necessary to monitor the reactor monomer and acetone concentrations during feed forward operation.

In the normal operation mode, the recycle mode, the reactor feed streams are augmented by the recycle stream of condensed vapor from the monomer stripper. The composition of this stream is somewhat variable, subject to the losses in the stripper bottoms and to the deviations from target nonvolatiles in the reactor effluent. As a practical matter, it is necessary to monitor the relative proportions of VCl, IB and acetone in

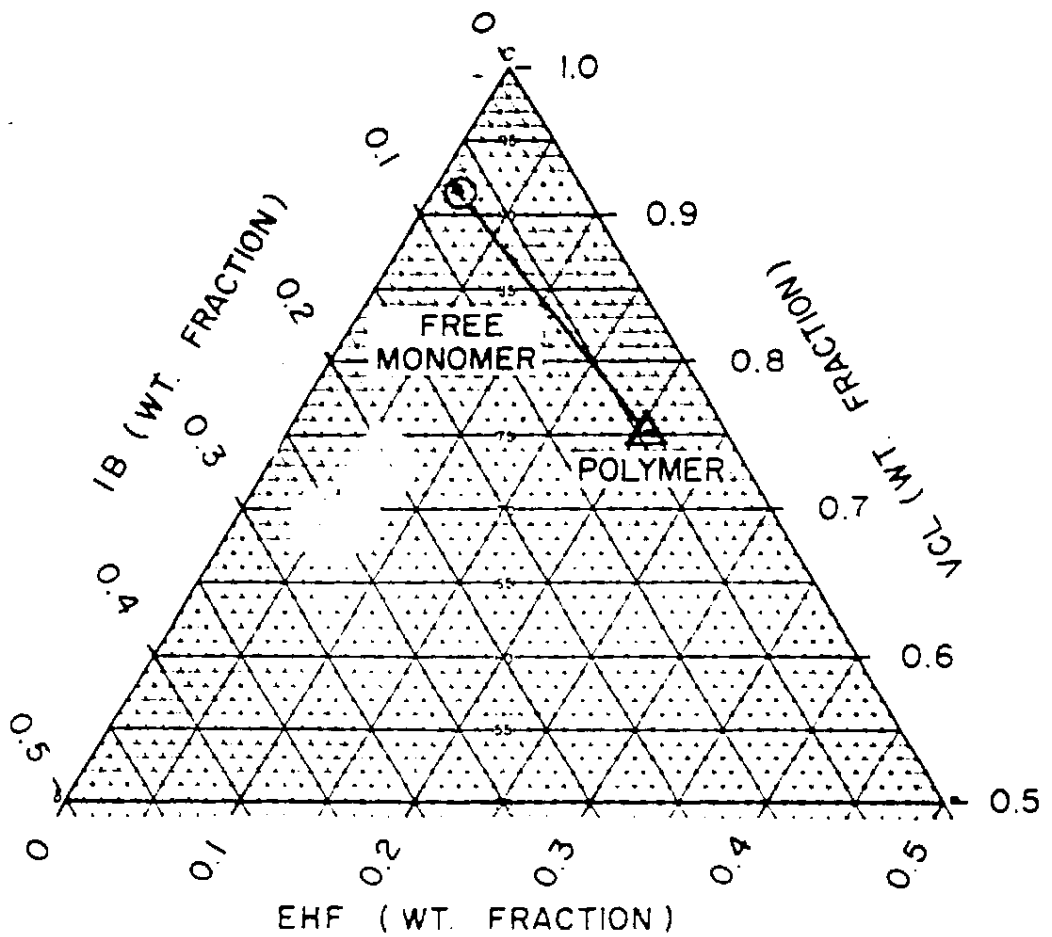

FIGURE 7

FREE MONOMER IN REACTOR CHARGE AND COMPOSITION OF POLYMER

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the reactor effluent and make small adjustments in the monomer feeds as necessary to maintain the proper proportions of these materials in the reactor. The VCl, IB and acetone determinations are made by gas chromatography.

As in the feed forward mode, the proportion of nonvolatiles in the reactor effluent during recycle opeation is adjusted by adjusting the concentration of AZBN in the AZBN-acetone solution feed. In making these corrections, the AZBN concentration is adjusted in direct proportion to the deviation of observed nonvolatiles from the desired level of nonvolatiles. Experimentation showed that this linear adjustment was to be preferred to making the change in initiator feed proportional to a power or root of the deviation.

The water content of the acetone feed has some effect on monomer conversion. In general, about 5%-10% more initiator was required to obtain 30% nonvolatiles in the reactor effluent when acetone containing 2% water was used than when acetone containing 0.5% water was used.

The hydroxyl content of EHF monomer may vary from about 7.8% to 8.2% (5). The polymer material balance assumes use of EHF monomer containing 8.0% hydroxyl. If the EHF monomer does not contain 8.0% hydroxyl, the EHF feed rate is adjusted to give the same hydroxyl feed rate as if the 8.0% monomer were being used.

Details of the development of the feed plan for a typical pilot plant run are given in Appendix A.

3. Instrumentation and Control Analyses for the Polymerization Process

a. Reactor Pressure Control

In most of the pilot plant work the reactor pressure was controlled well above the autogenous pressure by feeding a small stream of nitrogen to the reactor and setting the reactor pressure controller (PRC-1) to bleed nitrogen as required to control the set pressure. In other cases the reactor was operated at autogenous pressure. Operation at the higher controlled pressure was preferable because it gave a constant head for the feed metering pumps (the outputs of which were quite sensitive to discharge pressure) to work against.

In the plant it will be desirable to dispense with the nitrogen stream and operate the reactor at or near to autogenous pressure.* If the reactor is sufficiently leak-free, there may be enough inerts in the feed streams to permit operation above autogenous pressure without adding nitrogen.

*Conditions should be adjusted so that there is no flashing in the reactor effluent filter (F-1). See Section IX-A-7.

b. Reactor Temperature Control

In the pilot plant the reactor temperature was controlled by a temperature controller (TRC-1) cascaded with a temperature controller (TRC-2) in the jacket water supply. This was necessary to eliminate upsets due to water supply pressure and temperature fluctuations. In the plant a cascaded system may or may not be necessary depending on local conditions. Reactor temperature must be controlled to 80° ± 1°C.

c. Reactor Level Control

Reactor liquid level must be controlled very precisely in the VYSET RE process both because fluctuations in level produce severe upsets in the monomer stripper (D-1) and because of upsets in conversion.

No commercially available level transducer was suitable for use in the small and rather cramped space of the pilot plant reactor. A transducer (LT-5) which measures level by measuring the tangential force on a paddle inserted into the surface of the swirling liquid in the reactor was developed. This transducer performed excellently. It was able to detect the withdrawal of 20 cc of fluid from the two-gallon reactor charge and was not subject to troublesome zero drift. A plant version of this device has been built and tested in a 30-gallon baffled reactor. It is recommended that this device be used on the interim plant reactor.

In the plant reactor it will be necessary to cascade the reactor level controller with a flow controller in the line leading from the reactor to the monomer stripper. This will ensure a steady flow of feed to the stripper. Without it much difficulty with flooding in the stripping column would be expected.

d. Reactor Feed Metering

Successful operation of the VYSET RE pilot plant required accurate metering of the various liquid streams fed to the reactor. Until this was done through installation of the metering standpipes (T-1, T-2, T-3 and T-4), control of product composition, conversion and product viscosity was impossible.

The metering system permitted control of the feed rates to ± 2% of the desired feed rate. This specification should be met by any plant feed metering system.

With respect to a plant installation it is noted that 1) metering pumps will not meet this specification for accuracy unless they are continuously calibrated and reset; 2) continuous recording of feed rates should be provided, and 3) independent calibrating equipment (volumetric tanks or weigh tanks) should be provided for each feed stream.

e. Nonvolatiles Determination

The nonvolatiles are determined by evaporating a weighed sample of reactor effluent to dryness and weighing the residue on a moisture balance.

In a plant operation the nonvolatiles measurement might possibly be replaced by a measurement of the heat evolution in the reactor following the methods of Wotring (12). This could not be investigated in the pilot plant because of the relatively large radiation losses from the small reactor. Installation of equipment to measure heat transferred to the cooling water in the plant is recommended.

f. VCl, IB and Acetone in Charge

For control analyses in the pilot plant, the proportions of VCl, IB and acetone in the reactor effluent were determined using a standard laboratory gas chromatograph. This method, if good technique in sampling and sample injection is used, is accurate. However, it requires about 20 minutes to take a sample and run and interpret the chromatograms. The use of a process gas chromatograph in a plant would be desirable; however, a suitable sampler and sample vaporizer would have to be developed.

4. Polymerization Reactor Fouling

The reactor was opened frequently to check for fouling. Each time a thin film (less than 0.01 in.) was found deposited on the reactor wall, the agitator and the sensing lever of the reactor liquid level transmitter. In addition, a slight accumulation of deposits was observed on unwetted stainless steel parts of the sensing lever and the feed nozzles in the proximity of the liquid interface in the reactor. The amount of deposits did not appear to increase with operating time of the reactor.

Analyses of these polymer deposits indicated approximately 1% nitrogen which suggests the possible presence of toxic decomposition products of AZBN. (Micro analysis of precipitated VYSET RE polymer showed 0% N.) The deposits were soluble in hot cyclohexanone and partially soluble in acetone.

It is considered probable that much of the slight deposits found in the reactor were polymer which remained on the walls when the reactor was drained. There was never enough polymer deposited to interfere with reactor operation. On present evidence the possibility that a plant reactor would have to be given an occasional cleaning with hot cyclohexanone cannot be ruled out, although it is considered unlikely.

5. Reactor Agitation

The reactor was stirred by an anchor type agitator operated at 345 rpm. Since the polymerization is a solution process, the only requirements on the

agitation system are that it provide good mixing of the feed streams into the charge, minimize temperature gradients in the charge and support adequate heat transfer to the reactor walls. Design on the basis of the correlations given by Perry, Chilton and Kirkpatrick (8) should be satisfactory.

6. Use of a Reactor Reflux Condenser

In very large reactors it would probably be desirable to cool the reactor by using a reflux condenser. This was not investigated extensively in the pilot plant; however, there would appear to be no serious impediment to using a reflux condenser when needed.

7. Reactor Effluent Filtration (Grit Removal)

Midway in the process development work it was reported by the Springfield evaluation group that the pilot plant product contained small but objectionable amounts of insoluble polymer called "grit" (13). This "grit" caused roughness in coatings applied to metal.

The problem was solved by installing a reactor effluent filter (F-1). The filter used is made especially for filtering paints and resin solutions used in paint manufacture. The use of a filter of this type in plant operation is required.

The pilot plant filter was operated upward of 100 hours without evidence of much solids accumulation. For plant applications, it is recommended that two filter stations be used in parallel so that they can be changed without interrupting operation. Gauges should be provided upstream and downstream of the filters to indicate when the cartridges should be changed.

The operating reactor pressure and the static head on the filter combined should be high enough that there is no vaporization in the filter cartridge due to the pressure drop across the filter.

B. MONOMER STRIPPING

In the monomer stripper (D-1), the unreacted VCl and IB monomers are stripped from the reactor effluent for recycle to the polymerization reactor. The distillate contains acetone, VCl and IB; the bottoms 50% polymer in acetone solution containing not more than 1% VCl and IB combined. The column is operated by open superheated acetone vapor.

1. General Considerations

Vapor-liquid equilibrium data for the system VCl-IB-acetone-polymer are not available, so an exact plate-to-plate calculation for the stripper is not possible. Inferences about how the system behaves can, however, be drawn from available physical data. These inferences are:

a. The boiling points of VCl (-13.8°C) and IB (-6.9°C) are so much lower than acetone (56.5°C) that there is little likelihood of VCl-acetone or IB-acetone azeotropes--and there is no chance at all of azeotropes containing large proportions of acetone, which is the region of concentration of interest in stripper design. No interference by azeotropes can logically be expected.

b. Polymer in solution apparently has only moderate effect on the volatility of its solvents. This is inferred from the fact that a 50% solution of polymer in acetone boils only about 2°C higher than the pure solvent.

It is therefore concluded from these general considerations that a separation giving VCl-IB-acetone as distillate and polymer-acetone as bottoms is technically feasible. This was demonstrated in the pilot plant to be fact.

2. Consideration of VCl-Acetone System

To show what must be considered in designing and selecting operating conditions for a stripping column, the binary system VCl-acetone is now considered.

Figure 8 is an idealized material balance for the stripping system. In this material balance the moles of VCl correspond to the actual moles of VCl and IB combined as taken from Figure 1. The moles of acetone correspond to the acetone flows of Figure 1. The other components--polymer, EHF, water and initiator--are ignored.

Figure 9 is an x-y diagram and a composition-temperature diagram for the system VCl-acetone estimated from vapor pressure data using Raoult's Law.

In the idealized material balance, Figure 8 , the internal column liquid and vapor rates are considered fair approximations of the minimum liquid and vapor rates which actually existed in the pilot plant column. Part of the feed to the pilot plant column was vapor which merely passed through the top of the column without contacting the liquid on the top plate. This vapor stream is the stream J' on Figure 8 . A large part of the open acetone vapor was condensed in the column to supply sensible heat and to make good radiation losses. This is the stream L' in Figure 8 .

The operating line for the stripping section with open acetone vapor is ( )

$$y = \frac{\overline{W}}{\overline{V}} x - \frac{\overline{W}}{\overline{V}} x_w$$

$$y = 2.52 x - 0.0363$$

This operating line is plotted on the x-y diagram, Figure 9 , and the theoretical stages are stepped off, starting from the specified bottoms

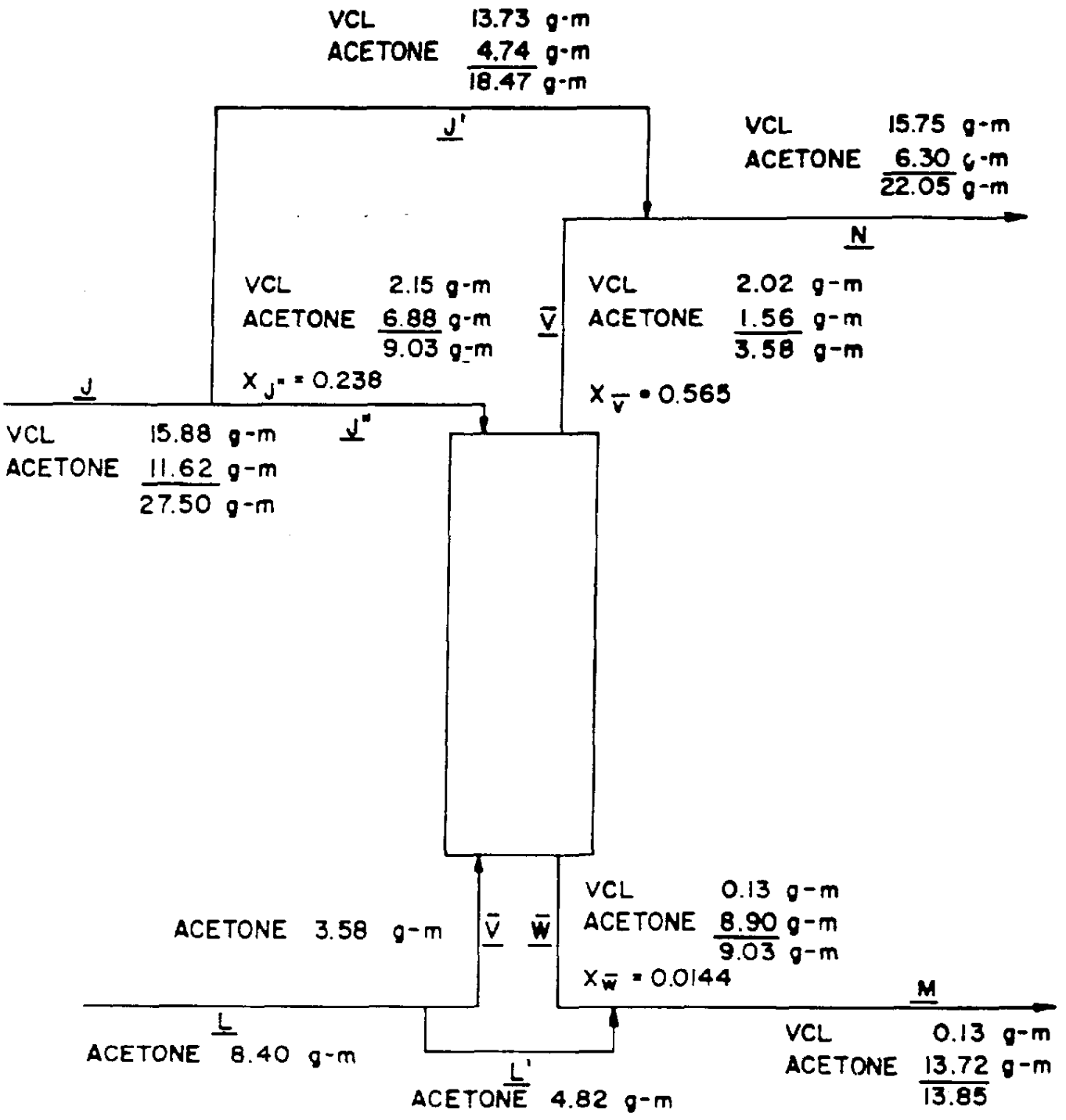


FIGURE 8

RSV 0017365

DRAWN	MONSANTO CHEMICAL COMPANY	PROJ. NO.
CHECKED	800 N. LINDBERGH BLVD. ST. LOUIS 66, MO.	LOCATION
DATE	SIMPLIFIED MATERIAL BALANCE FOR STRIPPING SYSTEM	DIVISION
SCALE		DWG NO.

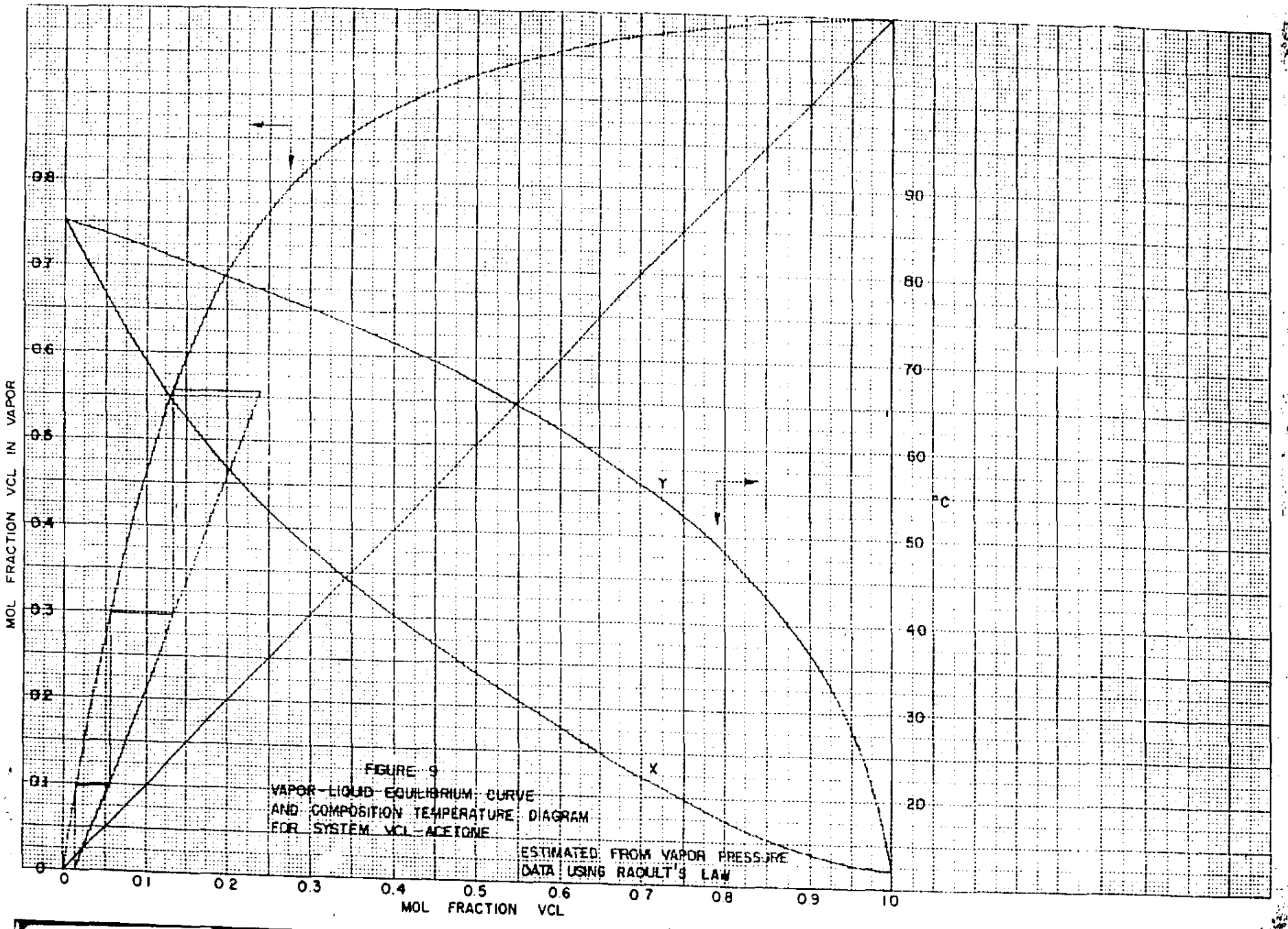


FIGURE 9
VAPOR-LIQUID EQUILIBRIUM CURVE
AND COMPOSITION TEMPERATURE DIAGRAM
FOR SYSTEM VCL-ACETONE

ESTIMATED FROM VAPOR PRESSURE
DATA USING RAOULT'S LAW

concentration, $x_w = 0.0144$. It is seen that about three theoretical stages are required. This is reasonable in view of the fact that the pilot plant column had five trays plus the sump at the column bottom.

The criterion of operability of the stripping process is that the operating line be under the equilibrium line up to the feed composition, the liquid coming to the top tray. If this is satisfied, it is only a question of providing an adequate number of theoretical stages to attain the desired separation.

If an adequate number of theoretical stages is provided for an operable set of flow rates, the operation of a stripping column is virtually self-regulating, i.e., an excess of theoretical stages will only result in a slight lowering of the low boiler content of the bottoms below specification.

Changes in the slope of the operating line can be made either by changing the temperature of the feed, which changes the split of vapor and liquid in the feed, or by changing the vapor feed rate.

3. Consideration of the Real Column

Returning to consideration of the real pilot plant column, the following differences between the simplified case and the real case should be noted.

a. The vapor-liquid equilibrium relations for the real case are undoubtedly different from the simplified case. Probably the relative volatilities for the real case are less than for the simplified case.

b. The assumption of constant molal overflow cannot possibly hold exactly in the real case because a large part of the liquid stream is nonvolatile polymer which must be heated as it descends the column.

c. The pilot plant column had, despite tracing, rather large radiation losses.

All these factors would tend to make the pilot plant theoretical stage requirement greater than found in the analysis of Section IX-B-2. For this reason, it is recommended that the plant be designed on the basis of 1½ times the number of theoretical stages indicated in Figure 9 and that the slope of the operating line in no case be greater than that used in Figure 9.

The independent operating variables for a real column are 1) the temperature of the feed, which controls the rate and composition of the liquid feed to the top of the column and 2) the superheat in the open acetone vapor feed. The problem in column control is to adjust these independent variables so that the stripper bottoms will contain the correct amount of acetone and be at or below specification in VCl content.

The instrumentation of a plant stripping column should include pressure control at the vent, measurement and control of feed temperature, control

of the open acetone feed rate, control of the temperature at some selected tray in the column by control of the temperature of the superheated acetone vapor feed, measurement of temperature on all trays, and measurement of either the bottoms flow rate or the bottoms density.

The column operating pressure should be as high as is acceptable to permit the use of the highest cooling water temperature in the recycle condenser (E-3). Pilot plant experimentation showed this to be 21 psig; above this pressure the polymer solution from the bottoms was overheated (above 85°C) and was discolored.

The split between vapor and liquid in the column feed should not result in a liquid phase containing much more than 50% polymer because the solution would be too viscous to flow properly in the column. The theoretical case (Section IX-B-2) indicated a 58% solution. For the reasons indicated above, the actual concentration in the pilot plant was probably somewhat lower.

4. Addition of Stabilizer

There is reason to suspect that it would be desirable to add the Paraplex G-62 stabilizer to the column feed rather than to the bottoms. Advantages might include improvement of polymer stability and alleviation of a very slight corrosion problem in the column. This was not done in the pilot plant; however, provision of nozzles so that it can be tried in the plant is recommended.

C. PRECIPITATION

Solid VYSET RE polymer is precipitated from the monomer stripper (D-1) bottoms solution by mixing with water in a special high intensity mixing vessel. The use of the high intensity mixer is critical; attempts in the pilot plant to use stirred tanks and pipeline mixers resulted uniformly in unmanageable sticky, gooey messes.

The mixing device used in the precipitation is called the SRC disintegrator. This mixer was developed by Shawinigan Resins Corp. for use in precipitation of polymers from solution. Readers of this report are cautioned that the existence of this device is a closely held Monsanto trade secret. The SRC disintegrator is a vertical cylindrical tank with two intermeshing beater type agitators. The action of these beaters is identical with the ordinary kitchen egg beater.

In operation polymer solution and water are fed to the top of the cylinder through separate nozzles. Slurry is withdrawn from the bottom nozzle through a leg with syphon break so that the mixer always runs full.

The experimental work on precipitation was done using a 4 in. ID x 6 in. high pilot plant SRC disintegrator loaned by Shawinigan Resins Corp. The standard production SRC disintegrator is 16-1/4 in. ID x 24-3/16 in. high.

Shawinigan Resins Corporation have scaled up numerous polymer precipitation processes using this equipment. In their aggregate experience, as outlined by Dabagian and Crozier (14), it has been possible to run in the production units all products which were successfully run in the pilot plant unit and, additionally, to run some products in the production unit which could not be run in the pilot unit. Since VYSET RE was successfully run in the pilot plant under a variety of conditions (cf. Volume II, Sections XVIII and XIX) there is little doubt that it can be run in a production unit satisfactorily.

The independent variables in the precipitation operation are operating temperature, water/polymer solution ratio, feed rate and beater (rotor) tip speed. The dependent variables are polymer particle size distribution and bulk density. The Shawinigan experience does not provide a method for predicting the exact operating conditions for a plant SRC disintegrator to obtain particle size distribution and bulk density which duplicates a pilot plant material. Indeed, some experimentation with plant rotor speed and operating temperature are almost always necessary.

The pilot plant experimental work was designed to find the range of feasible operation and to show, within this range, in what direction changes should be made to change bulk density and particle size to match specifications.

The results of the experimental work are given in detail in Section XVIII. The following general observations were made.

1) Bulk density increased from 17-20 lb/cu. ft. to 21-25 lb/cu. ft. upon increasing the slurry outlet temperature from 10°-20°C to 30°-35°C.

2) Beater tip speed had to be 1350 ft/sec or above for satisfactory operation.

3) In the range 1350-1740 ft/sec beater tip speed had little effect on particle size distribution or bulk density.

4) Operation with volumetric total feed rates from 0.41 to 1.46 SRC disintegrator volumes/minute gave satisfactory precipitate having essentially the same particle size distribution and bulk density.

5) The maximum operating temperature limit for routine operations should be 30°C for 5% acetone in the water phase of the slurry.

Using the maximum feed rates listed above, a 10,000,000 lb/yr VYSET RE plant would require at least two standard SRC disintegrators operating in parallel. It might be desirable to design and develop a larger SRC disintegrator for a large plant.

Following precipitation in the SRC disintegrator, the precipitate must be hardened by leaching residual acetone from the solid particles. Shawinigan Resins Corporation does this in a second-stage SRC disintegrator. The pilot plant results indicate that this can best be done in the VYSET RE process in an agitated hold tank (T-14) having volume equal to about one hour's slurry production.

In the pilot plant VYSET RE was also successfully precipitated from solution in a one-gallon Waring blendor operated either as a batch or a continuous overflow operation. Scale-up to plant scale of the Waring blendor type operation would be difficult because no plant-scale analog of a Waring blendor exists. *

D. FILTRATION AND CAKE WASHING

The hardened polymer slurry which overflows the slurry hold tank is filtered and washed on the filter to remove residual EHF and acetone.

Two types of filters -- rotary vacuum filter and perforate basket centrifugal -- were tested in the plant. Both types of filter were used successfully.

The rotary vacuum filter (F-5) was chosen because of a probable difficulty with glazing of the filter cake heel in a perforate basket centrifugal in a plant operation. This common difficulty encountered in polymer filtration in perforate basket centrifugals is caused by the effect of the discharge plow on the surface of the heel of polymer which remains in the basket to produce an impervious glazed surface. This could not be evaluated in the pilot plant because the pilot plant did not produce enough material to permit a test in an automatic discharge machine. **

The rotary vacuum filter operated well in the pilot plant and seems an ideal choice for the VYSET RE process. Dry cake production was 50 lb/hr-sq. ft.

Some pilot plant tests were also run on dewatering (but not washing) VYSET RE in a batch solid bowl centrifugal. It was found that all polymer in the slurry feed settled to the periphery of the bowl. This suggests, but does not prove, that a continuous solid bowl centrifuge could be used for dewatering VYSET RE.

E. DRYING

VYSET RE powder discolors in air above 65°C and fuses to a sticky mass at 70°-80°C. Any drying process must necessarily avoid these limiting conditions.

---

*A high-shear bottom driven mixer known as the Papenmeier mixer (Welding Engineers, Inc., Norristown, Pa.) was tested. It failed because it uses a round tank with baffle rather than the four-leaf clover type tank used by the Waring blendor. The baffle quickly became fouled with polymer deposits.

**The Decatur Acrilan polymer plant uses both rotary vacuum filters and Baker-Perkins or Meer type perforate basket centrifugals for polymer filtration and washing. They prefer the rotary vacuum filters because of the difficulty with glazing of the heel in the basket centrifugals.

The VYSET RE produced in the pilot plant was routinely dried in a mechanical air convection tray dryer. The long (18-24 hour) drying cycle and low capacity of tray dryers make their use in a plant completely impractical.

Several types of drying equipment which were potentially suitable for a plant operation have been given preliminary consideration. These were continuous through-circulation, direct rotary, fluidized bed, flash and vacuum tumble dryers. The vacuum tumble dryer was ruled out because of low capacity and high cost. The flash dryer works, but offers serious control problems. The continuous through-circulation, direct rotary and fluidized bed types probably would be satisfactory; however, more work must be done in order to make a proper choice and obtain information for sizing. This was not done in the pilot plant because the experimental work can be done much more economically and reliably using larger quantities of material which will become available from the projected Springfield interim plant.

The Springfield facility will use a direct rotary dryer which is already installed. Enough work has been done in the Springfield pilot plant to show that this dryer can handle the output of the proposed interim plant.

Tests of the continuous through-circulation and fluid bed dryers can be carried out in established test facilities. The Decatur (Chemstrand) pilot plant have an excellent through-circulation drying test set up including the necessary pelleting equipment. General American Transportation Corporation maintains a fluid bed test installation.

Polymer product quality can deteriorate severely during drying. Evaluation of drying tests must definitely include product property evaluations. Any drying system chosen must be shown to be capable of producing a product having good application properties.

Polymer dried in the pilot plant tray dryer was somewhat lumpy. These lumps were generally aggregates of smaller particles which persisted from the filter cake. These lumps were considered objectionable by the product evaluation groups. They were broken up either by screening or by running the dry product through a Model M Fitzpatrick Commutating Machine (The Fitzpatrick Company, Chicago, Illinois) without screens. In the plant if polymer is dried in a rotary dryer, a fluid-bed dryer or a flash dryer, it may not be necessary to install equipment to break up lumps. If the polymer is dried in a through-circulation dryer (which requires pelleting prior to drying) some grinding apparatus to break up the dry pellets will probably be required.

F. ACETONE RECOVERY

Acetone is distilled from the filtrate from the rotary vacuum filter (F-5). This predominately aqueous stream contains about 4.95% acetone, a trace of EHF and any solid polymer which may, through a cloth defect or otherwise, have passed the rotary vacuum filter. The design and operation of the recovery system are considered below.

1. Filtration of Column Feed

Any solid particles in the acetone column (D-2) feed will inevitably become deposited on the feed tray or on the trays immediately below. Such deposits would inevitably be difficult and expensive to remove. For this reason it is important that an efficient means for removing solids from the column feed be provided.

In the pilot plant this was accomplished by two filters in series. The primary filter (F-6) was a pressure-leaf filter in which the bulk of the solids was removed. The secondary filter (F-7) was a cartridge filter which removed any traces of very small particles which had passed the primary filter. This system worked satisfactorily in the pilot plant.

For plant applications, it is recommended that filters having internals which can be easily cleaned, e.g. Sparkler filters, be used. The possibility that difficultly removable solids might accumulate inside the leaves of pressure filters cannot be ruled out on present knowledge.

2. Column Stage Calculations

Extensive vapor-liquid equilibrium data are available for the systems acetone-water (15). This makes it possible to calculate the theoretical stages required to effect any given separation with precision. Figures 10 and 11 show the calculation for the number of stages required for the separation given in the material balance, Section VI, for reflux ratio two.

The modified latent heat of vaporization method was used to calculate theoretical stages. This method was chosen after a few test calculations showed that sensible heat effects had little effect on the location of critical sections of the operating lines. *

The calculation shows that for feed at 25°C, four theoretical stages are required above the feed tray and four below.

The minimum reflux ratio for the acetone-water separation is substantially influenced by the temperature of the feed. In general, the slope of the operating line for the stripping section is very steep and increases with increasing temperature of the feed. This increases the minimum reflux ratio required to obtain an intersection of the stripping and rectifying operating lines below the equilibrium line .

* Heat of mixing and acetone vapor heat capacity data are available (16, 17), so plate-to-plate enthalpy balances can be made if it is ever considered necessary.

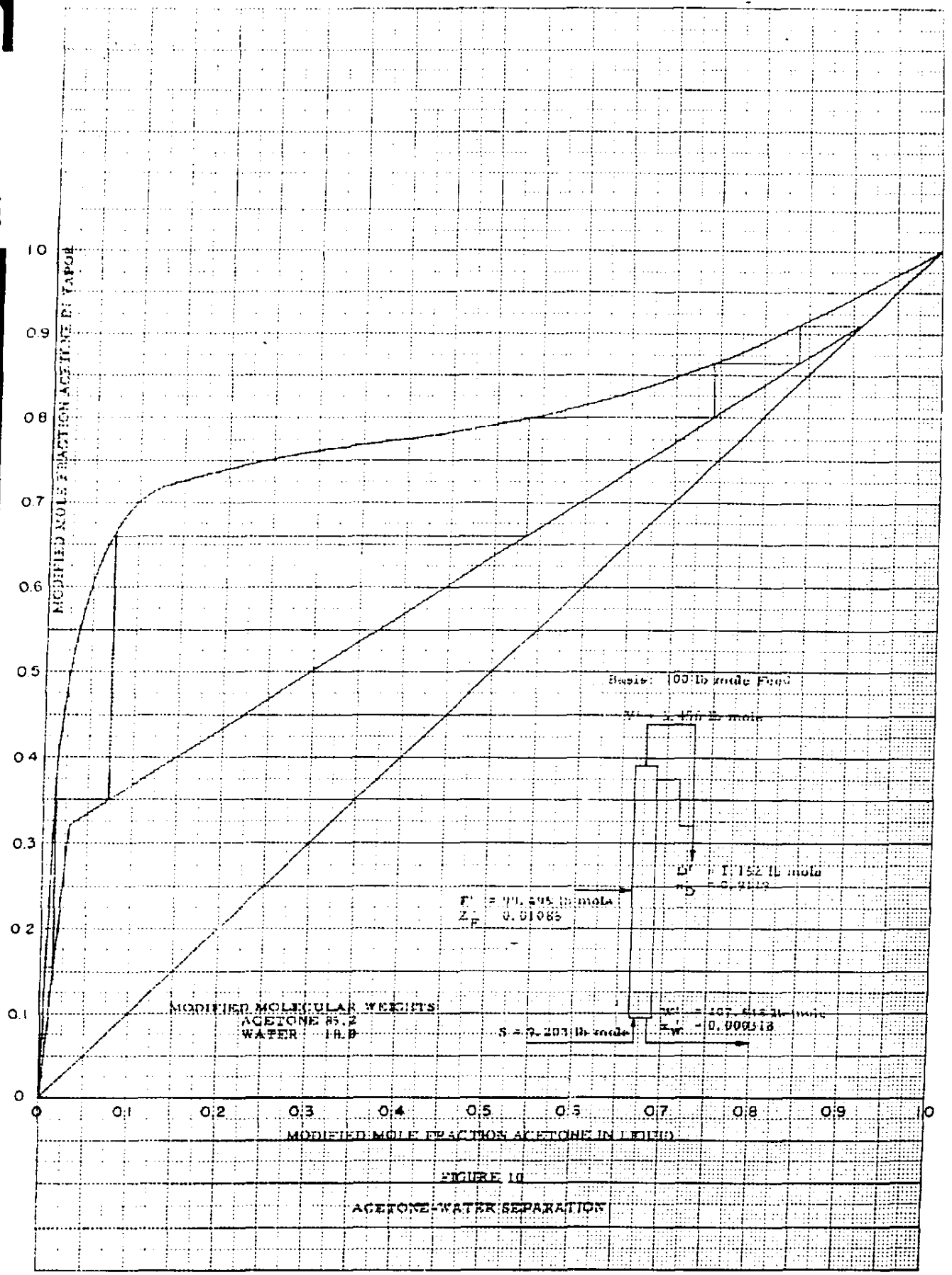


FIGURE 10

ACETONE-WATER SEPARATION

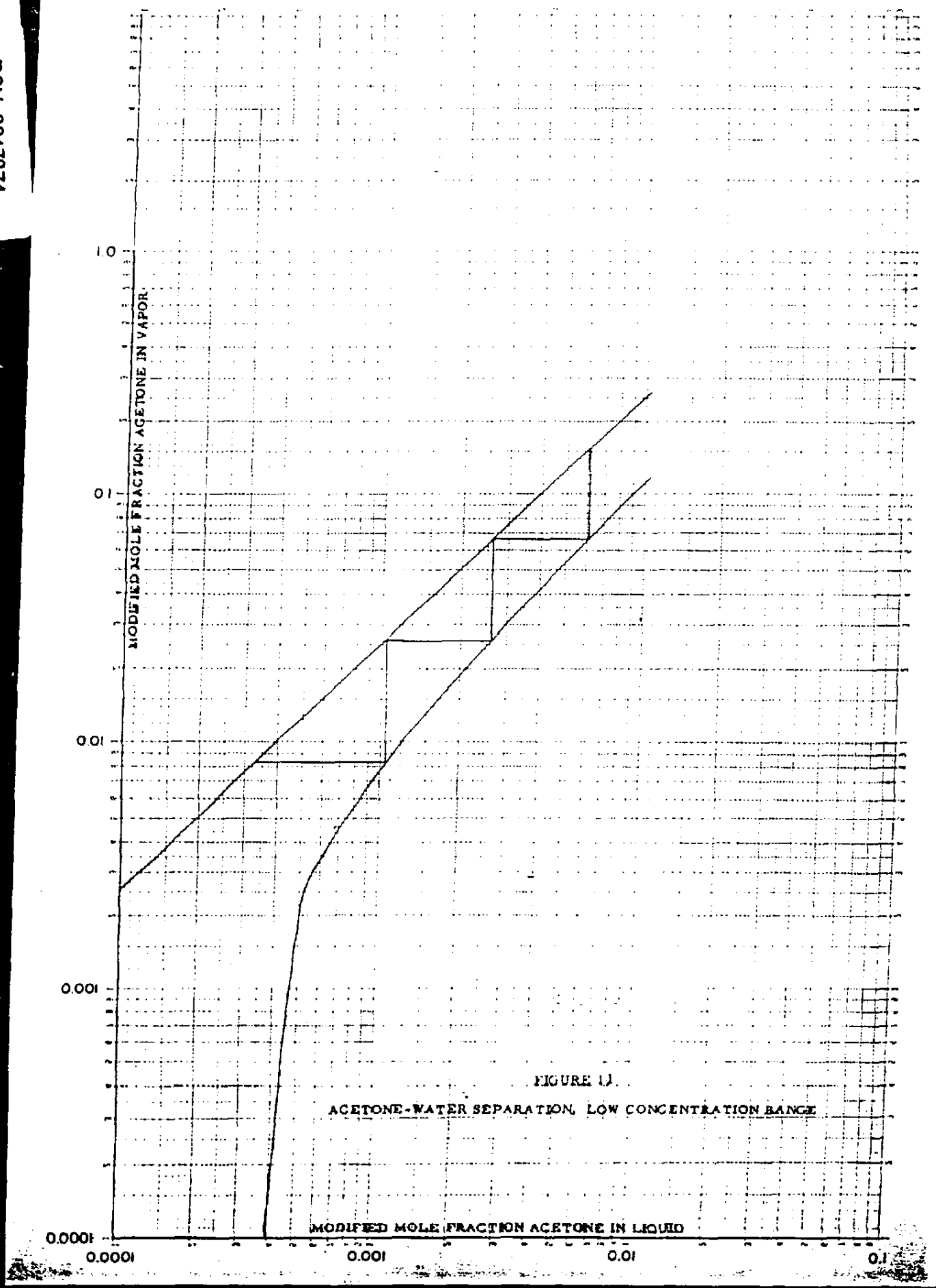


FIGURE 1.1

ACETONE-WATER SEPARATION, LOW CONCENTRATION RANGE

In the pilot plant the acetone recovery column was successfully operated at reflux ratio 2 with feed temperatures up to 45°C. Operation was better with feed at 35°C-45°C than at 25°C because the higher vapor rate in the stripping section caused much difficulty with flooding. In a plant column with properly sized downcomers, there would seem no good reason other than possible heat economy by using waste heat for preheating the feed.

In the pilot plant distillation column, Figures 5 and 6, the 1 in. ID 10-sieve tray Oldershaw rectifying section achieved a separation equal to about five theoretical stages. The 24 in. Goodloe wire mesh packed stripping section achieved about seven theoretical stages or 3.4 in. height equivalent to a theoretical stage. This suggests that stage efficiencies in the acetone-water system tend toward the low side and that a conservative approach to tray rating in a plant column is desirable.

3. Mechanical Design of Acetone Column

The unusual feature of the acetone column operation is the high liquid rates in the stripping section. In the pilot plant, glass Oldershaw columns could not be used in the stripping section because the downcomers were too small to handle the liquid flow at vapor rates high enough to operate the column. In a plant column, unusually large downcomers will certainly be required in the stripping section.

It is further recommended that in a plant column, the oversize downcomers be continued for two trays above the feed tray. Bashar (18) has reported that this is needed for acetone-water separations and pilot plant observations tend to confirm this. The presumed reason for the difficulty is boiling in the downcomers in the region where temperature changes rapidly.

Either a sieve tray or a bubble tray column could be used in the plant. A sieve tray column is recommended because it would be easier to clean in the event that mechanical cleaning is ever necessary.

The pilot plant acetone recovery column was heated by open steam rather than by a reboiler. Open steam is clearly preferred because a reboiler would undoubtedly be subject to some fouling.

4. Control of the Acetone Column

The pilot plant acetone column was controlled by setting the reflux ratio at two, setting the open steam feed to the bottom of the column to maintain 5 in. H_2O g pressure at the bottom, and adjusting the feed to maintain the feed plate temperature at 71°-72°C. This is the proper procedure to obtain maximum throughput at the established reflux ratio.

In a plant the column feed will be established by the rate of production of filtrate by the rotary vacuum filter. In this case the proper procedure will be to set the column feed to equal the filtrate production rate and to

adjust the open steam feed to maintain a selected temperature at a control point in the column.

The control point of the pilot plant acetone column was the temperature of the vapor above the feed tray. Figure 12, the boiling point-composition curve for the acetone-water system, shows this to be a region of substantial sensitivity. In a plant column thermowells on the feed tray and on several trays near the feed tray should be provided for possible use as control point.

Although it was not tested in the pilot plant, a continuous differential refractometer would appear to be a desirable instrument for monitoring the distillate water content. This may also be done in the field by specific gravity measurement: however, extremely careful observations must be taken to obtain accurate results.

5. Water Content of Recycle Acetone

The water content of recycle acetone affects conversion in the polymerization reactor. For this reason it is important that the water content of the recycle acetone be maintained constant in the 1.7%-2.3% range.

Any fresh acetone added to the recycle system should also be diluted to 2% water content.

6. Column Fouling

The acetone recovery pilot plant was operated a total of 78 hours. During this time a very small amount of yellow solid accumulated on the packing in the section just underneath the feed inlet. This material appeared to be partially but not entirely soluble in hot acetone. The amount of material accumulated was so small that it could not be properly characterized.

In the design of a plant column it is recommended that provision be made for washing the column with hot solvent and for easy access to the trays for cleaning.

There is at least a remote possibility that the solid deposits were catalyst residue and possibly quite poisonous. This point is discussed in Section XII-A-3.

G. MATERIALS OF CONSTRUCTION

1. Reactor and Recycle System

Pilot plant operation of the polymerization reactor and the recycle system indicated that glass-lined steel and stainless steel are suitable materials of construction. Stainless steel coupons placed in the vapor space above the reactor, in the reaction mixture and in the top of the stripping column showed no evidence of corrosion. The stainless steel flanges on the reactor and the stainless steel recycle condenser were not corroded. One

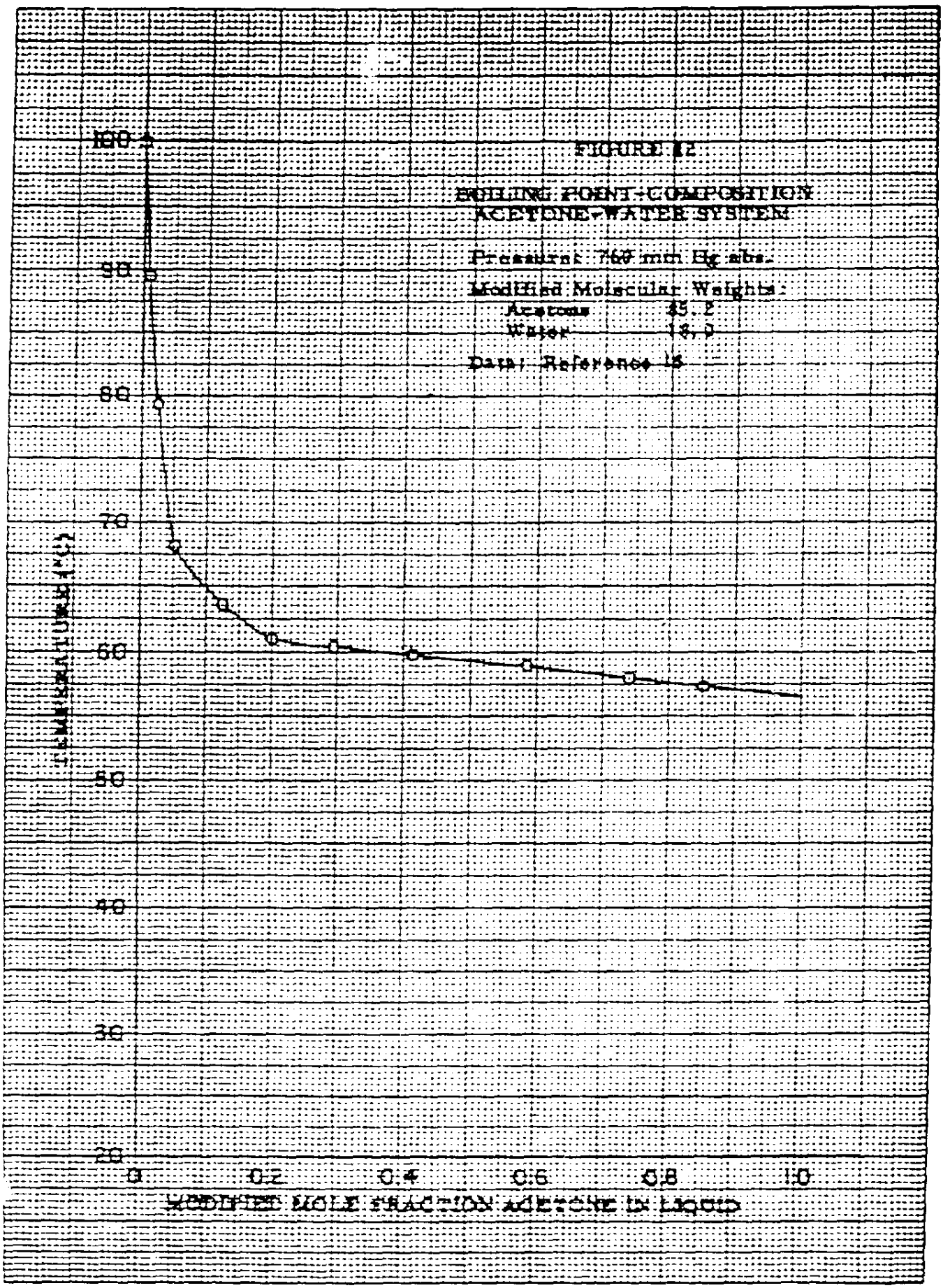
FIGURE 12

BOILING POINT-COMPOSITION
ACETONE-WATER SYSTEM

Pressure: 760 mm Hg abs.

Modified Molecular Weights:
Acetone 45.2
Water 16.0

Data: Reference 15



incident of corrosion was observed when polymer solution in the monomer stripper was accidentally overheated to decompose the polymer. Stainless steel parts exposed to the decomposition products showed spots of rust. It is possible that rusting due to accidental decomposition of polymer solution can be minimized by supplying the epoxy resin stabilizer feed to the stripping column inlet* although this was not tried.

2. Precipitation and Filtration

Materials of construction used in precipitation and filtration equipment should be stainless steel with exception of the slurry hold tank (T-14) which requires glass or resin-lined steel. In the early stages of pilot plant work an open stainless steel slurry hold tank was replaced with a polyethylene tank when traces of corrosion were observed on the stainless steel vessel wall in the proximity of the liquid-air interface. This change was made before epoxy resin stabilizers were added routinely to the polymer solution, subsequently no evidence of corrosion in the pilot plant system was observed.

3. Acetone Recovery

Stainless steel is an acceptable material of construction for the acetone recovery system. Possibly carbon steel could be used except in the condenser and reflux splitter.

H. PACKAGING AND STORING VYSET RE POWDER

Dried VYSET RE powder was routinely packaged in polyethylene-lined Leverpacks and stored at room temperature. There was no evidence of deterioration during storage.

I. PRODUCT PROPERTIES

The definitive test of the quality of a VYSET RE product is how it performs in applications. Product made by the methods of the Tentative Process and meeting the specifications listed in Section XIV has been judged satisfactory by Central Research and Plastics evaluation groups for metal coating applications.

The impact specification $\geq$ 50% pass was the most important specification. Damage to the polymer during drying was the most common cause of failure to meet this specification, provided the viscosity and chemical composition was within specification.

*Occurrence of accidental decomposition of polymer solution appears unlikely in the plant where heat addition to the monomer stripper is effected by addition of open superheated acetone vapor only.

The impact resistance of pilot plant polymer was substantially better at the upper end of the viscosity range than at the lower end.

J. RAW MATERIALS

The suppliers for raw materials listed in Section V are those found by Dr. A. D. Gott of the Monsanto Central Purchasing Department to be the most likely sources for a manufacturing operation located in New England. All these materials were tested in the pilot plant.

The vinyl chloride used in the pilot plant was obtained from Texas City in 200 lb steel cylinders, which frequently contained rust, polymer and presumably ferric chloride. It was necessary to purify this VCl monomer according to the procedure given in Section XX, Appendix A. The bulk monomer delivered by tank car to a plant will presumably be transported under clean conditions and therefore not require purification. This was tested in the pilot plant by obtaining a shipment of VCl in new cylinders from Texas City and using it successfully without purification.

The acetone used in the process was obtained from a plant which makes acetone by isopropanol dehydrogenation. Laboratory experimentation should precede any attempt to use acetone made by the cumene-phenol process, since traces of phenol would be expected to inhibit polymerization.

EHF monomer is not an article of commerce and must be made by Monsanto. A tentative process for EHF manufacture is available (5).

K. WASTE DISPOSAL

The principal waste stream from the plant is the bottoms from the acetone column, which is mostly water with a trace of EHF and possibly minute amounts of catalyst residues. Disposal of this stream would presumably not be difficult; however, it must be evaluated with respect to the existing local conditions.

During polymerization reactor start-up and shutdown operations, substantial amounts of VCl, IB and acetone mixture may have to be disposed of. The magnitude of this disposal problem will depend on the scale of operation and local conditions. It is noted that in some cases where VCl is flared, it is necessary to scrub the combustion products with caustic to remove acid prior to discharge to the atmosphere (19).

Small amounts of acetone used in reactor and column cleaning will have to be disposed of periodically.

L. PRODUCT STABILIZATION

The practice of adding an epoxy-type stabilizer to the polymer solution effluent from the monomer stripper (D-1) was adopted midway through the pilot plant work. This was done because the unstabilized dry powder showed a tendency to rust mild steel when stored in contact with it. Evaluation groups have agreed that addition of stabilizer has eliminated this problem.

Addition of stabilizer has had ancillary advantages. It virtually eliminated the problem of corrosion in the precipitation and led to a slightly lighter colored product.

Two epoxy stabilizers -- Epon 828 and Paraplex G-62 -- were used in the pilot plant. Both were effective. Paraplex G-62 was preferred by Plastics Division Research (13).

X. COST ESTIMATE (by E. C. Dybdal)

Estimated manufacturing costs and capital requirements for the production of 5, 10, and 20 million lb VYSET RE (designated as VCl/EHF/IB terpolymer in the memorandum to Dr. R. W. Schuler) were prepared by Dybdal (4). Summaries of these estimates are given in Tables II and III.

Detailed estimates were prepared for the base case; 10,000,000 lb a year, and conversion costs and capital requirements for 5,000,000 and 20,000,000 lb a year were factored ("0.6" factor for capital) from the base case.

For 10,000,000 lb a year (Table II) estimated raw material cost is 17.84¢ a lb. Estimated raw material requirements and costs as well as details of the estimated conversion cost (7.2¢ a lb) are shown in Table III. An over-all yield of 86% was assumed which included an estimated 5% loss for scrap and a yield of approximately 90% on monomers. The estimated bulk manufacturing cost is 25.0¢ a lb. Estimated M&E is $1,350,000 and fixed capital is $2,175,000 based largely on the estimate that nonmanufacturing capital will be about 50% of M&E. Working capital ($1,300,000) was assumed to be 28% of net annual sales. Selling price for a 20% return after Federal income taxes is 46¢ a lb (based on a tax rate of 52% of net profit).

At 5,000,000 lb a year the estimated raw material cost becomes 20.3¢ a lb (approximately 1,100,000 lb EHF at 55¢ a lb are required). Conversion cost is 10.1¢ a lb and the bulk manufacturing cost is 30.4¢ a lb. Estimated M&E is $891,000 and fixed capital, $1,437,000. The selling price for a 20% return after Federal income taxes is 58¢ a lb.

At 20,000,000 lb a year, estimated raw material cost is 16.3¢ a lb (approximately 4,430,000 lb EHF at 37¢ a lb). The conversion cost is 5.1¢ and the bulk manufacturing cost is 21.4¢ a lb. Estimated M&E is $2,047,000 and fixed capital: $3,321,000. Selling price for a 20% return after Federal income taxes is 39¢ a lb.

Prices for EHF at the three production rates are estimated prices and were presented in a memorandum to Dr. R. W. Schuler, Cost Estimate for the Manufacture of Ethyl, β Hydroxyethyl Fumarate, Revised July 30, 1963.

The following is a brief description of the projected process of manufacture on which these estimates were based:

1. VYSET RE is produced in an overflow reactor by continuous addition of four streams: (a) vinyl chloride and EHF dissolved in a portion of the required acetone, (b) isobutylene fed separately, (c) azo catalyst dissolved in acetone, and (d) a recycle stream of unreacted vinyl chloride dissolved in the remaining acetone. The effluent from the reactor is a 30% solution of terpolymer in acetone and unreacted monomers. Reaction temperature

TABLE II

ESTIMATED PRODUCTION COSTS, CAPITAL REQUIREMENTS, AND SELLING PRICES FOR THE MANUFACTURE OF VCl/EHF/IB TERPOLYMER

Composition - 74.5% vinyl chloride, 19.6% EHF. and 5.9% isobutylene
Plant location - Springfield
Yield on monomers - 86%

Production rate, lb/yr	5,000,000	10,000,000	20,000,000
Raw material cost, ¢/lb	20.3	17.84	16.3
Conversion cost. ¢/lb	10.1	7.16	5.1
Bulk manufacturing cost, ¢/lb	30.4	25.00	21.4
M&E, $	891,000	1,350,000	2.047,000
Fixed capital, $	1,437,000	2,175,000	3,321,000
Working capital, $*	809,000	1,300,000	2,159,000
Total fixed plus working capital	2,246,000	3,475,000	5,480,000
Selling price, 20% return after taxes, ¢/lb**	58	46	39

*28% of net sales
**SARE expenses 15% of net sales, Federal income taxes 52% of net profit

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TABLE III

COST ESTIMATE

FOR: VCl/EHF/IB Terpolymer (Revised 7/31/63)

SHEET NO. OF

PRODUCTION	PER YEAR AS				JOB NUMBER
10,000,000 lb	product in bulk storage				
LOCATION	**OPERATION**	**YIELD**	**ON**	**BY / DATE**	**OR'D. / DATE**
Springfield	8000 HRS./YR.	86 %	Monomers		

M&E - $1,350,000
Mfg. Bldg. - $150,000

	UNIT	QUANTITY	$ PER UNIT	$ PER YEAR	$ PER 100 LBS.
RAW MATERIALS					
vinyl chloride	lb	8,755,000	0.0706	618,100	6.18
EHF	lb	2,216,700	0.44	975,400	9.75
isobutylene	lb	688,600	0.0796	54,800	0.55
azo catalyst	lb	60,000	1.70	102,000	1.02
acetone	lb	961,900	0.0355	34,200	0.34
Total Gross R.M.				1,784,500	17.84
CREDITS					
TOTAL NET R.M.					
DIRECT EXPENSE					
LABOR	ManHr	26,670	3.60	96,000	0.96
SUPERVISION				12,000	0.12
PAYROLL CHARGES				17,000	0.17
STEAM	M lb	78,000	0.889	69,340	0.69
ELECTRICITY	CKWH	19,560	1.131	22,120	0.22
COMPRESSED AIR					
REPAIRS				183,600	1.84
WATER-COOLING	M gal	75,000	0.126	9,450	0.10
WATER-PROCESS-CITY WATER	M gal	16,260	0.126	2,050	0.02
FUEL-GAS					
FACTORY SUPPLIES				6,750	0.07
LABORATORY				56,000	0.56
CLOTHING & LAUNDRY				840	0.01
TOTAL D.E.				475,150	4.76
INDIRECT EXPENSE					
DEPRECIATION - M & E				112,500	1.13
DEPRECIATION - BLDG.				7,500	0.08
TAXES AND INSURANCE	} 25% D. E.			118,800	1.19
OTHER INDIRECT					
TOTAL I.D.E.				238,800	2.40
BULK MANUFACTURING COST				2,498,450	25.00
PACKAGING & SHIPPING					
TOTAL P & S COST					
TOTAL MANUFACTURING COST f.o.b.					

is 80°C and the pressure, 200-225 psig. The reactor is a one-thousand gallon jacketed, stirred vessel of 304 stainless steel for a capacity of 10,000,000 lb terpolymer a year.

2. The product stream from the reactor passes through a letdown valve and the pressure is reduced to 20-60 psig depending on the cooling water temperature. A heat exchanger is provided to supply the heat of vaporization of VCl, IB, and acetone and compensate for the cooling on expansion. Vapor and liquid are separated in the letdown tank. The liquid phase containing the dissolved terpolymer is pumped to the feed tank for polymer precipitation.

3. Polymer is precipitated by pumping the product stream through a nozzle into a high-velocity stream of water in a pipe loop formed by withdrawing slurry from the bottom of the precipitation tank through a 500 gpm pump and discharging the slurry into the top of the tank. The capacity of the precipitation tank is 500 gallons. Slurry from the precipitation tank is filtered by centrifugation to recover the polymer. *

4. Two 48-inch suspended-basket programed batch centrifugals are assumed. The cake is washed with water before it is discharged into the cake hopper for the dryer. Filtrate and wash water are kept separate. The filtrate contains about 7.5% acetone which is recovered by distillation. *

5. The centrifuge cake contains 60% water and is dried in a Proctor and Schwartz continuous through-circulation dryer to about 0.5% water in the product. The cake is preformed in a Bonnot pelletizer before it is fed to the dryer. The polymer is then transferred to product storage.

*The tentative process calls for precipitation in an SRC disintegrator and filtration on a rotary vacuum filter. The numbered equipment costs for this equipment have been compared with the costs for the same steps in the estimate. It was found that the costs would be insignificantly less than those used in the estimate; hence the estimate may be considered valid for the tentative process.

XI. PATENT STATUS (Prepared by J. D. Kennedy)

The following patent applications are on file at the Patent Office. They have not yet been on file long enough to receive any official action by the Patent Office.

RE 2744 - Hydroxyalkyl alkyl fumarate copolymers with vinyl chloride; high solids solutions of such copolymers in aromatic solvents: process of preparing such copolymers, particularly from monomer of low acid content.

RE 2819 - The use of organic amines in the interpolymerization of vinyl chloride with hydroxyalkyl fumarates, with or without isobutylene, specifically the use of trialkyl amines in amounts stoichiometric to the monoalkyl fumarate in the monomer to deactivate same.

RE 2820 - Terpolymers of vinyl chloride, fumarate esters (particularly alkyl hydroxyalkyl fumarates) and isobutylene; such polymers containing particular ranges of monomers; methods of conducting the polymerization.

RE 2824 - Interpolymers of vinyl chloride with bis(hydroxyhydrocarbyl) fumarates, optionally including dialkyl fumarates as additional monomer, and polymerization processes.

The filing of additional applications covering interpolymers from related monomers, process details, and curing and stabilization systems is contemplated. The prospects for sound patent protection, such as composition of matter claims, are better for the terpolymers containing isobutylene as third monomer than for the two component polymers.

No infringement problems, i.e., adverse patents, of sufficient significance to prevent commercialization of these polymers have been found. Information concerning studies which have been made can be obtained from the Patent Department.

XII. TOXICITY AND HAZARDS

A. HAZARDOUS OPERATIONS

1. Polymerization

The polymerization operation, carried out according to the operating procedure of Section VIII, is straightforward. It has only the hazards normally associated with high-pressure exothermic reactions of flammable materials.

Particular attention should be paid to protection of personnel from the consequences of leaks or errors during reactor sampling. While taking samples operators should wear face shields, chemical goggles and gloves.

In the event of cooling water, power or mechanical failure, the reaction in a large plant reactor will have to be stopped to prevent overheating and overpressuring the reactor. The most effective way to do this is to vent the volatile vinyl chloride and isobutylene monomer to a safe place. In cases where the reactor stirrer is still operating, a free radical acceptor such as hydroquinone might be pumped into the charge to stop the reaction.

2. Precipitation

The acetone content of the liquid phase of slurry produced by precipitation of stripped polymer solution is about 5% (wt.) acetone. At 90°F a concentration of about 7.3% acetone in water will produce explosive vapors.* Under the operating conditions outlined in Section VIII, the acetone concentration in the vapor over the precipitated polymer slurry would be below the lower explosive limit. However, an operating upset which resulted in too much acetone in the stripper bottoms or one in which filtrate rather than wash filtrate were recycled to the precipitation could lead to acetone vapor concentration in the explosive range.

A small amount of unreacted VCl and IB monomer is present in stripped polymer solution. Some of this monomer may be present in the vapor over the precipitated polymer slurry, thereby adding to the fire and explosion hazard. Designs should provide for proper venting of unreacted monomer vapor from the slurry hold tank (T-14).

*The lower explosive limit for acetone in air is 2.55 % (vol.). The vapor-liquid equilibrium data given by Chu (15) indicate that this vapor acetone concentration corresponds to about 7.3% (wt.) acetone in the water.

3. Filtration

The problem with potentially explosive vapors is the same as that discussed in Section XII-A-2 above. Proper precautions against fire and explosion should be taken.

4. EHF Handling

EHF monomer used in this process causes severe skin irritation by contact even in dilute form as in the reactor effluent. The only way to avoid skin irritation when handling EHF is to avoid all contact with the skin. In achieving this, the following principles should be kept in mind:

a. The fumarates are essentially nonvolatile; hence they remain where they are spilled. Spills may be washed up with isopropanol, ethanol or copious amounts of water. Tools may be cleaned with hot water.

b. Temporary protection is obtained with rubber or vinyl gloves; however, the fumarates are soluble in rubber and vinyl and soak through in time. Gloves which have been exposed to fumarates should be discarded immediately.

c. Leather also absorbs fumarates. Any shoes which have come in contact with fumarate material should be discarded.

d. Janitors and others handling contaminated waste may be affected. Special provisions for handling waste should be provided.

e. Clothing which has been contaminated with fumarate should be changed immediately. A system should be worked out so that laundry workers will not be exposed to the contaminated clothing. At the Research Center, contaminated clothing is sent to the laundry in polyethylene bags and laundry workers have been warned to dump the clothing into the washers directly from the bags.

Details of EHF toxicity studies are given by Carter (5).

5. Handling Azo-bis-Isobutyronitrile (AZBN) (20)

Packaged AZBN should not be exposed to temperatures in excess of 50°C as vigorous, but not explosive, decomposition is liable to occur with the risk of fire. Since some of the potential decomposition products are highly toxic, it is strongly recommended that all operations be carried out with adequate ventilation. Avoid contact with eyes, skin and clothing. Use of dust masks, rubber gloves and protective clothing is recommended.

AZBN can be decomposed by mechanical impact without explosion. An explosive hazard appears to exist only for solutions of AZBN in acetone (20). The maximum safe concentration of AZBN in acetone is unknown; in the pilot plant solutions up to 4% wt concentration were handled without difficulty. The temperature of the solution should not exceed 35°C.

During preparation of initiator solution, the initiator should be added to the bulk of solvent in an agitated vessel. Configurations of equipment leading to entrapment of partially dissolved initiator should be avoided.

In some experimental work AZBN which had been recrystallized from ethyl acetate was used. The recrystallization procedure is given in Section XX-B. Do not attempt to recrystallize AZBN from acetone.

B. HAZARDOUS COMPOUNDS

1. Acetone (21)

Description: Colorless liquid fragrant mint-like odor
Boiling point: 56.48°C
Flash point: 0°F (closed cup)
Explosive range in air: 2.55-12.8%
Autoignition temperature: 1000°F
Fire extinguishers: CO_2, dry chemical
Toxic hazard rating:*
Acute local: Irritant 1, Ingestion 2, Inhalation 2
Acute systemic: Ingestion 2, Inhalation 2, Skin Absorption 2
Chronic local: Irritant 1
Chronic systemic: Ingestion 1, Inhalation 1, Skin Absorption 1
Maximum allowable concentration in air: 1000 ppm
I.C.C. classification: Flammable liquid, red label

2. Azo-bis-Isobutyronitrile (20)

Description: White crystalline solid; stable at room temperature
Flash point: Can be ignited readily with an open flame. Will decompose vigorously, but not explosively, at temperatures above 50°C
Fire extinguishers: CO_2, dry chemical
Toxic hazard: Decomposition products highly toxic. Toxic effects produced through inhalation of dust or vapors and absorption through skin or eyes.
Explosive hazard in acetone solution: Maximum allowable. Concentration unknown. Do not heat solutions of AZBN in acetone above 35°C. Do not attempt to recrystallize in acetone.

*TOXIC RATING CODE: 0 = None, 1 = Slight, 2 = Moderate, 3 = High, U = Unknown

3. Ethylhydroxyethyl Fumarate (5)
Reference (5) gives details of a toxicological study of EHF.

Description: Straw colored liquid
Boiling point: > 250°C
Flash point: Unknown, probably high
Explosive range in air: Unknown, probably not explosive
Autoignition temperature: Unknown
Fire extinguishers: CO_2, dry chemical
Toxic hazard: Powerful skin irritant, very dangerous to eyes, moderate toxicity when ingested.
I. C. C. classification: Not established

4. Epoxy Resin (Epon 828, Paraplex G-62) (22)

Toxic hazard: Primary skin irritant. Sensitizing agent giving rise to some forms of hypersensitivity

5. Isobutylene (21)

Description: Volatile liquid or easily liquefied gas
Boiling point: - 6.9°C
Flash point: < 20°C
Explosive range in air: 1.8-8.8%
Autoignition temperature: 869°F
Fire extinguishers: CO_2, dry chemical
Toxic hazard rating: Details unknown. May have asphyxiant or narcotizing action
Maximum allowable concentration in air: Unknown
I. C. C. classification: Flammable compressed gas, red label

6. Methyl Isobutyl Ketone (21)

Description: Colorless liquid
Boiling point: 115.1°C
Flash point: 75°F (open cup)
Autoignition temperature: 860°F
Fire extinguishers: Foam, CO_2, dry chemical
Toxic hazard rating:
Acute local: Irritant 2, Ingestion 2, Inhalation 2
Acute systemic: Ingestion 2, Inhalation 3, Skin Absorption 2
Chronic local: U
Chronic systemic: U
Maximum allowable concentration in air: 100 ppm
I. C. C. classification: Flammable liquid, red label

7. Vinyl Chloride (21)

Description: Colorless liquid or gas; faintly sweet
Boiling point: - 13.4°C
Flash point: - 108°F (Cleveland open cup)
Explosive range in air: 4-22%
Fire extinguishers: CO_2, dry chemical
Toxic hazard rating:
Acute local: Irritant 1
Acute systemic: Ingestion 2, Inhalation 2
Chronic local: U
Chronic systemic: Ingestion 1, Inhalation 1
Very dangerous when heated to decomposition, will emit phosgene.
Maximum allowable
concentration in air: 500 ppm
I.C.C. classification: Flammable gas; red label

XIII. ANALYTICAL METHODS

A. NONVOLATILES IN THE REACTOR CHARGE

Connect sample bomb (SB-1) (Figure 13) to the reactor sampling manifold as shown in Figure 14. Purge the sampling manifold of residues of previous samples by sweeping a small amount of reactor charge through valves SV-1 and SV-2 into the purge volume. Valve SV-3 is opened to permit withdrawal of a reactor sample into the sample bomb (SB-1). Subsequently valve SV-3 and SV-1 are shut off and the amount of reactor charge trapped in the purge volume is flushed through valve SV-4 into the purge receiver. The sample bomb is then removed from the sampling manifold, any spill over from the reactor is washed off with acetone, and the net weight of the reactor sample determined.

The determination of nonvolatiles is carried out on an Ohaus moisture balance (Model 6000). Adjust zero balance with an aluminum liner in place on the pan of the moisture balance. Discharge the contents of the sample bomb on the aluminum liner. The residue in the bomb is rinsed onto the liner with acetone to insure that the entire reactor sample was transferred. Commence to drive off the volatile components of the sample at a heater setting of 35 (approximately 65°C) on the Ohaus balance for 40 minutes and weigh the dried sample. A nitrogen purge of the interior of the Ohaus balance must be provided to prevent explosion of the acetone vapors in the balance. From the net reactor sample weight and the dry weight calculate the nonvolatiles of the reactor charge:

$$\% \text{ nonvolatiles} = \frac{\text{weight dry sample}}{\text{net weight reactor sample}} \times 100$$

The sample bomb SB-1 is cleaned thoroughly with acetone, dried and tared prior to the next sampling.

B. REACTOR CHARGE ASSAY

For reactor control purposes, the volatile monomer and solvent charge in the reactor (VCl, IB and acetone) can be determined by a moderately fast (10 min.) isothermal gas chromatographic method without internal standards.

Gas chromatograph:	Perkin Elmer Model 154
Column:	⅛ in. OD x 10 ft copper
Packing:	5% 2, 2'bis(cyano ethoxy) dipropyl ether on Teflon 6
Helium flow:	75 ml/min
Oven temperature:	55°C
Injection block power:	65 (setting)
Sample size:	1 µl

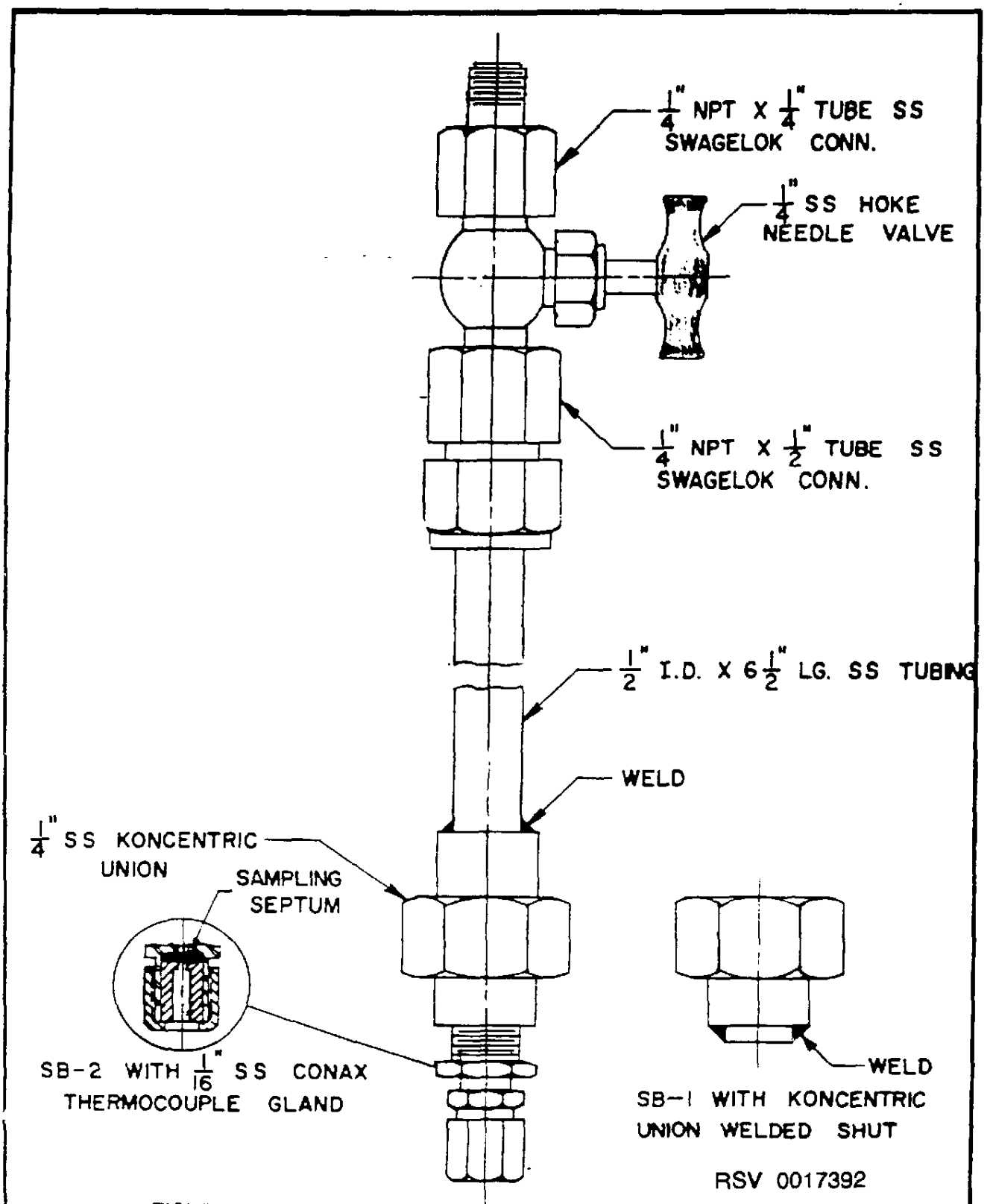
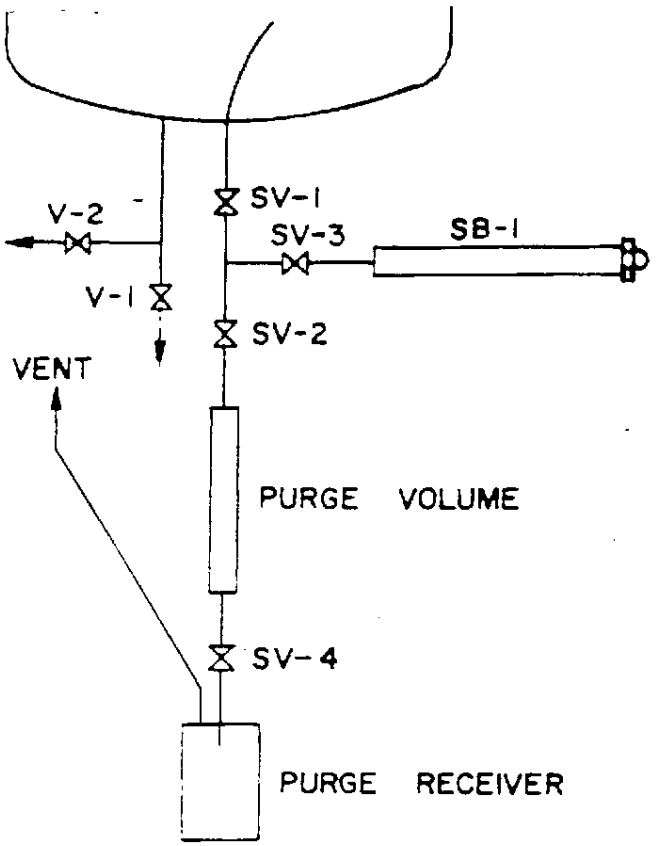


FIGURE 13

DRAWN	MONSANTO CHEMICAL COMPANY	PROJ. NO.
CHECKED	800 N. LINDBERGH BLVD. ST. LOUIS 66, MO.	LOCATION
DATE		DIVISION
SCALE	SAMPLE BOMB SB-1 & SB-2	DWG. NO.



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DRAWN	MONSANTO CHEMICAL COMPANY	PROJ. NO.
CHECKED	800 N. LINDBERGH BLVD. ST. LOUIS 66, MO.	LOCATION
DATE	FIGURE 14	DIVISION
SCALE	REACTOR SAMPLING SYSTEM	DWG. NO.

Sample the reactor using sample bomb SB-2 (see Figure 13) which has been charged with 20 ml methyl isobutyl ketone. The reactor sampling procedure is the same as outlined in Section XIII-A. The sample weight need not be determined. Shake the bomb and withdraw a 1 µl sample with a syringe directly from the sample bomb through the sampling septum. Measure the area response of IB, VCl and acetone on the chromatograph. The area response factors for IB, VCl and acetone are determined from a standard consisting of approximately 90% wt MIBK, 0.5% wt IB, 5% wt VCl and 4.5% wt acetone.

Calculate for the standard:

$$F_i = \frac{\% \text{ wt (i)}}{\% \text{ area response (i)}}$$

where i = IB, VCl or acetone

(Note: $\%$ area response (i) $= \frac{\text{area response (i)}}{\text{total area response}} \times 100$)

From the area response of the reactor sample calculate:

$\%$ wt IB = $\%$ area response (IB) x F_{IB}
$\%$ wt VCl = $\%$ area response (VCl) x F_{VCl}
$\%$ wt acetone = $\%$ area response (acetone) x $F_{Acetone}$

In order to express the above distribution of volatile constituents in terms of the reactor charge they must be multiplied by the following correction:

$$\left(\frac{100 - \% \text{ nonvolatile}}{100}\right)$$

The peak for the sample diluent MIBK will appear on the chromatogram approximately 10 minutes after injection of the sample.

2,2'bis(cyano ethoxy) dipropyl ether is not available commercially but has been synthesized in laboratory quantities at the Research Center (23).

C. RECYCLE STREAM ASSAY

Assays for IB, VCl and acetone in the recycle stream (G) are carried out identically to Section XIII-B.

D. VOLATILE RESIDUE IN POLYMER SOLUTION

Assays for IB, VCl and acetone in the polymer solution (M) from the stripper bottom are carried out identically to Section XIII-B. Since the polymer solution is at atmospheric pressure, a 5 ml sample can be taken directly into glassware containing approximately 30 ml MIBK. During normal operation of the polymerization system, the area response of IB is negligible.

E. RESIDUAL EHF IN THE REACTOR CHARGE

For control purposes, up to 2% EHF may be determined in the reactor charge by a quick isothermal gas chromatographic method employing dibutyl phthalate as an internal standard.

Gas chromatograph:	Aerograph A-90-P (Wilkens Instrument and Research Co.)
Column:	¼" OD x 32" stainless steel
Packing:	1% Carbowax 6000 on acid washed Chromsorb W 60/80 mesh
Helium flow:	60 ml/min
Oven temperature:	239°C
Detector temperature:	273°C
Injection block temperature:	268°C
Sample size:	1 µl

Prepare a standard by charging about 25 ml MIBK to a 50 ml volumetric flask and weigh in about 5 g dibutyl phthalate. Make to the mark with more MIBK and shake well.

Sample the reactor, proceeding in the same manner as outlined for Section XIII-A. Discharge contents of the sample bomb into about 30 ml MIBK. (If necessary, rinse sample bomb with MIBK to insure complete transfer of sample.)

To make a determination, charge 2 ml of standard solution to the MIBK solution containing the reactor sample. Run this mixture on the chromatograph and measure the area response of the EHF and DBP. Simultaneously prepare a MIBK-EHF reference solution in the ratio of approximately 150:1. Add 2 ml standard solution to this mixture and again determine the area response of EHF and DBP.

Calculate for the reference solution

$$F = \left(\frac{\frac{\text{area response EHF}}{\text{weight EHF}}}{\frac{\text{area response DBP}}{\text{weight DBP}}} \right)_{\text{standard}}$$

From the area response of the reactor sample

$$\% \text{ wt EHF} = \left(\frac{\text{area response EHF}}{\text{area response DBP}} \right) \left(\frac{\text{weight DBP}}{F} \right) \left(\frac{100}{\text{weight reactor sample}} \right)$$

F. RESIDUAL EHF IN POLYMER SOLUTION

Assays for residual EHF in polymer solutions are carried out identically to Section XIII-E. Since the polymer solution is at atmospheric pressure, sampling can be handled directly in glassware.

This method is applicable to polymer solution from the bottom of the stripper as well as dry polymer redissolved in either acetone or MIBK.

G. ACIDITY AND HYDROXYL CONTENT OF VYSET RE (by R. J. Slocombe)

1. Hot Acidity Test

   a. Weigh 0.5 to 1.0 g sample into 250 ml round-bottom flask.

   b. Add 10.0 ml Analytical Reagent grade pyridine with moisture adjusted to 0.3-0.5% based on Karl Fischer analysis.

   c. Reflux 40 minutes under an air condenser (ground glass joint greased with "Lubriseal") in a constant temperature oil bath adjusted to 126 ± 0.1°C. The 40-minute reflux time is checked with a stop watch to the nearest second after reflux drops begin falling from the condenser tip.

   d. Cool immediately in ice bath.

   e. Remove condenser and wipe grease from the ground glass joint.

   f. Pour contents of flask into 250 ml beaker, rinse the joint of the flask with a tiny amount of acetone, put the condenser back into the flask and rinse down the condenser with 15 ml acetone. Swirl the flask to completely rinse the sides with acetone, and pour it into the beaker.

   g. Pipette 25.0 ml cyclohexanone (best quality available) into the flask, swirl to completely rinse the sides and add it to the beaker.

   h. Add 10.0 ml distilled water to the flask, swirl to completely rinse the sides and add it to the beaker.

   i. Put the beaker in a plastic or glass ice bath, mount on a magnetic stirrer and allow the temperature to drop to about 5°C.

   j. Titrate potentiometrically using 0.1 N NaOH. Approach the pH of 8.0 carefully, then reduce the additions of caustic to 0.10 ml between pH readings.

   k. The largest break is usually observed between pH values of 9.5 and 10.5. The end point is determined by interpolating from the largest breaks to give the value of the titre to the hundredth of a milliliter.

   l. Run a blank using everything exactly the same except omit the sample of polymer.

   m. Calculate as follows:

$$\frac{\text{(titre for sample) - (titre for blank) x N of base}}{\text{weight of sample}} = \text{meq. acidity per gram of polymer}$$

2. Cold Acidity Test

a. Weigh a one-gram sample (accurately) of polymer into a 250 ml beaker.

b. Add 25.0 ml cyclohexanone and 15.0 ml acetone to the beaker.

c. Add a magnetic stirring bar, mount the beaker on a magnetic stirrer and allow the sample to dissolve.

d. Cool the solution to about 5°C by setting the beaker in a glass or plastic ice bath on the magnetic stirrer.

e. Add 10.0 ml distilled water.

f. Titrate potentiometrically (while stirring in the ice bath) with 0.1 normal NaOH. Approach the pH of 8.0 carefully, then reduce the additions of caustic to 0.10 ml between pH readings.

g. The largest break is usually observed between pH values of 9.5 and 10.5. The end point is determined by interpolating from the largest breaks to give the value of the titre to the hundredth of a milliliter.

h. Run a blank using everything exactly the same except omit the sample of polymer.

i. Calculate as follows:

$$\frac{\text{(titre for sample) - (titre for blank) x N of base}}{\text{weight of sample}} = \text{meq. acidity per gram of polymer}$$

3. Hydroxyl Determination

a. Weigh 0.5 to 1.0 g sample into 250 ml round-bottom flask.

b. Add 10.0 ml hydroxyl reagent. (Hydroxyl reagent prepared daily as follows: Add 30.0 ml acetic anhydride, AR grade, into a 250 ml volumetric flask. Fill to graduation mark with AR grade pyridine containing 0.3 to 0.5% water based on Karl Fischer determination.)

c. Reflux 40 minutes under an air condenser (ground glass joint greased with "Lubriseal") in a constant temperature oil bath adjusted to 126 ± 0.1°C. The 40-minute reflux time is checked with a stop watch to the nearest second after reflux drops begin falling from the condenser tip.

d. Cool immediately in ice bath.

e. Remove condenser and wipe grease from the ground glass joint.

f. Pour contents of flask into 250 ml beaker, rinse the joint of the flask with a tiny amount of acetone, put the condenser back into the flask and rinse down the condenser with 15 ml acetone. Swirl the flask to completely rinse the sides with acetone, and pour it into the beaker.

g. Pipette 250 ml cyclohexanone (best quality available) into the flask, swirl to completely rinse the sides and add it to the beaker.

h. Add 10.0 ml distilled water to the flask, swirl to completely rinse the sides and add it to the beaker.

i. Put the beaker in a plastic or glass ice bath, mount on a magnetic stirrer and allow the temperature to drop to about 5°C.

j. Titrate potentiometrically using 0.5 N NaOH. Approach the pH of 8.0 carefully, then reduce addition of caustic to 0.10 ml between readings.

k. The largest break is usually observed between pH values of 9.5 and 10.5. The end point is determined by interpolating from the largest breaks to give the value of the titre to the hundredth of a milliliter.

l. Run a blank using everything exactly the same except omit the sample of polymer.

m. Calculation:

V_1 - vol. base used in hot acidity test
V_2 - vol. base used in hot acidity blank
V_3 - vol. base used in hydroxyl test
V_4 - vol. base used in hydroxyl test blank
N_1 - normality of 1/10 N NaOH for hot acidity test
N_2 - normality 0.5 N NaOH for hydroxyl test
wt_1 - weight of sample for hot acidity test
wt_2 - weight of sample for hydroxyl test
A - acidity correction

$$\frac{(V_1 - V_2) \times N_1 \times wt_2}{N_2 \times wt_1} = \text{Acidity Correction} = A$$

$$\frac{(V_4 - A) - (V_3) \times 0.01701 \times 100 \times N_2}{wt_2} = \% \text{ OH}$$

H. PHYSICAL PROPERTY TESTS FOR VYSET RE (by H. P. Holladay)

Early in the VYSET RE program a routine procedure was adopted which gave a good comparative evaluation of research polymers. The early polymers varied considerably from lot to lot in tendency to release HCl to cause premature

reaction of Resimene. The following solution procedure essentially removes that variable.

Solutions are prepared according to the following formula:

Polymer	-	50 pts
Xylene	-	25 pts
MIBK	-	25 pts

If the polymer does not contain stabilizer, 1 pt epoxy stabilizer is added. Complete dissolution is normally obtained by rotational mixing 60 minutes at 60°C. The solution is then equilibrated at 75°F overnight. Resimene U 920 (6.25 pts) diluted with MIBK (12.5 pts) and xylene (12.5 pts) is added with stirring, followed by 30 minutes of mixing on a 2 rpm solution wheel. The resulting solution is allowed to stand five minutes before castings are made. Two solutions are prepared from each polymer lot.

Castings are made on SAE 1010 cold rolled steel (Gardner PG-1300B) to give 1.5 mil thick coatings when dry. Three panels are prepared from each solution. Castings are dried 15 minutes in 75°F, 50% RH air before baking 15 minutes at 150°C. Baked coatings are conditioned at 75°F and 50% RH overnight before testing.

Testing procedure emphasizes impact resistance. Twenty-four reverse impacts (50" lbs) are run for each polymer and rated according to degree of failure and number of failures. Ratio of "no failures" to number of tests run is reported. A Gardner Impact Tester is used.

Bend tests are run by quickly deforming the panel, coating side up, over a ½" rod. A test strip ¾" wide is cut in a transverse direction to coating. Test is run parallel to coating direction. Degree and type of failure is reported.

Adhesion is observed as part of impact and bend tests. Additionally a 1/16" grid is cut in coating with sharp razor blade and tested by a fast pull, at 90° to plate, with "Scotch-Tape" firmly attached to coating. Percent lift of grid squares is reported.

Pencil hardness is measured using graded engineering drawing pencils with lead flattened by sanding at a right angle to pencil. The sharp edge is used to gouge completely through the coating. The hard lead pencils are used progressively to softer leads until a softness is reached which will not cut through coating but next harder lead will cut through. The hardness of the pencil just too soft to penetrate coating is reported.

Color of baked coating is reported in qualitative terms.

Viscosity is measured in Gardner-Holdt Bubble Viscometers at 75°F. Polymer solutions are prepared as indicated under "Solutions" at 50% polymer solids and without Resimene. Increase of tube temperature by hand heat is avoided. Viscosity is reported to nearest ½ letter grade by comparison of bubble rise of temperature equilibrated solution with reference tubes.