

# REFERENCE BOOK

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1. Plastimer III, prepw. (for floor tile  
formlu.), tent. proc.

2. Ethylene/vinyl chloride copolymer (Plastimer III), prepw., tent proc

Monsanto Company  
Organic Chemicals Division  
St. Louis Research Department

*7-5-65*  
C.M.R. 8-5-65  
M.W.F. 8/9/65

(Supersedes P-1366; Job 4733, dated 3/25/65) ✓

St. Louis Research Report No. P-1381 ✓

## TENTATIVE PROCESS

FOR

PRODUCTION OF

PLASTIMER III

ETHYLENE/VINYL CHLORIDE COPOLYMER

-----  
Job No. 2-02-760.01-4733 ✓

July 7, 1965

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AMENDMENT A

TO THE

TENTATIVE PROCESS FOR

PRODUCTION OF PLASTIMER III ETHYLENE/VINYL CHLORIDE COPOLYMER

Written by M. E. Gibbs et al; Dated July 7, 1965  
Report No. P-1381; Job No. 2-02 760.01-4733

-----  
FINAL DISPOSITION

Sub Title: Elimination of heat treatment prior to washing of polymer.

Reject amendment since it causes  
problems in the subsequent centrifugation  
steps.

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Signed: M. E. Gibbs

Date: 12/5/66

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TENTATIVE AMENDMENT A

to the

TENTATIVE PROCESS FOR PRODUCTION OF PLASTIMER III  
ETHYLENE/VINYL CHLORIDE COPOLYMER

Report No. P-1381; Job No. 2-02-760.01-4733

Objective: Elimination of heat treatment prior to washing of polymer.

Present Practice:

The Plastimer III copolymer slurry is agitated for 1 hour at 60°-65°C. with an equal weight of filtered tap water, the slurry is then cooled to 30°C or less and centrifuged.

Proposed Change:

The Plastimer III copolymer slurry is to be agitated at 30°-35°C. for 1 hour with an equal weight of water (227 pound/100 lbs. of polymer).

Justification:

Laboratory experiments indicate that a lower residual lauric acid content results when the heat treatment is eliminated. The expected lauric acid content will be in the range of 0.70-0.85% by weight. The heat stability of polymer will not be affected by cold washing.

Precaution:

No unusual hazards exist.

R. W. Bucknell

Approved:

H. L. Hubbard

Date

R. W. Bucknell

Date

C. E. Butts

R. D. Smith

11/15/65

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## INTRODUCTION

Research studies on the ethylene/vinyl chloride reaction were initiated within the Central Research Department (CRD), and a recipe was developed for Plastimer III, a copolymer high in vinyl chloride content. Plastimer III was prepared in quantity by CRD for application and evaluation in floor tile formulations at Armstrong Cork and Kentile. Preliminary results from these evaluations indicated favorable application properties. As a result, the responsibility of completing the process development was transferred to the Organic Division Research Department in March, 1965. Modifications of the recipe were made and a process developed.

The purpose of this tentative process is to provide a basis for design and operation of manufacturing facilities to produce 1.0-1.5 million pounds per year of Plastimer III copolymer.

## SYNOPSIS OF PROCESS

This process consists of reacting ethylene with vinyl chloride in the presence of a persulfate redox catalyst system. The reaction is carried out as a semi-batch type reaction in a single reactor at a pressure of 850 psig. and a temperature of 30°C. The initial charge to the reactor includes an aqueous solution of the redox catalyst system, a surfactant and a buffer; and a mixture of ethylene and vinyl chloride monomers containing 68-69% vinyl chloride by weight.

Ammonium persulfate (APS) which serves as an initiator for the catalyst system is continuously added at a constant rate to the reaction mass. Vinyl chloride is added continuously and concurrently with the APS upon demand in order to maintain a constant pressure in the reactor. Ammonium persulfate is added to the reactor in such quantity that the reaction rate approaches zero when sufficient vinyl chloride has been added to give a product latex containing 45.5-47.5% total solids. When all of the vinyl chloride has been added, the VCl feed stream is stopped and the unreacted monomers in the reactor are vented. When the reactor pressure reaches atmospheric pressure, the latex is drained, frozen in a cold stage at -15°C. and subsequently thawed. The polymer slurry is diluted with water, heat-treated at 60-65°C. batchwise and separated from the mother liquor by centrifugation. The polymer solid is washed on the centrifuge and dried at 35-45°C.

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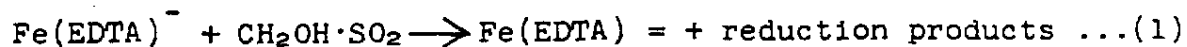
TABLE I  
Abbreviations and Molecular Weights

| <u>Compound</u>                          | <u>Formula</u>                                                       | <u>Abbreviation</u>      | <u>Molecular Weight</u> |
|------------------------------------------|----------------------------------------------------------------------|--------------------------|-------------------------|
| Ammonium hydroxide                       | $\text{NH}_4\text{OH}$                                               | $\text{NH}_4\text{OH}$   | 35.05                   |
| Ammonium laurate                         | $\text{C}_{11}\text{H}_{23}\text{COONH}_4$                           | AL                       | 217.34                  |
| Sodium dodecyl benzene sulfonate         | $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ | ABS                      | 349.49                  |
| Ammonium persulfate                      | $(\text{NH}_4)_2\text{S}_2\text{O}_8$                                | APS                      | 228.20                  |
| Ethylene                                 | $\text{C}_2\text{H}_4$                                               | $\text{C}_2\text{H}_4$   | 28.05                   |
| Ferric ammonium sulfate                  | $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   | FAS                      | 484.21                  |
| Sodium formaldehyde sulfoxylate          | $\text{NaHSO}_2 \cdot \text{CH}_2\text{O}$                           | SFS                      | 154.12                  |
| Sodium pyrophosphate                     | $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$         | SPP                      | 446.11                  |
| Tetrasodium ethylenediamine tetraacetate | $\text{Na}_4\text{EDTA}$                                             | $\text{Na}_4\text{EDTA}$ | 380.2                   |
| Vinyl chloride                           | $\text{VC1}$                                                         | $\text{VC1}$             | 62.50                   |
| Water                                    | $\text{H}_2\text{O}$                                                 | $\text{H}_2\text{O}$     | 18.02                   |

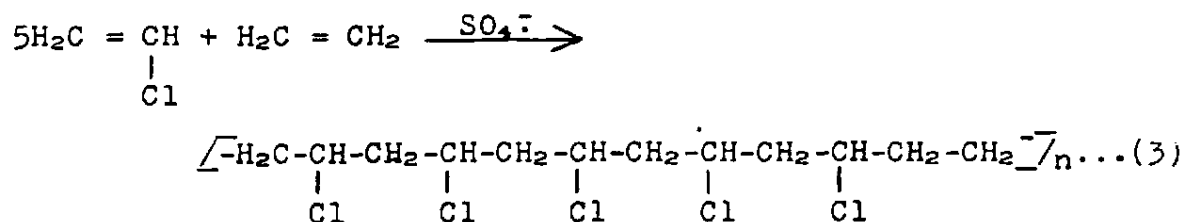
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Simplified equations follow:

Persulfate Redox System

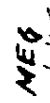


Polymerization Reaction



FLOW SHEETS

A schematic flow diagram is given in Figure 1. The material balances in Tables III and IV are keyed to this diagram and are based on 100 pounds of product produced (containing 98.6 pounds of E/VCl polymer).



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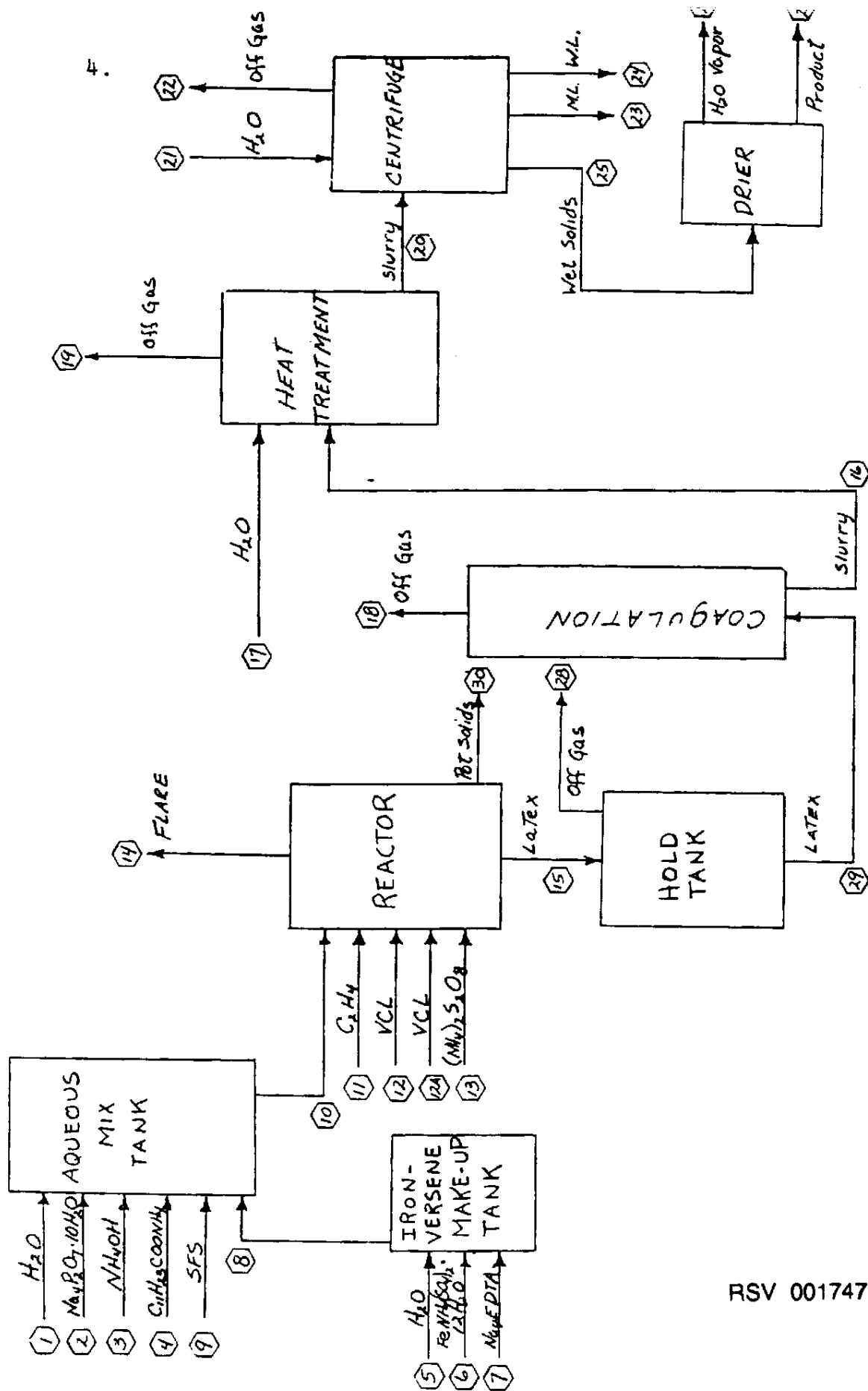


FIGURE I  
PLASTIMER III MATERIAL BALANCE  
FLOW SHEET

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MATERIAL BALANCEA. Bill of Materials for Plastimer III made with Ammonium Laurate

(Basis: 100 pounds of product (98.6 pounds E/VCl polymer);  
total reactor volume 31.7 gallons.)

| <u>Material</u>               | <u>Pounds Consumed</u> | <u>Pounds Produced</u> |
|-------------------------------|------------------------|------------------------|
| NH <sub>4</sub> OH (28%)      | 1.26                   |                        |
| APS                           | 0.421                  |                        |
| AL                            | 3.22                   |                        |
| SPP                           | 2.35                   |                        |
| FAS                           | 0.040                  |                        |
| Na <sub>4</sub> EDTA          | 0.062                  |                        |
| SFS                           | 0.427                  |                        |
| C <sub>2</sub> H <sub>4</sub> | 29.3                   |                        |
| VCl                           | 106.                   |                        |
| H <sub>2</sub> O              | 3321.                  |                        |
| Vent gas to flare             |                        | 33.9                   |
| Pot solids                    |                        | 0.420                  |
| Mother liquor                 |                        | 340.                   |
| Wash liquor                   |                        | 2968.                  |
| Off-gases                     |                        | 3.89                   |
| Drier gases                   |                        | 17.9                   |
| Product polymer               |                        | <u>100.</u>            |
| Total                         | 3464.080               | 3464.110               |

6.

B. Bill of Materials for Plastimer III made with ABS

(Basis: 100 pounds of product  $\sqrt{98.6}$  pounds E/VC1 polymer<sub>7</sub>; total reactor volume 32.5 gallons.)

| <u>Material</u>               | <u>Pounds Consumed</u> | <u>Pounds Produced</u> |
|-------------------------------|------------------------|------------------------|
| NH <sub>4</sub> OH (28%)      | 1.27                   |                        |
| APS                           | 0.424                  |                        |
| ABS                           | 5.21                   |                        |
| SPP                           | 2.36                   |                        |
| FAS                           | 0.040                  |                        |
| Na <sub>4</sub> EDTA          | 0.062                  |                        |
| SFS                           | 0.429                  |                        |
| C <sub>2</sub> H <sub>4</sub> | 29.8                   |                        |
| VC1                           | 105.                   |                        |
| H <sub>2</sub> O              | 3338.                  |                        |
| Vent gas to flare             |                        | 32.5                   |
| Pot solids                    |                        | 1.27                   |
| Mother liquor                 |                        | 343.                   |
| Wash liquor                   |                        | 2983.                  |
| Off-gases                     |                        | 5.18                   |
| Drier gases                   |                        | 17.8                   |
| Product polymer               |                        | 100.                   |
| Total                         | 3482.595               | 3482.75                |

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C. Yield

Yield figures are given in Table II in terms of monomer conversion as pounds per 100 pounds of product polymer formed.

TABLE IIMonomer Conversion

|                                                              | <u>Monomer</u>                | <u>Pounds Charged</u> | <u>Pounds Converted to Plastimer III</u> | <u>Percent Conversion</u> |
|--------------------------------------------------------------|-------------------------------|-----------------------|------------------------------------------|---------------------------|
| <u>C<sub>11</sub>H<sub>23</sub>COONH<sub>4</sub> Process</u> | VC1                           | 105.6                 | 87.3                                     | 82.6                      |
|                                                              | C <sub>2</sub> H <sub>4</sub> | 29.3                  | 11.3                                     | 38.7                      |
|                                                              | Total Monomer                 | 134.9                 | 98.6                                     | 73.0                      |
|                                                              |                               |                       |                                          |                           |
| <u>ABS Process</u>                                           | VC1                           | 105.3                 | 86.7                                     | 82.2                      |
|                                                              | C <sub>2</sub> H <sub>4</sub> | 29.8                  | 11.3                                     | 37.9                      |
|                                                              | Total Monomer                 | 135.1                 | 98.0                                     | 72.6                      |
|                                                              |                               |                       |                                          |                           |

D. Material Balance Sheet

Detailed material balance sheets are given in Tables III (C<sub>11</sub>H<sub>23</sub>COONH<sub>4</sub> Process) and Table IV (ABS Process). Three significant figures to the right of the decimal point are carried throughout Tables III and IV to effect complete mathematical balances. The significant places in these two tables do not necessarily indicate required accuracy. Required accuracy is indicated in the remainder of this report.

TABLE III  
er III Material Balance for Ammonium Laurate

|     | 12    | 14     | 15      | 16      | 17      | 18    | 19    | 20      | 21       | 22    | 23      | 24       | 25      | 26     | 27                | 28    | 29      | 30   |
|-----|-------|--------|---------|---------|---------|-------|-------|---------|----------|-------|---------|----------|---------|--------|-------------------|-------|---------|------|
|     |       |        |         |         |         |       | 0.320 |         |          | 0.036 |         |          |         |        |                   |       |         |      |
|     | 0.004 |        | 0.750   |         |         |       |       |         |          |       |         |          |         |        |                   |       |         |      |
|     | 0.421 |        | 0.421   |         |         |       |       |         |          |       |         |          |         |        |                   |       |         |      |
|     |       |        | 3.222   | 3.222   |         |       |       | 3.222   |          | 1.777 | 0.445   | 1.000    |         |        | 1.000             |       | 3.222   |      |
|     |       | 15.886 | 2.027   | 0.853   |         | 0.466 | 0.473 | 0.380   |          | 0.380 |         |          |         |        |                   | 0.708 | 1.319   |      |
|     |       |        | 0.040   |         |         |       |       |         |          |       |         |          |         |        |                   |       |         |      |
|     |       |        | 0.062   |         |         |       |       |         |          |       |         |          |         |        |                   |       |         |      |
|     |       |        | 0.427   |         |         |       |       |         |          |       |         |          |         |        |                   |       |         |      |
|     |       |        | 2.350   |         |         |       |       |         |          |       |         |          |         |        |                   |       |         |      |
| '98 |       | 17.317 | 0.680   | 0.092   |         | 0.233 | 0.088 | 0.004   |          | 0.004 |         |          |         |        |                   | 0.355 | 0.325   |      |
|     | 1.680 | 0.657  | 120.106 | 120.106 | 226.979 |       | 0.799 | 346.020 | 2973.459 | 0.028 | 335.971 | 2963.814 | 18.266  | 17.867 | 0.399             |       | 120.106 | 0.07 |
|     |       |        | 4.030   |         |         |       |       | 3.376   |          |       | 1.819   | 1.521    |         |        |                   |       | 4.030   |      |
|     |       |        | 98.678  | 98.678  |         |       |       | 98.678  |          |       |         |          | 98.678  | 0.077  | 98.601            |       | 98.678  | 0.35 |
| 798 | 2.103 | 33.860 | 228.743 | 226.981 | 226.979 | 0.699 | 1.680 | 452.280 | 2973.459 | 0.448 | 339.567 | 2967.780 | 117.944 | 17.944 | 100.000           | 1.063 | 227.680 | 0.42 |
| 58  | 0.23  | ---    | 24.6    | 24.2    | 27.2    | ----  | ----  | 51.30   | 357.0    | ----  | 40.4    | 356.3    | ----    | ---    | 24.0 <sup>h</sup> | ----  | 24.3    | ---  |
| --  | ----  | 433    | ----    | ----    | ----    | 7.33  | 29.20 | ----    | ----     | 6.20  | ----    | ----     | ----    | 357    | ----              | 11.1  | ----    | ---- |

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TABLE LV  
Plastimer III Material Balance for ABS

| 2    | 12A    | 12    | 14     | 12      | 10      | 17      | 18    | 19    | 20      | 21       | 22    | 23      | 24       | 25      | 26     | 27     | 28    | 29      | 30    |
|------|--------|-------|--------|---------|---------|---------|-------|-------|---------|----------|-------|---------|----------|---------|--------|--------|-------|---------|-------|
|      |        | 0.004 |        | 0.734   |         |         |       | 0.322 |         |          | 0.035 |         |          |         |        |        |       |         |       |
|      |        | 0.424 |        | 0.424   |         |         |       |       |         |          |       |         |          |         |        |        |       |         |       |
|      |        |       | 15.684 | 5.206   | 5.206   |         | 0.680 | 0.685 | 5.206   |          |       | 2.904   | 0.726    |         |        | 1.576  |       | 5.206   |       |
|      |        |       | 2.672  | 1.048   |         |         |       |       | 0.383   |          | 0.383 |         |          |         |        |        | 0.924 | 1.748   |       |
|      |        |       | 0.040  |         |         |         |       |       |         |          |       |         |          |         |        |        |       |         |       |
|      |        |       | 0.002  |         |         |         |       |       |         |          |       |         |          |         |        |        |       |         |       |
|      |        |       | 0.429  |         |         |         |       |       |         |          |       |         |          |         |        |        |       |         |       |
|      |        |       | 2.354  |         |         |         |       |       |         |          |       |         |          |         |        |        |       |         |       |
| .723 | 40.593 | 1.691 | 16.247 | 1.517   | 0.504   | 227.503 | 0.445 | 0.500 | 0.004   | 2991.383 | 0.004 | 338.295 | 2980.729 | 18.109  | 17.708 | 0.401  | 0.568 | 0.749   | 0.211 |
|      |        |       | 0.583  | 118.772 | 118.772 |         |       | 0.804 | 345.811 |          |       |         |          |         |        |        |       | 118.772 |       |
|      |        |       |        |         |         |         |       |       | 3.593   |          |       | 2.009   | 1.583    |         |        |        |       | 4.053   |       |
|      |        |       |        |         |         |         |       |       | 98.100  |          |       |         |          |         |        |        |       | 98.100  | 1.055 |
| .723 | 40.593 | 2.119 | 32.513 | 230.129 | 227.503 | 227.503 | 1.125 | 2.111 | 452.895 | 2991.385 | 0.450 | 345.208 | 2982.838 | 117.785 | 17.785 | 100.00 | 1.492 | 228.638 | 1.266 |
| .63  | 5.42   | 0.23  | 411    | 24.7    | 24.4    | 24.4    | 11.5  | 35.2  | 51.3    | 359.1    | 6.10  | 40.8    | 358.1    | ---     | ---    | 24.0   | ---   | 24.4    | ---   |
|      |        |       |        |         |         |         |       |       |         |          |       |         |          |         | 353    | ---    | 15.1  | ---     | ---   |

PROCESS IN DETAILA. Summary

This process for the manufacture of ethylene/vinyl chloride copolymer suitable for floor tile resin consists of four major steps: reaction, coagulation, washing and drying. The reaction is accomplished by an emulsion polymerization of ethylene and vinyl chloride under a pressure of 850 psig. at 30°C. in a reactor with a volume of 31.7 gallons. The latex formed in the reaction is then frozen to coagulate the polymer solids. The polymer solids are recovered from the two-phase liquid-solid mixture after first undergoing a heat treatment to facilitate washing. After the catalysts and surfactant have been washed from the polymer, the polymer solids are dried under a vacuum of 15-30 mm. Hg at 40°C.

The reaction may be carried out with alternate surfactants. Complete material balances are given in Tables III and IV using both ammonium laurate and dodecyl benzene sulfonates (ABS) as surfactants. However, the Process in Detail Section is based only on the ammonium laurate process. The process for ABS is very similar except for small changes in material balance which can be obtained from Table IV and reaction volume (per 100 pounds product, 31.7 gallons for AL and 32.5 for ABS).

B. Reaction1. Reactor Feedsa. Iron-Versene Catalyst (Stream 8 in Material Balance)

The ferric versene catalyst is made up batchwise from the following charge procedure:

|                                          |             |
|------------------------------------------|-------------|
| Tetrasodium ethylenediamine tetraacetate | 0.062 lbs.  |
| Ferric ammonium sulfate hydrate          | 0.040       |
| Demineralized water                      | <u>1.63</u> |
| Total                                    | 1.732 lbs.  |

A nitrogen atmosphere is maintained above the solution while mixing to prevent the solution from being contacted with oxygen which acts as a reaction retarder.

b. Aqueous Catalyst Charge (Stream 10 in Material Balance)

The aqueous catalyst charge is made up batchwise from the following charge procedure in the order given below:

|                                 |         |      |
|---------------------------------|---------|------|
| Demineralized water             | 103.    | lbs. |
| Ammonium hydroxide (28%)        | 1.25    |      |
| Sodium pyrophosphate            | 2.35    |      |
| Ammonium laurate                | 16.8    |      |
| Ferric versenate                | 1.75    |      |
| Sodium formaldehyde sulfoxylate | 0.427   |      |
| Total                           | 125.557 | lbs. |

A method for the preparation of ammonium laurate is given in Appendix B. A nitrogen atmosphere is maintained above the solution while mixing to prevent the solution from being contacted with oxygen.

c. Reactor Charge

A 31.7-gallon reactor (based on 100 pounds of AL product polymer) is first evacuated, purged with ethylene and evacuated again. Then 126 pounds of aqueous catalyst solution is added, brought to  $30^{\circ}\text{C.} \pm 0.2^{\circ}\text{C.}$ , and 63.8 pounds of vinyl chloride is fed to the reactor without agitation resulting in a reactor pressure of 40 psig. at  $30^{\circ}\text{C.}$  Ethylene is added batchwise to the reactor until the reactor pressure reaches 875 psig. At this point, the primary pressure sensing device is shut off from the reactor and agitation started. The pressure in the reactor will drop rapidly (to about 400 psig.) when agitation is begun and the contents in the reactor will begin to foam. At this point, reactor pressure is obtained by a gage in the ethylene charge line to the reactor. More ethylene is added with agitation until a reactor pressure of 850 psig.  $\pm 15$  psi. at  $30^{\circ}\text{C.} \pm 0.2^{\circ}\text{C.}$  is obtained, corresponding to the addition of 29.3 pounds of  $\text{C}_2\text{H}_4$ . After the addition of nearly all the ethylene, the primary sensing device can be opened to the reactor, allowing the trapped monomers at 875 psig. to blow back into the reactor at 850 psig. and thus avoiding deposition of foam in the pressure sensing line during charging.

The temperature and pressure in the reactor are allowed to equilibrate. (Premixing and emulsification were accomplished in the laboratory 1-gallon autoclave by utilizing an agitator speed of 400-600 rpm. A more complete description of the agitation system used in process development is given in Appendix A.)

Before the reaction is started, the agitation is decreased to a point where complete emulsion is sustained but excessive shear of the reaction mass is eliminated. (This point corresponded to 400 rpm. in the laboratory autoclave.)

d. Continuous Feeds

The APS solution is added to the reaction continuously at the rate of 0.65-0.70 pounds per hour until 97-98% of the vinyl chloride which is to be fed during the reaction has been added (40.5-41.0 pounds). The reaction rate is controlled by APS feed rate, higher APS feed rates resulting in higher reaction rates. An APS feed rate of 0.65 pounds/hour results in an over-all reaction time of 3 hours. A discussion of the effect of APS feed rate upon reaction rate and, consequently, reaction time is given in Discussion of Important Variables, Section B. Vinyl chloride is added upon demand to maintain a constant pressure in the reactor. A typical vinyl chloride addition curve is shown in Figure 2. The limiting factor governing the maximum VCl addition rate is the heat removal capacity of the reactor cooling system. Typical reaction time is 3 hours, although reaction times shorter than 2 hours can be achieved and result in satisfactory product. The vinyl chloride feed stream is added subsurface.

2. Reactor System

The reactor consists of a single, backmixed stage provided with heating (for start-up) and cooling media, and automatic temperature control. A pressure control system is also provided to maintain constant reactor pressure by regulation of vinyl chloride addition rate. An increase in vinyl chloride monomer

concentration in the reactor causes the reactor pressure to increase, and a decrease in vinyl chloride monomer concentration causes pressure to decrease. The operating conditions are:

Temperature 30°C. controlled to  $\pm 0.5^\circ\text{C}$ .  
 Pressure 850 psig. controlled to  $\pm 15$  psi.  
 Reactor volume 31.7 gal.

Agitation sufficient to maintain adequate emulsion but not vigorous enough to cause excessive liquid shear is required.

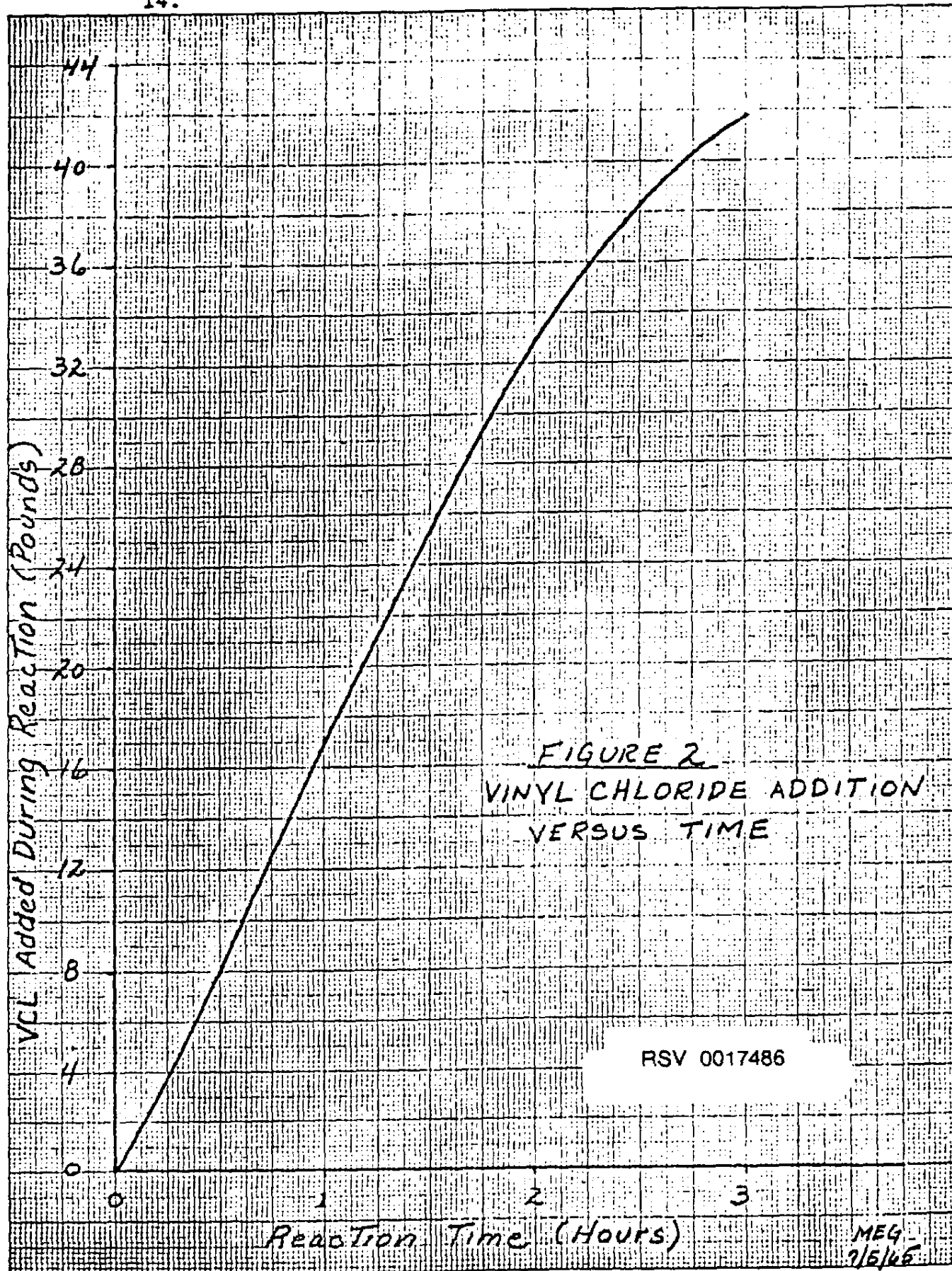
Reaction continues until the solids content of the latex reaches 45.5-47.5%. The addition of 41.8 pounds of VC1 during reaction results in a solids content of 46.0%. To terminate the reaction at this point, the APS feed is stopped when 40.8 pounds has been added. The reaction rate will begin to decrease sharply. When 41.8 pounds of VC1 has been added, the VC1 feed line is closed and the unreacted monomers vented off the top of the reactor. Venting is started immediately after the reaction has stopped and agitation is used while venting. The gas phase is vented over a 30-60 minute period such that no latex is obtained from the vent. The agitator may be turned off at 50-150 psi. to facilitate venting without foaming. When the reactor pressure has reached atmospheric pressure, the latex is drained out of the reactor by gravity. The liquid composition after letdown is:

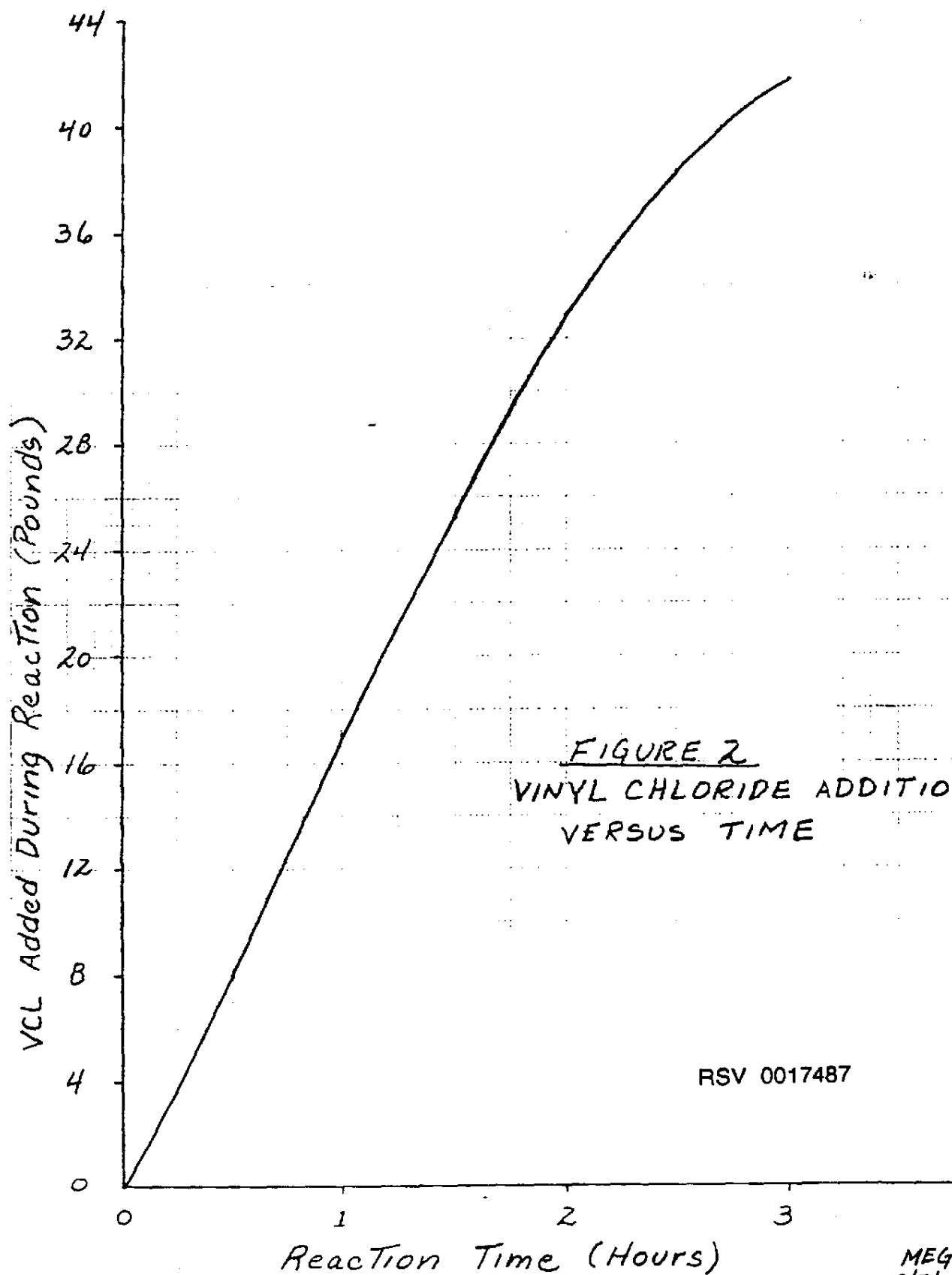
| <u>Component</u>                        | <u>Weight Percent</u> |
|-----------------------------------------|-----------------------|
| Water                                   | 52.5                  |
| Polymer solids                          | 43.1                  |
| Soap                                    | 1.4                   |
| Dissolved VC1                           | 0.3                   |
| Dissolved C <sub>2</sub> H <sub>4</sub> | 0.9                   |
| Inorg. and Org. salts                   | <u>1.8</u>            |
| Total                                   | 100.0                 |

The reactor vent gas composition is:

| <u>Component</u> | <u>Weight Percent</u> |
|------------------|-----------------------|
| Ethylene         | 47.0                  |
| Vinyl chloride   | 51.1                  |
| Water            | <u>1.9</u>            |
| Total            | 100.0                 |

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If provision is made for a hold tank prior to coagulation, degassing of dissolved monomers will occur. Degassing continues throughout the work-up steps until the final dried polymer is obtained. The average off-gas composition for a 4-hour period in the hold tank is:

|                |       |
|----------------|-------|
| Ethylene       | 66.8% |
| Vinyl chloride | 33.2% |

#### C. Coagulation

The liquid latex is coagulated by freezing in a cold stage tube at  $-15^{\circ}\text{C}$ . The volume of latex charged to the tube is such that 20% of the height of the tube is retained as freeboard for expansion and degassing. The tube is vented to a flame arrestor or suitable device to dispose of degassed monomers and ammonia. The amount of degassing that occurs upon charging and freezing is about 0.5% of the latex charge to the tube. The latex is charged to the tube such that free fall of latex down the tube is avoided (such as charging the latex into the bottom of the tube). Free fall of latex when charging produces appreciable foaming and causes the latex to overflow the top of the tube.

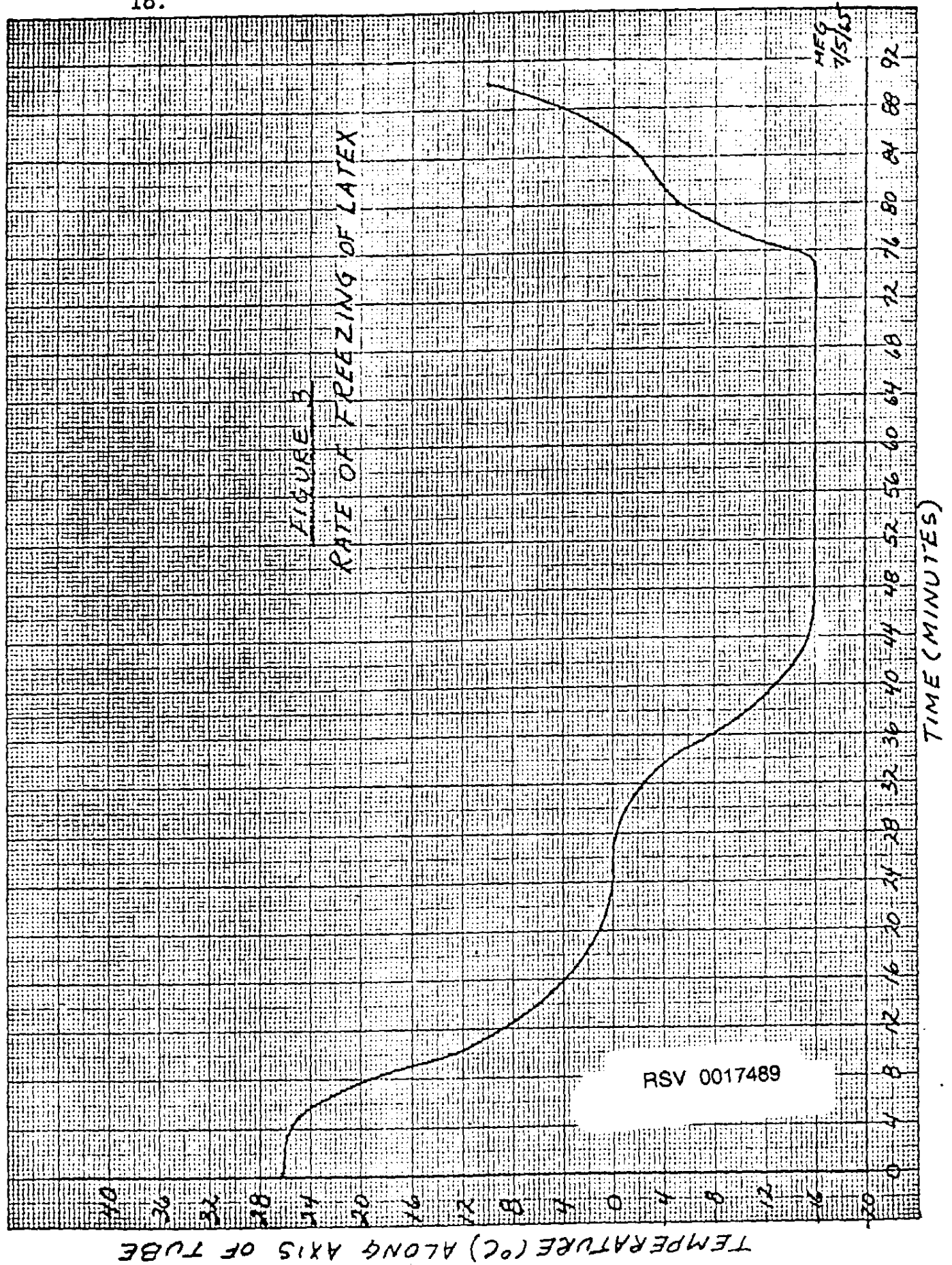
Since the rate of freezing of the latex affects the particle size of the polymer, the latex is frozen at a prescribed rate as shown in Figure 3. An over-all freezing cycle of 75 minutes is obtained when a 1-1/2 inch OD, 1-3/8 inch ID tube is utilized as the cold stage.

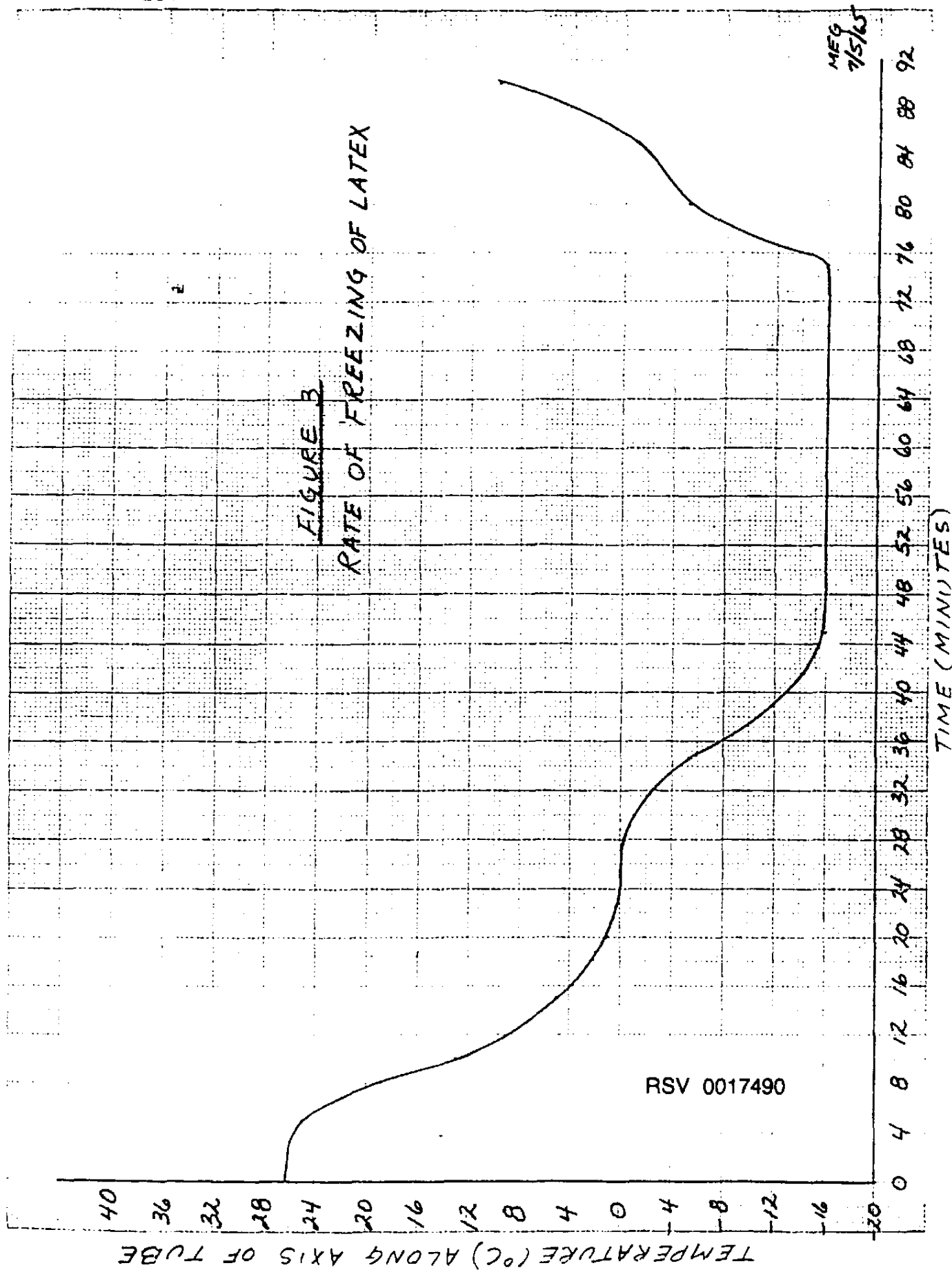
A thawing cycle of 15-20 minutes is required to sufficiently melt the latex so that it may freely fall from the tube. The center core of the latex, however, is not sufficiently melted to form a free flowing slurry. Provision is made to break off the frozen latex into small sections as it drops. The temperature of the tube jacket during the thaw cycle is  $35-45^{\circ}\text{C}$ . The two phase mixture of polymer and other solids in water is subsequently washed.

#### D. Washing

The washing procedure consists of two steps:

1. Batch washing and heat treatment.
2. Continuous washing of centrifuge cake.





In the first step, the polymer slurry is charged batchwise into a well-agitated vessel with an equal weight of filtered tap water (227 pounds). The mixture is heated to 60-65°C. under agitation and maintained at 65°C. for 1 hour. The vessel is vented to dispose of unreacted monomers and ammonia which degas during the heating period and total to 0.74% of the polymer slurry charged. The vessel is sized to retain all the foam created by the degassing of the dissolved monomers. A volume of foam approximately equal to the volume of diluted polymer slurry is formed. A greater amount of foam may be formed if the temperature of the slurry becomes greater than 65°C. or if it is heated too rapidly.

The heat treatment off-gas composition is:

| <u>Component</u> | <u>Weight Percent</u> |
|------------------|-----------------------|
| Ammonia          | 19.0                  |
| Ethylene         | 28.2                  |
| Vinyl chloride   | 5.2                   |
| Water            | <u>47.6</u>           |
| Total            | 100.0                 |

The polymer slurry is cooled to 30-35°C. and subsequently dropped to a centrifuge.

In the second step, the polymer slurry is centrifuged to separate the solids from the mother liquor. Some degassing occurs during centrifugation; consequently, it is recommended that the centrifuge be closed and that it be purged with nitrogen during operation. The composition of the gases coming off the centrifuge are:

| <u>Component</u> | <u>Weight Percent</u> |
|------------------|-----------------------|
| Ammonia          | 8.0                   |
| Ethylene         | 84.8                  |
| Vinyl chloride   | 0.9                   |
| Water            | <u>6.3</u>            |
| Total            | 100.0                 |

The polymer cake is washed on the centrifuge with filtered tap water (2970 pounds) and wrung as dry as possible.

### E. Drying

The washed polymer is dried at 35-45°C. and 30 mm. Hg pressure or less until a moisture content of less than 0.5% is obtained. Turnover of the solid as it is drying reduces drying time. A drying time of 6-8 hours is required at 40°C. and 15 mm. Hg in a vacuum rotary drier to achieve a moisture content of 0.2-0.4%.

### F. Reactor Washout

The reactor is washed out after each run with a solvent to remove reactor fouling. Polymer solids amounting to 0.2% of the discharged latex adhere to the inside of the reactor and will accumulate in successive runs if the reactor is not cleaned. A solvent mixture of 50% (by volume) benzene in acetone is charged to the reactor (after the latex has been drained) in sufficient quantity so that the reactor is 97-98% full. The solvent is heated to 50°C. with agitation for 1 hour, drained and stored for subsequent cleaning. The last traces of solvent are removed from the reactor by a water rinse.

The solvent is reused until the dissolved polymer content reaches 3.0-3.5%, which normally requires 15-20 runs. The solvent may be recovered by charging it to a straight take-over still and collecting 80-84% of the charge as still overheads. The still is operated at atmospheric pressure and a still pot temperature of 61-64°C. The overhead vapor temperature rises to 57°C. When 80-84% of the charge has been distilled, the still is shut down and the still pot residue drained while hot. The still pot residue is a highly viscous, yellow-colored fluid which solidifies at room temperature. It is difficult to remove from the still pot if allowed to cool. The residue is disposed of as waste solvent. The condensed still overhead is reused for reactor washout.

## DISCUSSION OF IMPORTANT VARIABLES

### A. Reactor Charge

#### 1. Persulfate Redox System and Surfactant

The chemical species serving to initiate monomer and partially reacted polymer thereby causing polymerization is the sulfate radical-ion ( $\text{SO}_4^{\cdot-}$ ). The sulfate

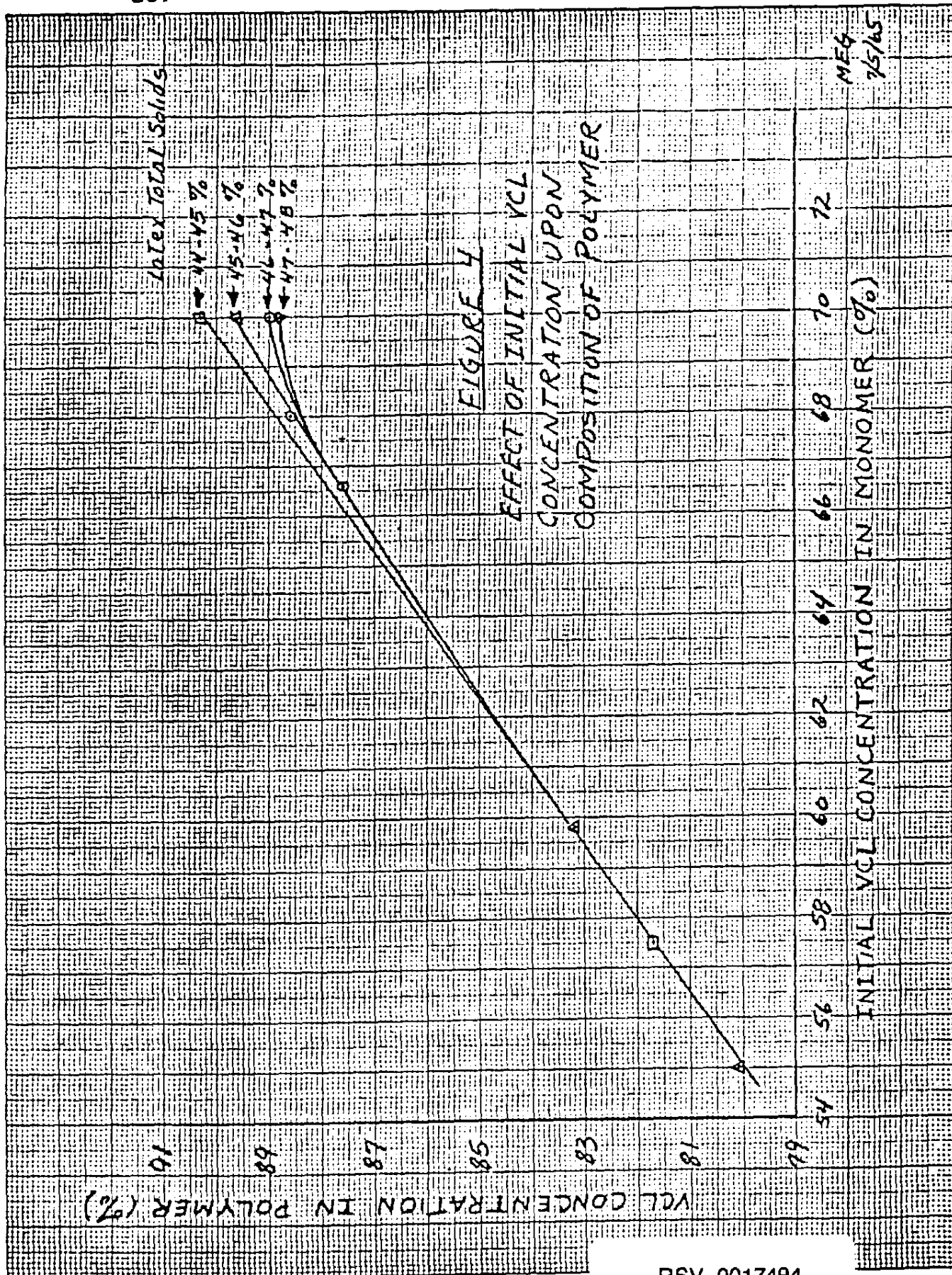
radical-ion is formed from the following oxidation-reduction system. Ferric versenate is reduced by SFS to ferrous versenate which serves to decompose persulfate forming a sulfate radical ( $\text{SO}_4^\cdot$ ) and a sulfate radical-ion ( $\text{SO}_4^{\cdot-}$ ). The ferrous versenate is oxidized back to the ferric state, thereby being regenerated. The SFS activates the system; the iron acts as a catalyst; and the persulfate when decomposed serves as an initiator for polymerization. The formation of  $\text{SO}_4^{\cdot-}$  from persulfate decomposition occurs only in a limited range of pH. For this reason, sodium pyrophosphate is used as a buffer to retain the pH of the reaction mass at 9.0-10.0. Ammonium laurate or sodium dodecylbenzene sulfonate is used as a surfactant or emulsifying agent. Reaction usually takes place in the liquid phase and, since the ethylene and VC1 monomers are only slightly soluble in water, it is necessary to emulsify the monomers in the liquid phase.

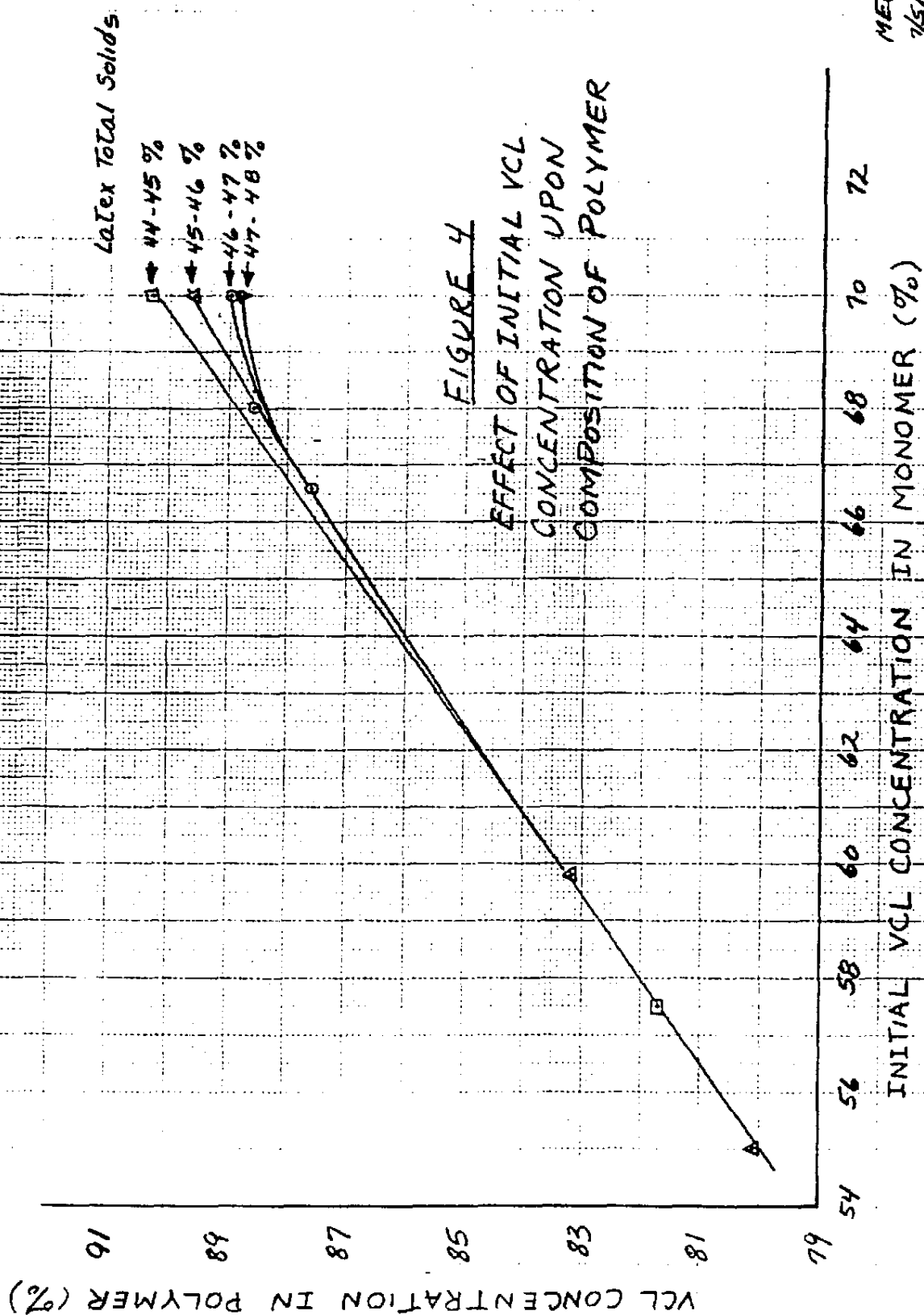
## 2. Oxygen a Retardant

The presence of a small amount of oxygen in the reactor will inhibit the reaction and prevent it from starting. To prevent oxygen from getting into the reactor, the aqueous catalyst solution is made up in an atmosphere of nitrogen and charged into a reactor which has been evacuated, purged with ethylene, and evacuated again. Charge lines are also purged and evacuated.

## 3. Aqueous and Monomer Charge

Since the aqueous charge and initial VC1 charge are charged by weight and the ethylene by difference (until a pressure of 850 psig. is reached), any error in water or VC1 charge will cause an error in ethylene charge and, consequently, an error in VC1/ $\text{C}_2\text{H}_4$  ratio. Close tolerances must be maintained in the initial reactor charges in order to achieve polymer compositions within specifications. The effect of the initial monomer composition upon final polymer composition is shown in Figure 4. At 46% total solids in latex, by Figure 4, the initial VC1 composition must be  $68.5\% \pm 1.0\%$  in order to obtain a final polymer composition of  $88.5\% \text{ VC1} \pm 0.4\% \text{ VC1}$ . Figure 5 shows the effect of error in aqueous and VC1 charges upon initial monomer composition. If a





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FIGURE 5

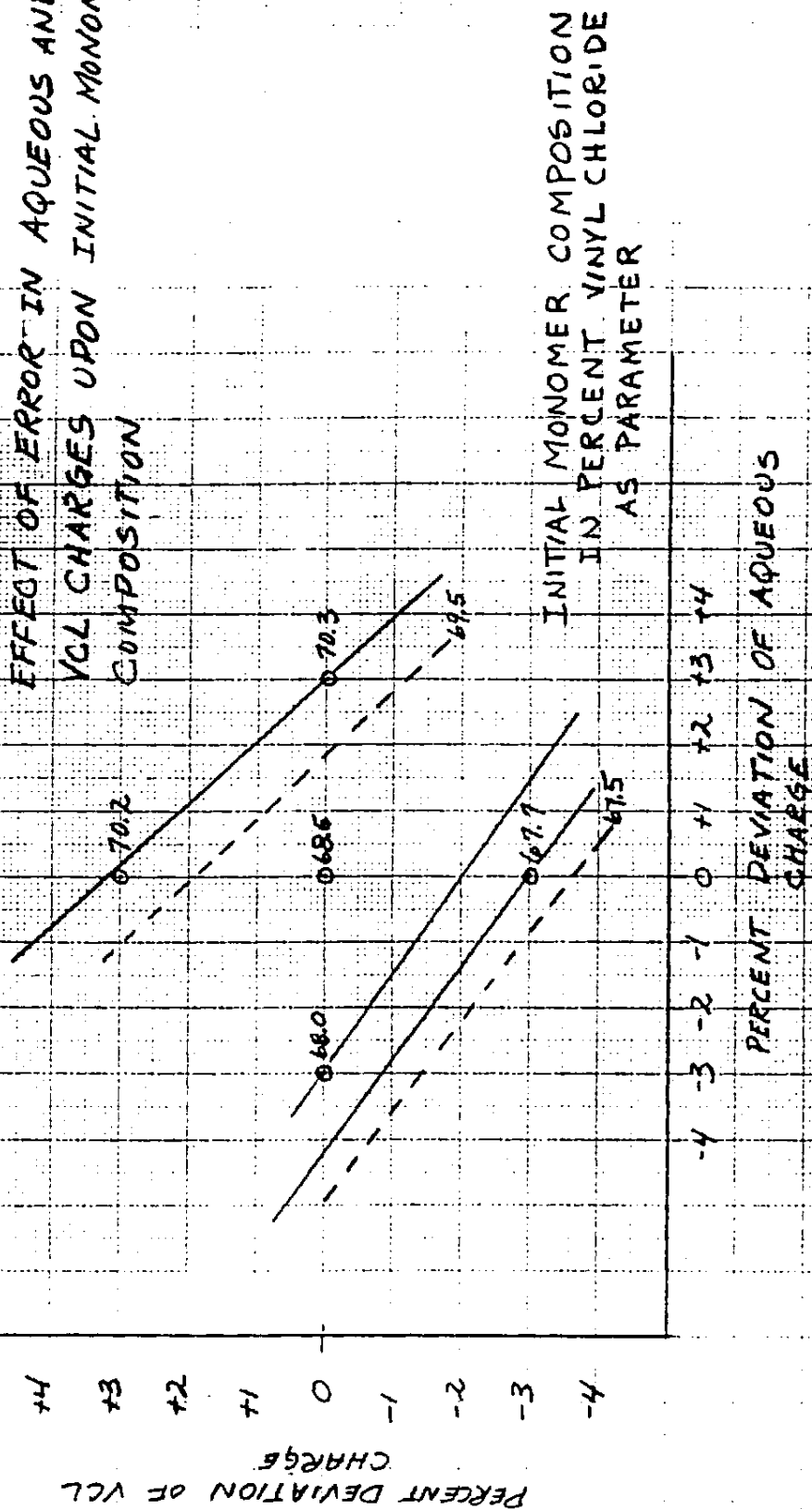
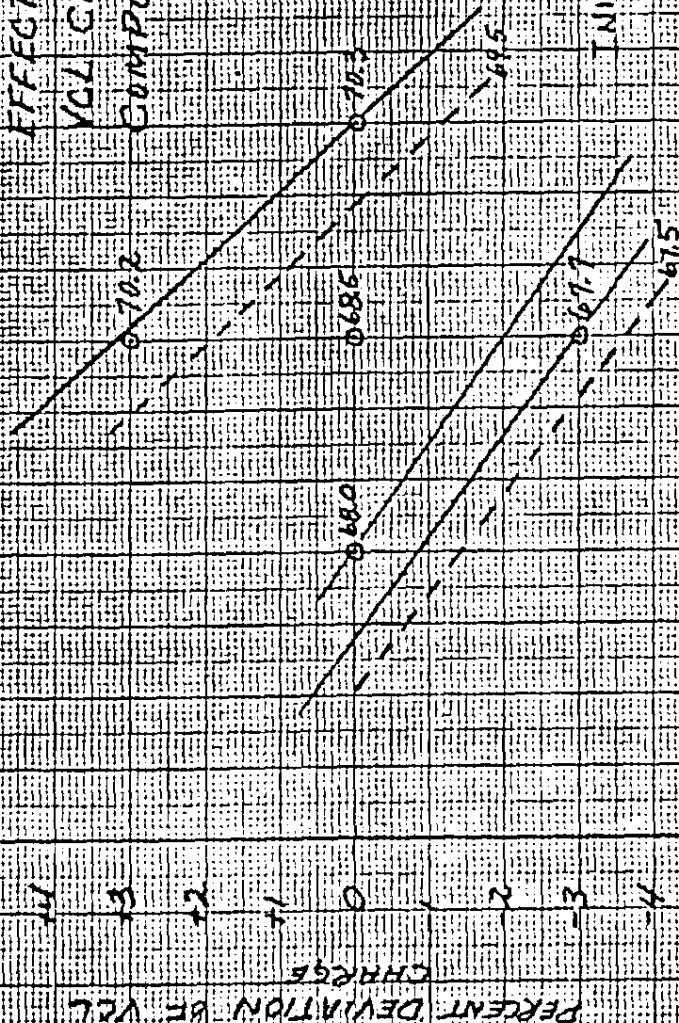
EFFECT OF ERROR IN AQUEOUS AND  
VCL CHARGES UPON INITIAL MONOMER  
COMPOSITION

FIGURE 5  
 EFFECT OF ERROR IN AQUEOUS AND  
 VCL CHARGES UPON INITIAL MONOMER  
 COMPOSITION



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positive deviation in aqueous charge is followed by an appropriate negative deviation in VC1 charge (or vice versa), an initial monomer composition of 68.5% VC1 can still be obtained. However, since the type or amount of deviation would be unknown in any plant charge, the deviations having maximum effect must be assumed. Positive deviation in both water and VC1 charges have maximum effect. A positive deviation of +1.0% in both results in a monomer composition of 69.5% which in turn will result in polymer just within specification at 88.9% VC1. Conclusions from this data indicate that both the aqueous and VC1 charges be within 1.0% of the specified amount.

Because of the nonlinearity of the partial molal volume of vinyl chloride, the addition of vinyl chloride to ethylene or to a mixture of ethylene and vinyl chloride can cause the pressure of the mixture to raise or lower, depending on conditions. At a concentration of 68.5% VC1 in a mixture of  $C_2H_4$  and VC1 and a pressure of 850 psig., addition of more VC1 to the mixture causes the total pressure to increase. At low concentrations of VC1 (below 55%), the total pressure will decrease.

Addition of all the  $C_2H_4$  to the reactor in the initial batch charge before any VC1 is added results in a total reactor pressure of greater than 1000 psig. To avoid exceeding a maximum pressure of 1000 psig., the initial batch charge of VC1 is added first, resulting in a pressure of 40 psig. The ethylene is then added (without agitation) until a reactor pressure of 875 psig. is reached. The line leading to the pressure-sensing device is closed prior to start-up of agitation to prevent the foam caused by agitation to be forced into the pressure sensing line as more ethylene is added. In the presence of agitation, a significant amount of ethylene will dissolve in the VC1 causing the reactor pressure to decrease. As the remainder of the ethylene is added, the pressure will rise and, at temperature and pressure equilibration, a pressure of 850 psig. at 30°C. is achieved. The pressure-sensing line can be opened during pressure equilibration allowing monomer to blow from the line back into the reactor leaving the line unplugged by dense foam.

#### 4. pH of Ammonium Persulfate Solution

The APS solution is made up as 20% APS in water with enough  $\text{NH}_4\text{OH}$  added to bring the pH to 7.0-8.0. An acidic solution such as an aqueous mixture of APS and water without  $\text{NH}_4\text{OH}$  will cause the reaction to stop by lowering the pH of the reaction mass. The appropriate sequence of reactions in the persulfate redox system only exists in a basic media. Addition of  $\text{NH}_4\text{OH}$  to the APS solution also serves to prevent corrosion to the APS feed system. A 20% APS- $\text{H}_2\text{O}$  mixture is quite corrosive to 316 stainless steel.

### B. Control of Reaction

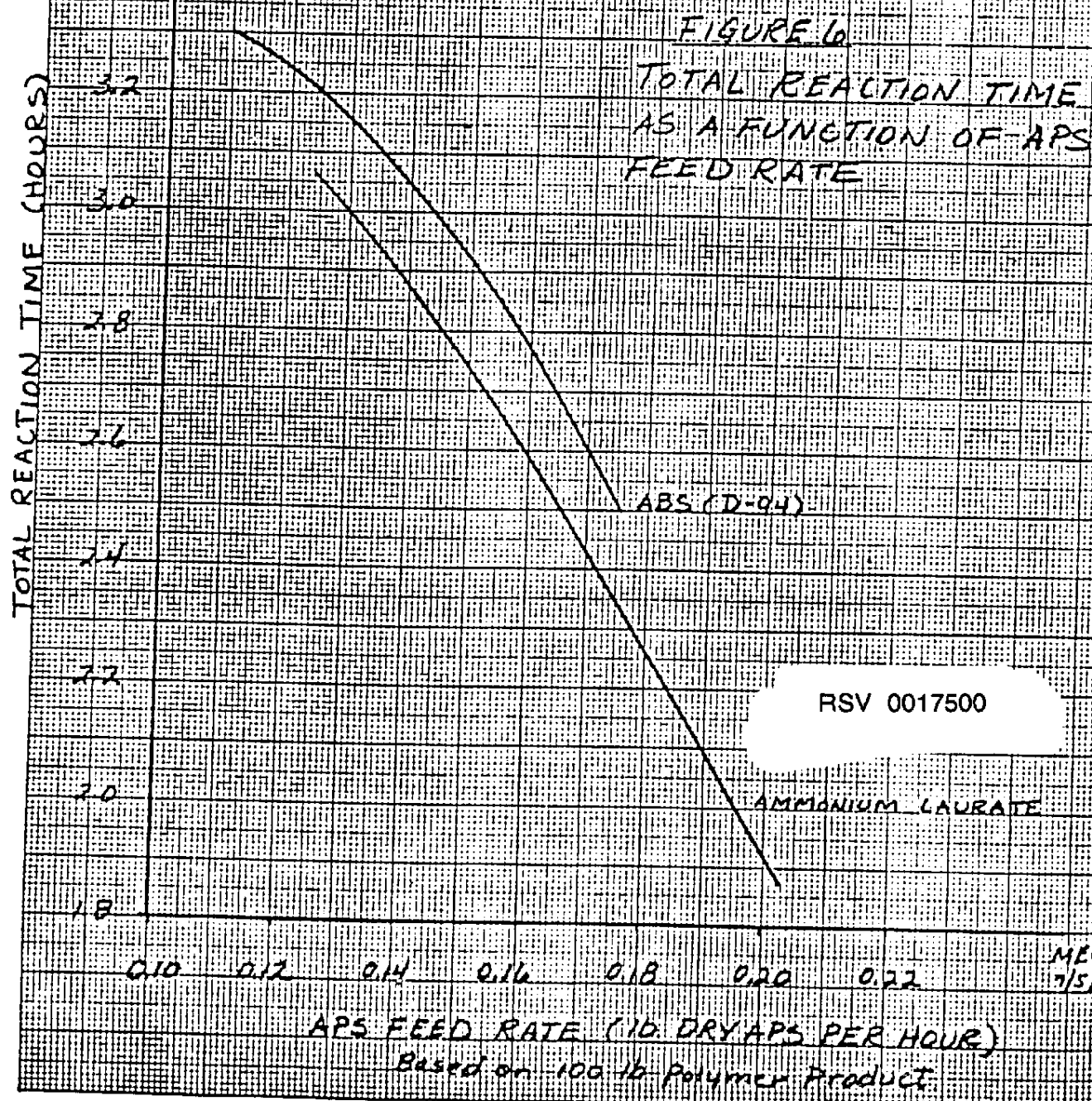
#### 1. Rate

The SFS charged in the initial aqueous charge is present in slight excess of the amount needed. The ferric versenate is regenerated as it is used. Therefore, the limiting reagent in the catalyst system is the APS and the reaction rate is controlled by the amount of unreacted APS in the reactor. Total reaction time as a function of APS feed rate is shown in Figure 6. For an equivalent APS feed rate, the ammonium laurate process has a higher reaction rate. The over-all APS usage (or efficiency), however, is only slightly better when ammonium laurate is used as when D-94 is used.

#### 2. Pressure Control

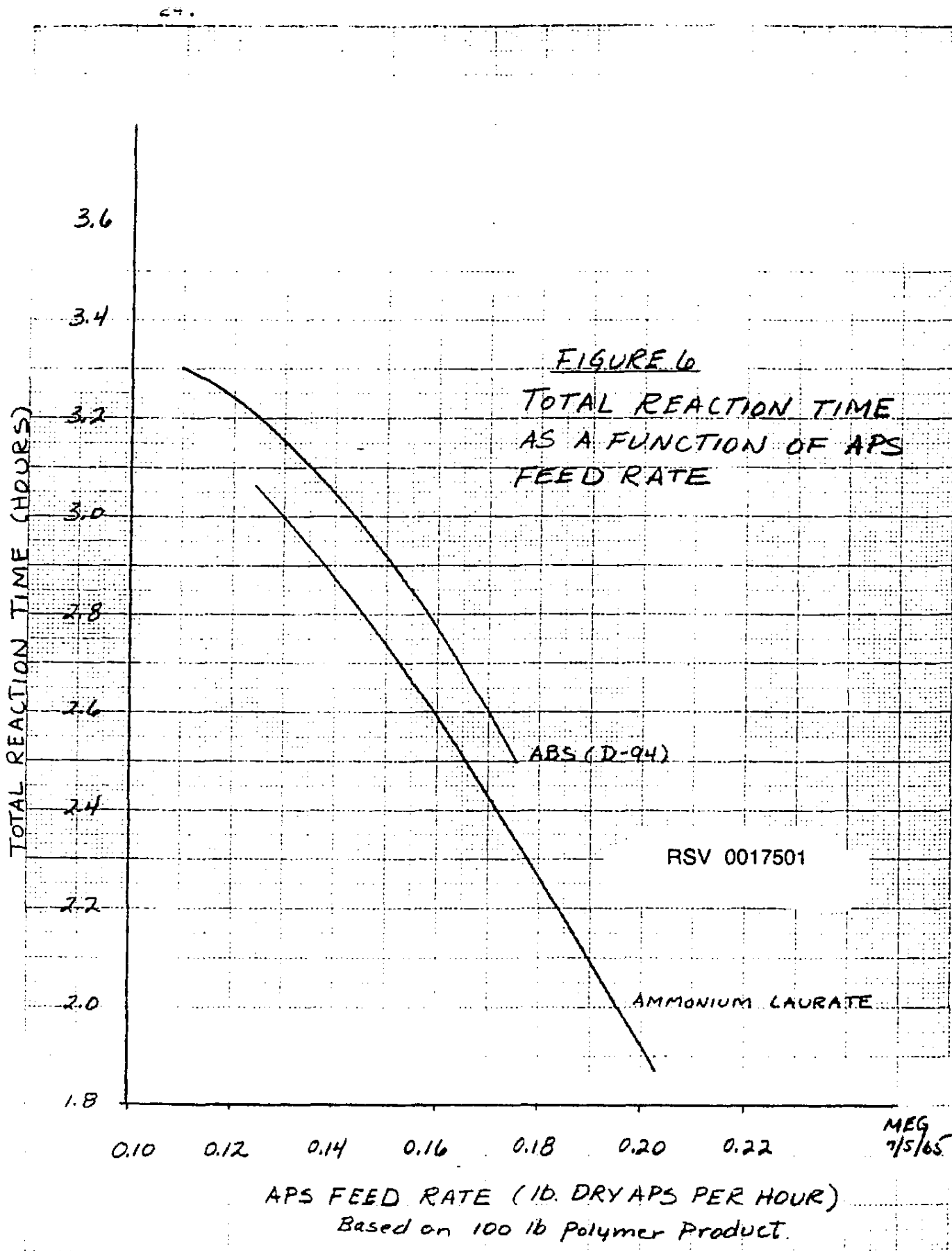
The appropriate composition of  $\text{VC1}$  in the reaction mass is controlled by reactor pressure. As reaction takes place and polymer is formed, the reactor pressure decreases since the product polymer is more dense than the reactant monomer. Reactor pressure is increased by addition of  $\text{VC1}$  to the reactor. Since  $\text{VC1}$  is used in a 5/1 weight ratio to ethylene in the reaction, the addition of pure  $\text{VC1}$  to maintain reaction pressure is adequate to retain a sufficiently high concentration of  $\text{VC1}$  in the reactor. The initial  $\text{VC1}$  composition in the reactor is 68.5% by weight; the final  $\text{VC1}$  composition is 50% by weight. Therefore, total pressure is a sufficiently good control media for control of reaction mass composition.

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### C. Reaction End Point

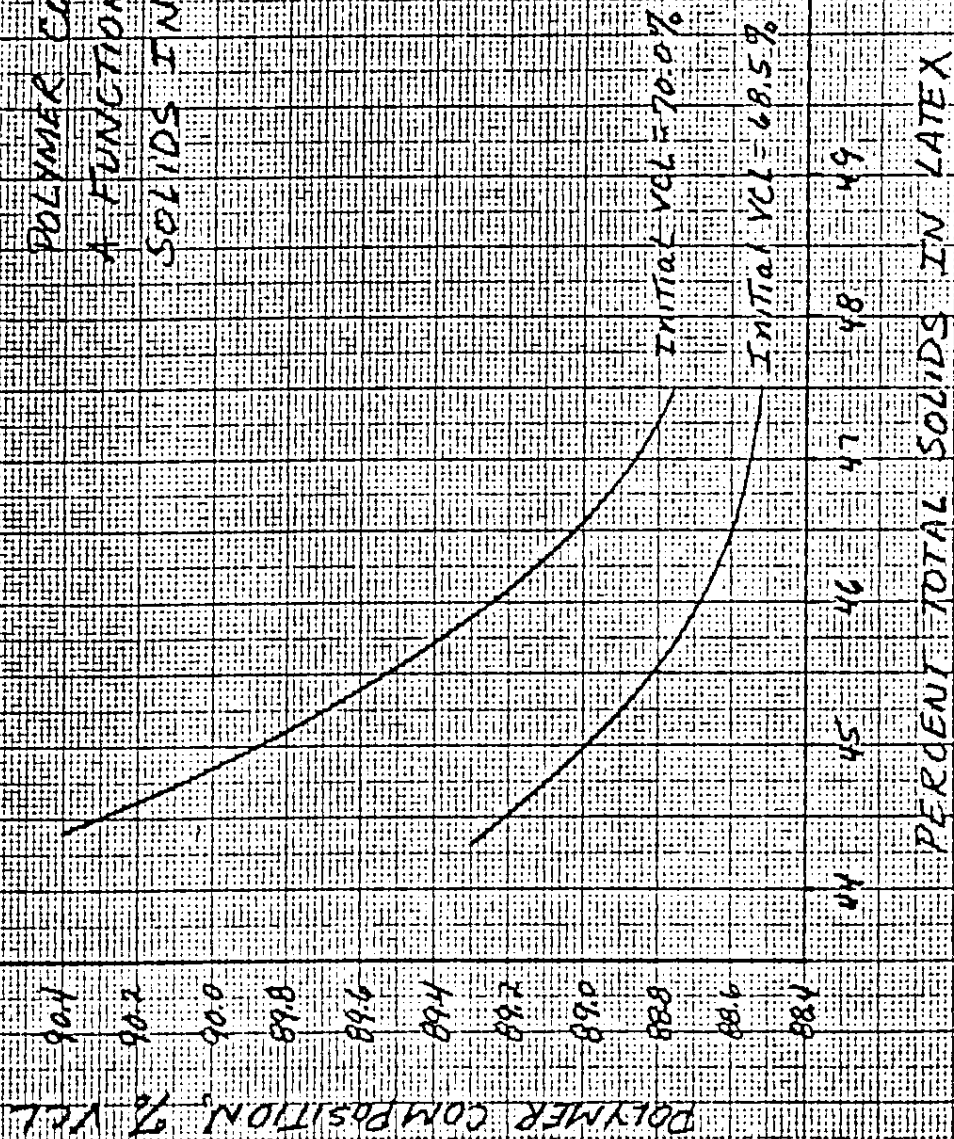
Sufficient reaction is achieved when the solids content of the latex reaches 45.5-47.5%. Reaction can proceed beyond this point, but latices with higher solids content are difficult to vent and result in higher deposits of solids in the reactor. Latices made with ammonium laurate are less stable than those made with ABS. Since the stability of a latex is also a function of polymer solid content, the total solids content of ammonium laurate latices are kept below 46.5%. D-94 latices may be taken to 47.5% total solids or higher without becoming too unstable. At 49% total solids, the D-94 latices will become unstable enough to coagulate prematurely. To reach the desired end point, the appropriate amount of APS is added such that the reaction will cease when 41.8 pounds of VCl has been added. The response of reaction rate to APS feed rate is very rapid causing the reaction rate to reach almost zero very shortly after the APS feed is stopped. If the APS feed is stopped when 97-98% of the total amount of VCl has been added, the active amount of APS present in the reactor will reach zero when 41.8 pounds of VCl has been added (this will take 8-10 minutes). The reaction end point has an effect upon final polymer composition as shown in Figure 7.

### D. Formation of Solids in Reactor

#### 1. Solids Due to Shear

Coagulated solids may be formed during the reaction or during pressure letdown. An increased amount of coagulum is formed in the latex during the reaction if the reaction is carried out in the presence of high shear agitation. Low shear agitation is desirable and minimizes formation of solids. A flat-bladed turbine-type impeller, turning at 350-400 rpm., was found satisfactory in process development work using a 1-gallon autoclave. An agitator speed of 600 rpm. was used to premix the initial batch charge but caused an increase in coagulum if used during polymerization.

FIGURE 7  
POLYMER COMPOSITION AS  
A FUNCTION OF TOTAL  
SOLIDS IN LATEX



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## 2. Solids as Function of Extent of Reaction

The extent of completion of the reaction has an effect upon the amount of coagulated solids formed in the reactor. As the total solids content increases above 45%, the coagulated solids increase from 0.36% (based on product polymer obtained) to greater than 2% at 50% total latex solids. When ammonium laurate is used as the surfactant, a significantly smaller amount of solids is formed than when ABS is used. However, the stability of the ammonium laurate latex is less than that of the ABS latex at equal solids content and may form more coagulated solids after being drained from the reactor.

### E. Pressure Letdown

The unreacted monomers are vented from the top of the reactor with agitation as soon as the reaction is completed. The monomers may be vented as rapidly as possible such that no foam or liquid is carried out the vent. The venting will occur rapidly (10-15 minutes) until the pressure in the reactor reaches 50-150 psig., when a great deal of foaming will occur in the reactor. At this point, the agitation is stopped and the venting rate decreased such that foam and latex are still prevented from being vented. To reach atmospheric pressure in the reactor from the point where the venting rate has been decreased takes 20-40 minutes. The reactor pressure must be decreased to atmospheric pressure before the latex can be drained. The latex will coagulate if subjected to even a small pressure gradient caused by dissolved monomers. To transfer the latex from one point to another, either gravity or 10-15 psig. nitrogen pressure should be used.

### F. Coagulation of Latex

The rate of freezing has a pronounced effect upon particle size. Rapid freezing causes formation of small polymer crystals; slower freezing results in larger crystals. For this reason, the rate of freezing should be sufficiently fast to give a particle size such that 85% of the particles are smaller than 20 mesh and larger than 140 mesh. An adequate freezing time for coagulation in a 1.5 inch tube (OD) is 1-2 hours. Experiments in which latex was frozen in trays in 8-16 hours resulted in particle sizes greater than 10 mesh. All of the latex must be frozen. A mixture of unfrozen latex and thawed coagulum presents a difficult material handling problem.

The latex may coagulate prematurely if it is allowed to remain in the latex form too long. Ammonium laurate latices will coagulate in 3 days at the 46% solids level. ABS latices will remain uncoagulated for several weeks. If a latex does coagulate before being frozen, it cannot satisfactorily be worked up as Plastimer III polymer. Subsequent freezing will not further coagulate it.

#### G. Polymer Washing

As the diluted polymer slurry is heated during the heat treatment step, foaming occurs. The volume of foam formed at 60-65°C., the maximum temperature in the heat treatment step, is approximately equal to the original volume of slurry. If the temperature is allowed to reach 80-85°C., an even greater volume of foam is formed and may cause overflowing from the heat treatment vessel. The temperature of the slurry appears to be much more sensitive to heat input at 55-60°C. than below 50°C. Consequently, the same rate of heat input above a temperature of 50°C. as below it may cause the temperature of the slurry to rapidly rise to 80-85°C. Adequate control of slurry temperature must be maintained.

The heat-treated polymer slurry is dropped to the centrifuge at 25-35°C. If dropped above 50°C., the polymer tends to cake in the centrifuge and cannot be adequately washed. Off-gas fumes also become a problem at a temperature of 50°C. At a temperature of 25-35°C., the slurry does not cake in the centrifuge and does not give off as much monomer and ammonia. However, even at a slurry temperature of 25-35°C., the centrifuge should be closed and purged with nitrogen to keep objectionable gases away from operating personnel and to purge explosive mixtures of monomer from critical areas.

#### H. Polymer Drying

Much of the moisture to be dried from the wet polymer is actually in the pores of the solid particles. The surface moisture dries relatively quickly, but a much longer time is needed to remove the internal moisture. Large polymer particles take much longer to dry than smaller ones since they contain more internal moisture and the moisture must travel through longer capillaries to reach the particle surface. Tube frozen particles at an average size of 60 mesh dry in 6-8 hours at 40°C. and 15 mm. Hg. Tray frozen particles at a size of about 10 mesh require 24-48 hours to dry at the same conditions. Turning over of the polymer particles during drying to expose new surface also aids in increasing the drying rate.

The polymer is heat sensitive and cannot be subjected to temperatures above 50°C. for a very long period of time without discoloring. The drier temperature is maintained below 45°C.

I. Coagulation Tube Washout

A small quantity of solids adhere to the coagulation tube, amounting to about 0.2% of a latex charge per run. The solids will build up in subsequent runs, especially near the top of the tube. A water washout is used every 20 runs and the polymer recovered. If the tube is not sufficiently clean after a water washout, an acetone rinse may be used to thoroughly clean the tube.

J. Materials of Construction

316 stainless steel is used for all surfaces exposed to reactants, product latex or polymer solids. No corrosion studies on other types of materials have been done.

K. Conversion

Vinyl chloride conversion is 82.6%. Conversion of both VC1 and C<sub>2</sub>H<sub>4</sub> may be increased by increasing the aqueous charge to the reactor. Increasing the aqueous charge requires less 68.5% VC1-31.5% C<sub>2</sub>H<sub>4</sub> monomer mixture, as initial charge, to reach the required pressure of 850 psig. at 30°C. To reach the same total solids content, a greater amount of VC1 is added during the continuous addition. The net result is a higher quantity of latex formed per unit volume of reactor and less off-gas to vent. An increase in aqueous charge by 10% results in an increase of VC1 conversion to 88%. However, a fivefold increase in pot solids and a lower VC1 composition in the final product polymer makes such a conversion increase undesirable.

MATERIAL SPECIFICATIONS, ANALYTICAL METHODS

A. Raw Materials

1. Vinyl Chloride

Uninhibited or polymerization grade vinyl chloride from the Texas City Plant (Monsanto) is used. It is passed through activated alumina (8-14 mesh) before use (maximum usage of 0.88 pounds of alumina per 100 pounds VC1).

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2. Ethylene

Monsanto Texas City ethylene, polymerization grade, is used. Polymerization grade ethylene from U. S. Industrial Chemical, Tuscola, Illinois is used as an alternate. The ethylene is passed through a charcoal and alumina absorber in series (0.01 pounds charcoal and 0.01 pounds alumina per 100 pounds  $C_2H_4$ ).

3. Persulfate Redox Catalyst System Materials

a. Ferric Ammonium Sulfate

AR grade from Fisher Scientific Company.  
Typical analysis:

|                  |        |
|------------------|--------|
| Insoluble matter | 0.008% |
| Chloride         | 0.001% |
| Copper           | 0.003% |
| Ferrous iron     | 0.001% |
| Nitrate          | P.T.   |
| Zinc             | 0.003% |

b. Tetrasodium Ethylenediamine Tetraacetate

Technical grade from Fisher Scientific Company.  
Powder form with 1 gram chelating 215 mg. of  $CaCO_3$  at pH 11.

c. Sodium Formaldehyde Sulfoxylate

Technical grade from Fisher Scientific Company.

d. Ammonium Hydroxide

AR grade from Mallinckrodt Chemical Works.  
15 N solution with typical analysis:

|                           |            |
|---------------------------|------------|
| Carbon dioxide            | 0.002%     |
| Chloride                  | 0.00005%   |
| Heavy metals              | 0.00005%   |
| Iron                      | 0.00002%   |
| Phosphate                 | 0.002%     |
| Residue after<br>ignition | 0.002%     |
| Sulfur                    | 0.0002%    |
| Assay                     | 28.0-30.0% |
| Specific gravity          | 0.90       |

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e. Ammonium Persulfate

AR grade from Mallinckrodt Chemical Works, with following typical analysis:

|                                              |          |
|----------------------------------------------|----------|
| Acidity (as H <sub>2</sub> SO <sub>4</sub> ) | 0.20%    |
| Chloride and chlorate (as Cl)                | 0.001%   |
| Heavy metals (as Pb)                         | 0.005%   |
| Insoluble matter                             | 0.005%   |
| Iron                                         | 0.001%   |
| Manganese                                    | 0.00005% |
| Residue after ignition                       | 0.05%    |
| Assay (minimum)                              | 98.0%    |

f. Sodium Pyrophosphate

AR grade from Mallinckrodt Chemical Works, with following typical analysis:

|                            |         |
|----------------------------|---------|
| Arsenic                    | 0.0005% |
| Chloride                   | 0.002%  |
| Heavy metals (as Pb)       | 0.001%  |
| Insoluble matter           | 0.010%  |
| Iron                       | 0.001%  |
| Nitrogen compounds         | 0.001%  |
| Sulfate (SO <sub>4</sub> ) | 0.005%  |

4. Surfactanta. Ammonium Laurate

See Appendix B.

b. ABS (D-94-b)

Slurry D-94-b (linear sodium dodecylbenzene sulfonate) is obtained from the Richardson Corporation, Chicago, Illinois. Local outlet is Krystall Chemical Company Plant at Lamont, Illinois. D-94-b from Alkylate 215 has the following specifications:

|                      |              |
|----------------------|--------------|
| Total solids         | 46-49%       |
| Active SDDBS         | 44-47%       |
| Alcohol insolubles   | 1.7% max.    |
| Unulfonated oils     | 2.5% max.    |
| pH of a 10% solution | 7.3-8.5      |
| Iron                 | 50 ppm. max. |

c. ABS (WW-b)

Slurry WW-b (linear sodium dodecylbenzene sulfonate) is obtained from the Richardson Corporation, Chicago, Illinois. For the St. Louis area this is made by Richardson's Krystall Chemical Company Plant at Lamont, Illinois. WW-b slurry from Alkylate 215 has the following specifications:

|                      |              |
|----------------------|--------------|
| Total solids         | 43-46%       |
| Active SDDBS         | 40-43%       |
| Alcohol insolubles   | 1.7% max.    |
| Unulfonated oils     | 2.5% max.    |
| pH of a 10% solution | 7.3-8.5      |
| Iron                 | 50 ppm. max. |

5. Water

Demineralized water is used for all charges to the reactor. Filtered tap water is used in all washing steps.

6. Nitrogen

Nitrogen used in process development work was obtained from the Air Reduction Company. It is prepurified nitrogen with a maximum oxygen limit of 5 ppm. A typical analysis is:

|           |                        |
|-----------|------------------------|
| Purity    | 99.997% N <sub>2</sub> |
| Dew point | -90°F.                 |
| Oxygen    | 2 ppm.                 |

B. Product1. Reactor Latex Product

Latex from the reactor is obtained with the following typical analysis:

|                          |                                                                                       |
|--------------------------|---------------------------------------------------------------------------------------|
| % Total solids           | 46.0 (46.5% for ABS latex)                                                            |
| % Polymer solids         | 43.1                                                                                  |
| Ratio of soap to polymer | 0.0327 - with C <sub>11</sub> H <sub>23</sub> COONH <sub>4</sub><br>0.0531 - with ABS |
| Latex viscosity          | 6-8 cs.                                                                               |

2. Specifications for Solid Polymer Product

| <u>Property</u>                 | <u>Min.</u>                 | <u>Max.</u>      | <u>Method</u>                    |
|---------------------------------|-----------------------------|------------------|----------------------------------|
| Physical form and color.        | White, free-flowing powder. |                  | Visual comparison with standard. |
| Contamination                   | -----                       | To be determined | -----                            |
| VCl content by IR               | 88.1                        | 88.9             | 65-19                            |
| Molded density                  | 1.3250                      | 1.3330           | TM-C-2d and D-4a                 |
| Intrinsic viscosity             | 0.90                        | 1.10             |                                  |
| Moisture content                | 0.0                         | 0.5              | Karl Fischer                     |
| Heat stability                  | 120 min.                    | ---              | TM-H-2c                          |
| T <sub>g</sub> by DTA           | 39°C.                       | 49°C.            |                                  |
| Melt flow                       | 1.0                         | 3.5              | TM-F-5b                          |
| Equilibrium torque by Brabender | 2000                        | 2600             | TM-P-5a                          |
| Tensile properties              |                             |                  | TM-T-2b                          |
| a. % elongation                 | 210                         | --               |                                  |
| b. Tensile strength at yield    | 5600                        | --               |                                  |
| c. TEB                          | 8750                        | --               |                                  |
| Screen analysis                 |                             |                  |                                  |
| % on 20 mesh                    | --                          | Trace            |                                  |
| % on 40 mesh                    | --                          | 20               |                                  |
| % through 140 mesh              | --                          | 15               |                                  |

C. Analytical Methods1. Latex Solids

A 10 ml. aliquot of latex is weighed into a tared aluminum foil dish, diluted with 10 ml. of ethanol to prevent foaming and spattering, and evaporated to dryness in a 105°C. oven (about 16 hours). The net dry weight divided by the net latex weight equals the percent total solids in latex.

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2. pH

The pH is determined directly on the latex with a standard Beckman expanded scale pH meter.

3. Determination of Alkyl Benzene Sulfonate in Plastimer

Scope

This method is intended for the determination of alkyl benzene sulfonate in concentrations up to 3.0% in E/VCl copolymer. The method can also be used for a variety of sulfated or sulfonated anionic surfactants. The estimated accuracy of the method is  $\pm 0.15\%$  absolute.

Equipment and Reagents

- a. Chloroform.
- b. Methylene blue.
- c. Methylene blue solution - dissolve 0.1 g. methylene blue, NF contained in a 100 ml. volumetric flask, in distilled water and dilute to 100 ml. Transfer 30 ml. of this solution to a 1 liter volumetric flask containing 500 ml. of distilled water, 6.8 ml. of concentrated sulfuric acid and 50 grams of monosodium phosphate monohydrate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ) AR grade. Shake until solution is complete and dilute to volume with distilled water.
- d. Toluene and ethanol solvent - 68% absolute ethanol/32% toluene by weight.
- e. Hellige Testing Outfit No. 367DO.
- f. Usual laboratory apparatus and reagents.

Determination

- a. Accurately weight 1.000 grams of dried polymer into a 125 ml. iodine flask containing 100 ml. of solvent, stopper and swirl. Let stand with occasional swirling to extract the adsorbed ABS into the solvent (approximately 4 hours standing).
- b. Pipet 5 ml. of the above solvent layer into a 1 liter separatory funnel containing 750 ml. of distilled water and shake well (no real separation takes place, some toluene is seen on top of the water).

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- c. Place 50 ml. (graduate) of the water taken from the bottom in a 125 ml. separatory funnel. To this add 15 ml. (graduate or pipet) of the methylene blue solution and 10 ml. (pipet) of chloroform. Shake well, allow to separate and filter the chloroform layer through a cotton pledget into the Hellige cell. Compare with standard and record ppm. ABS.

#### Calculation

$$\frac{\text{ppm. read}}{10^6} \times \frac{750 \times 100}{0.05} = \% \text{ ABS in polymer or}$$

$$\text{ppm. read} \times 1.5 = \% \text{ ABS in polymer.}$$

#### Discussion

This method is an adaptation of the Hellige method (Hellige Instruments). The method depends on the forming of a complex between the methylene blue and ABS. This complex is then extracted from the water layer by the chloroform. The method can be applied to the water used in washing the copolymer. In this case, take 50 ml. of the wash water (1-2 ppm. range) and proceed as in Step 3. Cleaning of equipment is sometimes facilitated by the use of a 10% HCl solution which destroys the ABS.

#### References

Hellige, Inc., Garden City, N. Y., ABS Testing Outfit No. 367D0.

Swisher, R. D., JAOCS 40, 648-656 (1963).

#### 4. Determination of Water in Plastimer by Karl Fischer Reagent

##### Scope

This method is intended for the determination of water in dried polymer. It involves the solubilization of a sample to be analyzed in tetrahydrofuran and the titrimetric determination of the moisture present with Karl Fischer reagent. The end point may be detected colorimetrically or electrometrically. The estimated accuracy of the method is  $\pm 0.05\%$  absolute.

Equipment

- a. Tetrahydrofuran.
- b. Karl Fischer reagent.
- c. Usual laboratory apparatus and reagents.

Determination

- a. Accurately weigh 10.0 grams of sample into a 100 ml. volumetric flask and dilute to volume with tetrahydrofuran. (Some difficulty will be encountered in dissolving the sample. When using volumetric flasks without a bulb, allowing some room to shake the contents will be helpful. This step can be accelerated if the contents can be freed from the sides of the flask shortly after the addition of the solvent. This step will usually require a minimum of 24 hours contact between the sample and solvent.)
- b. Blank about 25 ml. of methanol in 125 ml. Erlenmeyer flask.
- c. Zero the Karl Fischer burette.
- d. Weigh into the blanked methanol approximately 10.0 grams of the above copolymer solution. (On contact with the methanol, the copolymer will be precipitated, presenting some difficulty in the following titration.)
- e. Titrate the supernatant liquid back to the same end point.

Calculation

- a. 
$$\frac{\text{ml. titre} \times \text{KF factor} \times 100}{\text{sample weight (copolymer soln.)}} = \% \text{ moisture contained in copolymer soln.}$$

$$b. \quad (\text{wt. of copolymer soln.})(\% \text{ H}_2\text{O copolymer soln.}) = \text{wt. H}_2\text{O copolymer soln.}$$

$$(\text{wt. of copolymer soln.})(1.0 - \frac{\text{wt. sample}}{\text{wt. soln.}}) =$$

$$(\text{wt. of solvent THF in copolymer soln.})$$

$$(\text{wt. of solvent in copolymer soln.}) * (\% \text{ H}_2\text{O in solvent THF}) = \text{wt. of H}_2\text{O in solvent THF}$$

$$(\text{wt. of copolymer soln.})(\frac{\text{wt. sample}}{\text{wt. soln.}}) = \text{wt. of}$$

copolymer

$$\frac{(\text{wt. H}_2\text{O copolymer soln.} - \text{wt. H}_2\text{O in solvent}) \times 100}{\text{wt. of copolymer}} =$$

% moisture in copolymer

#### Discussion

No known interferences appear to be present in sufficient amounts to affect the accuracy of the analysis.

#### Safety

No unusual hazards are involved in this operation when cognizance is taken of the flammability and toxicity of the reagents and solvents.

#### Reference

Standard Procedure Method No. 78-A, B, John F. Queeny Plant.

\* NOTE: The moisture of the THF used as solvent can be determined by proceeding from Step 2 through calculation (a), substituting 10.0 grams of the solvent used for 10.0 of copolymer solution in Step 4.

5. DETERMINATION OF INTRINSIC VISCOSITY OF PLASTIMER  
(A VARIANT OF ASTM D 1243-60 AND D 1601-61)

TM - None

Organic Research

I. Scope

This method describes a test procedure for the determination of the dilute solution viscosity of Plastimer using tetrahydrofuran as a solvent at 30° C. Directions are given for the determination of relative viscosity, specific viscosity, reduced viscosity and intrinsic viscosity.

II. Significance

Dilute solution viscosity values for Plastimer are related to the average molecular size of that portion of polymer which dissolves in the solvent. This method is limited to samples which give clear uniform appearing solutions at the test dilution. Where a viscometer, solvent or temperature other than those specified are used, data may not be comparable to that obtained by this procedure.

III. Outline of Procedure

A sample of Plastimer is weighed accurately and dissolved in the solvent. Relative viscosity, specific viscosity, reduced viscosity, and intrinsic viscosity are calculated from the measured efflux times of the solvent alone versus a specified solution of the polymer in the solvent.

IV. Apparatus and Materials

1. Cannon-Fenske Viscometer (ASTM D 445-64) No. 50.
2. Constant temperature water bath, capable of maintaining  $30 \pm 0.1^\circ$  C.
3. Stop watch.
4. Thermometer, ASTM No. 91C having a range of 20 to 50 C. with 0.1 C. subdivisions.
5. Mechanical shaker.
6. Transfer pipettes.
7. 125 ml. Erlenmeyer flasks with ground glass stopper.
8. 50 ml. volumetric flasks.
9. Funnel, coarse filter paper and cotton.
10. Tetrahydrofuran, THF, reagent grade.

V. Test Specimens

The test specimens should be washed and dried Plastimer.

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## VI. Procedure

1. Weigh 4 specimens of the following approximate weights to  $\pm 0.0002$  into 125 ml. glass stoppered Erlenmeyer flasks.

|            |                  |
|------------|------------------|
| Specimen 1 | 0.49 to 0.51 gm. |
| Specimen 2 | 0.39 to 0.41 gm. |
| Specimen 3 | 0.29 to 0.31 gm. |
| Specimen 4 | 0.19 to 0.21 gm. |

2. Add 50.00 ml. of filtered THF to the specimen flasks. Shake the flasks on the mechanical shaker until dissolved completely. When the solution is considered complete, examine visually to be certain that no undissolved particles, gel or particles of foreign matter are present.
3. Filter the solution through a coarse filter paper packed with cotton into a 50 ml. volumetric flask. Cover the funnel with a watch glass to reduce evaporation. When filtration becomes slow, discontinue and immediately stopper the volumetric flask to avoid evaporation. It is not necessary to collect all the solution.
4. The viscometer should be thoroughly cleaned with hot sulfuric acid and potassium dichromate solution followed by rinsing with distilled water and THF, and drying with vacuum. Traces of impurity in the viscometer may cause serious errors.
5. Pipette 10 ml. of the filtered THF into the viscometer and allow 10 minutes for the solvent to come to temperature equilibrium. Draw the liquid up above the upper gradation mark on the viscometer capillary by applying suction. By releasing the vacuum, allow the liquid to drain to the upper mark of the capillary. As the meniscus passes this point, start the timer and time the interval for the liquid to drain to the lower mark on the capillary. Measure the efflux time of the liquid at least 3 times. Three consecutive readings shall agree within 0.2 sec.
6. After each run, clean and dry the viscometer. If the viscometer is kept clean, the efflux time for the reference solvent, THF need not be redetermined on subsequent determination; however, periodic checks should be run to monitor cleanliness.
7. Pipette 10 ml. of the filtered polymer solution into the viscometer and determine the efflux time as described above for the pure solvent.

VII. Calculations

The relative viscosity, specific viscosity and reduced viscosity are calculated as follows:

$$\text{Relative viscosity, } \eta_r = \frac{\text{Average efflux time of polymer solution}}{\text{Average efflux time of pure solvent}}$$

$$\text{Specific viscosity, } \eta_{sp} = \eta_r - 1$$

$$\text{Reduced viscosity, } \eta_{red} = \frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c}, \text{ } c \text{ is in gm/100 ml.}$$

A plot of the 4 reduced viscosity numbers versus their respective concentrations on linear graph paper extrapolated to zero concentration gives the intrinsic viscosity.

$$[\eta] = (\eta_{red})_{c \rightarrow 0} = \left(\frac{\eta_{sp}}{c}\right)_{c \rightarrow 0} = \left(\frac{\eta_r - 1}{c}\right)_{c \rightarrow 0}$$

VIII. Report

The report shall include the following:

1. Complete identification of the material tested.
2. The intrinsic viscosity to 3 significant figures.

6. INFRARED DETERMINATION OF THE VINYL  
CHLORIDE CONTENT OF PLASTIMER III

SCOPE

This method describes a solution procedure for the infrared determination of the vinyl chloride (VCl) content of Plastimer III, an ethylene-vinyl chloride copolymer (EVC1), in the range of 72 to 94% VCl. The estimated accuracy of the method is  $\pm 0.5\%$  absolute.

PRINCIPLE

The infrared absorbance ratio of the C-H bending vibration of vinyl chloride at 6.97 microns relative to the C-H bending vibration of ethylene at 6.85 microns is plotted as a function of the per cent vinyl chloride for a series of dilute solutions of Plastimer III standards in trichloroethylene. The infrared absorbance ratio for an unknown sample is determined in the same manner and its vinyl chloride content obtained from the empirical calibration curve. This method is a solution variation of previous cast film methods (1,2).

APPARATUS AND REAGENTS

Double beam recording infrared spectrophotometer, such as the Perkin-Elmer Model 221 or equivalent

3.0 mm. rocksalt cell.

Variable 0.8-5.0 mm. rocksalt wedge cell (Barnes Engineering Company W-2B wedge cell) or a suitable 3.0 mm. compensating cell

125 ml. iodine flashes.

Water-cooled condenser.

Magnetic stirrer hot plate.

1.5" teflon-coated magnets.

50 ml. volumetric pipette.

Trichloroethylene - Fisher reagent grade.

Methylene chloride - Fisher reagent grade.

CALIBRATION

Fill the sample and compensating cells with trichloroethylene. Place the cells in the spectrophotometer and adjust the compensating cell until the effects of the solvent absorbance in the 6.9 micron region are cancelled. Record the solvent blank for the region of 6.80 to 7.00 microns using the following instrument parameters:

|                  |               |
|------------------|---------------|
| slit program     | 1 X 980       |
| scan speed       | slow - 6      |
| scale            | 50 cm./micron |
| source intensity | 0.35 amps     |
| 100% adjust      | set to 96%    |

Weigh duplicate 600  $\pm$  3 mg. samples of each resin standard into 125 ml. iodine flasks. Pipette 50 ml. of trichloroethylene into each flask, add a magnetic stirrer bar, attach the condenser and place the assembly on the magnetic stirrer hot plate. Reflux the sample with stirring until complete solution is attained (usually 5 to 15 minutes). Allow the solution to cool to about 35° C. Remove the solvent from the sample cell by aspiration. Fill the sample cell with the Plastimer III standard solution and record its infrared spectrum in the region of 6.80 to 7.00 microns using the instrument parameters above. Remove the sample solution from the cell by aspiration and clean the cell by pumping methylene chloride back and forth with a pair of hypodermic syringes and removing the methylene chloride by aspiration. Record the infrared spectra of either the duplicate or new standard in the 6.80 to 7.00 micron region. Repeat the process until all the standards are run.

Measure the absorbance difference between the sample spectrum and the solvent blank at 6.85 and 6.97 microns and calculate the absorbance ratio R by:

$$R = \frac{(\text{abs. of sample} - \text{abs. of blank}) \text{ at } 6.97 \mu}{(\text{abs. of sample} - \text{abs. of blank}) \text{ at } 6.85 \mu}$$

Plot the calculated absorbance ratio as a function of the vinyl chloride content of the standards to obtain the working calibration curve. The spectra of a typical solvent blank and sample are shown in Figure 8, and the working calibration curve for the method is shown in Figure 9.

METHOD NO. 65-19SAMPLE ANALYSIS

Weigh  $600 \pm 3$  mg. of sample into a 125 ml. iodine flask. Add 50 ml. of trichloroethylene and a magnetic stirrer bar to the flask, attach the condenser and reflux the stirred system on a heat plate until complete solution is attained. Cool the sample to about  $35^{\circ}$  C. Record the infrared spectra of the solvent blank and the sample solution in the 6.80 to 7.00 micron region under the conditions used in the calibration. Calculate the absorbance ratio of the vinyl chloride band at 6.97 microns relative to the ethylene band at 6.85 and read the vinyl chloride content corresponding to this ratio from the calibration curve.

ACCURACY

Very good agreement was obtained in the calculated absorbance ratio of the standards used in calibrating the method. The experimental data are:

| <u>Sample Identification</u> | <u>% VC1*</u> | <u>Infrared Ratio</u> |
|------------------------------|---------------|-----------------------|
| OVC 637                      | 93.4          | 3.76                  |
|                              |               | 3.74                  |
| P3-1-14U                     | 90.3          | 2.08                  |
|                              |               | 2.07                  |
| P3-1-20U                     | 89.1          | 1.84                  |
|                              |               | 1.83                  |
|                              |               | 1.83                  |
| P3-5-14U                     | 84.8          | 1.44                  |
|                              |               | 1.45                  |
|                              |               | 1.45                  |
| Ba #38U                      | 79.0          | 1.10                  |
|                              |               | 1.10                  |
| Ba #44U                      | 77.7          | 1.11                  |
|                              |               | 1.11                  |
| OVC 254                      | 77.5          | 1.07                  |
|                              |               | 1.07                  |
| OVC 182                      | 72.2          | 0.91                  |
|                              |               | 0.91                  |

\*Based on chlorine data obtained by the J. F. Queeny Analytical Laboratory using the Schoniger combustion method.

With these small variations, the vinyl chloride content of the samples can be read within  $\pm 0.5\%$  absolute.

REFERENCES

1. Central Research Center infrared film method documented in memo to R. W. Bucknell from H. P. Holladay, October 5, 1964.
2. Organic Division Research Department, Analytical Method 64-45.

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