CWR 8-6-65
MWF 8/9/65

1. Plastimer III, prepn. (for floor tile formln.), tent. proc.
2 Ethylene/vinyl chloride copolymer (Plastimer III), prepn., tent. proc.

Monsanto Company
Organic Chemicals Division
St. Louis Research Department

(Supercedes 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

Written by:

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DS 8-12-65

MONSANTO COMPANY
Organic Chemicals Division
St. Louis Research Department

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REJECTED ☒ AMENDMENT A
APPROVED ☐

TO THE

TENTATIVE PROCESS FOR

PRODUCTION OF PLASTIMER III ETHYLENE/VINYL CHLORIDE COPOLYMER

Written by M. E. Gibbs etal; 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 step.

RSV 0017464

Signed: M. E. Gibbs Date: 12/5/66

MONSANTO COMPANY
Organic Chemicals Division
St. Louis Research Department

November 9, 1965

SAFETY REVIEW COMMITTEE
APPROVED BY: [signature] 11-12-65
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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	C. E. Butts	11/15/65 Date
R. W. Bucknell	11/9/65 Date	R. D. Smith	11/15/65 Date

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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.

TABLE I

Abbreviations and Molecular Weights

Compound	Formula	Abbreviation	Molecular Weight
Ammonium hydroxide	NH_4OH	NH_4OH	35.05
Ammonium laurate	$C_{11}H_{23}COONH_4$	AL	217.34
Sodium dodecyl benzene sulfonate	$C_{12}H_{25}C_6H_4SO_3Na$	ABS	349.49
Ammonium persulfate	$(NH_4)_2S_2O_8$	APS	228.20
Ethylene	C_2H_4	C_2H_4	28.05
Ferric ammonium sulfate	$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	FAS	484.21
Soidum formaldehyde sulfoxylate	$NaHSO_2 \cdot CH_2O$	SFS	154.12
Sodium pyrophosphate	$Na_4P_2O_7 \cdot 10H_2O$	SPP	446.11
Tetrasodium ethylenediamine tetraacetate	Na_4EDTA	Na_4EDTA	380.2
Vinyl chloride	VCl	VCl	62.50
Water	H_2O	H_2O	18.02

Simplified equations follow:

Persulfate Redox System

$$Fe(EDTA)^{-} + CH_2OH \cdot SO_2 \longrightarrow Fe(EDTA) = + \text{reduction products} \quad ...(1)$$

$$Fe(EDTA)^{=} + S_2O_8^{=} \longrightarrow Fe(EDTA)^{-} + SO_4^{=} + SO_4^{\cdot-} \quad .....(2)$$

Polymerization Reaction

$$5H_2C = \underset{\displaystyle Cl}{\underset{|}{CH}} + H_2C = CH_2 \xrightarrow{SO_4^{\cdot-}}$$

$$\overline{\left/ -H_2C-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_2-\right/_n}^{\cdot-} \quad ...(3)$$

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).

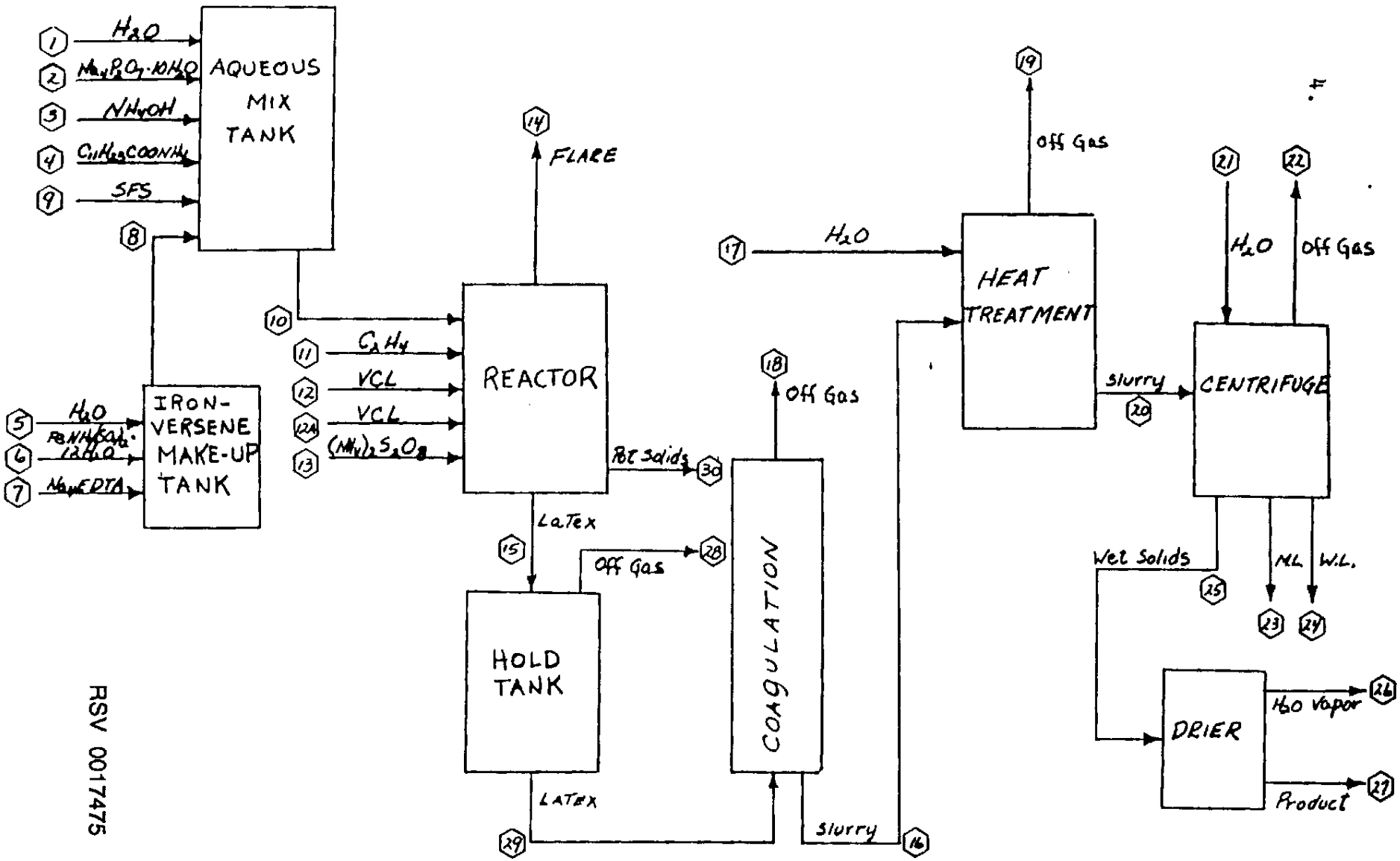

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FIGURE 1

PLASTIMER III MATERIAL BALANCE FLOW SHEET

MEG

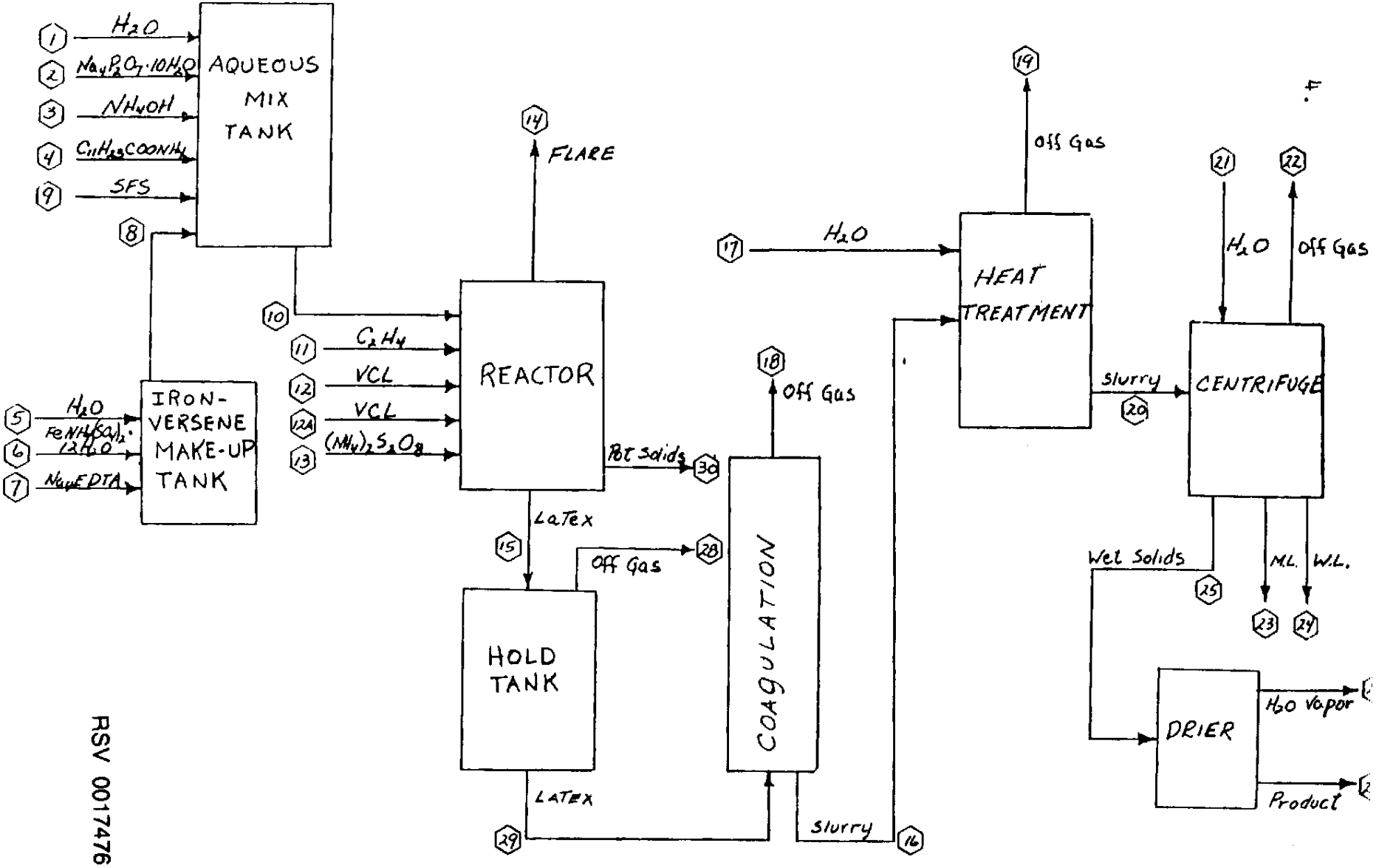

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FIGURE 1

PLASTIMER III MATERIAL BALANCE FLOW SHEET

MEG

MATERIAL BALANCE

A. 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.)

Material	Pounds Consumed	Pounds Produced
NH_4OH (28%)	1.26	
APS	0.421	
AL	3.22	
SPP	2.35	
FAS	0.040	
Na_4EDTA	0.062	
SFS	0.427	
C_2H_4	29.3	
VCl	106.	
H_2O	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		100.
Total	3464.080	3464.110

B. Bill of Materials for Plastimer III made with ABS

(Basis: 100 pounds of product /98.6 pounds E/VCl polymer/; total reactor volume 32.5 gallons.)

Material	Pounds Consumed	Pounds Produced
NH_4OH (28%)	1.27	
APS	0.424	
ABS	5.21	
SPP	2.36	
FAS	0.040	
Na_4EDTA	0.062	
SFS	0.429	
C_2H_4	29.8	
VCl	105.	
H_2O	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

C. Yield

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

TABLE II

Monomer Conversion

	Monomer	Pounds Charged	Pounds Converted to Plastimer III	Percent Conversion
$C_{11}H_{23}COONH_4$ Process	VCl	105.6	87.3	82.6
	C_2H_4	29.3	11.3	38.7
	Total Monomer	134.9	98.6	73.0
ABS Process	VCl	105.3	86.7	82.2
	C_2H_4	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 ($C_{11}H_{23}COONH_4$ 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

	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
							0.520			0.056								
	0.304		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	2965.814	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	0.3
798	2.105	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
98	0.23	---	24.6	24.2	27.2	----	----	51.30	357.0	----	40.4	356.3	----	---	24.0[a]	----	24.3	---
--	----	433	----	----	----	7.33	29.20	-----	-----	6.20	----	-----	----	357	----	11.1	----	---

TABLE IV

Plastimer III Material Balance for ABS

2	12A	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
								0.522			0.035								
		0.004		0.734															
		0.424		0.424															
				5.206	5.206				5.206			2.904	0.726	1.576		1.576		5.206	
			15.684	2.672	1.068		0.680	0.685	0.383		0.383								
				0.040													0.924	1.748	
				0.062															
				0.429															
				2.364															
.723	40.393		16.247	1.517	0.504		0.445	0.300	0.004		0.004						0.568	0.749	
		1.691	0.583	118.772	118.772	227.503		0.804	345.811	2991.383	0.028	338.295	2980.729	18.109	17.708	0.401		118.772	0.211
					4.053				3.391			2.009	1.383					4.053	
				98.100	98.100				98.100					98.100	0.077	98.023		98.100	1.055
.723	40.393	2.119	32.513	230.120	227.503	227.503	1.125	2.111	452.895	2991.383	0.450	343.208	2982.838	117.785	17.785	100.00	1.492	228.628	1.266
.63	5.42	0.25	---	24.7	24.4	24.4	---	---	51.3	359.1	---	40.8	358.1	-----	---	24.0	---	24.4	-----
---	---	---	411	---	---	---	11.3	35.2	---	-----	6.10	---	-----	-----	353	---	15.1	---	-----

PROCESS IN DETAIL

A. 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. Reaction

1. Reactor Feeds

a. 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	1.63
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	1.73	
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°C. ± 0.2°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°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. ± 15 psi. at 30°C. ± 0.2°C. is obtained, corresponding to the addition of 29.3 pounds of C_2H_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 ± 0.5°C.
Pressure	850 psig.	controlled to ± 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 VCl 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 VCl has been added, the VCl 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:

Component	Weight Percent
Water	52.5
Polymer solids	43.1
Soap	1.4
Dissolved VCl	0.3
Dissolved C_2H_4	0.9
Inorg. and Org. salts	1.8
Total	100.0

The reactor vent gas composition is:

Component	Weight Percent
Ethylene	47.0
Vinyl chloride	51.1
Water	1.9
Total	100.0

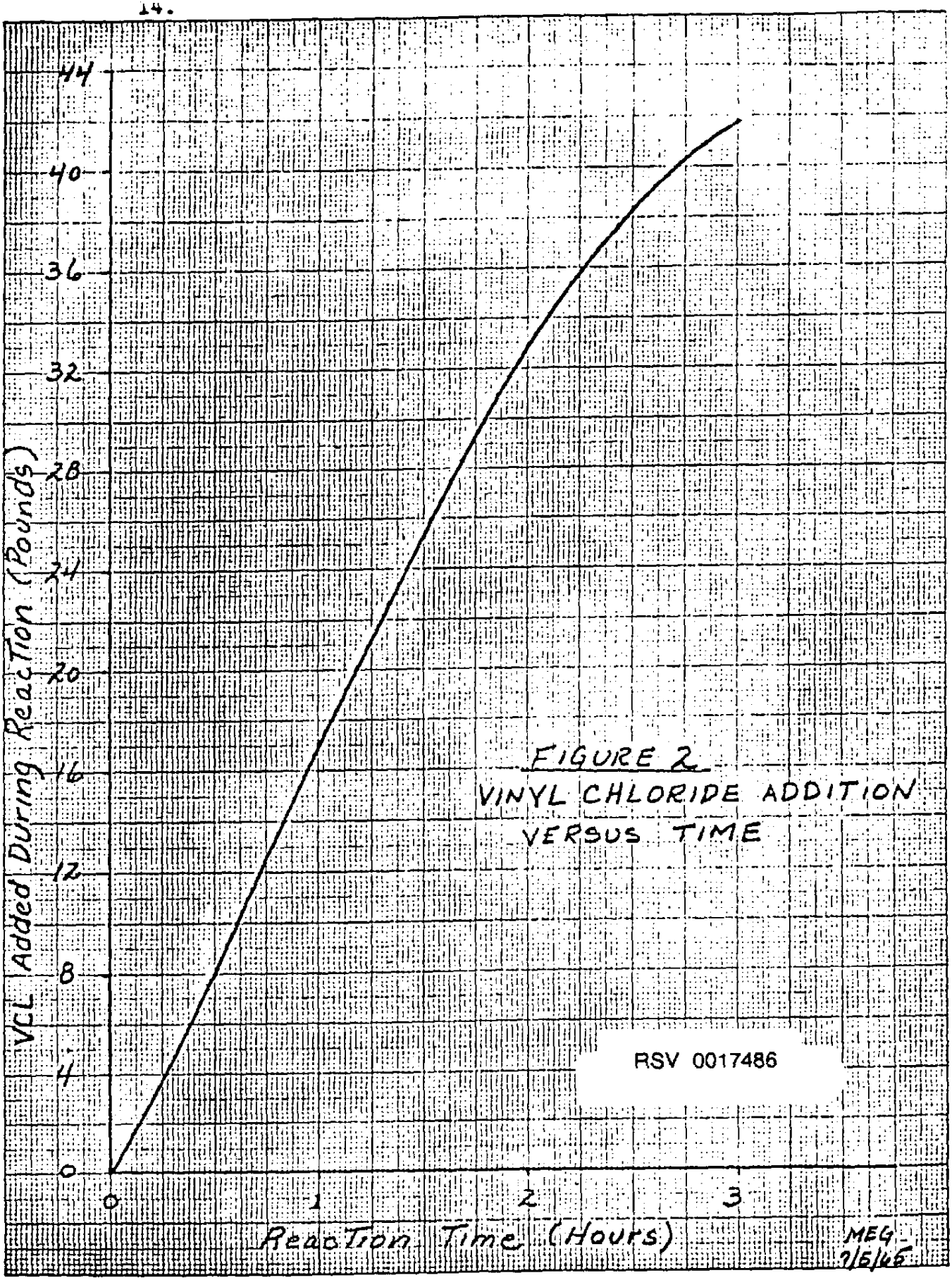

FIGURE 2
VINYL CHLORIDE ADDITION
VERSUS TIME

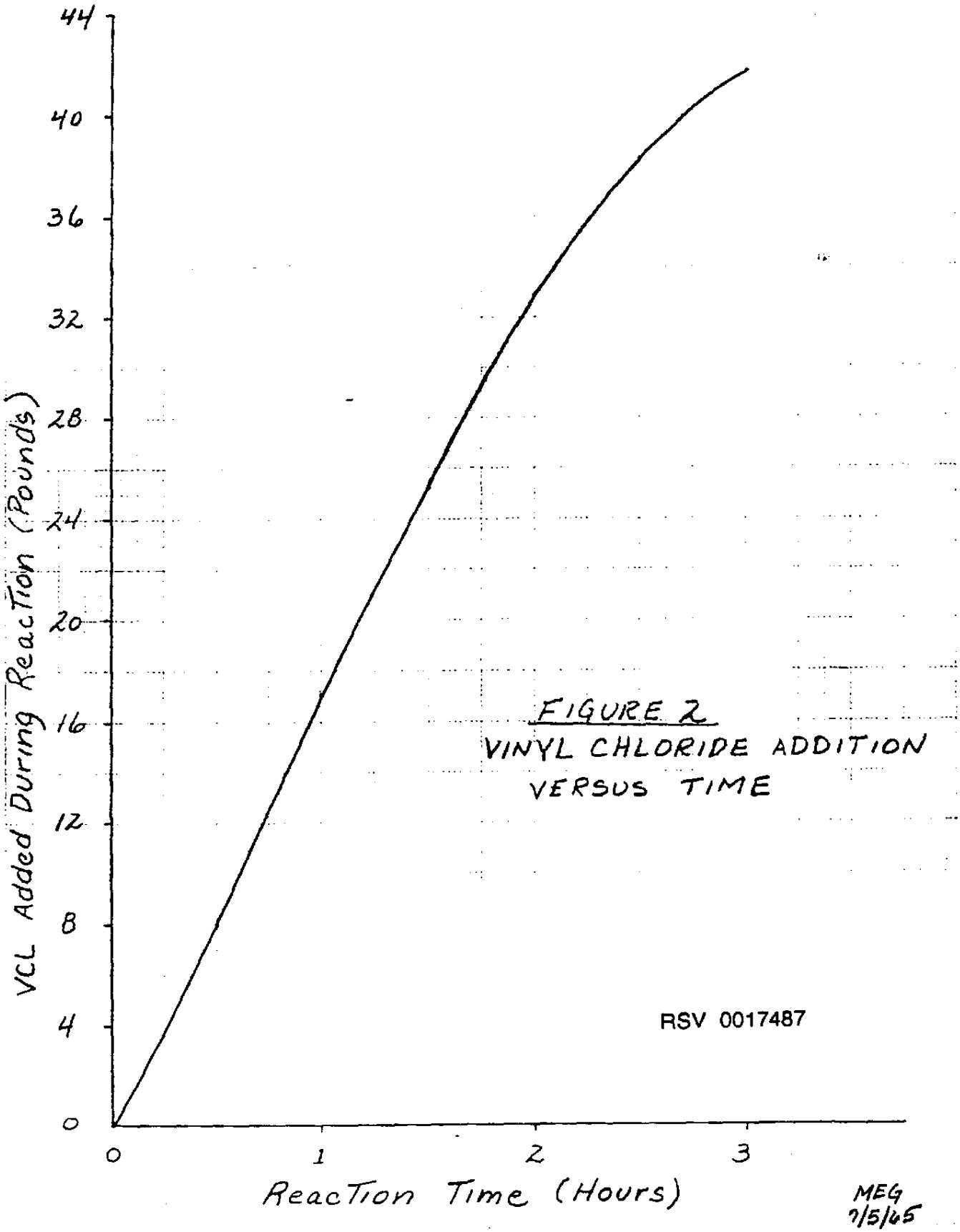

FIGURE 2
VINYL CHLORIDE ADDITION
VERSUS TIME

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°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°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.

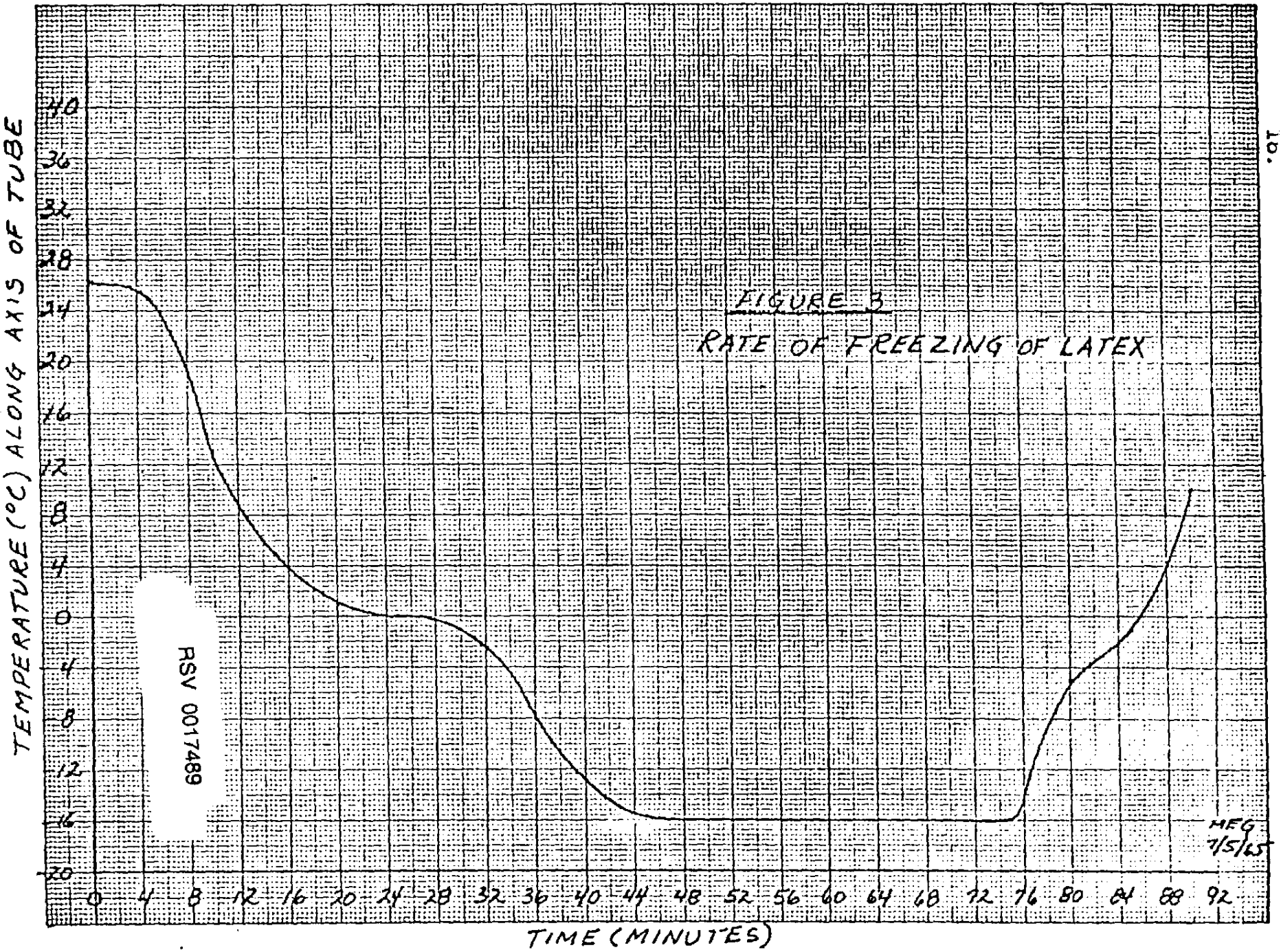

FIGURE 3

RATE OF FREEZING OF LATEX

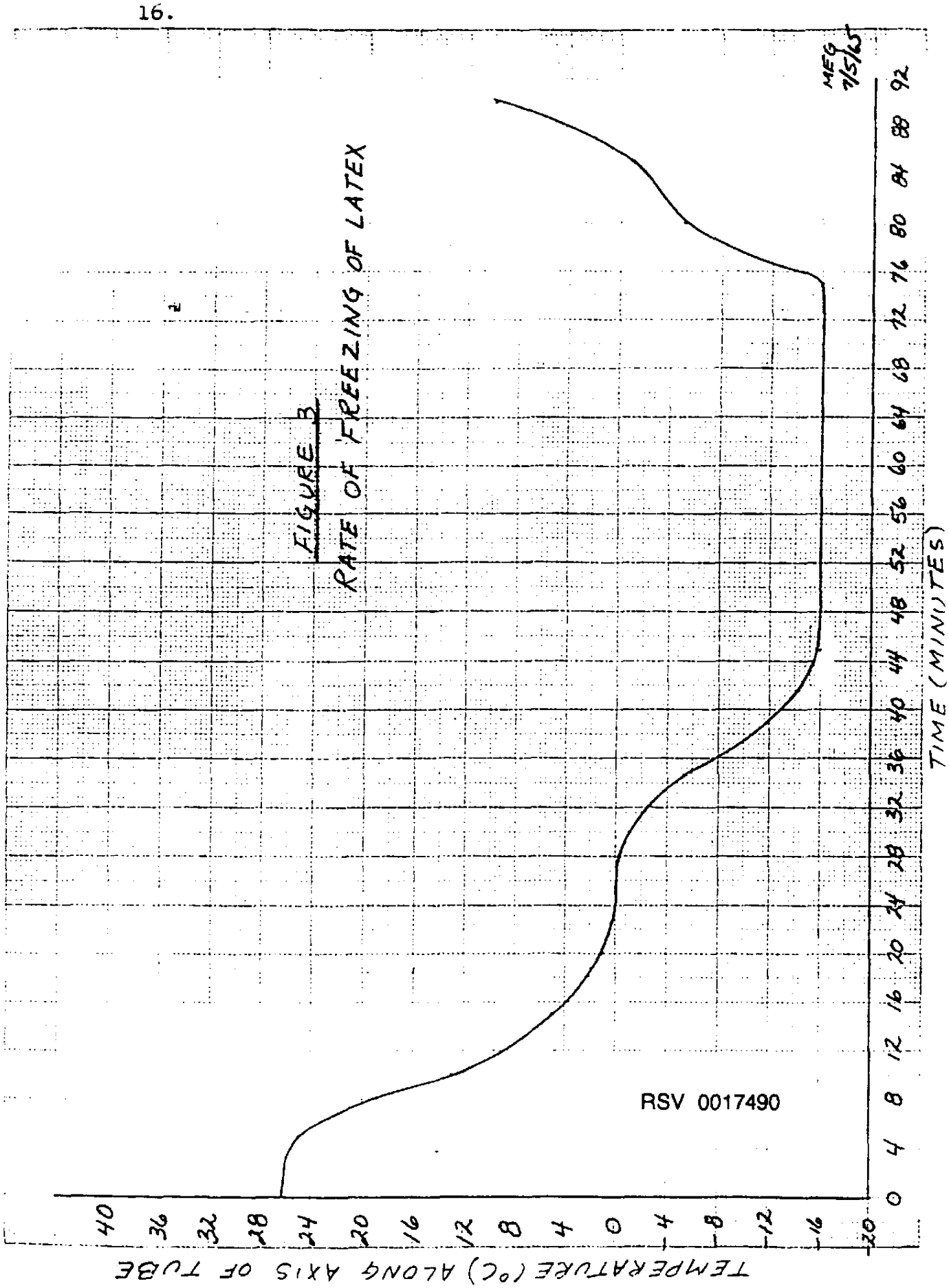

FIGURE 3
RATE OF FREEZING OF LATEX

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:

Component	Weight Percent
Ammonia	19.0
Ethylene	28.2
Vinyl chloride	5.2
Water	47.6
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:

Component	Weight Percent
Ammonia	8.0
Ethylene	84.8
Vinyl chloride	0.9
Water	6.3
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 (SO_4^-). 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 ($SO_4^=$) and a sulfate radical-ion (SO_4^-). 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 SO_4^- 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 VCl 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 VCl charge are charged by weight and the ethylene by difference (until a pressure of 850 psig. is reached), any error in water or VCl charge will cause an error in ethylene charge and, consequently, an error in VCl/C_2H_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 VCl composition must be 68.5% $\pm$ 1.0% in order to obtain a final polymer composition of 88.5% VCl $\pm$ 0.4% VCl. Figure 5 shows the effect of error in aqueous and VCl charges upon initial monomer composition. If a

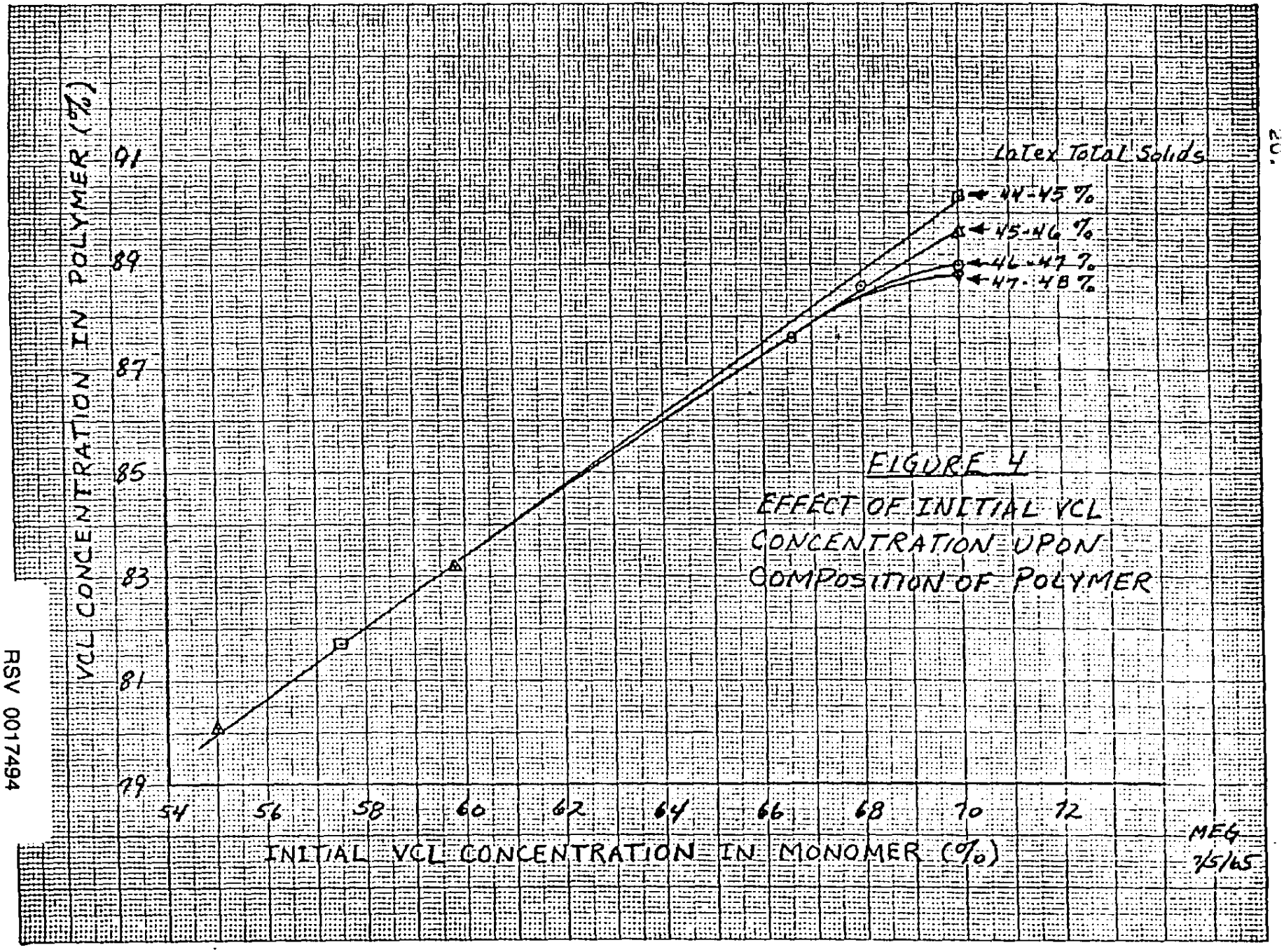

FIGURE 4

EFFECT OF INITIAL VCL CONCENTRATION UPON COMPOSITION OF POLYMER

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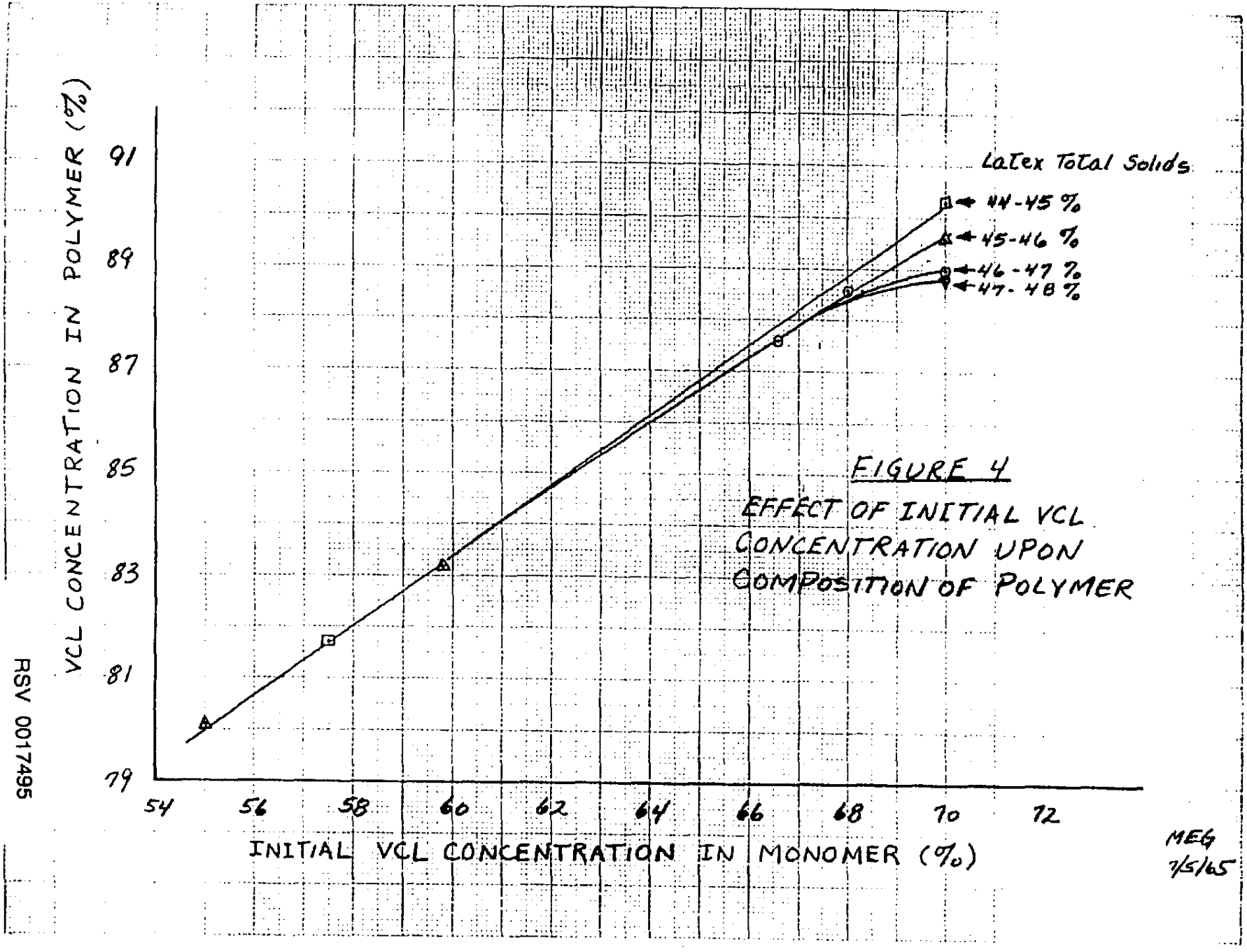

FIGURE 4

EFFECT OF INITIAL VCL CONCENTRATION UPON COMPOSITION OF POLYMER

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7/5/65

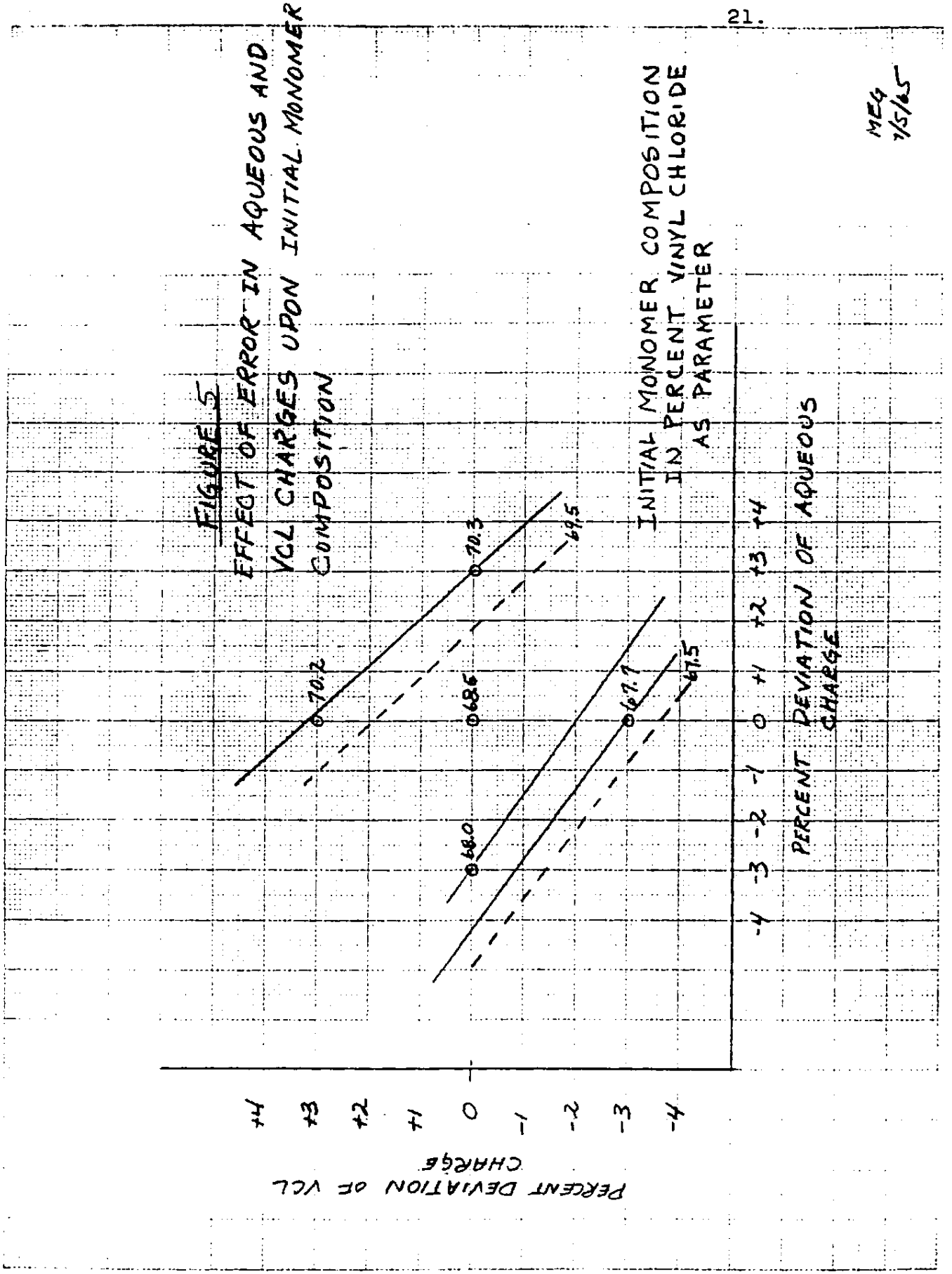


FIGURE 5
EFFECT OF ERROR IN AQUEOUS AND VCL CHARGES UPON INITIAL MONOMER COMPOSITION
INITIAL MONOMER COMPOSITION IN PERCENT VINYL CHLORIDE AS PARAMETER
PERCENT DEVIATION OF AQUEOUS CHARGE
+4 +3 +2 +1 0 -1 -2 -3 -4
70.2
68.6
68.0
70.3
69.5
69.1
67.5
PERCENT DEVIATION OF VCL CHARGE
+4 +3 +2 +1 0 -1 -2 -3 -4
MEG 1/5/65

positive deviation in aqueous charge is followed by an appropriate negative deviation in VCl charge (or vise versa), an initial monomer composition of 68.5% VCl 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 VCl 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% VCl. Conclusions from this data indicate that both the aqueous and VCl 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% VCl in a mixture of C_2H_4 and VCl and a pressure of 850 psig., addition of more VCl to the mixture causes the total pressure to increase. At low concentrations of VCl (below 55%), the total pressure will decrease.

Addition of all the C_2H_4 to the reactor in the initial batch charge before any VCl 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 VCl 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 VCl 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 NH_4OH added to bring the pH to 7.0-8.0. An acidic solution such as an aqueous mixture of APS and water without NH_4OH 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 NH_4OH to the APS solution also serves to prevent corrosion to the APS feed system. A 20% APS-H_2O 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 VCl 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 VCl to the reactor. Since VCl is used in a 5/1 weight ratio to ethylene in the reaction, the addition of pure VCl to maintain reaction pressure is adequate to retain a sufficiently high concentration of VCl in the reactor. The initial VCl composition in the reactor is 68.5% by weight; the final VCl composition is 50% by weight. Therefore, total pressure is a sufficiently good control media for control of reaction mass composition.

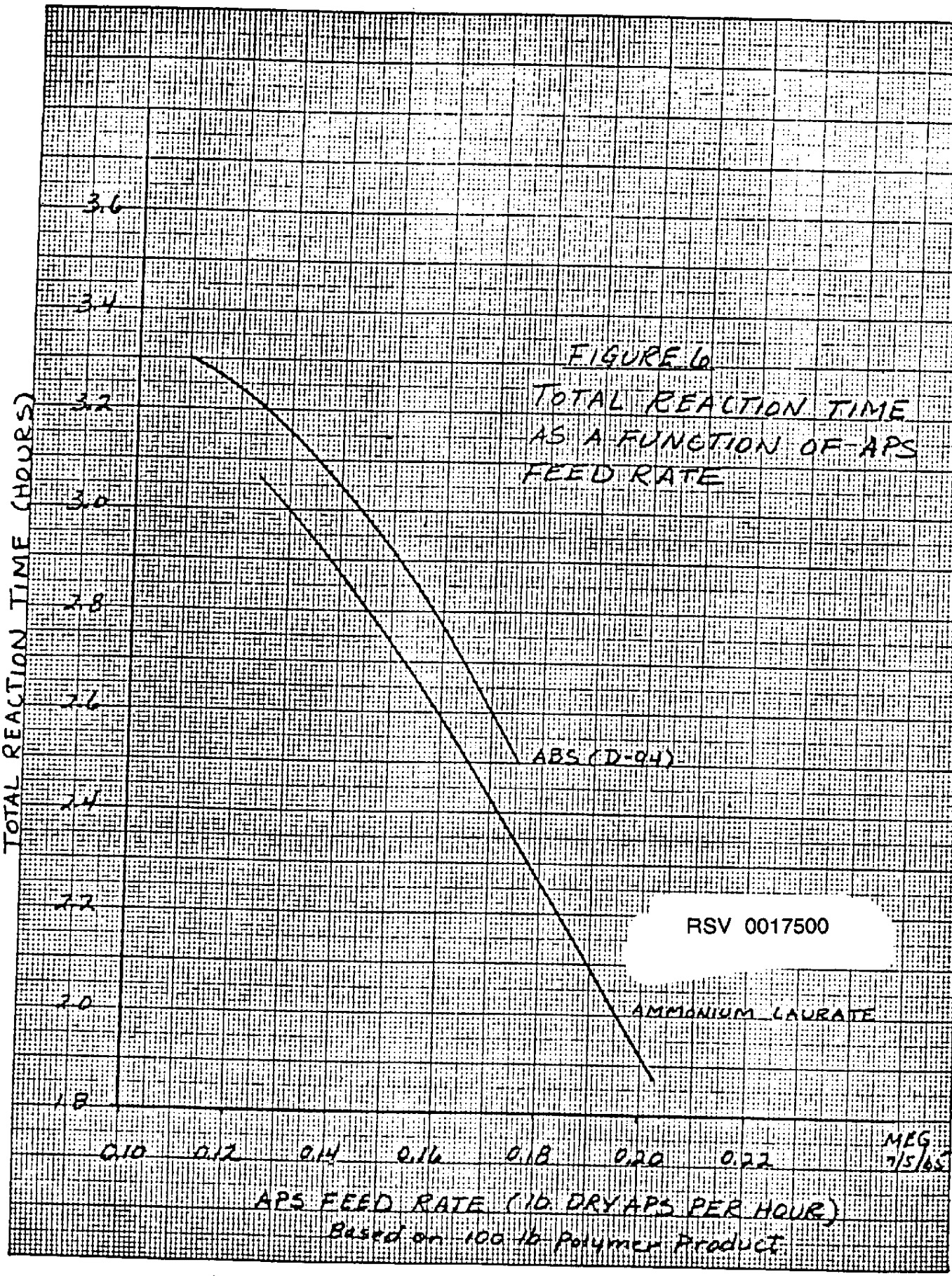


FIGURE 6
TOTAL REACTION TIME
AS A FUNCTION OF APS
FEED RATE

RSV 0017500

MEG 7/5/65

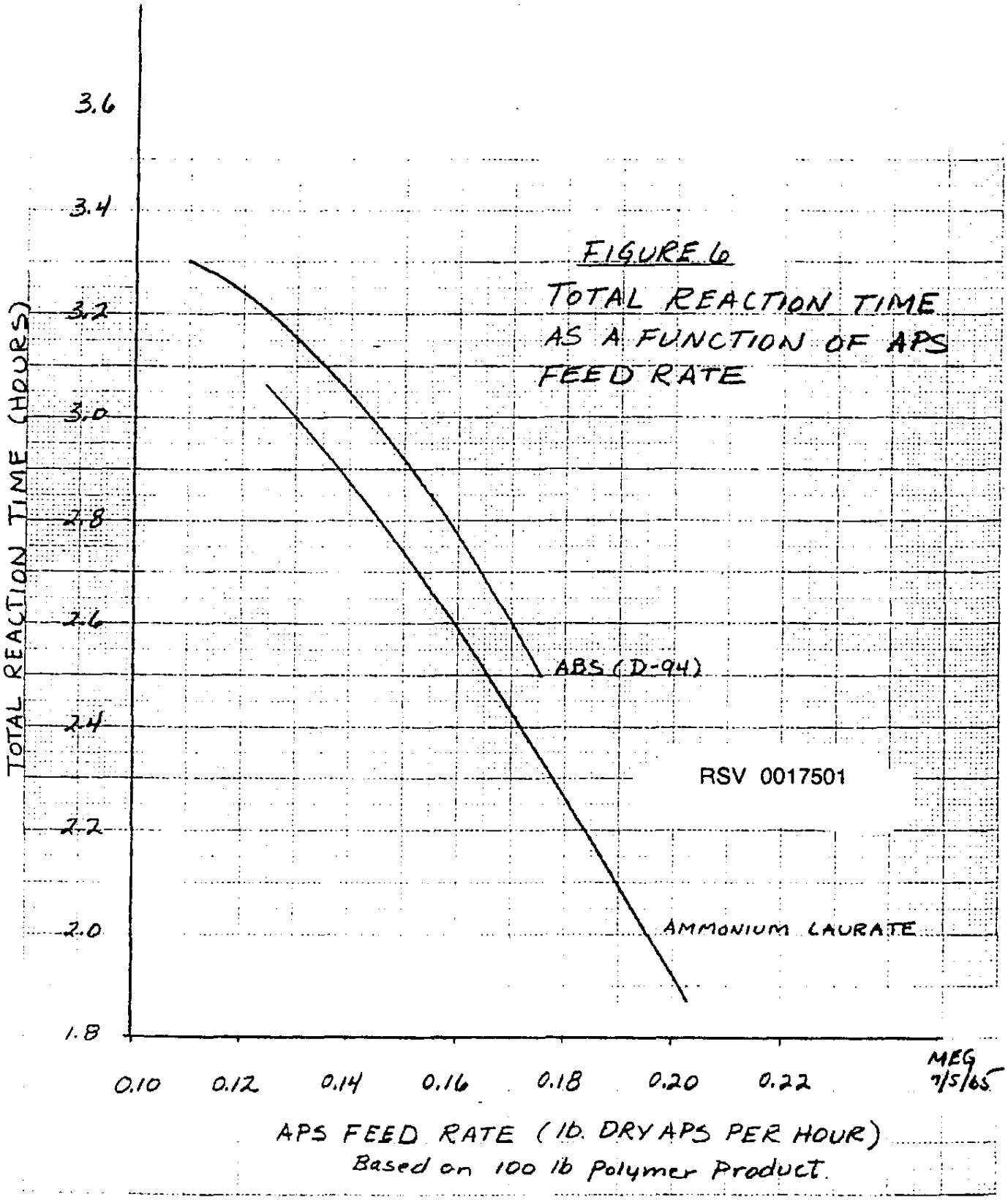


FIGURE 6

TOTAL REACTION TIME AS A FUNCTION OF APS FEED RATE

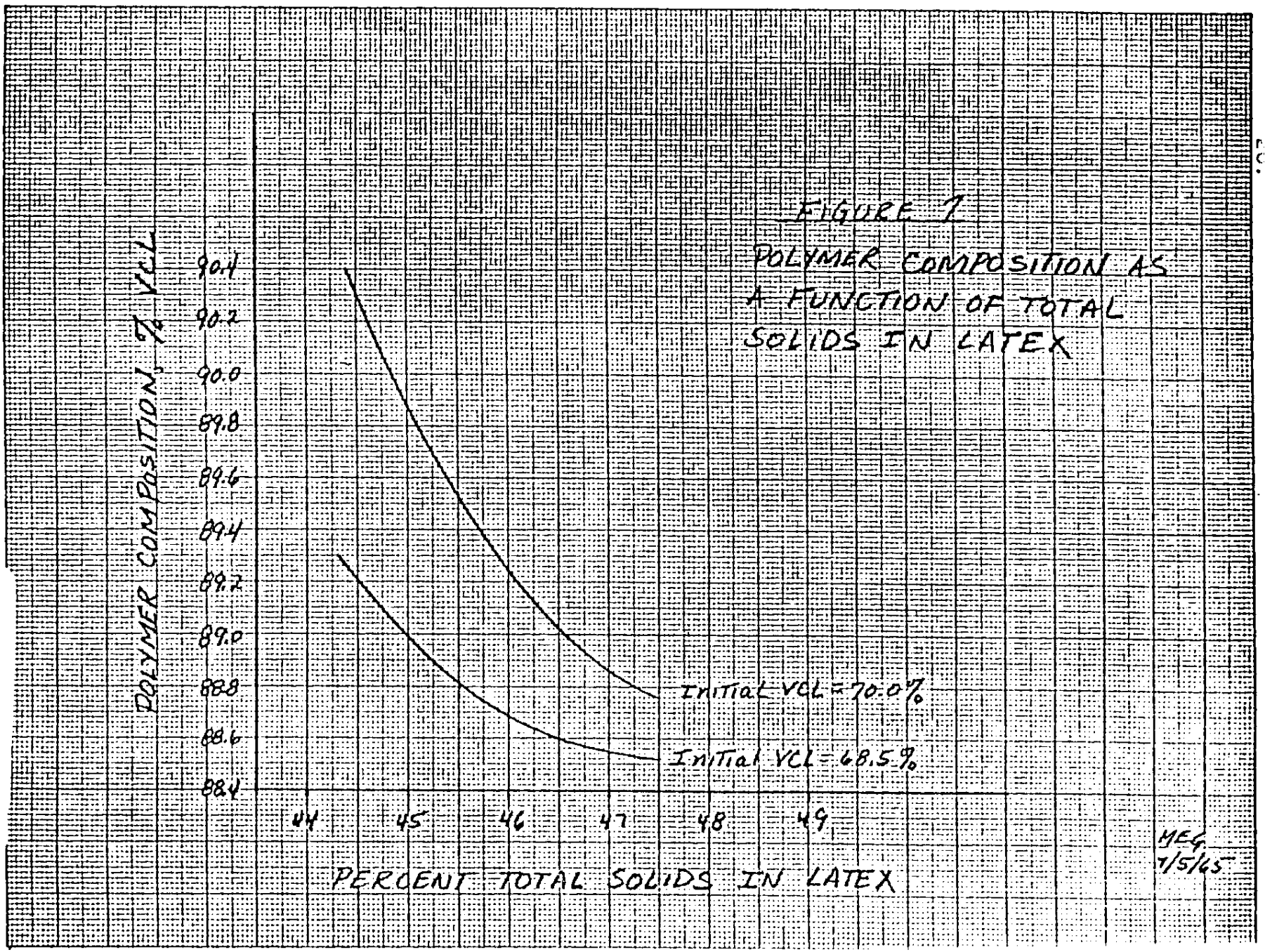
C. Reaction End Point

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.



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 VCl and C_2H_4 may be increased by increasing the aqueous charge to the reactor. Increasing the aqueous charge requires less 68.5% VCl-31.5% C_2H_4 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 VCl 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 VCl conversion to 88%. However, a fivefold increase in pot solids and a lower VCl 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 VCl).

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 ignition	0.002%
Sulfur	0.0002%
Assay	28.0-30.0%
Specific gravity	0.90

e. Ammonium Persulfate

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

Acidity (as H_2SO_4)	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_4)	0.005%

4. Surfactant

a. 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.
Unsulfonated 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.
Unsulfonated 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_2
Dew point	-90°F.
Oxygen	2 ppm.

B. Product

1. 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 $C_{11}H_{23}COONH_4$
	0.0531 - with ABS
Latex viscosity	6-8 cs.

2. Specifications for Solid Polymer Product

Property	Min.	Max.	Method
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_g 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 Methods

1. 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.

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 ± 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 ($NaH_2PO_4 \cdot H_2O$) 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).

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

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

ppm. read x 1.5 = % 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 ± 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. $\frac{\text{ml. titre} \times \text{KF factor} \times 100}{\text{sample weight (copolymer soln.)}} = \%$ moisture contained in copolymer soln.

b. (wt. of copolymer soln.)(% H_2O copolymer soln.) =

wt. H_2O copolymer soln.

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

(wt. of solvent THF in copolymer soln.)

(wt. of solvent in copolymer soln.)*(% H_2O in

solvent THF) = wt. of H_2O in solvent THF

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

copolymer

$$\frac{(\text{wt. } H_2O \text{ copolymer soln.} - \text{wt. } H_2O \text{ in solvent}) \times 100}{\text{wt. of copolymer}} =$$

% 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 ± 0.1° 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.

VI. Procedure

1. Weigh 4 specimens of the following approximate weights to ± 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:

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

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

Reduced viscosity, $\eta_{red} = \frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c}$, C 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.

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

VIII. Report

The report shall include the following:

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

METHOD NO. 65-19

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 (EVCl), in the range of 72 to 94% VCl. The estimated accuracy of the method is ± 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 flashs.

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.

METHOD NO. 65-19

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 ± 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.

SAMPLE ANALYSIS

Weigh 600 ± 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° 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:

Sample Identification	% VCl*	Infrared Ratio
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 ± 0.5% absolute.

METHOD NO. 65-19

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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