Monsanto Company
Organic Chemicals Division
St. Louis Research Department

St. Louis Research Report No. P-1366

TENTATIVE PROCESS

FOR

PRODUCTION OF

PLASTIMER III

ETHYLENE/VINYL CHLORIDE COPOLYMER

Job No. 2-02-760.01-4733

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INTRODUCTION

Research studies on the ethylene/vinyl chloride reaction were initiated within the Central Research Department, 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.

The purpose of this tentative process is to provide a basis for design of manufacturing facilities to produce 1.0-1.5 million pounds per year of Plastimer III copolymer. Work will be continued after this process is issued for the purpose of optimization in certain areas. Amendments for this process will be issued as these optimizations are developed.

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 70% 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 46.7% 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 -10°C., and subsequently thawed. The two phase liquid-solid mixture is separated, and the solid phase is washed with sufficient water and dried at about 40°C.

TABLE I

Abbreviations and Molecular Weights

Compound	Abbreviation	Molecular Weight
Ammonium hydroxide	NH_4OH	35.05
Ammonium persulfate	$(NH_4)_2S_2O_8$	228.20
Ethylene	C_2H_4	28.05
Ferric ammonium sulfate	$Fe(NH_4)(SO_4)_2 \cdot 12H_2O$	484.21
Sodium dodecylbenzene sulfonate	D-94	349.49
Sodium formaldehyde sulfoxylate	SFS	154.12
Sodium pyrophosphate	SPP	446.11
Tetrasodium ethylenediamine tetraacetate	Na_4EDTA	380.2
Vinyl chloride	VCl	62.50
Water	H_2O	18.02

Simplified equations follow:

Persulfate Redox System

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

$$Fe(EDTA)^= + S_2O_8^= \longrightarrow Fe(EDTA)^- + SO_4^= + SO_4^- \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Polymerization Reaction

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

$$\left(-H_2C-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_2-\right)_n \quad \ldots(3)$$

FLOW SHEETS

A schematic flow diagram is given in Figure 1. The material balance in Table III is keyed to this diagram and is based on 100 pounds of polymer solids produced.

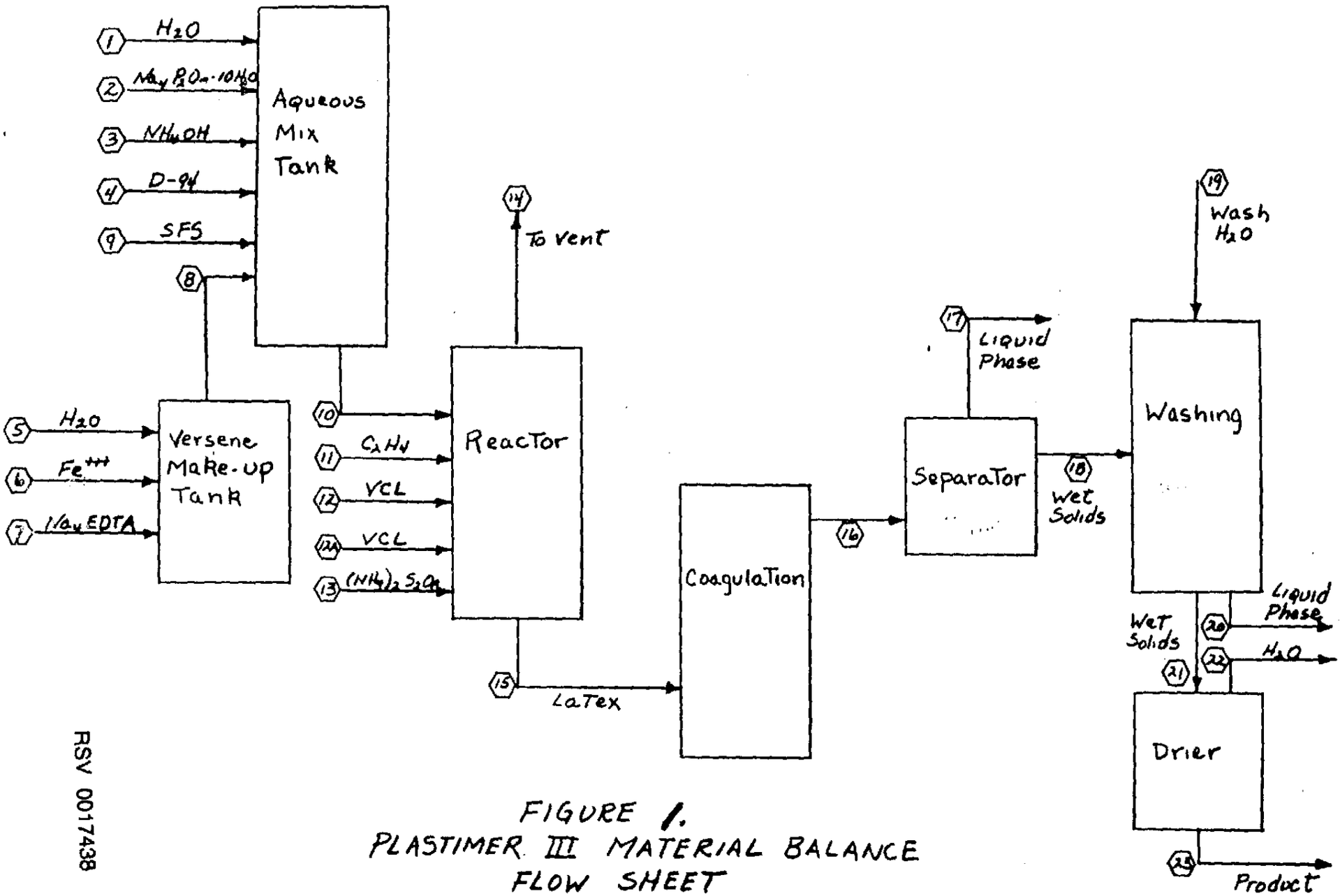

FIGURE 1.
PLASTIMER III MATERIAL BALANCE
FLOW SHEET

RSV 0017438

3.

MATERIAL BALANCE

A. Bill of Materials

(Basis: 100 pounds of polymer solids; total reactor volume 33.5 gallons.)

Material	Pounds Consumed	Pounds Produced
NH_4OH (15 N)	1.316	
$(NH_4)_2S_2O_8$	0.422	
SPP	2.455	
$FeNH_4(SO_4)_2 \cdot 12H_2O$	0.041	Inorganic salt solids
D-94 (43% soap)	12.567	9.143
Na_4EDTA	0.065	
SFS	0.442	
C_2H_4	30.692	22.101
VCl	116.753	25.444
H_2O	3116.272	3124.357
Polymer solids	--------	100.000
Total	3281.045	3281.045

B. Yield

Yield figures are given in Table II as pounds per 100 pounds of polymer solids formed.

TABLE II

Monomer Conversion

Monomer	Lbs. Charge	Lbs. Unreacted	Lbs. Used	% Conversion
VCl	116.753	25.444	91.309	78.2
C_2H_4	30.692	22.101	8.591	28.0
Total Monomer	147.445	47.545	99.900	67.7

C. Material Balance Sheet

A detailed material balance sheet is given in Table III.

TABLE III

Plastimer III Material Balance

Component/Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	12A	13	14	15	16	17	18	19	20	21	22	23
NH_3			0.590							0.590				0.004										
$(NH_4)_2S_2O_8$														0.442										
C_4H_6											30.692				22.101									
$FeNH_4(SO_4)_2 \cdot 12H_2O$						0.041		0.041		0.041														
D-94				5.404						5.404														
Na_4EDTA							0.065	0.065		0.065														
SFS									0.442	0.442														
SPP		2.455								2.455														
VCl												73.907	42.846		25.444									
H_2O	93.575		0.913	26.373	1.719			1.719		122.58				1.777	0.029		124.328	87.947	36.381	3000.000	3054.613	33.334	33.334	
Latex																233.471								
Inorganic solids																	9.243		9.243		9.143	0.100		0.100
Coagulated polymer solids																	99.900		99.900			99.900		99.900
Total	93.575	2.455	1.503	31.777	1.719	0.041	0.065	1.825	0.442	131.577	30.692	73.907	42.846	2.223	47.574	233.471	233.471	87.947	145.524	3000.000	3063.756	133.334	33.334	100.000
Temp. °C.	25	25	25	25	25	25	25	25	25	25	25	25	25	25	30	30	25	25	25	25	25	25	40	
Vol. (gal.)	11.23	--	0.17	3.72	0.21	--	--	0.22	--	15.45	--	--	--	0.24	--	24.80	24.80	10.50	--	360.14	367.79	--	4.00	

PROCESS IN DETAIL

A. Summary

A ferric-versene mixture is made up by mixing ferric ammonium sulfate hydrate and tetrasodium ethylene diamine tetraacetate in water under an atmosphere of nitrogen. The ferric versenate is added to an aqueous mix of ammonium hydroxide, sodium pyrophosphate, D-94, and sodium formaldehyde sulfoxylate. The resulting aqueous mixture is fed batchwise to a reactor which has been purged with ethylene and evacuated. A vinyl chloride charge is then added to the reactor followed by a batch charge of ethylene such that the resulting monomer mixture is 70% vinyl chloride by weight and the reactor pressure is 850 psig. at 30°C.

The contents of the reactor are allowed to equilibrate at 30°C. with adequate agitation. Upon temperature and pressure equilibration, the reaction is started by addition of ammonium persulfate (APS). Vinyl chloride is added upon demand during the reaction so as to maintain a constant reactor pressure of 850 psig. at 30°C. The APS is fed at a constant rate to achieve a reaction time of 3 hours. When 97% of the required amount of vinyl chloride has been added to the reactor, the addition of APS is stopped. When the vinyl chloride uptake stops, the unreacted monomers are vented off the top of the reactor until the reactor pressure reaches atmospheric pressure.

The latex is drained from the reactor by gravity, frozen in a cold stage at -10°C., and subsequently thawed. The two phase liquid, solid mixture is separated and the polymer solid is washed and dried at about 40°C.

B. Reactor Feeds

1. Iron-Versene Catalyst

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

Ferric ammonium sulfate hydrate	0.041 lbs.
Tetrasodium ethylene diamine tetraacetate	0.065
Demineralized water	1.719
Total	1.825 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.

2. Aqueous Catalyst Charge

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

Demineralized water	93.575 lbs.
Ammonium hydroxide (15 N)	1.303
Sodium pyrophosphate	2.455
D-94 (17% soap)	31.777
Ferric versenate	1.825
Sodium formaldehyde sulfoxylate	0.442
Total	131.377 lbs.

The sodium dodecylbenzene sulfonate (D-94) is commercially available as a 57% aqueous solution (43% D-94). Because of its very high viscosity, the 43% solution is diluted with demineralized water to a 17% solution before charging to the aqueous catalyst solution. Per 100 pounds of polymer solid formed, 19.210 pounds of water is added to 12.567 pounds of 43% D-94 to obtain 31.777 pounds of 17% D-94 which then is charged to the aqueous catalyst solution. A nitrogen atmosphere is maintained above the solution while mixing to prevent the solution from being contacted with oxygen.

3. Reactor Charge

A 33.5-gallon reactor (based on 100 pounds of polymer solids) is first evacuated, purged with ethylene, and evacuated again. Then 131.377 pounds of aqueous catalyst solution is added, brought to 30°C., and 73.907 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 900 psig. At this point, the primary pressure sensing device is shut off from the reactor and the 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. at 30°C. is obtained, corresponding to the addition of 30.692 pounds of C_2H_4. After the addition of all the ethylene, the primary sensing device can be opened to the reactor, allowing the trapped monomers at 900 psig. to blow back into the reactor at 850 psig. and 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 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.)

4. Continuous Feeds

The APS solution is added to the reaction continuously at the rate of 0.74 pounds per hour until 97% of the vinyl chloride which is to be fed during the reaction has been added (41.5 pounds). 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 3-3.5 hours, although reaction times as short as 2 hours can be achieved and result in satisfactory product. All continuous feeds are fed subsurface.

C. 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.

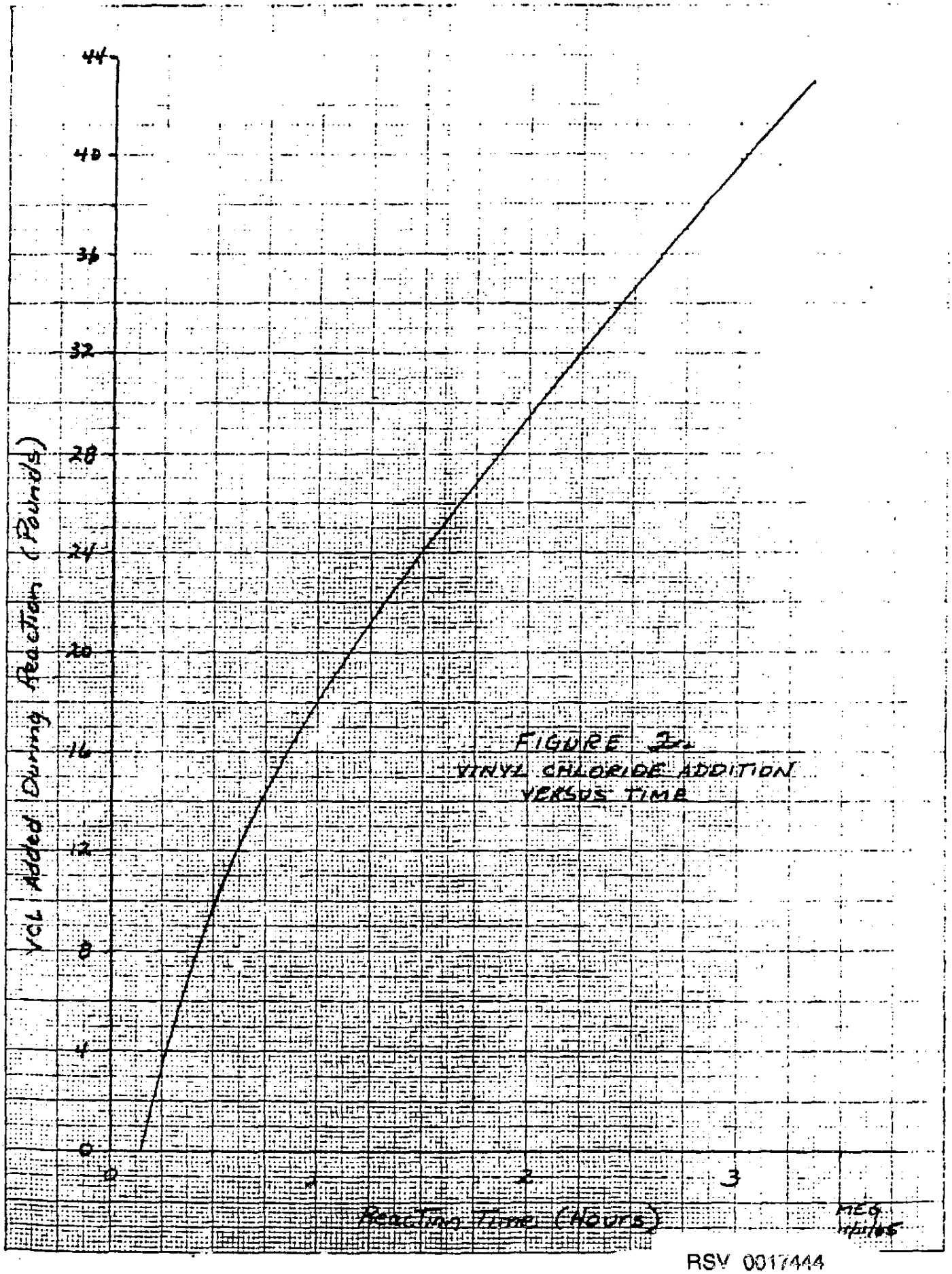

FIGURE 2.
VINYL CHLORIDE ADDITION
VERSUS TIME

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.	" " ± 15 psi.
Reactor volume	33.5 gal.	" " ± 0.2 gal.

Agitation sufficient to maintain adequate emulsion but not vigorous enough to cause excessive liquid shear is required. In the 1-gallon process development autoclave equipped with three 4-bladed flat impellers (see Appendix A for details and dimensions), an agitation speed of 400 rpm. was found to maintain satisfactory emulsion.

Reaction continues until the solids content of the latex reaches 46-48%. The addition of 42.846 pounds of VCl during reaction results in a solids content of 46.7%. To terminate the reaction at this point, the APS feed is stopped when 97% of the vinyl chloride has been added (41.5 pounds). The reaction rate will begin to decrease sharply. When the reaction has stopped, 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 30-35-minute period such that no latex is obtained from the vent. 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	53.23
Polymer solids	42.80
Soap	2.32
Other solids	1.65
Total	100.00

The reactor off-gas composition is:

Component	Mole (Vol.) Percent
Ethylene	65.84
Vinyl chloride	34.02
Water	0.14
Total	100.00

D. Coagulation, Washing, and Drying

The liquid latex is coagulated by freezing in a cold stage at -10°C. Slow freezing of the latex is required to maintain proper particle size. A freezing rate such that 85-90% of the polymer crystals are greater than 30 mesh is satisfactory. The cold stage is operated at atmospheric pressure. Subsequent thawing of the frozen latex such that the temperature of the polymer does not exceed 30°C. yields a slurry of polymer and other solids in water. The two phase mixture is separated and the solid phase washed with filtered tap water. The washing step requires 3000 pounds of water per 100 pounds of polymer solids for a washing stage having intimate mixing of wash water and polymer solids and a contact time of 1 hour. The washed polymer is dried at 40°C. until less than 0.1% moisture is obtained in the product.

E. Reactor Variables

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 ($SO_4^{\cdot}$). 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 ($SO_4^{=}$) and a sulfate radical-ion ($SO_4^{\cdot-}$). 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 $SO_4^{\cdot-}$ 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 9.0-9.5. Sodium dodecylbenzene sulfonate is used as a surfactant or emulsifying agent. Reaction actually 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. 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. An acidic solution such as an aqueous mixture of APS and water without neutralization will cause the reaction to stop immediately if it is not properly buffered. The appropriate sequence of reactions in the persulfate redox system only exists in a basic media. Reaction inhibition can therefore be caused by inadequate neutralization of the APS solution. 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, even to 316 stainless steel.

4. Monomer Charge

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 70% 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, 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 until a reactor pressure of 900 psig. is reached. In the presence of agitation, a significant amount of ethylene will dissolve in the VCl causing the reactor pressure to decrease. 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. 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.

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 3.

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 the 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

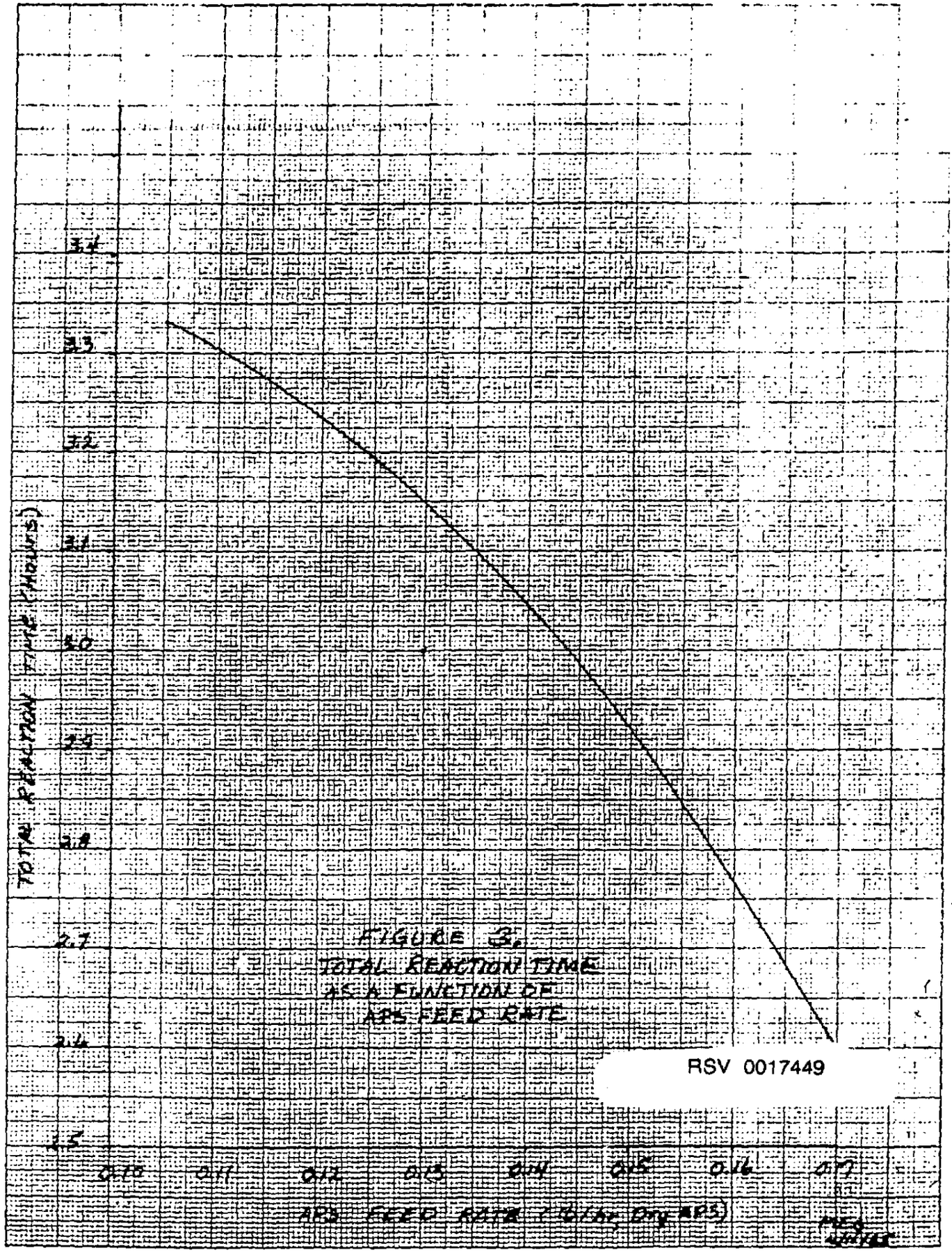

FIGURE 3.
TOTAL REACTION TIME
AS A FUNCTION OF
APS FEED RATE

VCl composition in the reactor is 70% by weight; the final VCl composition is 50-60% by weight. Therefore, total pressure is a sufficiently good control media for control of reaction mass composition.

C. Reaction End Point

Sufficient reaction is achieved when the solids content of the latex reaches 45-48%. Reaction can proceed beyond this point, but latices with higher solids contents are difficult to vent and result in higher deposits of solids in the reactor. To reach the desired end point, the appropriate amount of APS is added such that the reaction will cease when 42.846 pounds 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 97-99% of the total amount of VCl has been added, the active amount of APS present in the reactor will reach zero when 42.846 pounds VCl has been added.

D. Coagulated Solids Formation 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 Completion

The extent of completion of the reaction has an effect upon the amount of coagulated solids formed in the reactor. Above 48-50% total solids in latex, the amount of coagulated solids formed increases rapidly. The variation in total solids from 44-48% causes no significant difference in polymer quality.

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 until the pressure in the reactor reaches 50-100 psig. (10-15 minutes) 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 20-30 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.

F. Coagulation of Latex

The latex is coagulated by freezing at -10°C. 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. Due to a material handling problem in the washing stage, large polymer crystals are desired. For this reason, the rate of freezing should be sufficiently slow to give a particle size such that 85-90% of the particles are larger than 30 mesh and the number of particles smaller than 100 mesh are an absolute minimum. An adequate freezing time for coagulation in a 1.5-2-inch tube is 1-2 hours. All of the latex must be frozen. A mixture of unfrozen latex and thawed coagulum presents a difficult material handling problem.

G. Polymer Washing and Drying

Little information is known about polymer washing and drying at this time. Amendments to this process will be issued as new techniques and developments are obtained.

H. Reactor Washout

No research has been done on the method or frequency of reactor washout. Current solvents used to clean the reactor are water followed by either acetone or tetrahydrofuran. Amendments will be issued to cover this item.

I. Materials of Construction

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

MATERIAL SPECIFICATIONS, ANALYTICAL METHODS

A. Raw Materials

1. Vinyl Chloride

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

2. Ethylene

Monsanto Texas City, ethylene is used. It is passed through a charcoal and alumina absorber in series (.01 pound charcoal and .01 pound alumina per 100 pounds C_2H_4).

3. Persulfate Redox Catalyst System Materials

a. The following compounds from Fisher Scientific were used in process development work.

(1) Ferric Ammonium Sulfate

Typical analysis:

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

(2) Tetrasodium Ethylenediamine Tetraacetate

Powder, technical with 1 gram chelating 215 mg. of $CaCO_3$ at pH 11.

(3) Sodium Formaldehyde Sulfoxylate

Technical.

b. The following items were obtained from Mallinckrodt Chemical Works.

(1) Ammonium Hydroxide

15 N analytical, reagent grade with following 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

(2) Ammonium Persulfate

Analytical, reagent grade 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%

(3) Sodium Pyrophosphate

Analytical, reagent grade with following typical analysis:

Arsenic	0.0005%
Chloride	0.002%
Heavy metals (as Pb)	0.001%
Insoluble matter	0.010%
Iron (Fe)	0.001%
Nitrogen compounds (as N)	0.001%
Sulfate (SO_4)	0.005%

c. Nitrogen

Nitrogen used 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.

4. D-94

D-94 (sodium dodecylbenzene sulfonate) was obtained from the Richardson Corporation, Chicago, Illinois. The specifications are:

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

5. Water

Demineralized.

B. Product

1. Reactor Latex Product

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

% Total solids	46.7%
% Polymer solids	42.8%
Ratio of soap to polymer	0.054
Latex viscosity	9.42 cs.

2. Solid Polymer Product

% VCl	91.5%
Tensile break	7025 psi.
Elongation break	284%
T_f	42.5°C.

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.

2. pH

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

3. Latex Viscosity

The latex viscosity is determined by an Ostwald capillary viscometer, Model 150, at 30°C.

4. Particle Size

A weight average particle size can be obtained by dissymmetry on a diluted sample of latex. Absolute particle size and size distribution measurements are made by electron microscopy using a special cold stage technique.

5. Dry Polymer

The latex is coagulated by freezing at -10°C. After thawing, the coagulum is separated from the aqueous solution, filtered, and washed. The washed coagulum is dried by heating to 65°C. at 10 mm. Hg pressure.

6. Specific Viscosity

The specific viscosity is obtained with an Ostwald capillary viscometer, Model 50, at 30°C. 0.1 gram of solid polymer is dissolved in 100 cc. of tetrahydrofuran and run at 30°C. The specific viscosity is equal to the efflux time of the solution divided by the efflux time of the solvent minus 1.0.

7. Vinyl Chloride Content

Total chlorine in the dry polymer is obtained by Schoniger combustion and potentiometric titration with silver nitrate. Central Research Department Analytical Laboratory Method No. C-50-61.

8. Mechanical Stability

This test subjects a 40.0 gram, filtered sample of E/VCl copolymer latex suspension to a shearing force exerted by a 1-inch metal disc under a load of 6 kilograms, rotating at 1000 rpm., in contact with

a polyethylene surface. The sample container temperature is held constant at 35°C. by circulating water through the jacket. The test if timed for 20 minutes. Following this, the sample is filtered through a 200 mesh screen. About 300 ml. of water is used in transferring the sample and washing the coagulum retained on the filter. The coagulum formed is dried on the screen at 95-100°C. for at least 30 minutes. The weight of coagulum is a measure of sample stability.

TOXICITY AND HAZARDS

A. Vinyl Chloride

Vinyl chloride is a flammable liquid and a dangerous fire hazard. Its vapors form flammable mixtures with air at all temperatures down to 20°F. The limits of inflammability are 4-22% by volume in air. 10% vinyl chloride is dangerous to life of animals in from 30-60 minutes of exposure, whereas 5% causes symptoms in less than an hour. Vinyl chloride is stored in a cool, ventilated area away from open flame, acute fire hazards, or powerful oxidizing agents. Personnel exposed to it should heed the warning of dizziness and disorientation, and remove themselves at once from air contaminated with it.(4)

B. Ethylene

No appreciable reaction occurs in ethylene at 2,000 atmospheres below 100°C. and in ethylene at 250°C. below about 500 atmospheres. Nevertheless, even under these conditions, an uncontrollable reaction will propagate if by some mischance it is initiated. Ethylene is only safe from such propagations inside limiting conditions of which the following are examples:

Pressure	1,000 atm.	400 atm.	200 atm.
Temperature	20°C.	100°C.	210°C.

The flammability limits of ethylene with oxygen are 2.9-79.9% by volume and with air are 2.75-28.6% by volume.(3)

C. Ammonium Persulfate

Contact of ammonium persulfate with other material may cause fire or explosion.

POLLUTION CONTROL

The off-gas from the reactor may be recycled to subsequent batches or is flared to eliminate atmospheric pollution and an explosion hazard. Because of the relatively high density of vinyl chloride gas, high concentrations can accumulate near an atmospheric vent without a flare.

REFERENCES

1. Bovey, F. A., I. M. Kotthoff, A. I. Medalia, and E. J. Meehan, Emulsion Polymerization, Interscience Publishers, Inc., New York (1955).

2. Hileman, H. J., Progress Report, Central Research Department, September 1964, E/VCl Synthesis, Characterization and Applications, Job No. 2601, Issue 7.

3. Renfrew, A., and P. Morgan, Polythene, The Technology and Uses of Polymers, Interscience Publishers, Inc., New York (1957).

4. Sax, N. Irving, Handbook of Dangerous Materials, Reinhold Publishing Corporation, New York (1951).

ENGINEERING DATA

Cooling capacity per gallon of reactor volume as a function of reaction time is given in Figure 4. The heat of reaction per pound of polymer is 750 BTU/pound. Physical constants data are given in Tables IV and V.

ACKNOWLEDGEMENT

The exchange of information and contributions provided by the Central Research Department, notably from the group of Mr. H. J. Hileman, is greatly appreciated.

APPENDIX

Appendix A.

M. E. Gibbs Date

File Copy approved by: R. W. Bucknell Date

H. L. Hubbard Date
Mgr. of Res.

RSV 0017457

dm

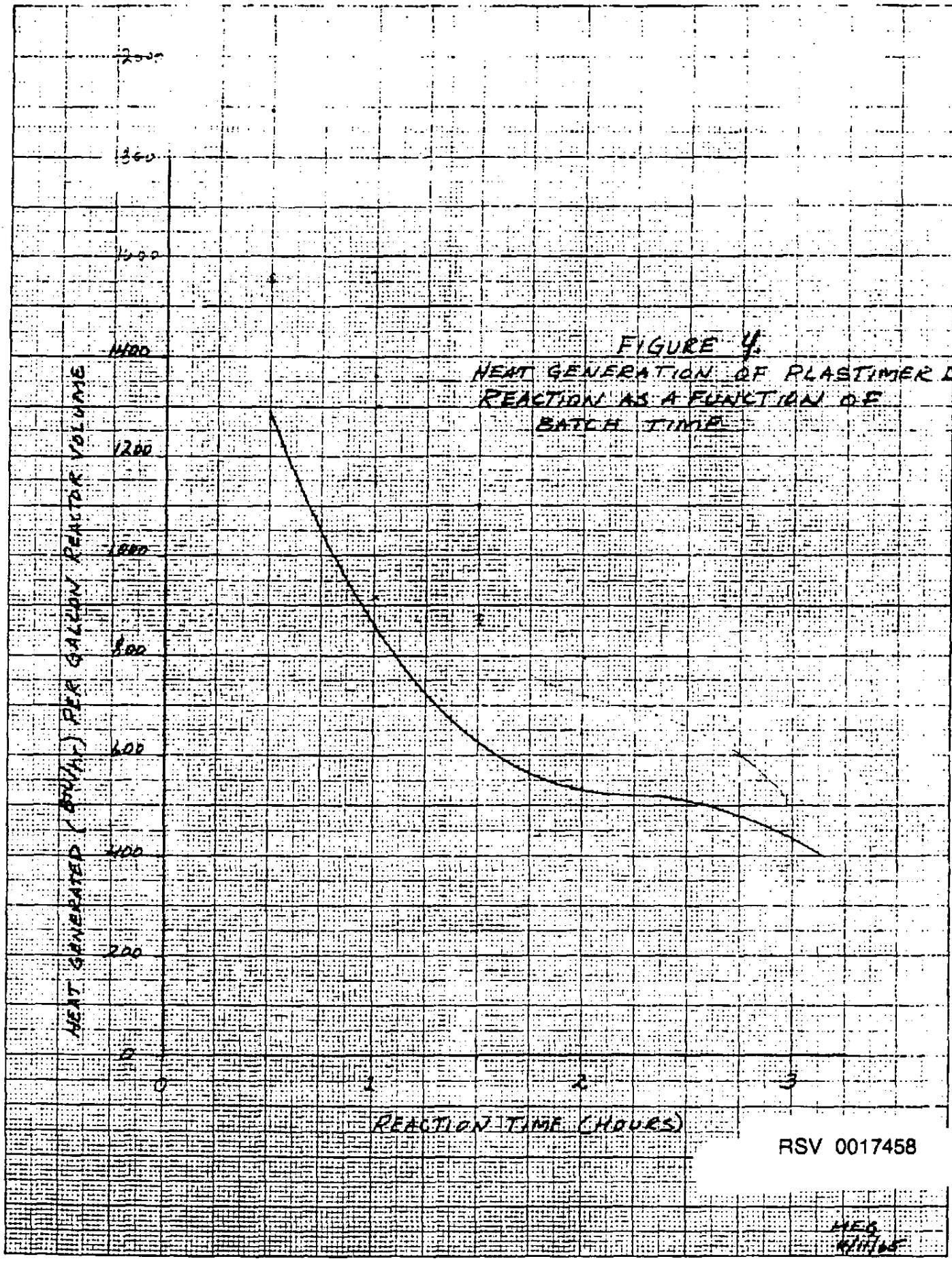

FIGURE 4.
HEAT GENERATION OF PLASTIMER III REACTION AS A FUNCTION OF BATCH TIME

PHYSICAL CONSTANTS DATA

SUBSTANCE	STRUCTURAL FORMULA
Ethylene	$CH_2 = CH_2$

COMPILED BY	DATE
M. E. Gibbs	3/17/65

NAME		SOURCE & DATE
Formula	C_2H_4	Physical Properties II,
Molecular Weight	28.052	Dreisbach, R. R.
Appearance		
Boiling Point at 760 mm	-103.71°C.	"
Boiling Point at 100 mm	-131.78°C.	"
Boiling Point at 30mm	-144.00°C.	"
Boiling Point at 10mm	-153.22°C.	"
Crystallizing Point	-169.15°C.	"
Melting Point		
Solution Point		
Specific Gravity @ -10°C.	0.384	"
Specific Gravity @ 0°C.	0.345	"
Pounds per Gal. @ °C		
Coefficient of Expansion		
Refractive Index @ n_D		
Infra Red Spectrum *(Reference)*		
Ultra Violet Spectrum *(Reference)*		
Viscosity @ -125°C.	0.23 cs.	"
Viscosity @ -105°C.	0.16 cs.	"
Surface Tension		
Solubility in Water		
Solubility in		
Solubility in		
Flash Point °F *(Method)*		
Fire Point °C		
Heat of Combustion at 25°C.	316.20 kcal/mole	"
Heat of Formation		
Thermal Stability (cal./kg/min.)		
Latent Heat of Fusion B.P.	115.39 cal./g.	"
Latent Heat of Vap. Vap. 300°K.	0.3725 cal./g. °K.	"
Specific Heat	9.90°C.	"
Critical Temperature	38380. mm.	"
Critical Pressure		
Dissociation Constant		
Critical Density	0.21 g./ml.	"
Other Constants		
Toxicity *(Give Reference)*		

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NOTE: *These data should not be released outside of Monsanto Chemical Company. Use additional sheets if necessary.*

TABLE V

PHYSICAL CONSTANTS DATA

SUBSTANCE	STRUCTURAL FORMULA
Vinyl Chloride Chloroethane	$CH_2 = CHCl$
COMPILED BY: M. E. Gibbs	DATE: 3/17/65

NAME		SOURCE & DATE
Formula	C_2H_3Cl	Physical Properties II
Molecular Weight	62.501	Dreisbach, R. R.
Appearance		
Boiling Point at 760 mm	-13.37°C.	"
Boiling Point at 100 mm	-55.8 °C.	"
Boiling Point at 30mm	-77.95°C.	"
Boiling Point at 10mm	-87.5 °C.	"
Crystallizing Point	-153.79°C.	"
Melting Point		
Solution Point		
Specific Gravity @ -20°C.	0.983	"
Specific Gravity @		
Pounds per Gal. @ °C		
Coefficient of Expansion		
Refractive Index @ -10°C. n_D	1.4046	"
Infra Red Spectrum *(Reference)*		
Ultra Violet Spectrum *(Reference)*		
Viscosity @ -20°C.	0.2780 cs.	"
Viscosity @ -10°C.	0.2563 cs.	"
Surface Tension -10°C.	20.88 dynes/cm.	"
Solubility in Water		
Solubility in		
Solubility in		
Flash Point °F *(Method)*	-78.0°C.	"
Fire Point °C		
Heat of Combustion		
Heat of Formation Liq. at 25°C.	-144.0 kcal/mole	"
Thermal Stability (cal./kg/min.)		
Latent Heat of Fusion	18.14 cal./g.	"
Latent Heat of Vap. at B.P.	79.53	"
Specific Heat Liq. at 293°K.	0.38 cal./g.°K.	"
Critical Temperature	156.5°C.	"
Critical Pressure	42000. mm.	"
Dissociation Constant		
Other Constants		
Toxicity *(Give Reference)*		

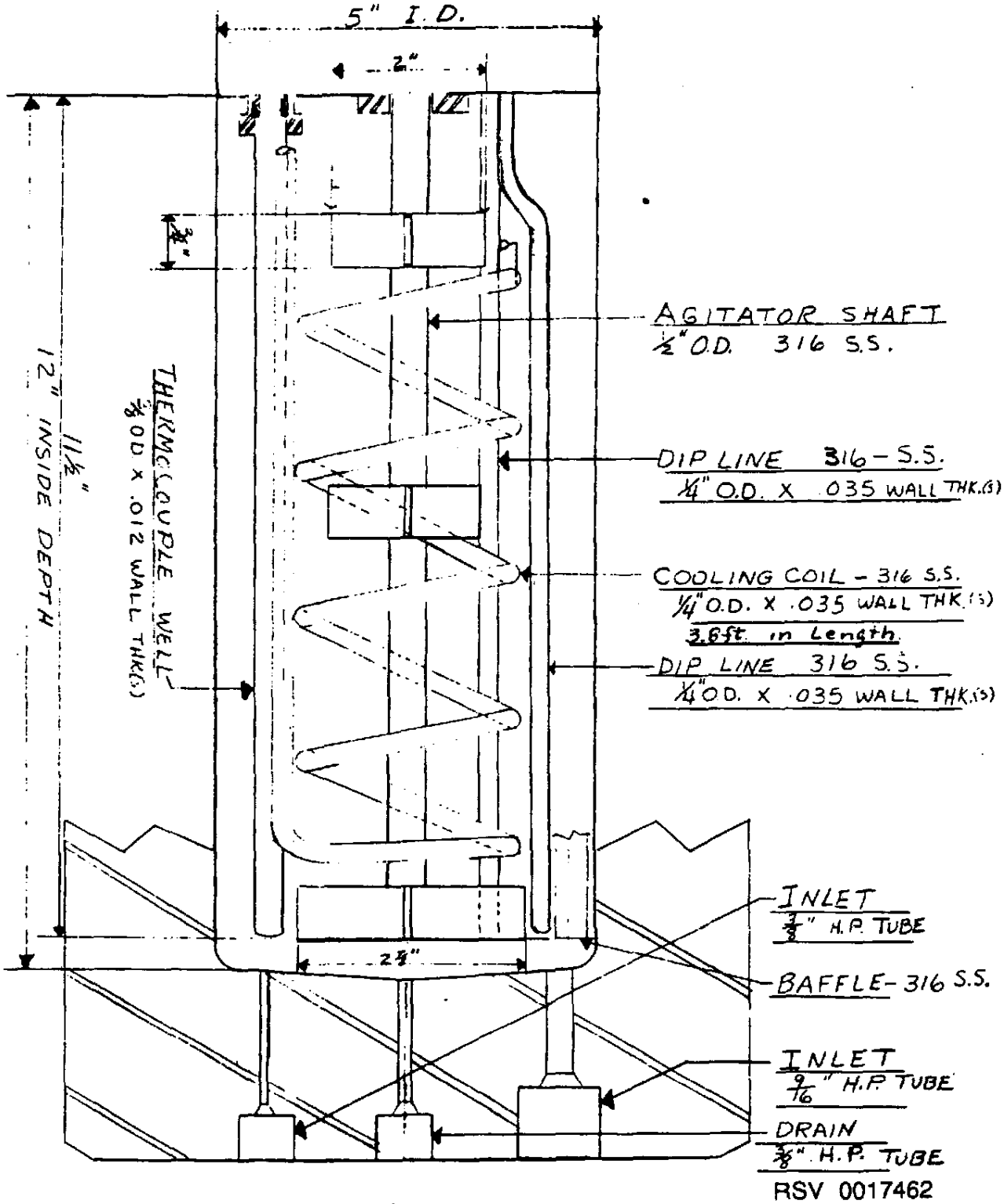
NOTE: *These data should not be released outside of Monsanto Chemical Company. Use additional sheets if necessary.*

APPENDIX A

LABORATORY AUTOCLAVE

APPENDIX A

Laboratory Autoclave



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1 GAL. AUTOCLAVE