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ACRYLIC RESIN MANUFACTURE
PROJECT: P-33

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"LUCITE"* ACRYLIC RESIN MANUFACTURE

BY: J. A. BURKE

Date Issued: 4/18/60
Project: P-33, New Polymer Alignment

PE-60-03

ABSTRACT

Information on plant scale manufacture of "Lucite"* acrylic resins is reviewed.

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I. SUMMARY

A. Origin of Investigation

Since 1954, Philadelphia Process Engineering has had the responsibility for scale-up and alignment of "Lucite"* acrylic resin manufacture in commercial plant equipment. Primary requirements were process development for plant scale operation, incorporation of process information in design of new facilities, manufacture of interim quantities in semi-works, and start-up of plant operations.

B. Objectives

1. Examination and refinement of polymerization processes for plant use.

2. Alter process conditions where dictated by equipment or production requirements.

3. Manufacture resins in interim quantities where plant operation was not feasible.

4. Assist plant production organizations in alignment for routine manufacture.

C. Results

1. Changes in raw materials, process conditions, process control, formulas, test methods and specifications were made in cooperation with Research.

2. Assistance was given to Flint, Parlin, and South San Francisco in designing facilities and starting manufacture of "Lucite"* resins at those locations.

3. Production of RC-909 in Toledo's 3000-gallon circulating resin kettle and Chicago's gas-fired resin kettle was demonstrated.

4. Process information was gathered so that scale-up problems with new variations of "Lucite"* resins could be minimized.

5. Blending limits for off-standard batches were obtained through Research and the Divisional Alignment Group.

6. **Assistance was given to "Lucite"* acrylic lacquer patent licensees for design and start-up of resin production facilities.**

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D. Recommendations

1. Alignment responsibility for "Lucite"* acrylic resins should be assumed by the Divisional Alignment Group.

2. Present plant operating conditions should be used as starting points for process development of new varieties of "Lucite"* resins by Research.

3. Batch size increases and changes to faster processes should be made by the plants involved.

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II. DISCUSSION

A. Introduction

Since the start of commercial manufacture of "Lucite"* acrylic resin at Flint in mid-1955, more than 4,000,000 gallons of the various resins have been produced. Most of the production took place at Flint, but Parlin and South San Francisco are now making significant quantities of the resins. The principal objectives of this report are to document the "know-how" gained since 1955 and to centralize other information pertinent to "Lucite"* resin manufacture.

The "Lucite"* resins referred to in this report are polymethylmethacrylate and copolymers of methylmethacrylate (MMA) with methacrylic acid (MAA), glycidyl methacrylate (GMA), ethyl methacrylate (EMA) or butyl methacrylate (BMA). These resins are polymerized in solution to molecular weight 65,000-105,000 using benzoyl peroxide (BPO) as the initiator. Heat of reaction is removed by refluxing monomers and solvent. The copolymer of MMA and GMA is reacted with anhydrous ammonia to form an hydroxy-amino methacrylate group in place of the epoxy methacrylate group in the original copolymer.

B. Acknowledgement

Most of the information in this report was developed by or in cooperation with other people. J. J. Sanderson, G. I. Mulholland, J. Blake, J. H. Lowell, C. M. Alsys, C. Ferstenberg and J. G. Schreckendgust of the Marshall Research Laboratory; C. R. DeBow, D. H. Stevenson and H. E. Newton of the Flint Plant; and C. J. Ryan of the Parlin Plant were especially helpful.

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C. PROCESS DESCRIPTION

During the period 1953-1960, a number of reports, letters, and formulas were written to describe processes and procedures to be used in "Lucite"* resin manufacture.

The chemical aspects of the polymerization are discussed in the following:

1. Marshall Laboratory Research Report No. 1228, "Development of a Batch Solution Polymerization Process for F. & F. Manufacture of OA Polymer", issued 1/20/53, written by C. Perstenberg.

2. Marshall Laboratory Research Report No. 1235, "Development of Solution Polymerization Process for OA Polymer - Laboratory Scale", issued 3/18/53, written by J. J. Sanderson.

3. Marshall Laboratory Memorandum Report M-595, "Manufacture of OA Solution Polymer", issued 6/3/53, written by C. M. Alsys.

4. Marshall Laboratory Research Report No. 1276, "The Development of a Short Cycle Polymerization Process for the Manufacture of OA Solution Polymer", issued 10/21/53, written by C. M. Alsys.

5. Marshall Laboratory Research Report No. R-58-29, "RC-917: Interim Process Development", issued 4/15/58, written by P. H. Roy.

Process scale-up and plant production are discussed in:

6. Philadelphia Process & Methods Group Report, "Manufacture of OA Resins", Study P-33 issued 7/55, written by J. A. Burke.

7. Letter J. A. Burke to J. S. Allen 3/19/56, "'Lucite'* Resin Manufacture - Plant Facilities and Operation." This letter is a supplement to Report (6).

8. Flint Process & Methods Group Report, "Instrumentation for 'Lucite'* Resin Manufacture", Study F-53, issued 6/1/56, written by E. A. Praschan.

9. Flint Plant Operating Instructions - "Manufacture of 'Lucite'* Resin in #2 Set Kettle" - 10/1/57.

The information contained in those reports will not be reproduced here except as necessary for continuity.

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Polymerization Conditions

"Lucite"* resins are made by the addition polymerization of methacrylate monomers in solution using benzoyl peroxide (BPO) as a free-radical initiator. The reactions are exothermic and use a time-temperature cycle for product control. Both monomers and polymers are soluble in the solvent system. In commercial production, heat of reaction is removed by refluxing monomers and solvent. There are no reaction by-products, such as water in esterification. Reaction temperature is at or above the atmospheric boiling point of the reaction mixture. The reactors operate under pressure when reaction temperatures are above the atmospheric boiling point.

Reaction temperature, reaction composition, and initiator concentration are adjusted to consistently produce polymer within a narrow average molecular weight range. Generally, conditions are selected to produce the shortest reaction cycles consistent with equipment capabilities. Resins made by a variety of processes have been shown to be alike as long as molecular weight and % conversion meet specifications.

Reflux cooling is used in plant operation because the peak exotherm of any of the standard processes cannot be removed by jacket cooling. Approximate peak exotherms for RC-909 are:

7.9	BTU/min.-lb.monomer	- 66-2/3%	monomer	- 100°C	(two-hour)
6.5	"	" - 50%	"	- 92°C	(six-hour)
5.9	"	" - 45%	"	- 92°C	(atmos.press.)

In a commercial scale production, 1900-gallon two-hour batches at Flint have normal peak exotherms of 49,000 BTU/min., 3400-gallon atmospheric pressure batches at Parlin peak at about 67,000 BTU/min. Solvent refluxing is used because the cooling area can be as large as necessary and heat transfer coefficients are higher for condensation of organic vapor than for conduction cooling of polymer solutions - 75 BTU/hr.-sq.ft.-°F vs. 50 BTU/hr.-sq.ft.-°F.

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General compositions of "Lucite"* resins are:

Code	Polymer Composition		Solvent Composition		% Solids
RC-909	100	MMA	30/70	H-30/H-47	40
RC-910	98/2	MMA/MAA	30/70	H-30/H-47	40
RC-913*	95/5	MMA/GMA	30/70	H-30/H-47	40
RC-914	95/5	MMA/GMA-P	41/59	H-30/H-47	30
RC-917	97.8/2.2	MMA/HAPMA	33/45/22	H-47/H-69/H-583	25
RC-918**	97.8/2.2	MMA/GMA	42/58	H-47/H-69	30
RC-921	60/40	MMA/EMA	30/70	H-30/H-47	44
RC-923	50/48/2	MMA/EMA/MAA	50/50	H-30/H-47	40
RC-927	50/45/5	MMA/EA/MAA	30/70	H-35/H-47	40

MMA - methyl methacrylate
EMA - ethyl methacrylate
BMA - butyl methacrylate
GMA - glycidyl methacrylate
GMA-P - glycidyl methacrylate - phosphated
HAPMA - hydroxy amino propyl methacrylate (GMA ammoniated)
EA - ethyl acrylate

* Intermediate for RC-914 - not active
** " " RC-917 - obsolete

Reaction conditions used in the preparation of these polymers are shown in Table No. 1.

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TABLE NO. 1

"LUCITE"* ACRYLIC RESIN POLYMERIZATION CONDITIONS

	% Monomer	Solvent Composition		Time	Temp.	Kettle Pressure	BPO Concen.	Remarks
RC-909	66-2/3	70/30	H-30/H-47	2 hrs.	100°C	14-28 psig	0.53 %	Reg.Prod.-Flint - 1900 G.
"	66-2/3	70/30	H-30/KH-1105	2 "	100°C	14-28 "	0.65	" " -SSF - 1900 G.
"	45	23.7/76.3	H-30/H-49	10 "	92-88°C	Atm.	0.47	" " -Parlin- 3500 G.
"	50	30/70	H-30/H-47	6 "	92°C	6-11 psig	0.52-0.48	Initial Prod. at Flint, SSF, Chicago
"	60	70/30	H-30/H-47	4 "	100°C	14-28 "	0.50	Temp.Prod. at Flint - reduce exotherm
"	45	23.7/76.3	H-30/H-49	12 "	92-88°C	Atm.	0.60	Parlin-Copper Ket.-1600 G.
"	50→40	30/70	H-30/H-47	8 "	92°C	5 psig	0.44	Toledo Circulating Resin Kettle - 1500 G.-Exp'l
RC-910	66-2/3	70/30	H-30/H-47	2 "	100°C	14-28 psig	0.61 %	Reg.Prod.-Flint - 1900 G.
"	66-2/3	70/30	H-30/KH-1105	2 "	100°C	14-28 "	0.75	" " -SSF - 1600 G.
"	45	23.7/76.3	H-30/H-49	10 "	92-88°C	Atm.	0.53	" " -Parlin- 3500 G.
"	50	30/70	H-30/H-47	6 "	92°C	6-11 psig	0.53	Initial Prod. at Flint, SSF - 1000 G.
RC-913	66-2/3	70/30	H-30/H-47	2 "	100°C	14-28 psig	0.82 %	Obsol.-Flint - 1400 G.
"	50	30/70	H-30/H-47	6 "	92°C	6-11 "	0.65	" " - 1400 G. Intermediate for RC-914
RC-918	50	70/30	H-47/H-69	6 "	92°C	4-8 psig	0.61 %	RC-917 Intermediate - Flint - 1600 G.
RC-921	60	60/40	H-30/H-47	6 "	92°C	9-22 psig	0.48 %	Flint - 1400 G.
RC-923	40	50/50	H-30/H-47	14 "	85°C	7-18 psig	0.35 %	Flint-750 G.(Unsatis.-Low Conv.-Low Mole.Wt.)
"	60	70/30	H-30/H-47	6 "	92°C	12-24 "	0.34	Marsh.Lab.S/W - 100 G.
RC-927	40	30/70	H-35/H-47	6 "	95-91°C	Atm.	0.495%	Marsh.Lab.S/W - 100 G.

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Monomers and solvents are used as received. Two items receive special attention; methacrylic acid which freezes at about 60°F is mixed in the drum prior to use to distribute inhibitor which separates on freezing, and benzoyl peroxide initiator is put into solution then assayed to get precise control of concentration.

Monomer, solvents and initiator solution are pumped into the empty kettle from weigh tanks or through meters. Agitation is begun and heat-up started. The reflux condensate return line is closed and the vent from the reflux receiver open so that the gases venting from the system during heat-up must pass through the condenser where solvent vapors will be condensed. When condensate shows in the receiver sight glass, the return line is opened because the liquid acts as a seal against vapor passage. Heat-up continues until the atmospheric boiling point of the kettle charge is reached; at this point the batch is allowed to boil to sweep most of the non-condensible gases from the system. Boiling is allowed to continue for about 5 minutes to insure sufficient reduction of inerts, to check the operation of the condenser at a non-crucial stage and to help keep the condenser tubes free of polymer by bathing them with condensing monomer and solvent.

In an atmospheric pressure reflux process, heating is stopped short of the boiling point to allow residual heat to dissipate before initial boil because it is the start of the reaction time and the peak of the exotherm. Heat is supplied to the batch by the exothermic reaction and removed by refluxing monomer and solvent. Reaction temperature is dependent on the composition of the batch and therefore drops during the reaction as monomer changes to polymer to alter the mol % of solvents and monomers present.

In a pressure reflux process, the kettle vent is closed after the 5-minute boil. Heating is continued until a predetermined temperature, short of the desired reaction temperature, is reached. Residual heat from the system and exothermic heat carry the temperature up to the desired level. Temperature rise is halted by dropping the condenser water temperature to increase refluxing. Temperature control is maintained by balancing heat gain due to exotherm with heat loss by reflux and radiation. Often, migration of non-condensible gases into the condenser reduces the effective area of the tubes so that cooling capacity is insufficient even with the coldest water. When that happens, the condenser must be vented to restore the area. Care must be exercised to minimize batch foaming when the pressure drops and to avoid over-cooling the batch with a cold condenser. In practice, a pressure drop of 1/4 psig with the condenser water either hot or not flowing has been found to be about a maximum if trouble is to be avoided. Since high viscosity magnifies any foaming problem, it has also been found advisable to vent the condenser deliberately, shortly after coming to temperature since a later vent can then usually be avoided.

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The same changes that cause a drop in reaction temperature with constant pressure cause an increase in pressure with constant temperature. In two-hour RC-909 batches, increases of pressure from 14 psig to 24 psig are common, the exact figures depend on precise temperatures and the amounts of non-condensible gas in the system.

As the exotherm diminishes, a point may be reached where it no longer can keep the batch temperature up to the desired level in the face of heat loss to minimal reflux plus radiation. Two techniques are used to help overcome this situation which otherwise leads to low conversion. In Parlin's atmospheric pressure, jacketed kettles, hot water (not steam) is used to supply heat and the condenser water temperature is allowed to rise to decrease reflux. In the gas-fired kettles at Flint and South San Francisco no heat can be supplied but condenser water temperature is allowed to rise and inert gas pressure is put on the kettle to raise the batch boiling point so that the residual exotherm can heat the batch.

"Lucite"* resins cannot be heated with steam or gas fires in the late stages because the polymer will "plate out" on the hot surface to stop heat exchange. For this reason, much of the process design is predicated on temperature conservation. In the case of RC-917 which must be ammoniated at an elevated temperature after thin-down, the thin-down solvents are heated to avoid a batch temperature drop.

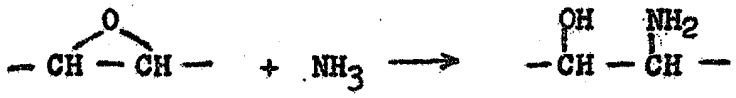
After thinning at the end of the prescribed reaction time, the batch is ready for filtration. Gel particles, initiator fragments and miscellaneous foreign matter are removed by filtration through paper. This filtration has been proven necessary on a number of occasions, gel particles getting into the dispersion system cause "grit" trouble. The throughput for a filter between changes may vary from 15 gallons to 500 gallons per square foot of surface as the cleanliness of the resin varies and seems most sensitive to resin gel particles which blind the filter paper. Filter aid and press precoating are not usually used.

In addition to the two processes in regular use for RC-909 manufacture; the two-hour process at Flint and South San Francisco and the atmospheric pressure process at Parlin, three other processes have been used for regular and special production. A six-hour, 92°C, 50% monomer polymerization was used in start-up at Flint and South San Francisco and for demonstration at Chicago. A twelve-hour, 92-88°C, 45% monomer polymerization with extra initiator was used to make RC-909 in Parlin's copper UF kettles for a time. RC-909 manufacture was demonstrated in Toledo's circulating resin kettle using an eight-hour polymerization at 92°C with 50% initial monomer concentration and progressive dilution to 45% and 40% for viscosity reasons.

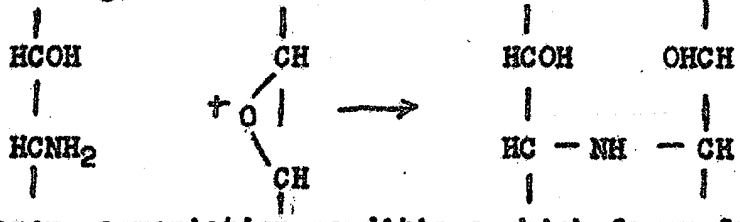
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Ammoniation Conditions

RC-917 manufacture requires preparation of a 97.2/2.2 MMA/GMA solution copolymer and subsequent reaction of the epoxy group of the GMA with ammonia to form adjacent hydroxy and amine groups.



If the reaction is not fast or complete enough, crosslinking which results in gelation can occur:



For this reason, ammoniation conditions which favor fast, complete reactions are used. Reaction temperatures that represent practical maximums for the thinned resin are obtained by heating the thin-down solvent to within a few degrees of the boiling point before charging it to the kettle. Ammonia pressures of 40 psig, the maximum allowable for the Flint kettle, are used to get the highest concentration of dissolved ammonia.

At the end of the ammoniation period, the excess ammonia is removed by distillation. The kettle pressure is cautiously dropped with the vapor going through the condenser so that solvent boiling off with the ammonia is condensed and returned to the kettle. Kettle pressure is reduced to 100 mm Hg absolute using a vacuum pump. Care must be taken to avoid excessive foaming because during the pressure reduction the batch boils and, as it reflux cools, gets more viscous. The batch is held at 100 mm Hg abs. pressure for one - five hours to get the free ammonia content of the resin down to the specified 0.08% max. level.

Process Peculiarities

Two main considerations override all others in scale-up: molecular weight and temperature control. As batch size increases, initiator level may have to be decreased to hold molecular weight constant. Chart No. 1 shows the adjustments made in the RC-909 initiator concentration as batch size is increased. Adjustments must be made in the six-hour process but not either the two-hour or atmospheric pressure processes which bracket it.

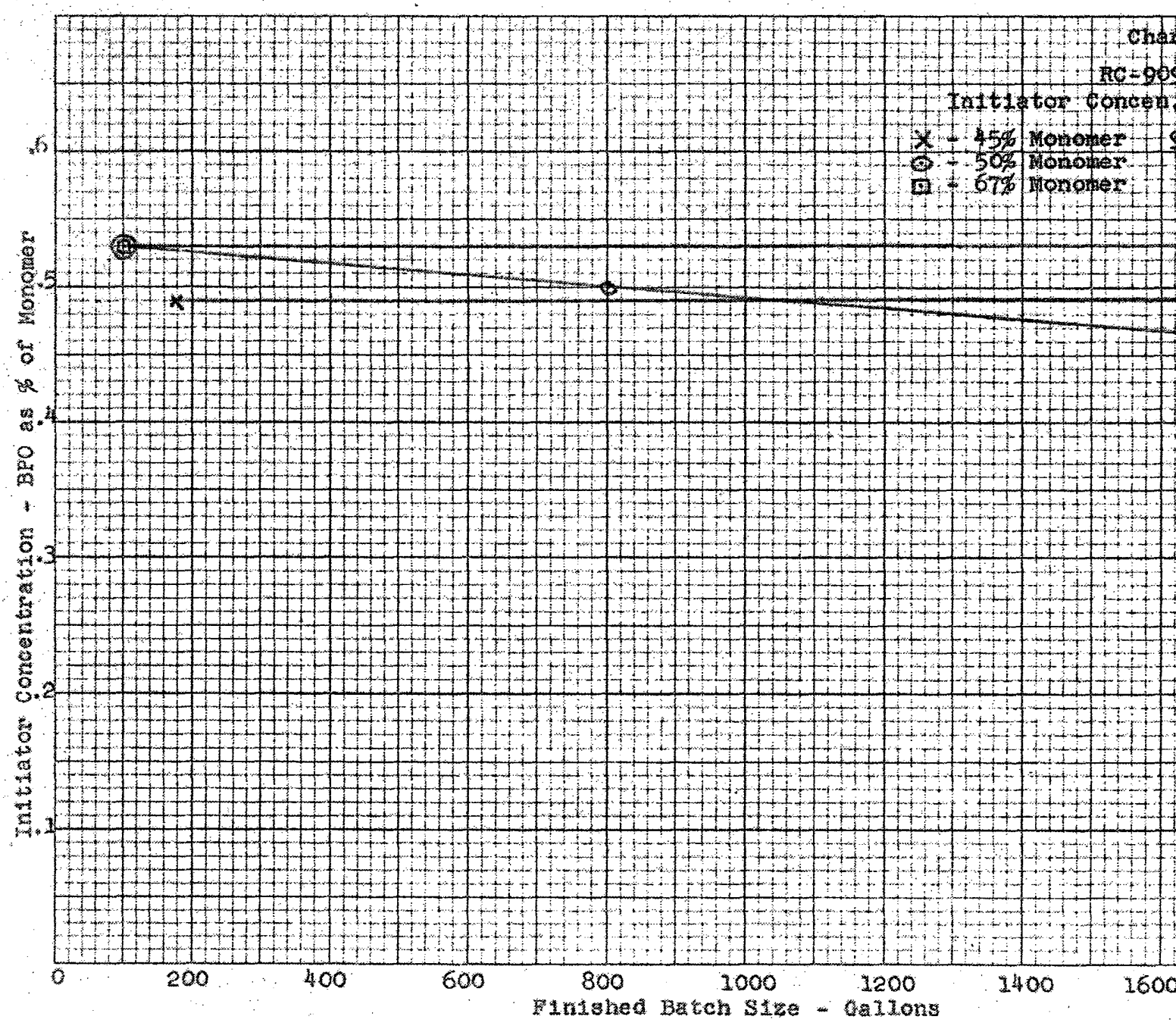
As might be expected in six years of operation, certain incidents or conditions have occurred to change process or product characteristics. In addition, some devices have been developed to avoid undesired process conditions. The history of "Lucite"*

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resin manufacture has been marked by a low incidence of "mystery" batches that either did not process normally or produce poor quality polymer. Of more than 2,500 factory batches made, less than 1% did not process normally and only one or two were not useable.

Raw material contamination caused trouble in RC-909 and RC-910 manufacture at South San Francisco. A major increase in RC-910 molecular weight was caused by methacrylic acid contamination by copper from a brass spigot on the drum. Discarding the contaminated acid and use of a stainless steel spigot corrected this. An overcharge of hydroquinone to a methylmethacrylate shipment by Polychemicals caused an increase in molecular weight of both resins which was compensated for by an increase of initiator concentration.

When RC-909 was made by the atmospheric pressure process in Parlin's copper U.F. resin kettles, it was found necessary to use a 0.60% BPO concentration instead of the 0.47% concentration used in stainless steel equipment. The polymerization inhibiting effect of the copper had to be overridden.

On two occasions, "run-away" reactions occurred in semi-works manufacture of RC-909 when an interruption of heat-up took place. In both cases, the batch was heated to 70-75°C then cooled when a mechanical failure occurred. Re-heating was started after delays of one-two hours. The exotherm on heat-up to reaction temperature was much more violent than normal and rupture discs were blown both times.

Consecutive manufacture of more than two batches of RC-913 at Flint had to be discontinued because of "popcorn" polymer formation. It was theorized that uninhibited glycidyl methacrylate monomer collected in pockets in the reflux system and started to autopolymerize to "popcorn" polymer. In subsequent batches the "popcorn" was washed back into the kettle where it seeded further popcorn formation. When care was taken to make several batches of RC-909 or RC-910 between each batch of RC-913, the problem disappeared. This situation did not hold with RC-917 manufacture, possibly because of the presence of isopropanol or because the ammoniation procedure causes any GMA present in the system to change to a non-reactive compound.

Stripping unreacted ammonia from RC-917 at the end of the ammoniation period is extremely difficult if there is even trace contamination of the resin with acetone. Ammonia reacts with the acetone to form an unstable compound that will not decompose during the stripping process, but does during the analytical test for total ammonia. The effect of making a batch of RC-909 or RC-910 in the RC-917 kettle can be noticed for a number of batches afterward. Contamination of RC-917 with acetone can also lead to the formation of brown compounds when the ammonia combines with the acetone.

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If the heat of reaction cannot be removed at a proper rate, the batch temperature will rise causing, in turn, the rate of heat generation to increase further. Unless this "snowballing" can be halted a runaway reaction will occur. Some correspondence on this subject is reproduced in the Appendix.

D. RAW MATERIAL PROPERTIES

Table No. 1 lists physical and chemical properties of the monomers used in "Lucite"* resin and some other commonly used monomers. The solvents used are acetone, toluene, xylene, and isopropanol; since they are common in our business, no descriptions are included here.

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TABLE NO. 1

PROPERTIES OF COMMONLY USED VINYL MONOMERS

Name		Methyl Methacrylate	Ethyl Methacrylate	Butyl Methacrylate	Glycidyl Methacrylate	Ethyl Acrylate	Ethyl Acrylate	Butyl Acrylate	Methacrylic Acid	Methacrylic Acid	Styrene	Acrylonitrile
Code		H-428	KH-1783	H-692	CP-105	KG-5625	KG-5727	G-723	G-285	G-475	H-627	G-481
Symbol		MMA	EMA	BMA	GMA	EA	EA	BA	MAA	MAA	S	AN
Mol. Wt.		100.11	114.14	142.19	142.15	100.11	100.11	128.17	85.08	85.08	104.14	53.06
Gal. Wt.	25°C	7.82	7.62	7.46	8.94	7.65	7.65	7.54	8.44	8.44	7.52	6.72
Sp. Gr.(60°F/60°F)	25°C	0.940	0.917	0.899	1.078	0.917	0.917	0.894	1.012	1.012	0.902	
Viscosity	25°C	0.53cp	0.65cs	1.05cs	2.05cs	0.6cs	0.6cs	.96cs	1.3cs	1.3cs	0.73cp	0.34cp
Refractive Index	n_{D}^{25}	1.412	1.411	1.426	1.448	1.403	1.403	1.416	1.428	1.428	1.544	1.388
Purity		99.5	98.8	98.0	98.0			97-99%	97-99%	97-99%	99.3	97% min.
Moisture Content		0.05	0.08%	0.15%	0.05	0.03	0.03%	0.18%	0.5%max.	0.5%max.	0.04%	
Inhibitor		HQ	HQ	HQ	MEHQ	HQ	MEHQ	HQ	HQ	HQ	tBC	HQ
Inhibitor Concen.	ppm	45-65	55	20-30	20	1000	200	100	1000	500	10-15	20-30
Boiling Point	°C	100	118.5	163	190	99.5	99.5	146	159-163	159-163	145.2°	77.3
Flash Point	Open Cup	75°F		132°F	183°F	50°F	50°F	105°F	170°F	170°F	88°F	32°F
Freezing Point		-48°C		<-75°C		<-75°C	<-75°C	∝ -50°C	14-16°C	14-16°C	-30.6	-83°C
Heat of Vaporization	BTU/#	155	130	111		149	149	128	139	139	185	264
Heat of Polymerization	BTU/#	234	205	171		281	281	253	334	334	289	604
Solubility 25°C in water		1.5%		2.0%		1.5%	1.5%	0.16%	∞	∞	0.03%	7.3%
Explosive limits in air		2-12.5%	1.8%-Sat			1.8%-Sat.	1.8%-Sat.	1.0%-Sat.	-	-	1.1-6.1	3-17%
Producers		duPont R&H	duPont R&H	duPont R&H	duPont	R&H Carbide Celanese Dow	R&H Carbide Celanese Dow	R&H Carbide Celanese Dow	duPont R&H	duPont R&H	Dow Koppers	Carbide Cyanamid Monsanto duPont (future

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C
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CC: F. H. BEADLES - WILMINGTON
J. S. ALLEN - "
C. R. DE BOW - FLINT

Philadelphia Plant
July 3, 1958.

R. H. BELL
PARLIN

ATTENTION: C. A. DORAN

M. L. BYRON
SOUTH SAN FRANCISCO

ATTENTION: H. C. ANDERSON

"LUCITE" ACRYLIC RESIN MANUFACTURE
RUN-AWAY REACTIONS
PROCESS ENGINEERING

We have been requested to review the causes of run-away "Lucite" polymerizations, the procedures to be followed to avoid them, and the actions to take if they occur. Since both Flint and Parlin have recently experienced a run-away reaction with attendant danger to personnel and equipment, the information should be of more than academic interest.

"Lucite" resins are made by exothermic polymerizations that proceed at rates varying with temperature, monomer concentration, and initiator concentration. If the heat of reaction is not removed as fast as it is generated, temperature must go up and with it the rate of heat generation; the interaction of these two brings on an "avalanche effect". The two-hour process, 66-2/3% monomer @ 100°C., has a normal peak exotherm of 7.9 BTU/min./# monomer which will raise the reaction mass temperature 5.8°C/min. if not removed. The six-hour process, 50 monomer @ 52°C., has a normal peak exotherm of 6.5 BTU/min./# monomer which will raise the reaction mass temperature 3.6°C/min. if not removed. In a closed system, pressure rises exponentially with temperature to provide a hazard to personnel and equipment because relieving high kettle pressures through rupture discs or relief valves puts large amounts of hot concentrated vapors into the atmosphere. The escape of solvent during heavy venting increases the batch viscosity so that the agitator may stall and the batch take on some of the characteristics of glass.

Since 1954, more than 800 batches of "Lucite" resin have been made; in that time there have been four run-away reactions. All of the run-aways occurred with the two-hour process but there have been several close calls with the six-hour process. Avoidance of run-away reactions requires meticulous attention to: equipment design, equipment maintenance, operator training, operating technique, process monitoring, and emergency procedures.

DUP030002238

Equipment Design

Consideration of this aspect is particularly important when existing resin units are being converted to "Lucite" production. Characteristics that require prime attention are: condenser design to obtain sufficient cooling surface and avoid flooding, pressure capabilities of the components, reflux return capacity, agitation type and power, instrumentation, relief valves, and systems for loading and discharging the batches.

Equipment Maintenance

Programmed inspection and repair systems must be used to avoid equipment failure during a batch. Instrument calibration, agitator seals, condenser shell-side fouling, pump and valve packing, and safety devices are some items that should receive routine attention.

Once a week, a mixture of acetone and toluene should be refluxed to remove any polymer deposits from the condenser and reflux system and the kettle walls. This mixture can be used in the "Lucite" batch that follows.

Operator Training

Because the "Lucite" process represents a substantial change from alkyd or U.F. resin processes, special attention must be given to operator instruction. It is especially important that the operator understand the chemical process and the principles of the temperature control system so that manual process control can be used in the event of instrument failure. The operator ought to be able to recognize the symptoms of an out-of-control situation such as: full reflux receiver, low condenser ΔT, rising kettle pressure, rising foam layer, poor response to control action, or poor control response to temperature rise, and take corrective action before the batch becomes a run-away. The best time for this training is on equipment start-up because that is the time when things are most likely to go wrong.

Operating Technique

After the operation has been aligned, an operating manual should be prepared and reviewed with the operators. The foreman should make sure that the prescribed operating technique is used by all operators. Refinements of operation should be incorporated into the manual as they develop. The operations over which the operator has control, such as: the kettle vent during heat-up, the condenser check during heat-up, and the time external heating is stopped, must be standardized.

Process Monitoring

Gradual changes in batch behavior provide information about changes in: operating technique, condenser efficiency, initiator analysis, reflux return system, and automatic control precision. Recognition of the changes and correction of their causes will help to avoid ragged operation that may result in a lost batch. Operators should be trained to recognize these changes and call them to the foreman's attention.

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Emergency Procedure

In the event that a batch does get out of control, two steps can be taken to prevent a run-away. The first step lowers the monomer concentration to lower the reaction rate, the second stops the reaction and is intended to protect the equipment.

1. Solvent Addition:

   Add all the thin-down solvent. This will reduce the exotherm in proportion to monomer concentration change and also provide cooling from the heat capacity of the solvent. Allow the batch to return to its former designated reaction temperature and extend the cycle by two hours.

2. $FeCl_3$ Termination:

   If solvent addition does not lower the exotherm enough to secure control, the reaction can be terminated by the addition of a 10% solution of ferric chloride in acetone to provide 1.5 lb. $FeCl_3$/lb. of benzoyl peroxide used in the batch. Since $FeCl_3$ solutions are corrosive, stand-by quantities should be stored in a glass, herisite, epoxy or karbate-lined pressure vessel so that they can be added by gas pressure in case of a power failure.

It is essential to avoid over-delay in using the emergency procedure because the residual heat and pressure plus the addition generated while the procedures are being carried out may make them ineffective. As soon as the operator realizes that the controls are not holding the temperature down, step I should be started.

In order to decrease the possibility of a run-away reaction, the two-hour process is being changed to use 60% monomer instead of 66-2/3%. This reduces the peak exotherm by 10% and makes the reaction mass less viscous. Initial checks of conversions vs. time indicate that no cycle extension will be necessary.

PROCESS ENGINEERING
C. F. KALB, MANAGER

BY: J. A. BURKE /s/

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C
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cc: J. A. Burke - Philadelphia
J. S. Allen - Wilmington

Flint 2, Michigan
July 29, 1958

H. R. STINE)IN
L. S. BAKER)TURN

"LUCITE" ACRYLIC RESIN MANUFACTURE
PREVENTION OF RUN-AWAY BATCHES
FLINT PLANT

A copy of J. A. Burke's letter of July 3, 1958, is attached. The letter lists six main points in avoiding run-away batches. Paint and Resin Area comments are listed below and follow the outline of J. A. Burke's letter.

Equipment Design

No comments.

Equipment Maintenance

A regular procedure has been established for cleaning the shell side on each "Lucite" Resin condenser with acid every three months. Instrument calibration is not scheduled periodically and with three independent temperature indicators the calibration does not seem necessary. The pressure relief valve is checked once each week with inert gas pressure. Replacement of electronic tubes is scheduled on an arbitrary six month basis. A mixture of Acetone and Toluene is boiled for two hours in each "Lucite" kettle each week. The mixture is converted into a four-hour batch of RC-909.

Operator Training

The Paint Area has five thoroughly trained "Lucite" Resin operators. Two additional operators are being trained. All operators can recognize the symptoms of an out-of-control batch and all know what corrective action to take.

Operating Technique

Some time ago, Flint prepared an operating manual. The manual needs revising to include reference to the four-hour process, RC-917, the setting of control point on TC-2 so that water application to the condenser will start at 203°F. and how much increase in temperature the condenser should undergo during the seven minutes of atmospheric boil.

DUP030002241

H. R. Stine
L. S. Baker

July 29, 1958

Process Monitoring

During the course of the year, the supply of water for the condensers changes from a high of 75 in the summer to a low of 36 during the winter months. This change does require an adjustment in the setting of the index of the condenser water controller. The foreman of this operation fully understands this situation.

Emergency Procedure

The Paint and Resin Area subscribes to methods No. 1 and No. 2 as presented. Method No. 2 will require the expenditure of some money to provide a 100-gallon vessel capable of withstanding 100 pounds of operating pressure and necessary pipe lines.

The last paragraph of Burke's letter is incorrect with respect to the length of time required to complete the polymerization of materials charged on the 60 per cent solids basis. Our index now indicates that four hours are required to reduce the monomer content below 2 per cent.

C. R. DEBOW /s/

CRD:nl
Attach.
(11)

DUP030002242

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Y

cc: J. A. Burke - Philadelphia
J. S. Allen - Wilmington

Flint 2, Michigan
December 15, 1958

H. R. STINE) IN
L. S. BAKER) TURN

"LUCITE" ACRYLIC RESIN MANUFACTURE
PREVENTION OF RUN-AWAY BATCHES
FLINT PLANT

C. R. DeBow's letter of July 29, 1958, regarding the above subject, with reference to J. A. Burke's letter of July 3, 1958, is revised to bring up to date procedures and practices followed by the Resin Area.

Equipment Design

Two 850-gallon solvent hold tanks have been made available to store thinning solvents for "Lucite" resins in process. Upon completion of the resin cook the solvents are pumped directly to the kettle when the batch is thinned. A high speed pump, 90 GPM, is used for this purpose.

Equipment Maintenance

A regular procedure has been established for cleaning the shell side on each "Lucite" Resin condenser with acid every two months. Instrument calibration is not scheduled periodically and with three independent temperature indicators the calibration does not seem necessary. The pressure relief valve is checked once each week with inert gas pressure. Electronic tubes for the kettle controls are not being replaced on an arbitrary six month basis. If any tubes should go bad, they can be immediately replaced with ones held in stock. A weekly solvent boil of Acetone and Toluene is no longer considered necessary to clean the equipment of hardened residual resin. The solvents refluxing during batch manufacture are deemed entirely satisfactory for this purpose.

Operator Training

The Resin Area has six thoroughly trained "Lucite" Resin operators. One additional operator is being trained for vacation and sickness relief. All operators can recognize the symptoms of an out-of-control batch and all know what corrective action to take.

DUP030002243

H. R. Stine
L. S. Baker

December 11, 1958

Operating Technique

Flint's "Lucite" Resin operating manual needs revision to include reference to the two hour process for RC-917. Since this process is not yet in operation, the revision will be delayed until actual operating experience has been gained.

Process Monitoring

During the course of the year, the temperature of the water supplied to condensers varies from a high of 75 in the summer to a low of 36 in the winter. This change requires an adjustment in the setting of the index of the condenser water controller. The foreman of this operation understands this situation.

Emergency Procedure

The Resin Area subscribes to method No. 1 wherein the thinning solvents are charged to the kettle in the event of a runaway batch. Inasmuch as these solvents are immediately available by virtue of the hold tanks and high-speed pump described under Equipment Design, we do not feel that additional facilities for process termination are necessary.

H. R. STINE, PLANT MANAGER

By: W. W. Jaeger /s/

WWJ:nr
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