EP P-634

Vinyl-Vinylidene Chloride Copolymers by Conoflow for Vinyl Asbestos Floor Tile

Part II. Semi-Plant Scale Up

by

W. G. MacPherson - C. D. Parker
F. M. Poindexter

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Vinylidene Chloride: polymer-co; vinyl chloride, properties

SUMMARY for floor tile,

This work is concerned with a study of polymerization variables and resin properties of vinyl-vinylidene chloride copolymers in a composition range of 85% to 91.0% vinyl chloride. Resins were prepared in both 50 gallon and 750 gallon Pfaudler glass lined reactors. Polymerization variables, composition distribution and polymer granulation data are presented and discussed. Physical properties of these resins, both alone and in floor tile formulations are compared with VYHH, the leading commercial resin in this field.

INTRODUCTION

The initial work in the development of a vinyl-vinylidene chloride copolymer resin for floor tile applications in 20 gallon Pfaudler type reactors has been presented in Saran Polymerization report EP P-547. It was hoped that a single resin composition could be produced having properties that would satisfactorily fit it into both fields of application. As a result some difference of opinion existed among various Coatings Technical Service groups as to the exact resin composition. It was decided to initiate a scale-up in both the 50 gallon and 750 gallon reactors to obtain the following information:

1) To gain information on possible scale-up problems.
2) Prepare resins having a composition of 85% and 88% vinyl chloride-15% and 12% vinylidene chloride in the 750 gallon reactor for a complete evaluation and a final decision on polymer composition.
3) To obtain resin in sufficient quantity to have a plant floor tile run made and prepare 5000 sq. ft. of floor tile. This tile was to be placed in service on the floors of the C. C. Kennedy Research Laboratory.

EXPERIMENTAL

Resins were prepared by suspension polymerization in glass lined 50 gallon and 750 gallon Pfaudler reactors. All resins were produced using the technique of automatic addition of mixed monomers by pressure. Resins were evaluated by the following lacquer and floor tile tests as recommended by the Asphalt Tile Institute.

Plasticizer Absorption or P.A.

152 grams of resin with 10 grams of Tribase E were premixed on a Kitchenaide mixer. 68 grams of plasticizer (18 pts. dioctyl phthalate, 50 pts tricresyl phosphate) was then added at slow speed over a period of 20 seconds, then stopped and the mixture checked for wetness. Resin was then mixed at high speed for an additional 20 seconds and checked again for wetness.

A plasticizer absorption No. 1 = dry free flowing mix.
A plasticizer absorption No. 6 = wet, paste mix.

Baker Perkins Flux

The following materials were premixed on a Kitchenaide Mixer:

152 grams Resin
68 grams Plasticizer (18 pts. DOP-50 pts. TCP)
10 grams Tribase E

This mixture was then placed in a Baker Perkins mixer at a temperature of 275°F and mixed until fused. The time to fuse this mixture is known as the initial flux time. To the above then was added the following:

36 grams Piccopale
320 grams Lesamite
115 grams No. 18 graining sand
54 grams TiO_2 (No. 510)

The mixture was then milled at the same temperature of 275°F until fluxed. The time to fuse this mixture is known as the final flux time.

Two Roll Mill Test

The following materials are dry blended.

300 grams resin
6 grams lead stearate

The rolls of a two roll compounding mill are adjusted so both are at a temperature of 200°F. The dry blend is then placed on the rolls and milled until it completely fused and banded on the rolls. The time to fuse and band is recorded as the flux time.

Floor Tile Recipe

210	grams	resin
27	"	plasticizer (DOP)
27	"	plasticizer Monoplex S-38
228	"	asbestos shorts (7 mm)
477.6	"	Lesamite ($CaCO_3$)
150	"	No. 18 graining sand
60	"	TiO_2 (R 510)
18	"	Metasap No. 624
1.2	"	aluminum stearate
1.2	"	paraffin wax

The above materials are dry blended and the plasticizer added. It then is fluxed on a two roll mill at a temperature of 280°F (front roll) and 230°F on the back roll. The fused material is then given two passes through a calender and then cut into 6 inch squares for testing.

Indentation

This test utilizes the McBurney Indentation Tester. The tile is subjected to a 30 lb. weight on a 1/4" ball for periods of one minute and ten minutes. The resulting indentation of the tile is measured and recorded in mils.

Impact

In this test a 1" diameter ball weighing 0.143 lbs. is dropped through a distance of 10 inches or 20 inches striking the tile.

The number of drops required to produce a fracture is recorded as the impact strength.

Dimensional Stability

A 6" x 6" tile is conditioned at 77°F for 15 minutes and then carefully measured. It then is placed on a steel plate and exposed to a temperature of 180°F for a period of 6 hours. After which it is cooled to room temperature. After again being conditioned at 77°F for 15 minutes it carefully is measured a second time. A change in tile dimensions, either plus or minus, is recorded as the dimensional stability in mils.

Heat Distortion

These tests were determined on a Boyer apparatus on flash molded samples of resin.

Tinius Olson Flow

This test was made on numerous samples of resin to try and determine if it were a more realistic test than the Baker Perkins in determining flux characteristics of the resins. A pelletizer was made up of stainless steel to prepare polymer pellets for testing. This consisted of a 3/8" hole bored into a block of steel and a plunger of the same dimension. The block is filled with polymer, the plunger inserted and this subjected to a pressure of 7600 lbs/sq. in. in a Preco Press. The compressed pellets then are run on a Tinius Olson at temperatures of 150°, 160° and 170°C at a constant pressure of 300 lbs/sq. in. Graphs were prepared, plotting time in seconds to flow 1" vs. temperature.

Brookfield Solution Viscosity

38 grams of resin are dissolved in 152 grams of a mixture of 2 pts methyl ethyl ketone to 1 pt. toluene. Solutions are held at a constant temperature of 25°C for a period of 16 hours, and the viscosity measured with a Brookfield Viscosimeter.

SECTION I

DISCUSSION

A total of eight polymerization runs were made in the 50 gallon reactors, none of which gave evidence of any scale-up problems. Polymerization and processing data on these runs are presented in Table I. The variables in these runs were in the granulator recipe, catalyst system, agitation and the percent monomer added to initiate polymerization. Although each run was charged the same i.e., 91% vinyl chloride-9% vinylidene chloride, the analyzed compositions varied from 80% to 92% vinyl chloride. This may be due to errors in the analysis, in weighing the monomer charge, incomplete mixing of the monomers or a combination thereof.

Absolute viscosities averaged approximately 1.05 with two exceptions, B5-1345 and B5-1346. These two runs had an average viscosity of approximately 0.97 which is considerably lower than the rest of the series. Data in Table I indicates two possible causes.

1. Higher vinylidene chloride content by analysis. This would result in lower resin viscosity as vinylidene chloride is a good chain transfer agent.
2. Slower agitation speed.
   This may effect the resin viscosity if the agitation is slow enough to result in poor heat transfer in the reactor. This could result in localized overheating or hot spots which would tend to reduce the resin viscosity.

Flux times on both the Baker Perkins and the two roll mill were quite uniform except for run B5-1347. This run had a flux time on the two roll mill of 2 minutes as compared to approximately 30 seconds for the others. It is suggested that the high O-D-B viscosity of this resin is due to a composition distribution containing high vinyl chloride fractions. If true, this would result in a higher viscosity and longer flux time at the same average composition level.

P.A. or plasticizer absorption is a function of polymer granulation and appears to be greatly influenced in this recipe by agitation. Referring to Table No. 1, runs B5-1345 and B5-1346 were made at an agitation speed of 120 RPM. Each had a P.A. of No. 4 indicating a wet resin-plasticizer mix. In comparison runs B5-1347 thru B5-1352 which were prepared at 150 RPM had P.A. values from 1 to 3 indicating a relatively dry, free flowing mix.

Figures 1 and 2 present graphically the Tinius Olson Flow and Heat Distortion data on these resins. With one exception, flow viscosity and heat distortion values are comparable to those obtained on resins prepared in the 20 gallon reactors at the same composition level. (Refer to Saran Polymerization Report No. EP P-547.) It is interesting to note that resin B4-1347 has a much higher flow viscosity and higher heat distortion values. This previously has been found to be due to the effect of higher vinyl chloride compositions or a broad composition distribution. This data appears to correlate with the high O-D-B viscosity and longer flux time of this resin which would substantiate the observations made earlier in this discussion.

SECTION II

Scale-up in the 750 gallon reactors involved the preparation of a number of both B8800 and B8500 compositions. Polymerization and processing data are summarized in Table II. As will be noted there was little or no variations in the polymerization recipe in either the B8800 or B8500 composition runs. The exceptions were in the amount of monomer added to initiate polymerization and the use of vinyl chloride to relieve the vacuum on the reactor prior to adding the initial shot of monomer. The addition of vinyl chloride at this point was made to shift the monomer composition in the water phase toward a higher vinyl chloride composition. Inasmuch as vinylidene chloride enters the polymer chain faster than vinyl chloride the initial polymer formed should be of a composition closer to the desired or charged monomer composition. This was discontinued however because it was found that the vinyl chloride was not being added as a vapor but as a raw liquid monomer. The

addition of liquid monomer would result in at least a portion being dissolved in the water phase. This could result in the initiation of polymerization in which the initial polymer formed would be polyvinyl chloride. This could be one explanation for some of the variation in resin viscosities, solubilities, etc.

Runs R5-8049 through R5-8052 in which vinyl chloride was not added to relieve the vacuum, were very uniform in both resin and processing properties. However, there was another variable here that is not shown. In explanation, when a conoflow or continuous addition run is made more monomer is mixed up in the monomer weigh tank than is added to the reactor. This results in a monomer heel left in the weigh tank. In the preceding runs, this heel was left in the weigh tank and additional monomers added to make the succeeding run. It was felt that this procedure could contribute greatly to a variable monomer composition and therefore to variable polymer composition and properties.

This variable was eliminated from the above mentioned runs by dumping this monomer heel and preparing a fresh monomer mix for each run. Although the actual composition of the monomer mixtures in these runs is unknown it is indicated here that an analytical method is needed to adjust monomer mixtures to a constant composition. Then and then only can reproducibility of resin composition and properties be attained. It is suggested that the method currently being used at V_1V_2 Production Plant based on refractive index would be excellent.

A comparison of B8500 and B8800 compositions indicates the former is a softer resin resulting in shorter flux times, higher indentation and lower impact values. Solutions prepared in a 65/35 methyl ethyl ketone-toluene solvent system, were quite uniform in viscosity, producing very clear solutions that were free of insolubles.

T.O. Flow and Heat Distortion

Figure 3 through 6 graphically present the Tinius Olson Flow and heat distrotion data on both the B8800 and B8500 compositions. In general these values compare very favorably with those obtained in both the 50 gallon and 20 gallon reactor batches at equivalent resin compositions. R8047 (B8500) and R8041 (B8800) appear to fall outside the general grouping in melt viscosity, indicating a higher vinyl chloride composition or a broad composition distribution. This appears to correlate well with the poor solubility and resin processing data on these resins.

Specific Gravity and Melting Point

A comparison of specific gravity and melting points of the various vinyl chloride-vinylidene chloride compositions with VYHH is presented in Table III. Specific gravity of the resin decreases with increasing amounts of vinyl chloride in the polymer, with VYHH being the lowest. This could reflect a cost advantage for VYHH if these resins were compared on a volume basis.

B8500 has the lowest melting point, which in conjunction with its good plasticizer absorption properties accounts for its fast fluxing properties.

Polymer Granulation

A comparison of the polymer granulation of B8500 and VYHH may be observed in Figures 7 and 8. VYHH consists of polymer particles on an average smaller than B8500, however, it does have some large particles which are probably agglomerates. On the other hand B8500 appears to have some very large spherical particles with a large amount of smaller agglomerates. These small irregular shaped agglomerates greatly increase the polymer surface area which accounts for plasticizer absorption properties comparable to VYHH. A critical comparison of these resins with VYHH as a lacquer resin was made by the Lacquer Section of C.T.S. and will be found in Coatings Technical Service Report L-815.

Following is a reprint of the summary of this report:

"Experimental Resin X2716 (B8500) a vinyl chloride-vinylidene chloride copolymer produced by a new manufacturing method was evaluated as an industrial maintenance lacquer resin. Solution and film properties were compared with those of three leading commercial all-purpose vinyl resins. Experimental resin X2716 was found to yield solutions with exceptional clarity in vinyl lacquer solvents. Viscosity is in the medium range and viscosity stability is equivalent to the commercial resins. Sprayability is equal to or better than the control lacquers.

Films of this resin are characterized by outstanding resistance to chemicals and solvents and an exceptionally low WVTR. This is enhanced by a high response to plasticizers; elongation being achieved at low plasticizer levels. This response also yields films of extra strength at desirable elongation values. The films were equivalent to commercial resins in heat and light stability. Adhesion to steel and wash primer was considered poor.

It is concluded that Experimental Resin X2716 will perform exceptionally well as an industrial maintenance lacquer resin."

A plant trial run with X2716 (B8500) was made by Flintcote in Chicago, Illinois, in which 5000 square feet of floor tile was prepared. In a discussion of the plant trial with these people at a later meeting, it was indicated the resin performed very well. They did mention that at one point in their process they had some trouble with the tile mixture falling off their compounding rolls. However, inasmuch as they were reluctant to give out any information concerning this problem it would be only a guess as to its cause.

The floor tile prepared in this plant trial is now in service on the floors of the C. C. Kennedy Research Laboratory (677 Building).

TABLE I

50 Gallon Semi-Plant Batches

Run Number	Charged Composition	Phase Ratio	Granulator	% Granulator	Catalyst	% Catalyst	Polym. Temp. °C	Agitation RPM	O.P. psig	Monomer 1st Shot, lbs.	Run Time Hrs.	Run Time Min.	ODB Viscosity	% $VeCl_2$	B.P. Flux Time/Minutes Initial	B.P. Flux Time/Minutes Final	2 Roll Mill Minutes	P.A.
B5-1345	B9100	2:1	MOC(50 cps) 0.1 Duponol ME 0.1		LR_2O_2	0.4	65°	120	130	45	15	15	0.979	20.0	1'-20"	5'-45"	-25"	4
B5-1346	"	"	"	"	"	"	"	"	"	17	20	-	0.962	19.0	1'-20"	5'-45"	-30"	4
B5-1347	"	"	"	"	"	"	"	150	"	15	10	50	1.096	16.0	1'-15"	6'-50"	2'-	1
B5-1348	"	"	"	"	"	"	"	"	"	12	12	45	1.057	14.0				2
B5-1349	"	"	"	"	"	"	"	"	"	11	17	-	1.061	10.0				2
B5-1350	"	"	MOC(50 cps) 0.1 Ultrawet DS 0.05		"	"	"	"	"	10	22	30	1.050	8.0				1
B5-1351	"	"	"		LR_2O_2 0.4 BZ_2O_2 0.1		"	"	"	10	11	25	1.054	12.5				1
B5-1352	"	"	"		"	"	"	"	"	10	12	30	1.010	17.5	1'-05"	5'-20"	-45"	3

TABLE II

Run Number	Charged Comp.	% Catalyst LR_2O_2	% Catalyst BZ_2O_2	% Ultrawet DS	% MOC(HG) 50%	lbs. monomer 1st shot	VCl added to relieve vac.	Run Time Hrs.	Run Time Min.	% VCl by Analysis	Bulk Density gms/cc	Abs. Viscosity 2.0% Sol'n in ODCB at 120°	% H_2O	Plasticizer Absorption	Sol'n. Visc. 20% in 2:1 MEK-Tol.	Polymer Properties: Baker Perkins Init. Flux	Baker Perkins Final Flux	Indentation of tile in mils. 1'	Indentation of tile in mils. 10'	Impact 10' drips	Tile Thickness in mils.
35-8036	B8800	0.6	0.15	0.1	0.04	*	yes	9	15	91.1	.501	1.086	.009	1	173	1'05"	6'25"	8.8	11.6	9	68
35-8037	B8800			0.1		*	yes	8	50	88.2	.582	1.068	.022	1-2	141	1'30"	8'00"	11.9	15.0	14	68
35-8038	B8800			0.1		monomer feed line plugged-run dumped															
35-8039	B8800			0.1		*	yes	8	30	90.9	.555	1.063	.102	1-2	142	55"	5'55"	9.5	12.2	12	69
35-8040	B8800			0.1		*	yes	10	15	89.7	.556	1.039	.102	1	100	50"	5'25"	9.2	11.9	8	69
35-8041	B8800			0.1	0.03	*	yes	12	-	91.5	.596	1.137		1-2	insol	2'15"	9'	8.7	10.5	13	68
35-8042	B8800			0.1	0.05	190	yes	9	-	92.5	.641	1.078		1-2	insol	1'	5'	9.2	11.4	12	69
35-8043	B8800			0.13	0.04	200	yes	10	50	88.4	.568	1.040	.020	1	95	50"	4'45"	11.5	14.5	24	72
35-8044	B8500	0.6	0.15	0.1	0.04	225	yes	9	10	87.4	.758	1.022		3-4	94	no tile evaluation					
35-8045	B8500			0.12		225	yes	9	22	89.4	.676	1.059		3-4	90	"	"	"			
35-8046	B8500					360	yes	14	30	84.5	.676	1.061		3-4	215	"	"	"			
35-8047	B8500					300	yes	8	30	89.0	.556	1.093	.018	1-2	167	1'15"	7'-	9.5	12.2	7	66
35-8048	B8500					300	yes	11	45	94.5	.676	1.012	.012	4+	45.5	no tile evaluation					
35-8049	B8500					300	no	9	50	85.0	.544	1.049	.021	1	61	50"	5'30"	11.1	14.0	7	66
35-8050	B8500					200	no	10	15	85.4	.596	1.034	.018	1	66	55"	5'30"	11.6	14.7	7	65
35-8051	B8500					200	no	10	30	86.0	.696	1.048	.033	2	94	1'10"	5'30"	10.2	13.3	8	67
35-8052	B8500					200	no	10	-	85.4	.625	1.042	.039	1	73.5	55"	5'13"	10.6	13.5	9	67
												1.050		1		55"	5'55"				
												1.177		4		2'15"	15'30"				
/Y1111	B8713G																				
(2708	B9000																				

All Runs: Phase Ratio - 2:1
Polym. Temp.- 65°C
Agitation RPM - 120
Control Press. PSIG - 125
* Added monomer to obtain 125 PSIG

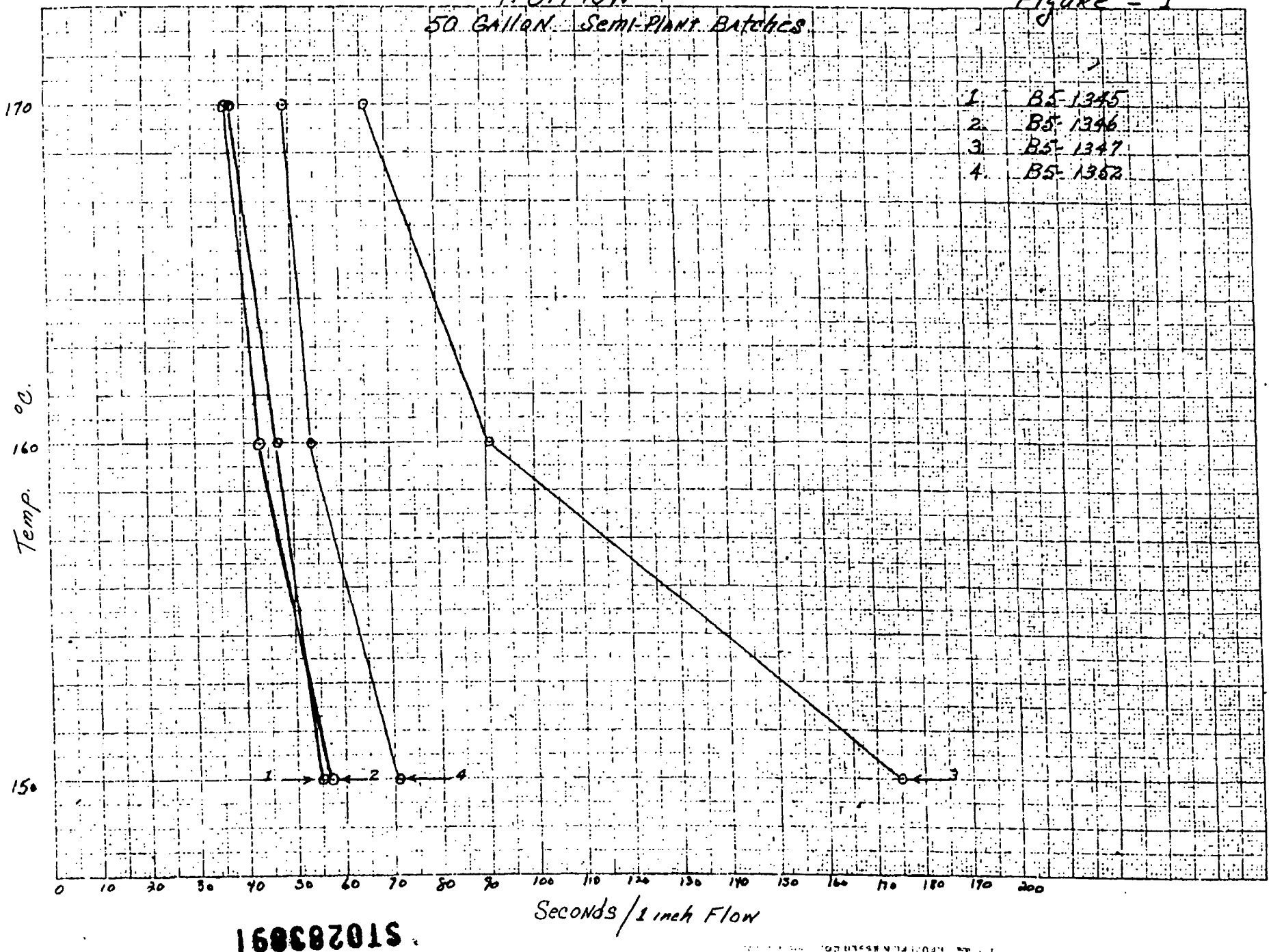
TABLE III

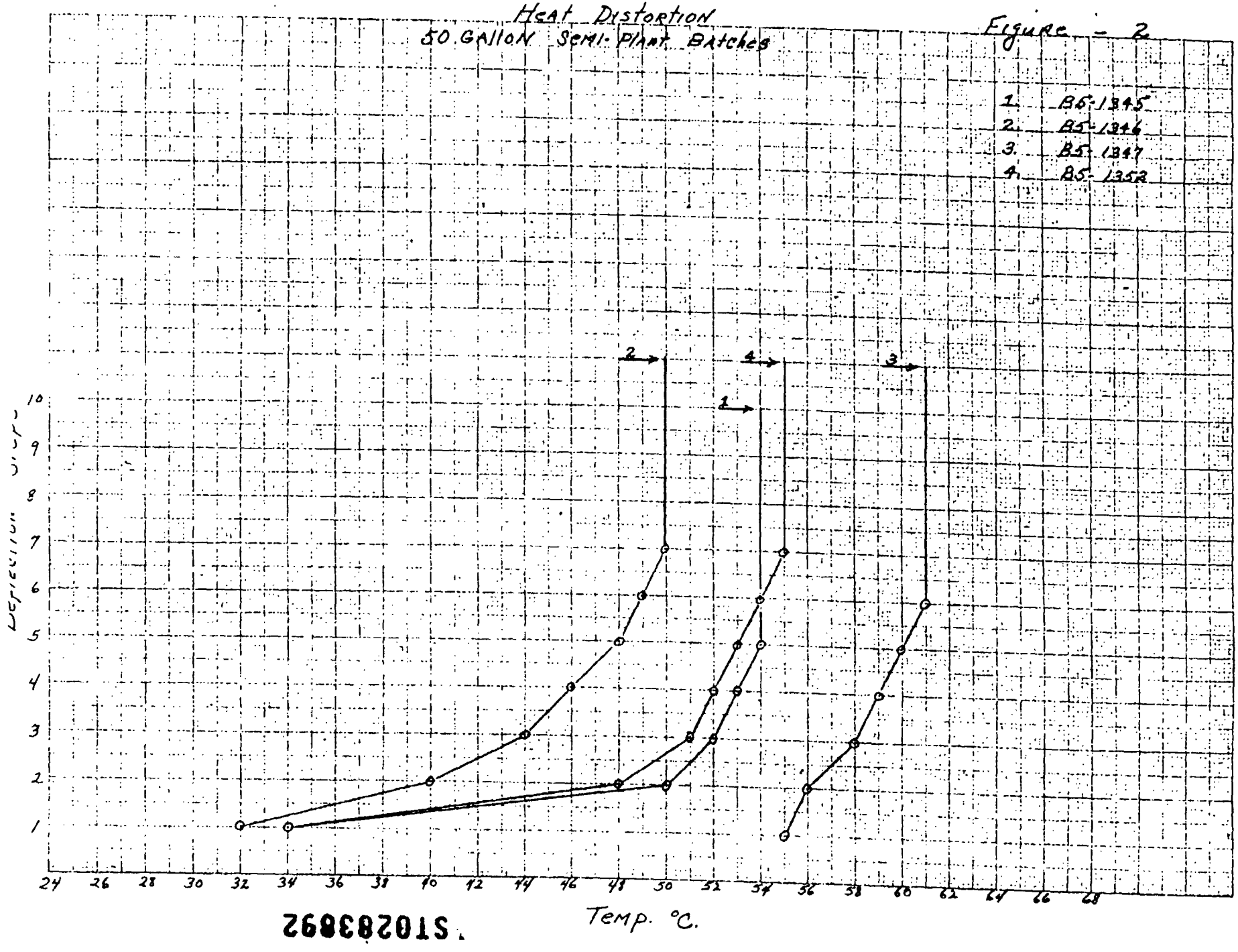
Type	Compositon	Run No.	Sp. Gr.	Melting Pt. in Oil
VYHH	13% Vinyl Acetate 87% Vinyl Chloride	-	1.36	135.3°C
X2708	10% Vinylidene chloride 90% Vinyl chloride	R9004	1.419	-
X2717	12% Vinylidene chloride 88% Vinyl chloride	R5-8039	1.426	136.3°C
X2716	15% Vinylidene chloride 85% Vinyl chloride	R5-8050	1.431	113.9°C

T.O. Flow

Figure - 1

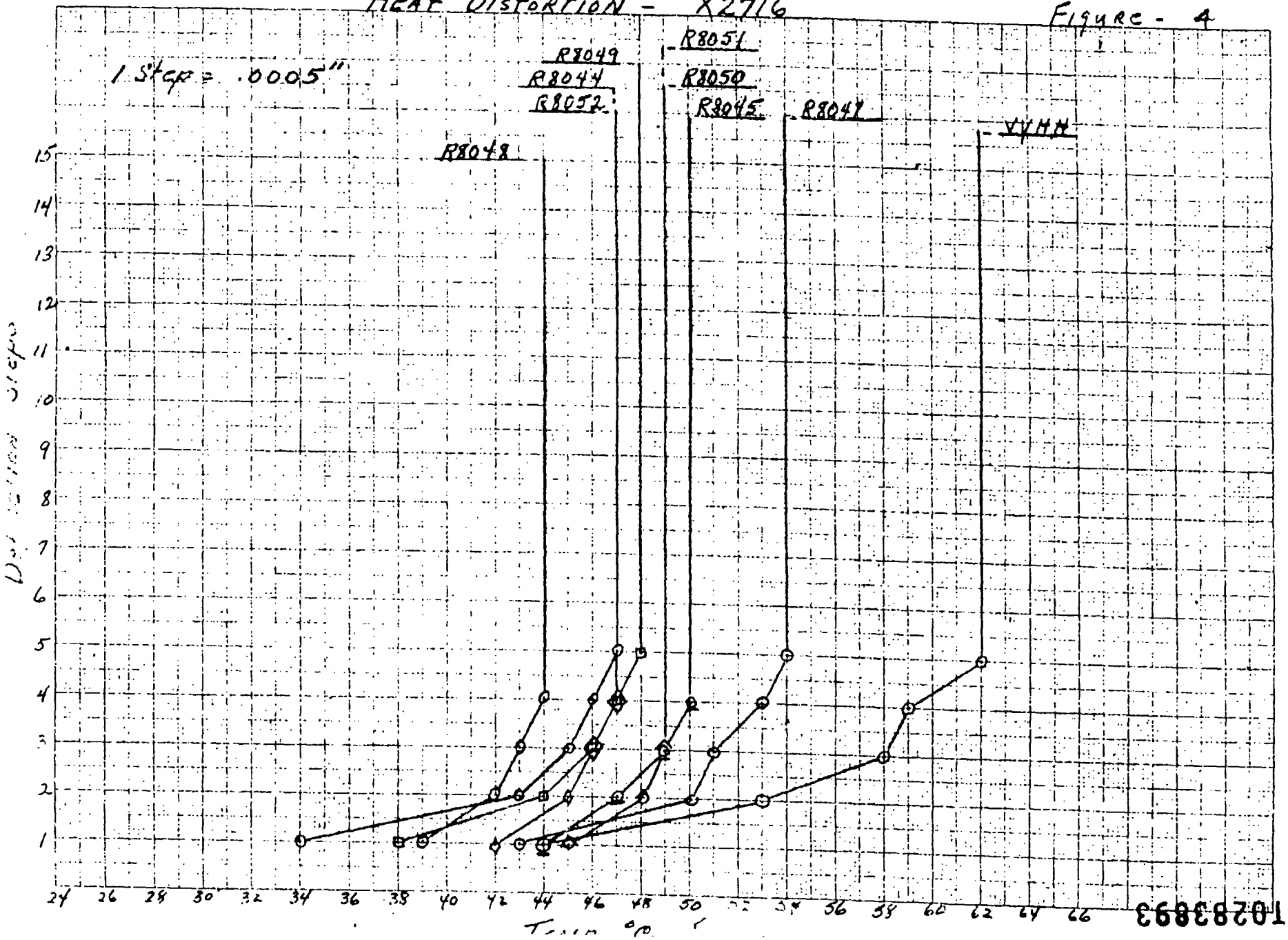
50 Gallon Semi-Plant Batches




Heat Distortion
50 Gallon Semi-Plant Batches
Figure - 2
1. B5-1345
2. B5-1346
3. B5-1347
4. B5-1352
Deflection, Inches
Temp. °C.
24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68
1 2 3 4 5 6 7 8 9 10

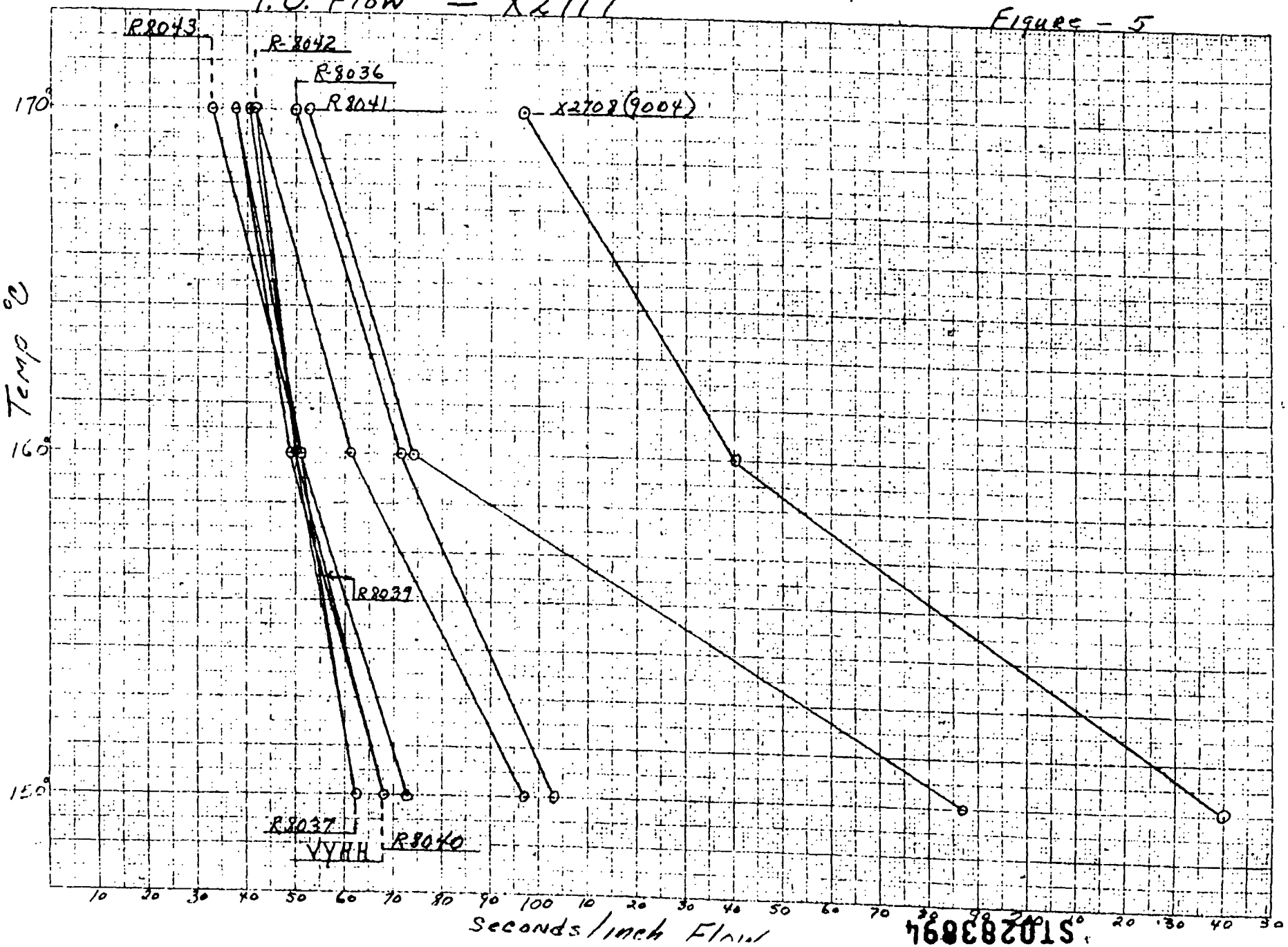
Heat Distortion - X2716

Figure - 4



T.O. Flow — X2717

Figure - 5



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Heat Distortion - X2717

Figure - 6

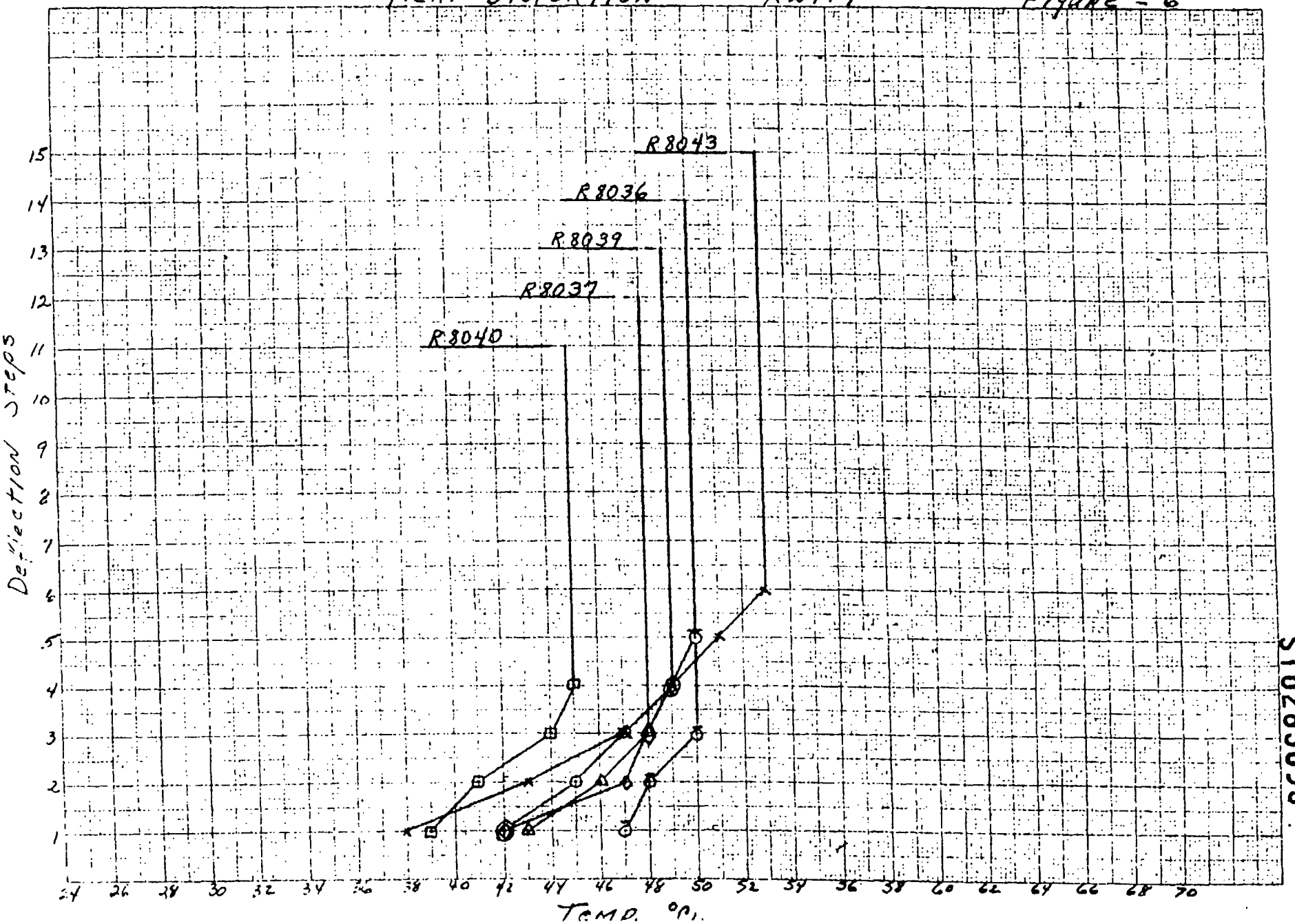

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Figure 7

E8500(R J0522) Magnif 180X

Figure 8

VYHH Magnif - 180X

Conclusions and Recommendations

Resin compositions of (85% vinyl chloride-15% vinylidene chloride) are comparable to VYHH in resin processing and basic floor tile properties. This composition has solution properties comparable and in some respects superior to VYHH as a lacquer resin.

Agitation in the range of 120 to 140 RPM appear near the optimum, however this may present a problem in scale-up to a 3500 reactor. These agitation speeds are not readily obtainable in the larger reactors.

An absolute viscosity of 1.04 to 1.05 appears to be the range for good resin properties. This is obtained by polymerizing at a temperature of 65°C and a constant pressure of 125 psig.

Heat distortion and Tinius Olson flow tests correlate very well with resin processing. The Tinius Olson flow test is recommended as a production control test.

An analytical method to adjust monomer mixtures to a constant composition is recommended. This would result in greater reproducibility of resin compositions and properties.

C. C. KENNEDY RESEARCH LABORATORY
The Dow Chemical Company

By: W. G. MacPherson — 3/16/59 Date

By: C. D. Parker — 3/17/59 Date

By: F. M. Poindexter — 3-16-59 Date

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