

BUSINESS CONFIDENTIAL**PROJECT REPORT****RECEIVED****JAN 3 1968****R. N. Wheeler****SUSPENSION VINYL RESINS: PROPOSED PROCESSES****TO PRODUCE A POWDERBLEND COPOLYMER RESIN****FOR THE SOUND RECORD MARKET****AUTHOR :** A. A. Peterson**DATE:** December 20, 1967**PROJECT NO.:** 333 A 10**SUPERVISOR:** Dean E. Richardson**FILE NO.:** 8646

SUMMARY The advent of powderblend feed for the manufacture of vinyl records has called for a vinyl chloride/vinyl acetate copolymer with good dryflow properties. To date, there is but one resin on the market with the excellent properties required, Borden VC 113 FSP. The Process-10 resins now made by UCC have poor flow properties due to static electricity and mediocre particle sphericity.

During the past few months, three processes have been found to produce good particle sphericity:

- 1) Continuous addition of vinyl chloride monomer withheld from the initial charge;
- 2) Batch addition of vinyl chloride monomer withheld from the initial charge;
- 3) Use of Elvanol 50-42 as suspending agent instead of polyvinylpyrrolidone.

All three methods have been successful in producing spherical particles. However, methods 1) and 2) still have the disadvantage of static electricity. Another disadvantage of method 1) is the fact that the north line autoclaves (those designated for VC1/VAc copolymer manufacture in 1968) are not equipped with meters for continuous vinyl chloride addition. Disadvantages of method 2) would be the additional attention required by operators, additional hold-up time in the charging of autoclaves, and possible failure of pumps during the critical addition period.

As stated, the Process-10 resins made with methods 1) and/or 2) still have the static electricity problem. This report includes a comparison of three additives which would alleviate the static problem and permit free flow of the spherical resin particles. Efforts are also being made by Dr. J. E. Glass of the Tech Center to study the effects of silicones and caprolactone/ethylene oxide copolymer upon the static electricity problem with the polyvinylpyrrolidone.

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As to the relative merits of the antistatic additives, the Magnesol and Cabosil were almost identical. On those resins which had spherical particles, but had the static problem, 0.1% of either the Magnesol or Cabosil greatly improved the flow properties. Two things are evident from these tests: 1) excellent dry flow requires spherical particles whether or not the static electricity is neutralized, and 2) the Process-10 copolymer will not flow well without the antistatic additives in spite of the improved sphericity gained by batch or continuous vinyl chloride addition.

An additional interesting and promising fact was found during the writing of this report. The Magnesol can be added at concentrations of 0.3%-0.5% to antistatic (with Catanac SN) VYCR-10 (a sticky, poor-flowing powder) and the resin flows better than the original VYCR-10 without the Catanac. This might prove valuable for RCA technical service or, for that matter, our own handling of the resin, if RCA is converted from VYAR-2 to the Catanac-modified VYCR-10.

The Process-10 resin with continuous vinyl chloride addition (or with 65% of the VCl added batchwise) with the aid of 0.1% Cabosil or Magnesol was equivalent in flow properties to the Borden resin. The VYCR made with Elvanol 50-42 was equivalent to the Borden resin without the aid of antistatic materials.

During the next few weeks, efforts will be made to scale-up the Elvanol 50-42 recipe for a powderblend record resin from the 10-gallon to the 600-gallon autoclave.

INTRODUCTION In July of 1966, pictures were made by the author of several blends of VYCR-10 resin. It was noticed at this time that a few blends of this resin had spherical particles. Most of the Process-10 copolymer (and homopolymer) observed had an irregular non-spherical character. At that time there seemed to be no particular desire for such a characteristic, since most resin was being compounded into pellets. During the past year, interest grew toward increasing the dry flow properties of the record resins for powderblend formulations in which good dryflow properties are critical. After looking at several blends of VYCR-10, it was decided that an increase in particle size and a decrease in fines should help the dry flow properties. After extensive efforts, consistently satisfactory blends were made with a good improvement in flow properties due to the larger particle size gained through lower agitator speed in the pilot plant and production autoclaves.

In the past few months, Bound Brook personnel have expressed a desire for an even greater improvement as the flow properties were still not as good as the best competitive resin, Borden VC 113 FSP. It was noted that this resin had regular, very spherical particles which accounted for the excellent flow properties. Thus, attempts were made to improve the sphericity of the UCC record copolymer.

DISCUSSION Three successful methods have been discovered to produce the desired particle geometry. The first came from pictures of old VYCR-10 blends made in late 1965. A report by H. H. Savage concerning the reduction of free vinyl acetate content of copolymer by continuous vinyl chloride addition mentioned that "the appearance of the resin made at 75% and 73% initial vinyl chloride was appreciably different from the others--the particles were very spherical and had a wider size distribution." From this observation a pilot plant run was made using the continuous vinyl chloride addition (controlled by feeding the remaining vinyl chloride to hold the reaction pressure constant). The initial vinyl chloride/vinyl acetate ratio was 75/25 and the final ratio was 87.6/12.4 for a VXKF-10 copolymer. The result was a resin with greatly improved sphericity and higher bulk density (also noted in H. H. Savage's report).

The 1968 schedule for production of VCl/VAc copolymer calls for the north line autoclaves to be used. These autoclaves are not equipped for continuous vinyl chloride addition. Thus, several pilot plant runs were made by withholding from the initial charge a fraction of the vinyl chloride, which was then batch-charged after a few hours of reaction had occurred. It was found that the larger the fraction of vinyl chloride withheld, the more spherical the particle. It is known that the suspension polymerization of vinyl acetate produces very spherical particles. Perhaps the lower vinyl chloride/vinyl acetate ratio at the beginning of the experimental copolymer runs is what causes the improved sphericity.

A third method for producing improved sphericity of copolymer was found: the use of Elvanol 50-42 polyvinyl alcohol to replace polyvinylpyrrolidone (PVP K-90) as the suspending agent. The Borden Chemical Company has been producing a polyvinyl alcohol in the molecular weight range which should theoretically make a good suspending agent, but for some reason they stopped marketing it. We suspect that they are still using it internally as a suspending agent for the Borden vinyl chloride/vinyl acetate copolymer series. A duPont product, Elvanol 50-42, is the most likely polyvinyl alcohol on the market with the molecular weight suitable for a good suspending agent. Elvanol 50-42 has been used in the past in pilot plant work, but the evaluation was not a high priority item.

A statistical series of polymerizations was made in the 10-gallon stainless steel autoclave using Elvanol 50-42 with the new Pfaudler agitation system. After defining the limits of the experiments with several agglomerated runs due to excessive agitation, eight successful runs were made studying four operation variables. The results will be reported separately from this report. All of the runs produced very spherical particles. Due to the study of the operating variables, all runs did not produce the desired particle size, but the sphericity attained was equivalent to the Borden VC 113 FSP. This can be seen in the accompanying photomicrographs.

Another feature of the resin produced by the Elvanol 50-42 system was the lack of electrostatic charge, which is a great shortcoming of the Process-10 resin. The study with the antistatic additives showed no improvement of funnel flow upon mixing the resin with them. It was quite evident from the drying, screening, and microscope visual observation that the static charge is immeasurable by sight or from resulting flow properties. After discussion with Dr. J. E. Glass, who theorized that the polyvinyl alcohol should be more difficult to remove from the resin particle

than the polyvinylpyrrolidone, it is thought that the polyvinyl alcohol may have some antistatic properties. Dr. Glass will be studying the effect of adding silicones or caprolactone/ethylene oxide copolymer to the polyvinylpyrrolidone recipe as a solution to the static problem with Process-10 resins.

Work is now being started to reproduce the Elvanol 50-42 recipe results in the 600-gallon autoclave and for possible scaleup efforts to production autoclaves.

From a suggestion by Bound Brook personnel, comparative funnel flow tests were made with resins produced by the continuous and batch vinyl chloride addition process, resin produced by the Elvanol 50-42 system, the Borden VC 113 FSP, VSKF-10 (B-6) made with the lower agitator speed of 104 rpm, and a recent production sample of VYCR-10 produced at the normal high agitator speed of 120 rpm.

The greatest improvement in flow properties upon the addition of an antistatic material was realized by the resin produced by the continuous vinyl chloride addition. The resulting flow properties were comparable to the Borden VC 113 FSP (without antistatic material). The next best improvement was the resin made with the largest amount of vinyl chloride withheld and charged by batch addition. Comparing these improvements with the sphericity of the resins, it would seem that the static of the Process-10 copolymer can indeed be overcome with antistatic materials, but to give flow properties comparable to the Borden resin, the sphericity must also be present. This can be seen in the minor improvement in those resins tested with poor sphericity.

The Magnesol, Cabosil, and carbon black gave similar improvement with few exceptions. Carbon black would not be a good additive as it has been found to segregate. For that matter, segregation may occur with the other materials also, but this has not been detected. All three materials are very dusty and would be difficult to handle, unless added while the resin was still wet (for example, between the Strong-Scott Solidaire and fluid-bed drier in the Texas City Number 7 Drying System).

CONCLUSIONS Through the examination of the flow properties and particle geometry of the resins and the effect of the three antistatic materials, the following conclusions have been made:

- 1) At present, the Elvanol 50-42 suspending system for copolymers gives the best candidate for a powderblend record resin. The scale-up of this recipe in the next month will determine the success of this approach. The Elvanol 50-42 process produces a resin particle unlike the Process-10 copolymer in that it possesses a great degree of sphericity, virtually no electrostatic charge, an 8-to 10-pound higher bulk density, and excellent flow properties.
- 2) The continuous vinyl chloride addition method with Process-10 gives improved sphericity over the normal Process-10 procedure, but the resin still has an electrostatic problem. This can be overcome with the addition of an antistatic material at low concentrations. With the antistatic material and improved sphericity the flow properties are equivalent to those of the Borden VC 113 FSP, and with the resins produced in the 10-gallon autoclave with Elvanol 50-42.

- 3) Batch addition of the majority of the vinyl chloride after two or three hours of reaction produces resin similar to that produced by the continuous addition method. When more than 50% of the vinyl chloride is charged in the initial charge, the resin produced begins to look more like the normal Process-10 resin, possessing mediocre sphericity.
- 4) Both Magnesol and Cabosil inhibit the electrostatic charge of the copolymer at very low concentrations. It was also found that the Magnesol will aid the flow properties of copolymer resin containing Catanac SN, without which the resin will not flow at all, as was experienced by a recent production run of Catanac-modified VYCR-10 (QEX-1323).

The only recommendation concerning future work is a study to determine the feasibility of adding Magnesol to the Catanac-modified VYCR-10 for RCA. A sample has been sent to Steve Krumm at Bound Brook for evaluation. Scale-up studies of the Elvanol 50-42 recipe are being made at this time. No future work is planned with the continuous or batch addition of vinyl chloride at this time. Dr. J. E. Glass is experimenting with caprolactone/ethylene oxide copolymer and silicones for the inhibition of the electrostatic charge accompanying the Process-10 copolymer.

EXPERIMENTAL The procedure for determining the flow properties of the resins were as follows.

- 1) Weigh the resin in a tared dry jar.
- 2) Add the antistatic material to the concentration desired.
- 3) Record total weight. This should be about 50 grams.
- 4) Mix the resin and additive vigorously by shaking with the jar-lid closed.
- 5) Transfer all the material to the steel funnel (see accompanying drawing) holding a finger at the bottom of the funnel to prevent leakage.
- 6) With a stopwatch, measure the time required for the resin to flow through the 1/8" aperture at the bottom of the funnel. Record this time.
- 7) Repeat test once.
- 8) Divide average time in seconds by resin weight in grams. Report this number.

ACKNOWLEDGEMENTS The author's thanks go to D. E. Richardson for his suggestions and help. The pilot plant work was coordinated by R. C. Robinson. Appreciation is due technicians E. W. Dennard, T. W. Oliphint, and J. R. Lytle for their work and suggestions at the pilot plant. Technicians W. J. Tumlinson and J. T. Canon assisted with the resin flow testing. Special thanks go to Monty Montague for the reproduction of the photomicrographs.

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- 1) Peterson, A. A., "Suspension Vinyl Resins: Pilot Plant Studies of Process-10 Copolymer Process Variables and Subsequent Scale-up Efforts", Project Report, July 19, 1967, file number 347B10.
- 2) Peterson, A. A., Letter to S. Krumm, October 16, 1967.
- 3) Savage, H. H., "VYCR-10 Copolymer Production: Reduction of Free Vinyl Acetate Content by Continuous Vinyl Chloride Addition", Status Report, December 29, 1965.

NOTEBOOK REFERENCE

Vinyl Chloride-Vinyl Acetate Copolymers, Number 9107 1 - AAP, pages 1 - 23.


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Attachments

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APPENDIX

Table I: Funnel Flow Test Results

Figure I: Drawing of Resin Flow Funnel

Figure II: Photomicrographs of Resin Examined

Figure III: Photomicrographs of Resin Examined

TABLE I FUNNEL FLOW TEST RESULTS

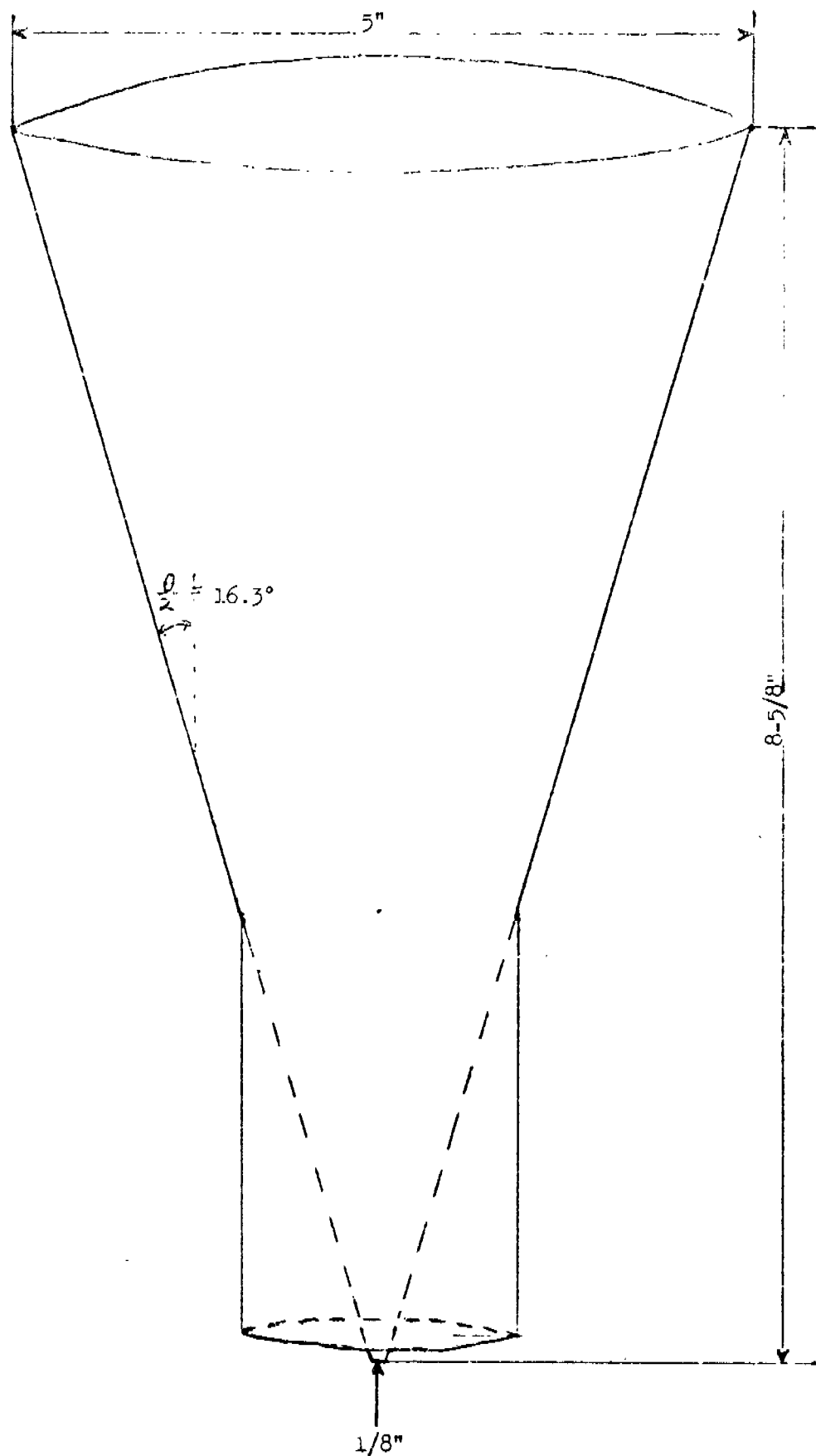
Sample	Remarks	Particle Size, Microns	Size Distribution	Appearance	Flow Time in Seconds/Gram for 50 Grams Resin ²					
					Control	Carbon Black	Cabosil		Magnesol	
						0.5%	0.1%	0.5%	0.1%	0.5%
VYCR-10 (B-208)	Normal Process-10 recipe at 120 rpm, particle somewhat larger than normal	132	0.59	Better than most Process-10 resins, but no sphericity	2.34	2.25	2.22	2.24	2.14	2.08
VXKF-10 (QEX1315)	Pilot Plant run with continuous VC1 addition	150	1.18	Good sphericity but poor distribution	2.20	1.65	1.56	1.57	1.51	1.65
Borden VC 113 FSP	Best competitive record resin with respect to flow properties	151	0.47	Very smooth spherical-to-egg-shaped particles, few agglomerates	1.57	1.49	1.66	1.97	1.41	1.44
11-67-7-10S	Elvanol 50/42 recipe in 10-gal. autoclave from statistical series	175	0.64	Very smooth, spherical-to-egg-shaped particles, few agglomerates	1.63	1.61	1.64	1.76	1.58	1.79
11-67-8-10S	Elvanol 50/42 recipe in 10-gal. autoclave from statistical series	107	1.31	Very smooth, spherical particles, very few agglomerates	1.93	1.98	1.92	2.05	2.00	2.26
11-67-5 FBD	54% of VC1 charged at end of third hour (600-gallon autoclave)	114	1.18	Fair sphericity, poor distribution	2.46	2.06	1.98	2.06	2.09	2.19
11-67-8 FBD	32% of VC1 charged at end of fourth hour (600-gallon autoclave)	161	0.90	Slightly more spherical than normal Process-10 resin	4.44	2.18	2.22	2.24	2.26	2.07
11-67-9 FBD	65% of VC1 charged at end of second hour (600-gallon autoclave)	162	1.12	Good sphericity, but poor distribution	2.06	1.66	1.70	1.65	2.04	1.71
11-67-10 FBD	32% of VC1 charged at end of 2nd hour (600-gallon autoclave)	181	0.88	Just slightly smoother than normal Process-10 resin	2.46	2.08	2.12	2.14	2.03	1.94
VXKF-10 (B-6)	Normal Process-10 recipe at 104 rpm	172	0.49	No sphericity	2.20	2.12	2.28	2.23	2.20	2.02

1) Distribution is (P 84% - P 16%)/ P50% from sieve analysis

2) 50 grams of resin was tested in duplicate on 1/8" aperture funnel as described on accompanying drawing

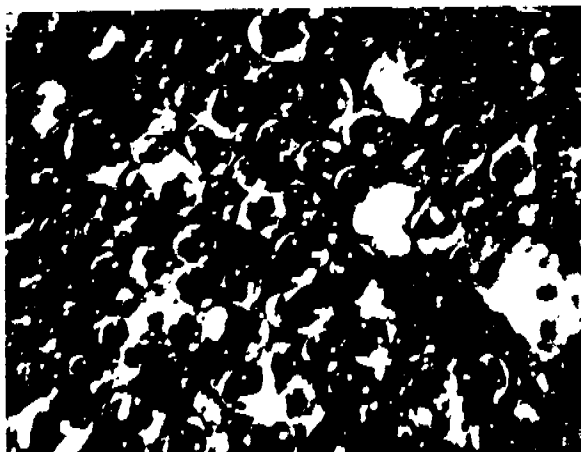
3) Industrial Grade magnesium silicate from Waverly Chemical Company, Inc.

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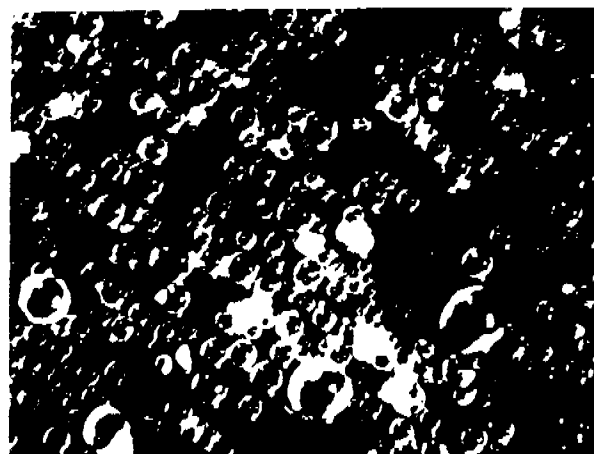


RESIN FLOW FUNNEL
FIGURE I

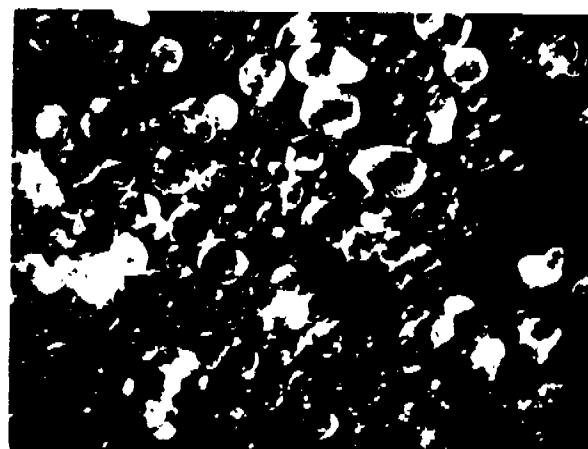
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11-67-7-10s made in 10 gal autoclave
with Elvanol 50/42

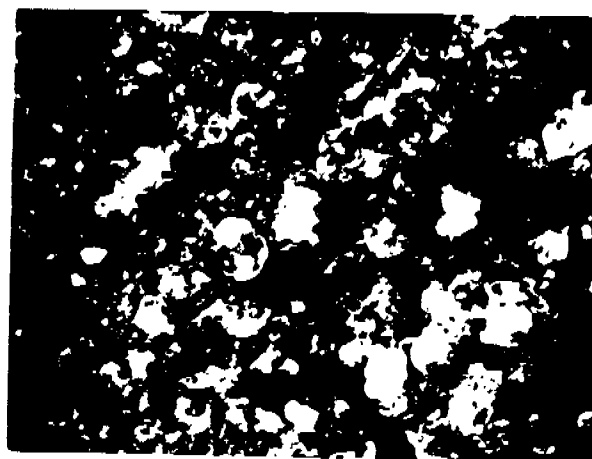


11-67-8-10s made in 10 gal. autoclave
with Elvanol 50/42

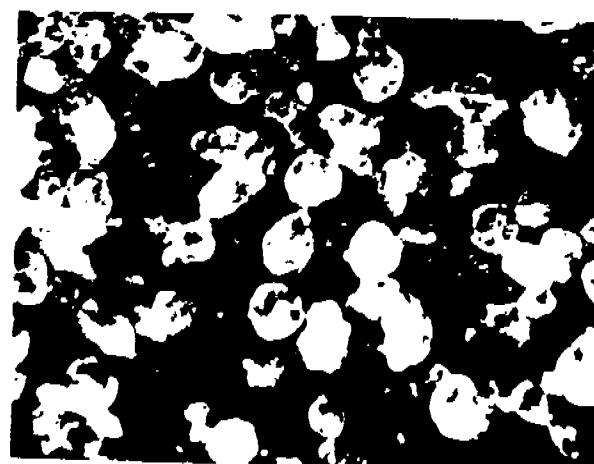


Borden VC113 FSP

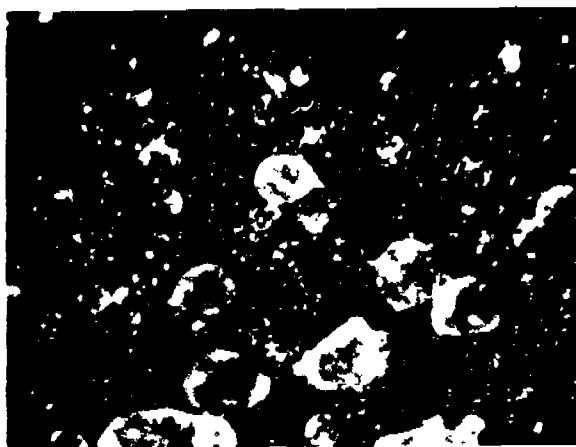
All pictures
at
40X magnification



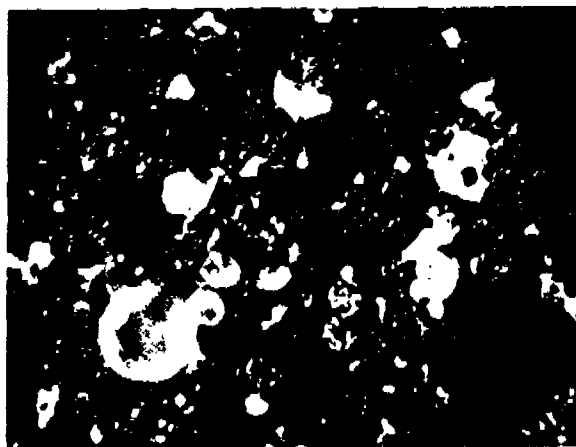
VYCR-10 (B-208) made in pro-
duction autoclaves at 120 rpm



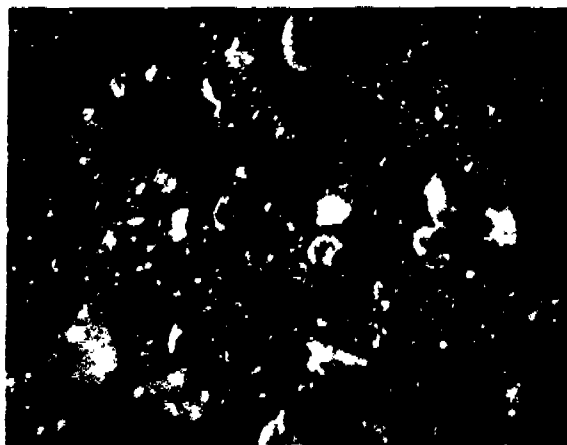
VSKF-10 (B-6) made in production
autoclaves at 104 rpm



10-67-3 (QEX-1315) made in 600 gal. autoclave via continuous VCI addition

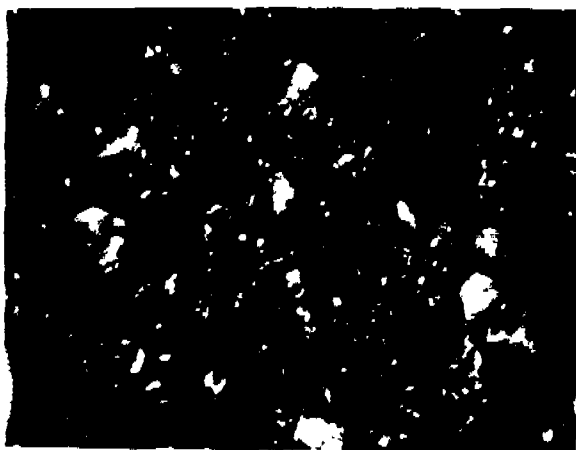


11-67-9 made in 600 gal. autoclave with 65% of VCI added at 2nd hr.

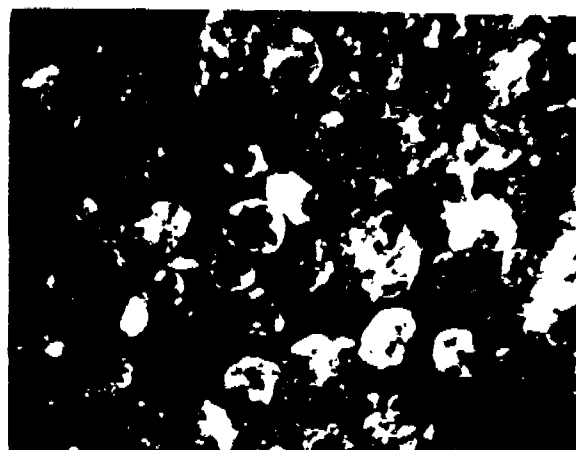


11-67-5 made in 600 gal. autoclave with 54% of VCI at 3rd hr.

All pictures
at
40x magnification



11-67-10 made in 600 gal. autoclave with 32% of VCI at 2nd hr.



11-67-8 made in 600 gal. autoclave with 32% of VCI added at 4th hr.

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