heat removal is consequently less crucial for the best product color in batch operation.

Cyclic operation in the Votator with a small shaft is chemically similar to batch operation as described above, and it produces products of equally good quality. The fact that it gave U values in the range of 200 to 250 is considered of minor influence. However it does lead to the conclusion that, if a Votator with a small shaft is to be used for continuous sulfonation, cyclic operation is preferred over once-through both for quality and efficiency of heat removal even though it may be somewhat less straightforward mechanically, as discussed above.

Summary and Conclusions

Two continuous processes for sulfonating detergent alkylate with sulfur trioxide vapor have been developed by using a Votator high-speed, scraping-blade heat-exchanger. Both procedures yield products suitable for household use without bleaching.

For the process of major interest, involving once-through operation, the ratio of shaft diameter to the enclosing shell is the prime factor governing equipment performance and product quality. This factor is not critical for the second method, involving cyclic operation. Numerous other process variables were studied for both procedures, with special emphasis on how they affect product quality and efficiency of heat transfer.

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Improved Process for the Preparation of Conjugated Soybean and Lower Alkyl Vinyl Ether Copolymers by Flash Polymerization[1]

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DURING THE PAST YEAR an extensive research program has been in progress at this laboratory on the preparation and evaluation of new vinyl ether monomers derived from soybean and linseed oils. Pure vinyl ethers capable of polymerization were produced without significant loss of unsaturation by reacting fatty alcohols with acetylene at atmospheric pressure (1, 2). Copolymerization of the fatty vinyl ethers with various comonomers was accomplished at room temperature by using Lewis-acid-type of catalysts and a flash technique in solvent (5). Baked copolymers dried to hard varnish-like films that had good resistance to acids, alkalies, and solvents. Among the comonomers studied, the lower alkyl vinyl ethers appeared most promising for baked metal and can coatings (4, 5, 6, 8).

From the view-point of economics and performance isobutyl and ethyl vinyl ethers were selected for more intensive industrial evaluation. The test samples were prepared both on a laboratory and pilot-plant scale. Isobutyl, ethyl, and n-butyl vinyl ethers were copolymerized by flash techniques with conjugated soybean vinyl ether at a mole ratio of 3:1 lower alkyl/fatty monomer, using stannic chloride catalyst in solvent. Improved techniques of polymerization and catalyst handling are reported from the standpoint of commercial process development. A simplified procedure for separation of catalyst, using hydrated lime, is described; turbo-agitation is proposed as a method for obtaining essentially water-white copolymers; and two solvent recovery processes are described.

Experimental

Materials and Equipment. Fatty vinyl ether monomers were prepared by atmospheric vinylation of conjugated soybean fatty alcohol in the presence of

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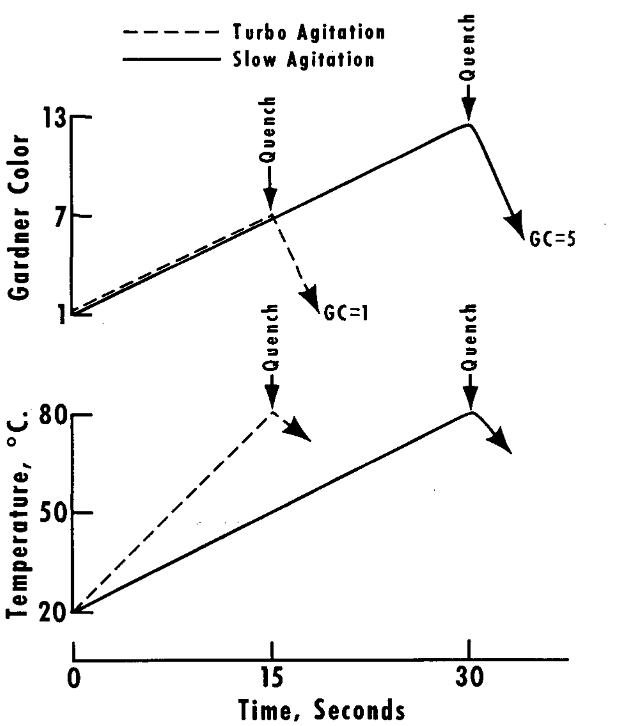

FIG. 1. Effect of agitation on temperature and color development during copolymerization.

potassium hydroxide as catalyst (1), and the distilled monomers analyzed 98-99.5% vinyl ether. Inhibitors in the lower alkyl vinyl ether comonomers, obtained as commercial grade, were removed by distillation.

Anhydrous stannic chloride was dissolved in dried toluene as an 8% solution by weight; lower concentrations were obtained by dilution.

Commercial-grade solvents were used exclusively and were dried prior to use. Sodium hydroxide and calcium sulphate were used as drying agents to reduce the moisture level of the solvents to below 0.005%. Effective drying of solvents was also obtained by the use of a molecular sieve-packed column.

Laboratory polymerizations were carried out in a 2-liter Pyrex beaker with flat-blade turbine agitator, stationary baffles, nitrogen inlet tube, thermocouple, and head-plate cover. The rise in polymerization temperature was followed by using a fast-response temperature recorder. Vacuum filtration was conducted in a conventional Büchner funnel and filtration flask. Desolventization was carried out by vacuum-distilling the polymer solution in a round-bottom flask, fitted with a nitrogen gas ebullator tube, distillation head, water condenser, and receiver.

Pilot-plant runs were conducted in stainless steel. For the polymerization the equipment consisted of a 30-gal, flat-bottom tank, flat-blade turbine agitator, explosion-proof motor, thermocouple, head cover, and nitrogen inlet tube. The agitator revolved at 570 r.p.m. Catalyst precipitation was carried out in a 30-gal., cone-bottom tank with an air-driven agitator. After filtering the precipitate through a 5-gal., Büchner type of filter, the polymer mixture was desolventized in a flash rotating-type evaporator, which operated under vacuum.

Analytical Methods. The vinyl ether content of the fatty monomers was determined by the iodometric method described by Teeter *et al.* (2). Water content of the solvents was analyzed by the Karl Fischer method. Number-average molecular weights of the copolymers were obtained by the cryoscopic method by using water-saturated cyclohexane as the solvent (7). The standard Gardner scales were used for viscosity and color.

Polymerization Procedure. In a typical laboratory copolymerization 50 g. (0.17 mole) of conjugated soybean vinyl ether and 51.5 g. (0.51 mole) of isobutyl vinyl ether were dissolved in 300 ml. of dried toluene. The vapor space in the reactor was purged with nitrogen, and agitation was started. The reaction was then initiated at 21°C. by the addition of 6 ml. of catalyst solution (4% $SnCl_4$ in toluene). The reaction was strongly exothermic, and a rapid temperature rise occurred. Within 10-30 seconds the temperature reached a maximum value of 80°C. The catalyst was deactivated at this point by quenching with 50 ml. of absolute methanol. The yellow color produced in the carbonium ion reaction was decolorized by the methanol. The water-white solution was then cooled to room temperature. Five grams of hydrated lime and 5 cc. of water were added, and the resulting mixture was stirred for 30 min. and filtered. When viscous solutions were encountered, a small quantity of Filter-cel was added in the filtration. After desolventizing by heating over a steam bath and stripping with nitrogen under reduced pressure, the filtrate yielded the pure, clear copolymer.

Pilot-plant runs were conducted by a similar procedure except that a 45-fold increase in the weight of materials was used.

Results and Discussion

Solvent Selection. The solvent serves to absorb exothermic heat and act as a soluble carrier for the copolymer. Such factors as the degree of polymerization desired, toxicity, dielectric constant, hygroscopicity, heat capacity, and cost must be considered in selecting the solvent. After testing several solvents, toluene was found to have important advantages and was used in the majority of the runs. The moisture of the toluene was reduced from approximately 0.03% to levels below 0.005% to prevent hydrolysis or inactivation of the catalyst.

Development of Water-White Copolymers. Copolymers were improved in color and molecular weight when turbulent agitation was provided during the polymerization. Also turbo-mixing resulted in more rapid and intimate dispersion of the catalyst than slow agitation. Consequently carbonium ion polymerization was carried out more rapidly, and color formation was minimized. Decolorization during deactivation was thus more complete than with slow agitation. The effects of agitation on decolorization are illustrated by Figure 1, where typical polymerization curves show the rate of temperature rise and degree of color development in the reactions for fast and slow agitation, respectively. The degree of color development was less pronounced when high purity (99% +) fatty monomers were used or when concentrations of the catalyst were low.

Typical data for laboratory copolymerizations are given in Table I.

The isobutyl-soybean and ethyl-soybean copolymer films were evaluated by being baked on glass at 200°C. for 10 min. and at 150°C. for 1 hr., with and without cobalt drier. When the dried films were tested for hardness and chemical resistance to acid, alkali, and

TABLE I
Typical Laboratory Polymerization Data and Analysis of Copolymers

Vinyl ether comonomer[a]	Reaction Data				Copolymer			
	Init. time	Init. temp.	Max. temp.	Total time	Mole wt.	D.P.[b]	Gardner	
							Color	Viscosity
	Sec.	*°C.*	*°C.*	*Sec.*				
Isobutyl	I[c]	21	80	15	7,400	50.0	1	Z6+
Isobutyl	I[c]	21	76	15	9,500	64.2	1	Z6+
Isobutyl	I[c]	21	67	30	9,525	64.3	1	Z6+
Isobutyl	I[c]	20	80[d]	10	5,100	34.5	4	Z6+
N-butyl	I[c]	21	74	83	5,700	38.6	2	Z6+
Ethyl	10	17	60	52	5,350	42.1	1	Z6+
Ethyl	4	21	80	24	5,130	40.4	1	Z6+

[a] 3:1 mole ratio of comonomer: monomer, where monomer is conjugated soybean vinyl ether.
[b] Degree of polymerization = M.W./Av. M.W. of vinyl monomer unit.
[c] Instantaneous.
[d] Calcium hydroxide used as catalyst deactivator.

solvents, they were found to be resistant to water, 95% ethanol, butanol, diethyl ether, hexane, acetone, and kerosene. Swelling occurred in the presence of chloroform and benzene. Sward hardness values and resistance to acid and alkalies are given in Table II. Films baked with cobalt drier were hardest, but increased alkali resistance resulted when no drier was used. Isobutyl was superior to ethyl copolymer film in hardness. Film properties for copolymers of this type are also reported by coworkers (4, 8).

Little or no change was observed in unsaturation or geometric isomerism of the fatty vinyl ethers during polymerization except for increased isolated *trans*, as shown in Table III.

TABLE III
Changes in Unsaturation and Geometric Isomerism of Soybean Vinyl Ethers During Copolymerization with Isobutyl Vinyl Ether

Material	Diene	Triene	Tetra-ene	*Cis-trans*	*Trans-trans*	Isolated *trans*
	%	%	%	%	%	%
Conjugated soybean monomer	41.8	0.5	0.04	32.9	12.2	0
Isobutyl-conjugated soybean monomer mixture (3:1)[a] before polymerization	20.6[b]	0.25[b]	0.02[b]	16.2[b]	6.0[b]	0[b]
Isobutyl-conjugated soybean copolymer (3:1)[a] after polymerization	21.9	0.2	0.01	17.1	8.4	15.3

[a] Molar composition.
[b] Calculated from conjugated soybean monomer.

By analyzing the copolymers for vinyl ether content the completeness of each copolymerization run was checked. The products consistently analyzed less than 1% vinyl ether.

Catalyst Concentration. Concentration of the catalyst was investigated over the range of 0.1 to 0.4 g. $SnCl_4$ per 100 g. of total monomers. Polymerization curves plotted in Figure 2 show the relationship between quantity of catalyst and a) initiation time, b) rate of temperature rise, and c) total reaction time. Molecular weights and other properties of the copolymers are presented in Table IV. The highest molecular weight obtained was at a $SnCl_4$ level of 0.2 g. per 100 g. of total monomer for both isobutyl and ethyl copolymers. Viscosity and degree of polymerization

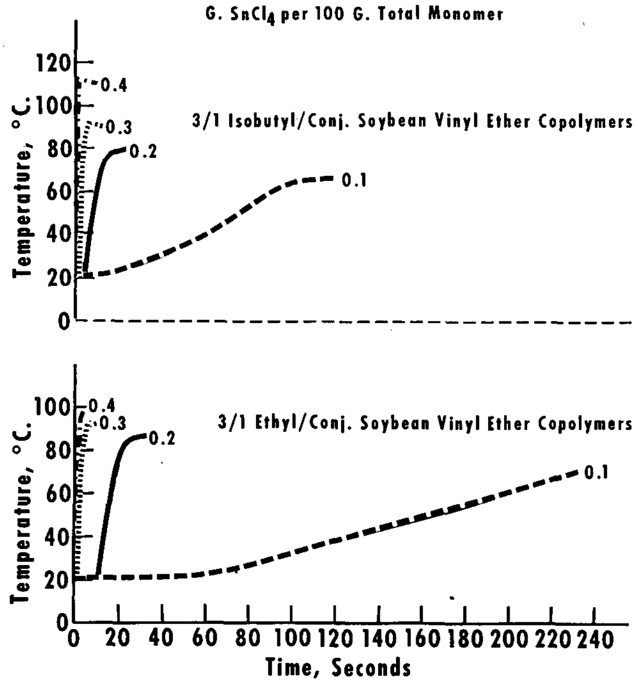

FIG. 2. Effect of catalyst concentrations on reaction rate and temperature.

TABLE II
Hardness and Chemical Resistance of Typical Baked Conjugated Soybean Vinyl Ether Copolymer Films

Tests	Isobutyl—Soybean[a, b]				Ethyl—Soybean[a, c]			
	With drier[d]		Without drier		With drier[d]		Without drier	
	200°C. 10 Min.	150°C. 1 hr.	200°C. 10 Min.	150°C. 1 hr.	200°C. 10 Min.	150°C. 1 hr.	200°C. 10 Min.	150°C. 1 hr.
Sward rocker hardness	10	18	2	Tacky	6	8	Tacky	Tacky
Chemical resistance								
18% HCl								
Frosted, hrs.	24[e]	24	24	3-6	24[e]	24[e]	4	1
5% NaOH								
Swelling, hrs.	4	3	24	4	2-8	1½	3	
Dissolved, hrs.	24	7		24[e]		3	5	1

[a] 3:1 mole ratio of alkyl:fatty vinyl ether.
[b] M.W. = 7,400.
[c] M.W. = 3,450; essentially the same results were obtained with M.W. = 5,400.
[d] Drier = 0.1% cobalt napthanate.
[e] Slight.

TABLE IV
Effect of Catalyst Concentration on Properties of Isobutyl and Ethyl Vinyl Ether Copolymers[a] with Conjugated Soybean Vinyl Ether

Soybean copolymer	Catalyst concentration g. $SnCl_4$/100 g. total monomer			
	0.1	0.2	0.3	0.4
Isobutyl				
Molecular weight	3,700	7,690	5,400	5,050
Degree of polymerization	18.2	62.0	36.5	34.1
Gardner color	1½	1	1	1
Viscosity, bubble seconds[b, c]	3,000	1,680	1,230	1,275
Ethyl				
Molecular weight	5,000	5,130	4,444	5.000
Degree of polymerization	39.4	40.4	35.0	39.4
Gardner color	2	1½	1½	1½
Viscosity, bubble seconds[b, c]	990	879	600	420

[a] Mole ratio of lower alkyl/soybean monomer = 3/1.
[b] Gardner tube; 7½ cm. × 10.6 mm. diameter.
[c] Gardner viscosity—Z6 + for all concentrations.

were slightly higher for the isobutyl copolymer. All the copolymers were approximately water-white, ranging from 1 to 2 in Gardner color value.

Catalyst Deactivators. Stannic chloride deactivators that were examined included aqueous and absolute methanol, calcium hydroxide, distilled water, and ammonium hydroxide. $SnCl_4$ undergoes decomposition to insoluble hydrolysis products with ammonia or hot water. After being heated in the polymerization reaction, an aqueous methanol quench converted the catalyst to a gelatinous precipitate. Drainage and cleaning of the reactor proved very difficult and required detergent and scouring. A drying step was then needed to make the vessel anhydrous for a subsequent polymerization.

When the polymerization mixture was quenched with absolute methanol, a clear, water-white solution was obtained, no hydrolysis of catalyst occurred; and $SnCl_4$ remained in the soluble anhydrous state. The reactor therefore drained quickly, could be rinsed with solvent, and was immediately available in anhydrous condition for the next polymerization. Since hydrolysis had not occurred, the removal of catalyst was facilitated.

Calcium hydroxide was used directly in one experiment (Table I, footnote d) as both the quench and precipitating agent for the catalyst. Although the catalyst was deactivated, the reaction resulted in less extensive decolorization than normally and in a yellow-colored product.

When ammonium hydroxide and distilled water were used as deactivators, white, highly turbid copolymers with low molecular weights were obtained. Absolute methanol was selected as the quenching agent for polymerization studies.

Catalyst Separation. An important step in the overall process consisted of the catalyst separation from the copolymers. Incomplete removal of catalyst resulted in their darkening upon aging. Two methods of separation were investigated, namely, solvent extraction with methanol and chemical precipitation with calcium hydroxide.

In the first method four or more batch extractions with 50% aqueous methanol were used to extract the catalyst. Hydrolysis of the catalyst resulted in a gelatinous precipitate, and separation of the emulsified layers required approximately 10-15 min. per decantation. The separation became even more difficult when more viscous polymer solutions were encountered. The initial emulsion was more effectively broken if the polymerization mixture was heated to approximately 95°C. After decantation, the polymer phase was further extracted with successive washes of 50% aqueous methanol at room temperature. A more rapid extraction was attained by this technique.

In the second method, hydrated lime and a trace of water were added to the copolymer mixture to produce an insoluble precipitate with stannic chloride. Adding water at this point increased the ionization and rate of calcium precipitation. The catalyst precipitate was then separated from the copolymer toluene solution by simple filtration, using filter aid, and a clear filtrate was obtained.

The hydrated lime procedure (5 g./100 g. of total monomer) represented a considerable reduction in number of steps and in processing time required to remove the catalyst. Although the quantity is in excess of the stoichiometric amount,[3] it represents a very small cost in a commercial process. Since only 0.2 g. of $SnCl_4$ is required to polymerize 100 g. of monomer, it would not be economical to recover $SnCl_4$. Lime precipitation seems the simpler procedure for catalyst separation and disposal.

Pilot-Plant Operations. The polymerizing process was carried out with approximately 10 lbs. of total monomers per batch. Flash reactions and temperature-rise curves obtained in the laboratory runs were reproduced in the pilot-plant unit. Processing data are shown in Table V, and a flowsheet, based on 100 lbs. of finished copolymer, is given in Figure 3.

Nearly water-white isobutyl copolymers in a molecular weight range of 4,200-5,300 were produced. Although higher molecular weights of 6,000-9,500 obtained in the laboratory could not be reproduced in the pilot plant, since similar film properties were found irrespective of molecular size, the relative differences of molecular weight are probably not significant. Pilot-plant products were lower in viscosity and re-

TABLE V
Polymerization Data and Analysis of Copolymers Prepared in the Pilot Plant

Vinyl ether comonomer[a]	Reaction data				Copolymer						
					M.W.	D.P.[b]	Gardner-Holdt[c]		Diene conjugation	Iodine value	Recovered[d, e]
	Init. time	Init. temp.	Max. temp.	Total time			Color	Viscosity (bubble test)			
	Sec.	*°F.*	*°F.*	*Sec.*				*Sec.*	%		*lb.*
Isobutyl	3	70	174	10	4,255	28.8	1	877	16.6	44.5	8.7
Isobutyl	5	70	183	32	4,350	29.4	1½	1,430	......	......	8.9
Isobutyl	3	70	171	10	5,000	33.8	1	938	16.5	50.4	8.6
Isobutyl	5	86	189	30	5,300	35.8	2	......	18.1	52.5	8.9
Ethyl	43	50	156	81	3,450	27.2	1	......	19.6	59.4	5.1

[a] 3:1 mole ratio of comonomer: monomer, where monomer is conjugated soybean vinyl ether.
[b] Degree of polymerization = M.W./Av. M.W. of vinyl monomer unit.
[c] Gardner tube; 7½ cm. × 10.6 mm. diameter.
[d] Comonomers charged—Isobutyl-soybean = 10.1 lb.
Ethyl-soybean = 6.0 lb.
[e] Losses due to processing rather than unreacted monomer.

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[3] 2½ moles $Ca(OH)_2$ per mole $SnCl_4$.

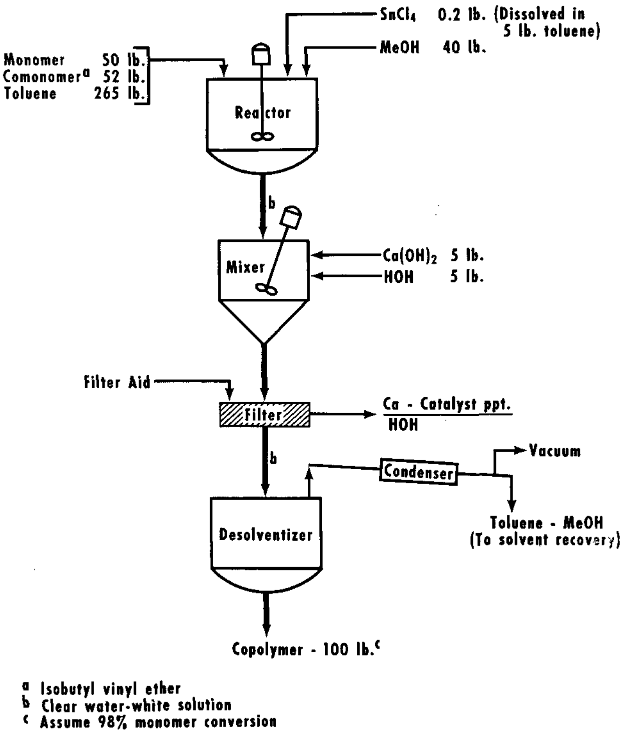

FIG. 3. Flowsheet of simplified process for preparation of conjugated soybean and lower alkyl ether copolymers.

mained quite fluid. In contrast, laboratory copolymers above 6,000 molecular weight were too viscous to pour without redissolving in solvent. The property of lower viscosity could be a significant advantage in industrial casting of copolymer films.

Solvent Recovery. Two alternate methods for solvent recovery, indicated in Figure 4, emphasize the complete separation of methanol from toluene since the recycled alcohol would serve as a catalyst deactivator in a subsequent polymerization. In Method 1 the quench is recovered and recycled as 100% methanol whereas in Method 2 the methanol is recovered as a binary azeotrope with toluene. Since the azeotrope can be used in this form as a quench, Method 2 appears to be a simpler process for commercial application.

In the copolymer-desolventizing step a trace of water may remain in the distillate, in which case it should be removed by an adsorbant such as sodium sulfate prior to use, as in Method 2.

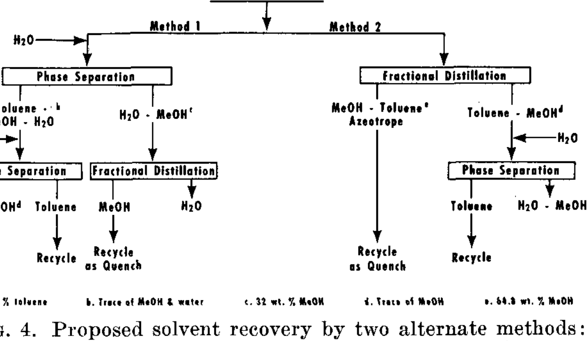

FIG. 4. Proposed solvent recovery by two alternate methods: a) 87 wt. % toluene; b) trace of MeOH and water; c) 32 wt. % MeOH; d) trace of MeOH; e) 64.8 wt. % MeOH.

Summary

An improved process was developed for the copolymerization of lower alkyl vinyl ethers in the presence of anhydrous stannic chloride catalyst and toluene. When a turbo-mixer was used for dispersing the catalyst, water-white viscous copolymers with molecular weight of 4,000-9,500 resulted. In contrast, slower agitation techniques produced yellow-colored copolymers with lower molecular weights.

The maximum degree of polymerization was found at a level of 0.2 g. $SnCl_4$ per 100 g. of monomer. By using absolute methanol as a terminator, decomposition of the catalyst to the gelatinous form, which occurs with use of aqueous alcohols, was prevented. This procedure gave clear, water-white copolymer solutions with the catalyst in nongelatinized state to facilitate its removal.

A low-cost lime precipitation method, developed to recover the catalyst, simplifies the over-all process and offers an efficient means of catalyst disposal. Since the catalyst used is very small, its recovery was not deemed economically justified.

Laboratory conditions were substantially duplicated on a larger scale in pilot-plant operations. Clear viscous copolymers in the molecular weight range of 3,500-5,500 were produced. Film properties remained unchanged although molecular weights were lower than comparative laboratory results. The pilot-plant product retained sufficient fluidity for pouring at room temperature whereas laboratory copolymers with higher molecular weight (> 6,000) did not.

Baked films obtained in these studies were hard and wrinkle-free and showed good resistance to acids, alkalies, and ordinary solvents.

The techniques involved in this work should be applicable to a large variety of monomers that can be copolymerized with $SnCl_4$ in solvent.

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