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FOR A HEAT STERILIZABLE BATTERY
Quarterly Summary Progress Report 5

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ABSTRACT

A 31:69 2-vinylpyridine-methyl methacrylate copolymer was selected as the separator material for large scale preparation. This polymer has excellent electrical properties after saponification and is adaptable for film preparation on a paper coater. A sufficient amount of this polymer to make a total of 100 linear feet of 18-inch wide 1.5-mil film was prepared and purified. Procedures for making film on the paper coater were developed and 40 feet of film in sections with lengths up to 25 feet were made in initial runs.

Methods to accelerate saponification of these copolymers during sterilization were studied. Some films that saponified completely within one 60-hour sterilization cycle were obtained by both pretreatment of copolymer films with methanol and by partial presaponification of the copolymer before film formation.

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I. INTRODUCTION

The primary objective of this program is the development of highly stable battery separator materials that will function satisfactorily in a sealed Ag-Zn secondary battery after heat sterilization at 135°C, and have sufficient flexibility and mechanical strength so that they can be incorporated into the battery system by practical fabrication techniques. Three types of ligand-containing polymers that showed a great deal of promise for use as heat sterilizable separators for the Ag-Zn cell in preliminary tests in our initial JPL 951524 program, namely, hydrolyzed copolymers of 2-vinylpyridine-methyl methacrylate, hydrolyzed styrene-maleic anhydride-methyl methacrylate terpolymers, and styrene copolymers containing 8-hydroxyquinoline substituents were chosen for development. Both the 2-vinylpyridine-methyl methacrylate copolymers and modified tetrapolymers of styrene-maleic anhydride-methyl methacrylate-methyl acrylate were proven to meet most of the project objectives and therefore are now being developed in preference to the other copolymer systems.

During this report period our objectives were as follows:

1. Determine film properties of partially saponified 2-vinylpyridine-methyl methacrylate copolymers;
2. Develop a method to accelerate saponification of 2-vinylpyridine-methyl methacrylate copolymer during sterilization;
3. Complete checks on reproducibility of polymer preparations;
4. Prepare a batch of polymer selected for scale-up and start arrangements for film preparation.

II. SUMMARY

The major part of the work done during this period was directed at development of our 31:69 2-vinylpyridine-methyl methacrylate copolymer as a separator material. We chose this material to prepare in large scale samples because it yields films with lower resistivities (about 5 ohm-in) after saponification than the saponified tetrapolymers (20 to 25 ohm-in). It is also more easily handled during film preparation on a paper coating apparatus. Several 100- to 200-gram batches of this polymer were made at 40 and 60°C to determine the best conditions for making large quantities of this material. In this study, we found that the polymer conversions of samples made in resin pots were lower than those we had prepared earlier under otherwise identical conditions in agitated pressure bottles. As a result of this work we now can consistently prepare polymers having a relative viscosity in 0.5% solutions of 2.1 to 2.6 in 50 to 60% conversions by polymerization in resin pots at 60°C with 0.04% azobisisobutyronitrile catalyst. These conditions have been used to prepare two large batches of copolymer.

The methods used to prepare films of this copolymer in the laboratory were also altered to simulate film preparation conditions on a paper coater. We found that 1.5-mil films with good mechanical properties could be prepared by using solutions containing 13% solids in 1:3 methanol:benzene solvent. This solution was then cast on release paper and dried quickly at 40 to 60°C. These conditions have been used to prepare 40 feet of uniformly good 1.4-mil thick, 18-inch wide film.

We also have been developing methods to accelerate saponification of the methacrylate groups in the copolymers during sterilization so that the films will have usable electrical properties after one 60-hour sterilization cycle. The sterilization time required for complete saponification of high molecular weight copolymers was lowered to under the 60-hour limit by immersion of the films in methanol immediately before sterilization. These films had resistivities of about 3 ohm-in after 60-hours sterilization. The copolymers with moderate molecular weights that we used to prepare large samples of film on the paper coater have greater solubility in absolute methanol, which prohibits the use of this technique with our new films. It is necessary to use moderate molecular weight polymers on the paper coater to obtain the proper solids content/viscosity relationship in the casting solution. With films of these polymers, acceleration of saponification was obtained by pretreatments with methanol diluted by 40% KOH. However, these pretreatments did not give entirely reproducible acceleration and therefore pretreatments using other alcohols such as the propanols are now being evaluated.

Preformed 2-vinylpyridine-methyl methacrylate-methacrylic acid terpolymers were also evaluated as separators during this quarter. These terpolymers are more hydrophilic than the acid-free copolymers and can be expected to wet and saponify more quickly during sterilization. Polymers with a range of acid contents were prepared both by direct polymerization of the monomers and by partial saponification of samples of copolymer. The polymers prepared by partial saponification of the copolymers has higher molecular weight and better film properties. A film of one of these polymers with 20% of the methacrylate content in the acid form attained a resistivity of 5 ohm-in after only one 60-hour sterilization cycle. This indicates a complete saponification. These films, however, have some opaqueness, which is caused by precipitation of an insoluble, crosslinked fraction formed by intermolecular bonding between pyridine nitrogen and the acid groups. This property of the polymers makes it difficult to obtain homogeneous films.

The separator properties of unmodified tetrapolymers prepared from a 18:29:9:44 styrene-maleic anhydride-methyl methacrylate-methyl acrylate charge were also compared to those of the same polymer modified with 10 weight % 2-chloroethyl vinyl ether. The electrical and mechanical properties of the films were about the same. The modified polymers, however, have the advantage that they give casting solutions with longer pot lives.

III. DISCUSSION OF RESULTS

A. PREPARATION OF 2-VINYLPYRIDINE-METHYL METHACRYLATE COPOLYMER FILMS

A paper coating technique was chosen as the method for scaling-up production of film samples to obtain samples with extended lengths. Our contract goal is preparation of a total of 100 linear feet of 18-inch wide film in samples, preferably 10 feet in length or longer. The requirements and limitations of the paper coater made it necessary to alter some of the conditions used previously in the laboratory to make small 6 x 24 inch film samples. Therefore, conditions simulating those that would be compatible with the paper coater were tried on a laboratory scale. Based on the results of these trials the following conditions were established for initial film preparation by the paper coating technique.

- - - Substrate - Transcote Patent Type AV release paper supplied by S. D. Warren Co.
- - - Concentration - 13% solid content. The viscosity of these solutions, that contain copolymers with relative viscosities in the range of 2.1 to 2.5, is 1600 to 1800 centistokes.
- - - Solvent - 1:3 methanol:benzene by weight.
- - - Roller Opening - approximately 18-mils to make 1.5-mil film.
- - - Drying Temperature - 50 to 60°C for two 4-minute passes.
- - - Coating Rate - 4 feet/minute.

A total of 40 feet of 18-inch wide film 1.4 mils thick was prepared during our initial trial with the paper coater. The chief difficulty encountered during the film preparation was the control of the oven temperature to avoid bubble formation in the films since the 50 to 60°C range is near their lower usable range of the drying ovens.

B. ACCELERATION OF SAPONIFICATION OF 2-VINYLPYRIDINE-METHYL METHACRYLATE COPOLYMERS DURING STERILIZATION

1. Methanol Pretreatment of Copolymers

Films of our 31:69 2-vinylpyridine-methyl methacrylate copolymer have required about 120 hours sterilization in 40% KOH

at 135°C to complete saponification of the methacrylate group and attain the low electrical resistivity required of the separator (ref. 1). Since it is advantageous that the separators be usable after a standard 60-hour sterilization cycle, various methods to accelerate saponification of the methacrylate groups are being studied. We have found that pretreatment with methanol effectively accelerated saponification rate during sterilization.

Films of high molecular weight copolymer (polymer 58039) were immersed directly in methanol for 1 to 2 minutes immediately before sterilization. The methanol treatment wetted and plasticized the films and, therefore, probably accelerated subsequent penetration by the 40% KOH into the films during sterilization. Saponification was also probably accelerated directly by potassium methoxide formed inside the film from the residual methanol.

These methanol-treated films had reproducible conductivities of from 3 to 6 ohm-in after 60 hours sterilization. The wet tensile strengths of these sterilized films (Table 1) fell into two groups, namely, those with strengths of 1100 psi and elongations of 12% and those with strengths of 335 psi and elongations of 100%. This dual behavior by films with apparently equivalent treatments has also been noted in untreated copolymer samples, and, therefore, may be caused by slight variations of alignment of the film with the direction of the grain during testing.

The solubility of the copolymers with moderate molecular weights (i.e., relative viscosities of 0.5% solutions of 2 to 2.5) is too high for immersion in methanol without dilution with a nonsolvent. Therefore, solutions containing varying proportions of methanol in either water or 40% KOH were used to pretreat these films. Immersion times from 1 to 30 minutes were used. The results of tests completed so far can be summarized as follows.

Pretreatment solutions containing methanol/40% KOH are more effective than those containing methanol/water for accelerating the rate of saponification. All of several films immersed in 1:1 methanol/water for 2 to 5 minutes before saponification had high resistivities after the 60-hour sterilization period.

Several films pretreated by immersion in 1:1 or 1:3 methanol/40% KOH had resistivities under 10 ohm-in after one 60-hour sterilization cycle. However, films with initial dry thickness over 1.8 mils as well as some of the normal 1.5-mil films had resistivities from 30 to over 100 ohm-in, indicating incomplete saponification in 60 hours.

All the films treated with the methanol/40% KOH solutions adsorbed 300 to 400% of their weight of solution during pretreatment indicating good wetting. However, these films are difficult to handle. Therefore, in future tests higher alcohols

Table 1
TENSILE STRENGTH OF MEMBRANES^a

Reference	Polymer Composition ^b	Film State ^c	Thickness, mils	Tensile Strength, psi	Elongation at Break, %
58040	33:67 2-VP:MMA	Sterilized 120 hrs	3.6	570(av 2)	38
58040	33:67 2-VP:MMA	"	3.3	2300	4
58039	31:69 2-VP:MMA	"	3.9	260(av 3)	92
58039	31:69 2-VP:MMA	Alcohol dip for 2 min. before 60 hr sterilization	4.5	1100(av 2)	12
58039	31:69 2-VP:MMA	"	4.6	335(av 6)	100
99194	30:70 2-VP:MMA	Sterilized 120 hrs	5.3	280(av 3)	70
99137-1	St:MA:MMA:MAC 18:29:9:44 cross- linked with 1% BAM	Sterilized 60 hrs	2.4	790(av 2)	7
99198-1	Same as 99137-1	"	2.9	725	7
99175-2	Same as 99137-1 ex- cept charge modified with 5% CVE and cross- linked with 2% BAM	"	3.5	715(av 2)	7
99175-2	"	"	2.4	625(av 2)	7
99183-A	Same as 99137-1 ex- cept charge modified with 10% CVE and cross- linked with 2% BAM	"	2.4	700(av 4)	9
99178-A	Same as 99137-1 ex- cept charge modified with 10% VCHO and crosslinked with 1.2% BAM	"	2.3	880(av 3)	12
99178-0	Same as 99178-A ex- cept crosslinked with 0.3% BAM	"	1.5	640(av 3)	10
99178-M	Same as 99178-A with addition of 2% LiNO ₃	"	1.8	770(av 4)	15

^a Instron Tensile Tester; "D" Cell; Chart Speed 5 in min⁻¹; Cross-head Speed 2 in min⁻¹; Gage Length 2 3/4 in ± 1/4 in

^b 2-VP is 2-vinylpyridine; MMA is methyl methacrylate; St is styrene; MAC is methyl acrylate; CVE is 2-chloroethylvinyl ether; and BAM is bis(4-anilino)-methane

^c Wet with KOH after exposure to 40% KOH at 135°C

such as the propanols will be used as pretreatment media to try to improve both film handleability and reproducibility of acceleration of the saponification rate.

2. Use of Films Containing Methacrylic Acid Groups

2-Vinylpyridine-methyl methacrylate-methacrylic acid polymers were also evaluated as separator materials because these polymers "wet" more readily than the 2-vinylpyridine-methyl methacrylate copolymers and therefore, might be expected to saponify more quickly. However, the acid groups also increase film brittleness, and the acid content of these polymers must, therefore, be limited. Samples of these terpolymers were prepared both by partial saponification of the copolymers and by direct polymerization of the three monomers (Section C). One film, prepared from a 31:69 copolymer in which 20% of the methacrylate groups had been pre-saponified to methacrylic acid completely saponified during the standard 60-hour sterilization cycle. Its resistivity was 5 ohm-in. However, films of these terpolymers are slightly opaque. The opaqueness is apparently caused by precipitation of insoluble crosslinked polymer formed by intermolecular salt formation. This interaction was greater with polymers with higher acid contents. Since this characteristic makes it difficult to obtain homogeneous films, the use of the terpolymers as separators is not being pursued further.

C. POLYMER PREPARATIONS

1. 2-Vinylpyridine-Methyl Methacrylate Copolymers

Two 1100-gram batches (110528 and 110531 in Table 2) of copolymer were prepared using freshly distilled monomers and with 0.04% azobisisobutyronitrile as catalyst at 60°C in resin pots under oxygen-free nitrogen. The reactions were stirred until the masses solidified after about 7 hours. These conditions yielded suitable samples of copolymer for film preparation. Their relative viscosities in 0.5% solution were 2.10 and 2.26 and their 2-vinylpyridine contents were 30 and 32%. Both polymers were purified by three successive precipitations with benzene/petroleum ether (30-60°) as solvent/nonsolvent pair.

These polymers were prepared at 60°C since we found that polymerizations (110524A and B) in resin pots at 40°C required excessively long times to reach conversions over 50%. Earlier we had found that polymerizations with small batches in pressure bottles (ref. 2) reached high conversions at 40°C as well as at 60°C. These pressure bottles had been shaken during the entire course of the polymerization and it is possible that the shaker movement increased mobility in the small mass sufficiently to maintain polymerization. Another possible cause of the difference in polymerization rates would be differences in amount of oxygen impurity that reach the polymer.

Table 2
POLYMER PREPARATIONS

Ref. No.	Mole Ratio Monomer Charge	Special Conditions	Catalyst* g/100g Monomer	Temp (°C)	Reaction Time (hr)	Conversion (wt-%)	n_D for 0.5% Solution	2-VP in Product (mole-%)**
99198	18:29:9:44 St:MA:MMA:MAC	- - -	0.2	40	1.5	5.7	1.92	----
110505	Same as 99198	- - -	0.2	40	2.8	7.4	2.36	----
110521	Same as 99198 except 10 wt-% 2-chloroethyl- vinyl ether added	- - -	0.2	40	6.3	49	1.58	----
99187	30:70 2VP-MMA	- - -	0.04	60	72	54	2.84	----
99192	Same as 99187	- - -	0.04	60	72	50	2.11	36
99194	Same as 99187	- - -	0.04	60	96	58	2.23	30
110507	Same as 99187	0.02g addtl. catalyst added after 45 hrs	0.04	60	90	75	2.11	32
110511	Same as 99187	0.02g addtl. catalyst added after 60 hrs	0.04	60	120	76	2.12	33
110513	Same as 99187	- - -	0.04	60	68	74	2.00	31
110518	Same as 99187	- - -	0.04	60	89	60	1.90	----
110524A	Same as 99187	- - -	0.40	40	192	40	1.6	33
110524B	Same as 99187	- - -	0.40	40	288	78	2.1	29
110528	Same as 99187	1100 g scale	0.04	60	95	54	2.26	30
110531	Same as 99187	1100 g scale; 0.02% addtl. catalyst added after 45 hrs.	0.04	60	119	60	2.10	32
110519A	26.4:56:17.7 2VP:MMA:MAA	- - -	0.04	60	46	16	1.2***	----
110519B	25.9:45:29.1 2VP:MMA:MAA	- - -	0.04	60	46	--	1.3***	----

* azobisisobutyronitrile

** by titration with perchloric acid (ref. 3)

*** soluble fractions

2. 2-Vinylpyridine-Methyl Methacrylate-Methacrylic Acid Terpolymers from the Monomers

Two terpolymers (Table 2) were prepared by polymerization at 60°C with 0.04% azobisisobutyronitrile catalyst. Monomer charges of 26:45:29 (110519B) and 26.4:56:17.7 (11059A) mole ratio 2-vinylpyridine:methyl methacrylate:methacrylic acid were used. The polymers were purified by three successive precipitations with methanol/hexane as the solvent/nonsolvent pair. However, an insoluble fraction, apparently caused by intermolecular salt formation, separated at each solution step of the cycle, making purification difficult. These insoluble fractions dissolved in methanol when sodium hydroxide was added.

Relative viscosities of 0.5% solutions of soluble portions of these polymers in methanol were only 1.15 and 1.30 for A and B, respectively, and the polymers gave brittle films.

3. 2-Vinylpyridine-Methyl Methacrylate-Methacrylic Acid Terpolymers by Partial Saponification of 2-Vinylpyridine-Methyl Methacrylate Copolymer

This method of preparation yielded terpolymers with higher molecular weight than those obtained by direct polymerization of monomers. In these preparations we used copolymers with high molecular weight (relative viscosity in 0.5% solution of 3.4), which has low solubility in methanol. The saponifications were, therefore, difficult to control because of the heterogeneous reaction media. The specific conditions that were used to make samples with 20, 58, and 91% conversions of methacrylate to methacrylic acid were as follows:

20% - 7 hours reflux in 10% HCl in methanol-water or from 65 hours in 40% KOH at 135°C;

58% - 22 hours reflux in aqueous 10% HCl;

91% - 89 hours in 40% KOH at 135°C.

We expect that different rates of saponification would be found for more soluble polymer samples. The polymers above also had the irregular solubility characteristics noted above for the terpolymers prepared directly from the monomers.

4. Tetrapolymers

The tetrapolymers characteristically undergo an exotherm at about 5 to 10% conversion during preparation in bulk, which makes large scale preparation difficult. We found that preparation of the tetrapolymer modified with 10 weight-% 2-chloroethylvinyl ether could be controlled with only moderate cooling during the exotherm when polymerization was carried out at 40°C with only 0.2 weight-% catalyst and one polymer (110521 in Table 2) of this type was carried to 49% conversion. The electrical and mechanical properties of this polymer are now being evaluated.

D. SEPARATOR PROPERTIES OF UNMODIFIED TETRAPOLYMER FROM 18:29:9:44 STYRENE-MALEIC ANHYDRIDE-METHYL METHACRYLATE-METHYL ACRYLATE CHARGE

Earlier (ref. 2) we had found that tetrapolymers with the above composition that were modified with 2-chloroethylvinyl ether and crosslinked during film formation with bis(4-anilino)methane had satisfactory properties for a sterilizable separator material. Since the unmodified polymers crosslinked by the same reagent also survived sterilization, a comparison of other separator properties of the two types of tetrapolymers was made as follows.

Several film samples made from the above unmodified tetrapolymer crosslinked with 1 or 2 weight-% bis(4-anilino)methane were sterilized and their electrical and mechanical properties measured. This polymer, like its analogs that are modified by either 2-chloroethylvinyl ether or vinylcyclohexene oxide, dissolves during sterilization unless first crosslinked. The mechanical and electrical properties of the crosslinked films after sterilization are similar to those of the modified polymers. For example, sterilized samples had about 700 psi wet tensile strength (Table 1) and 25 ohm-in resistivity. These data indicate that the amide linkage is sufficiently stable to sterilization in 40% KOH to preserve the good separator properties of the film. However, one property of unmodified polymer, namely, a very short pot life, reduces its usefulness for this application. The pot life of unmodified polymer containing bis(4-anilino)methane is less than 5 minutes compared to 15 to 30 minutes for the modified polymers.

E. REFERENCES

1. J.J. O'Connell, et al., "Separator Development for a Heat Sterilizable Battery," Summary Report, 1 May 1966 to 15 March 1967.
2. Ibid, Quarterly Report 4, October through December 1967.
3. T. Tamikado, J. Poly. Sci., 43, 489 (1960).

IV. PROGRAM PLAN

A. GENERAL

The overall approach to be followed in accomplishing our contract objectives can be divided into the following four phases:

1. Optimization of copolymers;
2. Optimization of modified tetrapolymers;
3. Comprehensive tests;
4. Preparation of film samples.

Our revised long-range program planning chart showing the proposed distribution of effort for each of these phases is given in Table 3. This program was revised to allow time to fully develop two polymer systems, namely, the 2-VP-MMA copolymers and the tetrapolymers, by eliminating study of new separator materials.

B. ANTICIPATED WORK FOR FINAL WORK PERIOD

1. Complete study of pretreatments to accelerate saponification of 2-vinylpyridine-methyl methacrylate copolymers.
2. Evaluate mechanical and electrical properties of samples of film prepared by paper coating technique.
3. Evaluate mechanical and electrical properties of tetrapolymers prepared at high conversions.

Table 3

REVISED PROGRAM PLANNING CHART

Program Phase	Per Cent of Total Research Effort										
	<u>July</u>	<u>Aug</u>	<u>Sept</u>	<u>Oct</u>	<u>Nov</u>	<u>Dec</u>	<u>Jan</u>	<u>Feb</u>	<u>March</u>	<u>April</u>	<u>May</u>
Optimization of copolymers	10	35	40	40	30	65	60	10			
Optimization of Modified Tetra-polymers	90	60	55	55	40	30	30	10			
Comprehensive tests		5	5	5	5	5	10	10	5	40	
Preparation of film samples					25			70	85	40	
Final report										20	100