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SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

Final Summary Progress Report Supplement

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ABSTRACT

Two ligand-containing polymers were developed as separator materials for heat sterilizable silver oxide-zinc cells. A pilot film sample of one of these polymers that is derived from a 33:67 2-vinylpyridine:methyl methacrylate copolymer was prepared and submitted to JPL for their evaluation. The pilot sample consists of a total of 150 square feet, in sections over 10 feet long, of 1.5 mil film which has 7000 psi dry tensile strength and shows electrical resistivity under 10 ohm-in. after sterilization in 40% KOH at 135°C. The film normally requires about 120 hours sterilization to reach this minimum resistance, but pretreatment of the film with alcohols shortens the time to under 64 hours.

The second polymer developed is a tetrapolymer made from an 18:29:9:44 styrene: maleic anhydride:methyl methacrylate:methyl acrylate monomer charge that is crosslinked during film formation by reaction with a diamine. Films of this material with 1 to 2 mil thickness have dry tensile strengths of about 6000 psi and reach electrical resistivities of about 20 ohm-in. after sterilization for 64 hours.

I. INTRODUCTION

The primary objective of this program was 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. Two types of ligand-containing polymers that showed a great deal of promise in our initial JPL 951524 program, namely, copolymers of 2-vinylpyridine-methyl methacrylate and polymers containing styrene, maleic anhydride, and methyl methacrylate units were chosen for development and optimization.

Our program was divided into the following four phases.

1. Optimization of the mechanical and electrical properties of the 2-vinylpyridine-methyl methacrylate copolymer films. This work involved both improvement of the method of preparation of this copolymer to obtain polymers with higher molecular weights, and the development of new techniques to insure complete hydrolysis of the films during sterilization.
2. Determination of the optimum compositions of the styrene-maleic anhydride-methyl methacrylate type polymers that give the lowest electrical resistivity compatible with good film mechanical properties.
3. Evaluation of the mechanical and electrical properties of separator films made from the optimized polymers.
4. Preparation of a total of 100 linear feet of 18-inch wide film made from our best polymer system. The film should be in lengths of 10 feet or longer.

II. SUMMARY

A. 2-Vinylpyridine-Methyl Methacrylate Copolymers

The first phase in the development of our 2-vinylpyridine-methyl methacrylate copolymers consisted of improving polymerization conditions to increase the molecular weight of the polymer. This increase in polymer molecular weight was necessary to obtain more durable films. A study of the polymerization conditions showed that the degree of polymerization (1) increased at high reactant conversions, (2) decreased significantly in the presence of traces of oxygen or other chain terminators, and (3) was relatively insensitive to changes in catalyst concentration and polymerization temperature. Polymers with intrinsic viscosities as high as 4.2 were prepared.

During testing of films of the new higher molecular weight copolymers (relative viscosity of 0.5% solution over 2) we found that the increase in polymer molecular weight had sufficiently improved the film mechanical properties so that copolymers with higher methacrylate contents (67-70%) than before (55%) could be used as separator materials. The higher methacrylate content is desirable since it lowers the electrical resistivity of the separator. For example, the new higher molecular weight copolymers with 67 to 69% methacrylate contents gave durable separators with resistivities under 10 ohm-in. after sterilization. Earlier, lower molecular weight copolymers with this composition dissolved during sterilization.

In the next phase of development, an evaluation was made of the film forming characteristics and of the mechanical and electrical properties of the films of a series of high methacrylate copolymers with different molecular weights to choose the best molecular weight for scale-up. The molecular weight affected two properties of the polymer that were considered in this choice, namely, polymer solubility in solvents used for film preparation and the time required to saponify the methacrylate groups under sterilization conditions. In this evaluation, polymers with moderate molecular weight (relative viscosity in 0.5% solutions of 2 to 2.7) were found to have better solubility characteristics and also to saponify at higher rates than polymers with very high molecular weight. Therefore, about 4500 g. of the 33:67 copolymer with moderate molecular weight was prepared. This material was used to make 150 square feet of 1.5 mil separator film using a pilot paper coater to coat the film. This film has 7000 psi dry tensile strength and reaches an electrical resistivity under 10 ohm-in. after sterilization for 120 hours in 40% KOH at 135°C.

Methods to obtain complete saponification of these polymers within one 64-hour sterilization cycle were also investigated. The most effective method was to accelerate saponification by incorporation of alcohols into the polymer. Complete saponification within 64 hours was best obtained by methanol pretreatment of the high molecular weight polymers and by octanol pretreatment of the moderate molecular weight polymers such as used to make the pilot separator sample. Complete saponification within 64 hours was also obtained with films made from 2-vinylpyridine-methyl methacrylate-methacrylic acid terpolymers. However, the film forming properties of these polymers are poor because of the adverse effect on solubility caused by intermolecular bonding between the pyridyl groups and the free acid groups.

B. Polymers Containing Maleic Anhydride

Several polymer modifications containing styrene and maleic anhydride were prepared and evaluated to improve both the mechanical and electrical properties of the co- and terpolymers that had been developed in our initial program. The results of these evaluations are summarized as follows.

- The usefulness of the styrene-maleic anhydride copolymer was previously limited because the low molecular weight samples that were used gave hard, brittle films in a dry atmosphere. High molecular weight samples of this copolymer having intrinsic viscosities of 4.3 and 1.8, compared to 0.8 for the earlier samples, were prepared. These polymers formed films with much greater flexibility and also slightly higher tensile strength. The polymer with 1.8 intrinsic viscosity has better film-forming properties than the highest molecular weight polymer, because of higher solubility in the casting solvent, but was not equal to the ter- and tetrapolymers developed later.

- The styrene-maleic anhydride-methyl methacrylate terpolymers used before gave films with good mechanical properties, but had electrical resistivities after sterilization that were close to the usable maximum of 60 ohm-in. Several terpolymers were prepared from reactants containing a high ratio of maleic anhydride. It was necessary to prepare these polymers in methylene chloride solvent to obtain high molecular weights. The strong azeotropic effect in polymerization of these monomers limited their anhydride content to under about 40%. For this reason, other modifications of these polymers were made to obtain larger improvements in their electrical properties than could be realized from this polymer composition.

- The major modification was to incorporate easily hydrolyzable methyl acrylate units in the polymer to make tetrapolymers. These polymers were readily prepared by bulk polymerization and had slightly higher molecular weights than the terpolymers.

Sample films of tetrapolymers prepared from 43:25:10:22 and 48:25:10:17 charges of styrene-maleic anhydride-methyl methacrylate-methyl acrylate had electrical resistivities from 35 to 70 ohm-in. after sterilization in 40% KOH. Films of tetrapolymers from charges containing higher contents of hydrolyzable anhydride and acrylate groups, that should have lower resistivities, could not be tested because of some solubility in 40% KOH after sterilization. These polymers were modified and crosslinked during film preparation to reduce solubility. Polymers prepared from monomer charges of 18:29:9:44 and crosslinked with 4, 4'-bis (anilino) methane gave films that were durable during sterilization and had resistivities of about 20 ohm-in. after one 64-hour sterilization cycle.

III. DISCUSSION OF RESULTS

A. Evaluation of Separator Properties

1. General

Film samples of polymers being evaluated as separator materials were routinely sterilized in 40% KOH at 135°C to test film durability and stability. The properties of these films that were measured were as follows:

1. Dimensions before and after sterilization.
2. Electrolyte absorption during sterilization.
3. Electrical resistivity after sterilization.
4. Appearance
5. Tensile strength of dry films before sterilization and wet films after sterilization.

The general procedures developed for evaluation of separators for silver oxide-zinc batteries (ref. 1) were used. Details of these tests are described in the Experimental Section of this report. With the exception of some of the early tests, the films were fastened in Teflon holders (Figure 1) during sterilization to retain film dimensions. Unfastened films shrank during sterilization.

The maximum acceptable electrical resistivity for a separator material to be usable is 60 ohm-in. However, an electrical resistivity under 10 ohm-in. is considered ideal. A single value of the minimum acceptable tensile strength can not be specified since film durability depends upon both tensile strength and flexibility (elongation). We found that dry film with elongations under 3% that had tensile strengths over 4500 psi were durable and resistant to tears under ordinary handling. Wet film with elongations above 10% were resistant to tears when tensile strengths were over about 200 psi.

Data describing the electrical properties of the separators are in Tables I, III and V and data describing their mechanical properties are in Tables II and IV.

2. 2-Vinylpyridine-Methyl Methacrylate Copolymers

The electrical and mechanical properties of these copolymers after sterilization depend upon polymer molecular weight, polymer composition and film thickness. In general, films made from polymers with the highest methacrylate contents had the lowest

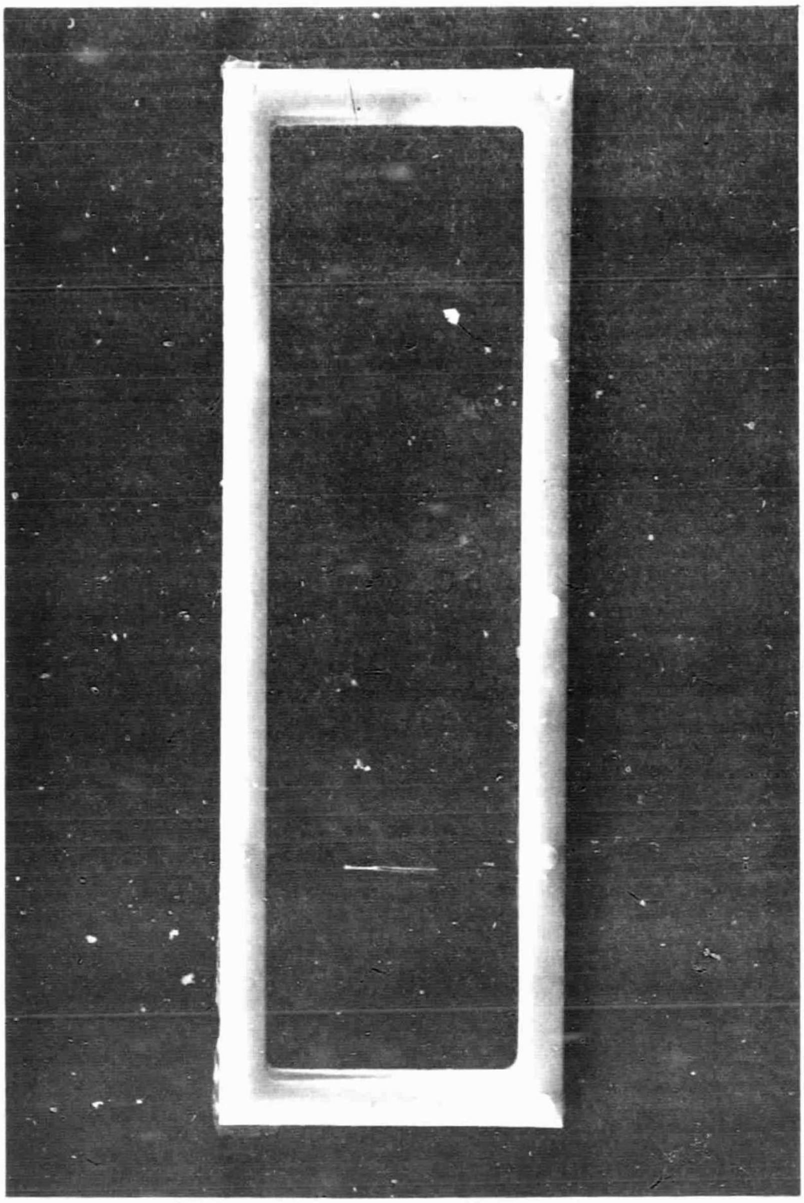

Figure 1. Teflon Film Holder for 2 by 5 1/2 Inch Films

electrical resistivities and wet tensile strengths, and the highest wet elongations after sterilization. As would be expected, mechanical strength and durability of the film increased with increase in molecular weight of the polymer. However, films made from high molecular weight polymers required longer or more drastic sterilization conditions to complete saponification of the methacrylate groups than those made from lower molecular weight polymers with the same methacrylate content.

Data summarizing the results of tests of the electrical properties of films of these copolymers are in Table I. Tests of mechanical properties are summarized in Table II. The test results can be summarized as follows:

- Electrical resistivity of copolymer films with methacrylate contents above 65% were under 10 ohm-in. after saponification during sterilization.

- Several films made from low and moderate molecular weight copolymers with methacrylate contents between 55 and 65% that were tested both last year (ref. 2) and this year had resistivities in the range 7 to 60 ohm-in. after sterilization. However, some required over 120 hours sterilization to complete saponification and reach the minimum resistance level.

- The sterilization time required for complete saponification of the methacrylate groups varied with the molecular weight of the polymer. All films made from copolymers with 65 to 70% methacrylate contents saponified completely within 120 hours when the relative viscosity of the polymer was under 2.3. Some films made from polymers with viscosities over 3 required longer time.

- The sterilization time required for complete saponification of all the copolymers could be lowered by pretreatment with saponification accelerators. These pretreatments are discussed in Section 3 following.

- Tensile strengths were 7000 to 7400 psi for dry films made from all copolymers with relative viscosities over 2.

- Tensile strengths of wet sterilized film with resistivity below 10 ohm-in. were 250 to 350 psi. Elongation of these films was over 100%. Tensile strengths of sterilized films made from copolymers with lower methacrylate contents that have resistivities between 10 and 60 ohm-in. (Table II and ref. 2) are higher.

Table I

PROPERTIES OF 2-VINYLPYRIDINE-METHYL METHACRYLATE SEPARATORS AFTER STERILIZATION IN 40% KOH AT 135°C

Reference	Polymer Composition	Pretreatment	Thickness Dry (mils)	Sterilization Time, Hours	Properties After Sterilization[a]		
					Thickness (mils)	Wt. Gain %	ρ (ohm-in)
Pilot Run #2	31:67 (n_R = 2.1)	none	1.4	120	2.9 (2.7-3.3)	378 (360-412)	7.0 (AV 6) (5.4-9.6)
Pilot Run #1	31:69 (n_R = 2.2)	none	1.8	120	3.5 (3.3-3.8)	354 (314-382)	3.8 (AV 5) (3.2-4.6)
		none	1.4	90	3.0	468 (369-557)	4.6 (AV 4) (4.5-..9)
		Soaked in octanol to 11% wt. gain	1.6	60	3.0	-	3.5 (AV 2)
		Soaked in octanol to 5% wt. gain	1.6	60	3.3	700	3.9
		Soaked in octanol to 1% gain	1.8	60	3.5	500	7.9
			1.6	60	3.7	450	2.9 (AV 4)
		Soaked in octanol to 0.4% gain	1.6	60	3.5	-	22 (AV 2)
			1.6	60	3.7	-	over 50 (2)
110536	34:66 (n_R = 1.9)	film contains 2.2% octanol	2.3	60	3.5	390	9.4
			2.6	60	3.7	310	8.5
		film contains 2.8% butyl stearate	2.3	60	3.7	250	12.3
			2.5	60	3.5	300	11.6
		film contains 6.9% butyl stearate	2.4	60	3.0	520	8.4
			2.0	60	2.5	550	9.6
Pilot Run #1	31:69 (n_R = 2.2)	1 min. soak in n-propanol	2.0	60	4.0	-	3.8 (AV 2)
		1 min. soak in n-propanol followed by 20 min. drain	1.7	60	5.0	-	24
			1.7	60	-	-	over 50
		15 min. soak in isopropanol	1.8	60	3.0	-	5.0 (AV 2)
		30 min. soak in isopropanol followed by 2 min. drain	1.8	60	(10)	-	9.3
			1.8	60	8	-	over 50
		5 min. soak in n-butanol	1.8	60	4.0	-	3.4

Table I (Continued)

PROPERTIES OF 2-VINYLPYRIDINE-METHYL METHACRYLATE SEPARATORS AFTER STERILIZATION IN 40% KOH AT 135°C

Reference	Polymer Composition	Pretreatment	Thickness Dry (mils)	Sterilization Time, Hours	Properties After Sterilization[a] Thickness (mils)	Wt. Gain %	ρ (ohm-in)
99194	30:70 (n_R = 2.23)	30 min. soak in 3:1 of 40% KOH:methanol (350 to 600% wt. gain)	1.4	60	3.3	600	3.0 (AV 2)
			1.8	60	-	-	over 50
		30 min. soak in 1:1 40% KOH:methanol	1.6 to 1.8	60	4.2 to 5.0	-	3 to over 50
58039	31:69 (n_R = 4.6)	none	1.3	114	2.8	283	13
		none	1.3	120	3.2	450	4
		none	1.5	120	3.0	215	>100
		none	1.6	120	3.0	173	>100
		none	1.5	120	4.2	---	17
		none	1.5	120	4.5	---	16
58040	33:67 (n_R = 3.2)	none	---	164	4.0	---	10
		none	1.0	114	4.0	300	6
		none	1.6	120	3.1	127	>50
		none	1.9	120	4.5	277	5
		none	2.0	120	4.2	217	5
		none	1.9	120	3.3	179	90
58019	38:62 (n_R = 1.5)	none	1.1	120	7	---	49
58027	40:60 (n_R = 1.7)	none	---	164	4.5	---	>100
		none	2.1	120	2.8	250	>100[b]
58036	36:64 (n_R = 2.5)	none	---	164	2.0	---	>100
		none	1.7	120	2.5	240	66[b]

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[a] Original area dimensions retained during sterilization by film holder

[b] 5 wt-% $LiNO_3$ in film.

Table II

TENSILE STRENGTH OF 2-VINYLPYRIDINE-METHYL METHACRYLATE MEMBRANES[a]

Reference	Polymer Composition	Relative Viscosity of 5% Solution of Polymer	Pretreatment	Film State	Thickness mils	Tensile Strength psi	Elongation at Break, %
Pilot Run #1	31:69	2.2	none	dry	1.6	7000 (AV 5)	<3
			none	wet after 120 hrs sterilization	3.5	270 (AV 11)	155
Pilot Run #2	31:67	2.1	none	dry	1.4	7400 (AV 5)	<3
			none	wet after 120 hrs sterilization	3.0	345 (AV 7)	145
			4 hr soak in 1-octanol to 1.1% wt gain	wet after 60 hrs sterilization	3.8	340	33
					2.5	775 (AV 2)	38
					2.4	125 (AV 2)	150
Pilot Run #1		2.2	7 hr soak in octanol to 3.3% gain	wet after 60 hr sterilization	3.2	31	170
			1 min. soak in n-propanol	"	4.1	195 (AV 5)	40
			15 min. soak in isopropanol	"	3.7	270 (AV 2)	50
			30 min. soak in isopropanol	"	6.8	130	35
			5 min. soak in n-butanol	"	6.8	60	47
99194	30:70	2.23	none	wet after 120 hr sterilization	5.3	280 (AV 3)	70
			film cut on bias	"	3.7	135	45
			30 min. soak in 3:1 of 40% KOH:methanol	wet after 60 hr sterilization	3.5	105 (AV 2)	115
			30 min soak in 1:1 of 40% KOH:methanol	"	3.8	130	43
			22% of ester groups prehydrolized	"	2.0	75	163

Table II (Continued)

TENSILE STRENGTH OF 2-VINYLPYRIDINE-METHYL METHACRYLATE MEMBRANES[a]

Reference	Polymer Composition	Relative Viscosity of 5% Solution of Polymer	Pretreatment	Film State	Thickness mils	Tensile Strength psi	Elongation at Break,%
10528	30:70	2.26	15 min. soak in 1:1 of 40% KOH:methanol	"	5.6	130 (AV 2)	47
99194	30:70	2.23	2 min. soak in 1:1 water: methanol	"	3.2	63	77
110531	32:68	2.10	30 min. soak in 1:1 40% KOH:methanol	"	2.6	375 (AV 3)	45
110536	34:66	1.88	cost film contains 2.2% octanol	dry	1.9	6500 (AV 2)	2.8
				wet after 60 hr sterilization	3.0	320 (AV 2)	85
			cost film contains 2.8% butyl stearate	dry	2.0	5600 (AV 3)	3.5
				wet after 60 hr sterilization	3.0	395 (AV 2)	75
			cost film contains 6.9% butyl stearate	dry	1.9	3700 (AV 2)	4.5
				wet after 60 hr sterilization	3.2	220 (AV 2)	115
58036	36:64	2.46	none	wet after 120 hr sterilization	3.5	2300	9
			5° to $LiNO_3$ in film	dry	1.5	8600	<3
58040	33:67	3.16	none	dry	1.3± 3	7100 (AV 10)	<3
			none	wet after 120 hr sterilization	3.2	660 (AV 2)	55
					3.6	570 (AV 2)	38
					3.3	2300	4
58039	31:69	4.65	none	dry	-	7000 (AV 7)	<3
			none	wet after 120 hr sterilization	2.8	640	18
					3.9	260 (AV 3)	92
			2 min. soak in methanol	wet after 60 hr sterilization	4.5	1100 (AV 2)	12
					4.6	335 (AV 6)	100
(58039)		(4.65)	58% of ester groups prehydrolyzed	wet after 60 hr sterilization	3.3	215 (AV 2)	175

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[a] Instron Tensile Tester; "D" Cell; Chart Speed 5 in min^{-1}; Cross-head Speed: Dry 0.5 in min^{-1}, Wet 2 in min^{-1} : Gage Length 2 3/4 in ± 1/4 in

3. Film Pretreatment to Accelerate Saponification of Methacrylate Groups During Sterilization

a. Film Pretreatment by Saponification Accelerators

Films of our 31:69 2-vinylpyridine-methyl methacrylate copolymer required 90 to over 120 hours, depending upon molecular weight, sterilization in 40% KOH at 135°C to complete saponification of the methacrylate group and attain the low electrical resistivity required of the separator. 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 were studied. We found that pretreatment with alcohol effectively accelerated saponification rate during sterilization.

The specific alcohol treatment that accelerated saponification with a minimum effect on the mechanical properties of the film was different for copolymers with different molecular weights. For example, films of high molecular weight copolymer (polymer 58039) could be immersed directly in methanol for 1 to 2 minutes immediately before sterilization. This methanol treatment wetted and plasticized the films and, therefore, probably accelerated subsequent penetration by the 40% KOH. 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 I) 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 film 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) was too high for immersion in methanol without dilution with a nonsolvent. Therefore, less drastic pretreatments were necessary. Solutions containing varying proportions of methanol in either water or 40% KOH were first used to pretreat these films. Immersion times were from 1 to 30 minutes. The most effective solutions were methanol: 40% KOH solutions containing over 50% methanol. Several 1.5 mil films pretreated by these solutions saponified completely within the 60 hour sterilization period. However, the treatment did not give completely reproducible results and also was less effective with films of thickness greater than 1.8 mils.

Next, a series of pure higher alcohols from n-propanol to 1-octanol were evaluated. n-Propanol, n-butanol and sec-butanol plasticized the films appreciably and generally caused a large loss in mechanical strength of the films during sterilization.

When the treatment with n-propanol was limited to 1 minute or less the films survived sterilization. For example, five samples of Pilot #1 films that were treated in this way had 195 psi average tensile strength after sterilization. However, this treatment is difficult to control to give reproducible up-takes of alcohol because of the high volatility of n-propanol.

Isopropanol and 1-octanol affected the modulus of the film very little. Only 2 weight % isopropanol was absorbed by the film during a 15-minute immersion, and the absorption of 1-octanol into the films during the same immersion time was much lower. The pretreatments by both isopropanol and 1-octanol resulted in complete saponification of the methacrylate groups on the copolymer within the 60 hour sterilization cycle when the alcohol uptake was over 1%. Of the two alcohols, 1-octanol is the preferred reagent. Due to its higher boiling point (194°C), it is more convenient to use, and also, it will not contribute to the vapor pressure in the sealed battery.

Octanol absorptions between 1 and 2% were found to be best: lower absorptions did not cause complete saponification during the 60 hour cycle and higher absorptions appreciably lowered the mechanical strength of the sterilized films. We also found that it was necessary to soak the films for 4 to 6 hours in octanol to obtain homogeneous absorption. Films containing 2% octanol absorbed on the outer surface during a short immersion had poor mechanical properties after sterilization.

Another and more convenient method to obtain homogeneous absorption of the saponification accelerator is to incorporate it directly into the film during casting. Films were prepared in this way using octanol or butyl stearate as accelerator. Both accelerators were effective (Table I). The stearate also plasticized the dry film, making it extremely easy to handle.

Another type of pretreatment tested to accelerate saponification consisted of pre-wetting the film surface with dilute potassium hydroxide before sterilization. The 40% KOH solution has a high contact angle (non-wetting) on the copolymer film. As this solution is diluted with water, the angle diminishes and good wetting ($\theta < 90^\circ$) is achieved in the range 10-13% KOH solution. Therefore, samples of copolymer film were immersed in solutions of this strength for either 64 hours at 72°C or 24 hours at 85°C before being sterilized in 40% KOH for 64 hours at 135°C. However, all the films had resistivities above 50 ohm-in. after the 64-hour sterilization period, indicating incomplete saponification.

b. 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 presaponified 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 was not pursued further.

4. Polymers Containing Maleic Anhydride

a. Linear Polymers

A series of co-, ter- and tetrapolymers containing maleic anhydride together with styrene, styrene and methyl methacrylate or styrene, methyl methacrylate and methyl acrylate, respectively, were tested. Their electrical properties are described in Table III and their mechanical properties in Table IV. These polymers completely hydrolyze within one 64-hour sterilization cycle unlike the untreated 2-vinylpyridine copolymers which require two cycles. During hydrolyses, however, only the anhydride and acrylate groups react. The methacrylate group in these polymers remains largely intact during sterilization.

The mechanical properties of dry films of these polymers improve with increase in methacrylate and/or acrylate content. The styrene-maleic anhydride polymer gives rather hard films. The flexibility and durability of films made from the high molecular weight copolymer 99119 and moderate molecular weight copolymer 99130B were much greater than those of films prepared from low molecular weight copolymer (Lytron® 810) that were tested last year (ref. 2), but were not equal to the ter- and tetrapolymers. Therefore, most of our efforts were directed at improving the electrical properties of the ter- and tetrapolymers.

Table III

PROPERTIES OF SEPARATORS MADE FROM LINEAR POLYMERS CONTAINING MALEIC ANHYDRIDE AFTER STERILIZATION IN 40% KOH AT 135°C

			Properties after Sterilization for 64 Hours				
Polymer No.	Polymer Composition	Dry Thickness(mils)	Thickness(mils)	Wt. Gain(%)	Area Retention(%)	ρ (ohm-in)	Appearance
99119	Styrene-maleic anhydride copolymer	0.69	1.8	228	(100)**	40.2*	Sl. yellow
		0.65	3.1	283	35	32.9	Shrunken
		0.65	1.1	350	70	----	
99130B	Styrene-maleic anhydride copolymer	1.16	2.3	192	(100)	39.4	
		1.1	1.5-3.8	296	64	(0.091 ohm-in^2)	Uneven surface
		0.93	1.5	174	(100)	55.7*	
99121	Styrene-maleic anhydride-methyl methacrylate terpolymer from 50:25:25 monomer charge	0.54	1.4	488	100	21	Some surface
		0.92	2.7	207	100	34	wrinkles
99117	Same as 99121 but from 40:45:15 monomer charge	0.47	film continuity lost during sterilization				
		0.49					
99118	Same as 99121 from 18:50:32 monomer charge	0.04	0.36	1000	film continuity lost during sterilization		
99115	Same as 99121 from 33:33:33 monomer charge	1.7	3.4	244	(100)	49.2*	
99127	Styrene-maleic anhydride-methyl methacrylate-methyl acrylate polymer from 43:25:10:22 charge	0.9	2.5	248	100	37.9	Wrinkled
		1.6	3.3	227	---	35.7*	Brown colored
		1.18	1.6	171	(100)	70.7	
		1.34	2.2	178	(100)	40.5	
		1.6	2.7	200	(100)	33.0*	
99129	Same as 99127 from 48:25:10:17 charge	2.1	2.8	189	105	49.7	
		1.0	2.6	258	77	37.9	
		1.2	3.9	335	90	----	
		1.2	2.7	99	100	86*	
99137	Same as 99127 from 18:29:9:44 monomer charge	1.1	film continuity lost				
99138C	Same as 99127 from 18:29:19:33 monomer charge	0.73	---	360	film continuity lost		
99132	Same as 99127 from 28:20:19:33 charge	film continuity lost					

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* Sterilized in 40% KOH containing 1M ZnO

** (100) indicates that area was controlled by fastening sample to Teflon frame with Teflon plugs

Table IV

TENSILE STRENGTH OF MEMBRANES DERIVED FROM POLYMERS CONTAINING MALEIC ANHYDRIDE[a]

Reference	Polymer Composition[b]	Film State[c]	Thickness mils	Tensile Strength, psi	Elongation at Break, %
99137-1	St:MA:MMA:MAC 18:29:9:44 cross-linked with 1% BAM	Sterilized	2.4	790 (av 2)	7
99198-1	Same as 99137-1	"	2.9	725	7
99128	St:MA:MMA:MAC 17:30:20:33 charge	Dry	-	4850 (av 3)	2
99150	St:MA:MMA:MAC from 18:29:9:44 charge modified with 10% CVE and crosslinked with 2% BAM	Dry	1.7	6000	<3
		Sterilized	3.5	720	6
		Sterilized	4.0	750	4
	Crosslinked with 1% BAM	Dry	1.5	5900	<3
		Sterilized	3.0	300	13
		Sterilized	3.0	500	8
99183A	Same as 99150 and crosslinked with 2% BAM	Sterilized	2.4	700 (av 4)	9
	Same as 99150 and crosslinked with 1% BAM	Sterilized	3.5	375 (av 2)	10
99153	St:MA:MMA:MAC from 18:29:9:44 charge modified with 5% CVE and crosslinked with 1% BAM	Dry	1.3	5400	<3
		Sterilized	5.0	520	7
		Sterilized	3.5	500	14
	Crosslinked with 0.5% BAM	Dry	1.4	4300	<3
		Sterilized	3.0	330	14
		Sterilized	3.0	435	14
	Crosslinked with 0.25% BAM	Dry	1.9	5800	<3
99175-2	Same as 99153 and crosslinked with 2% BAM	Sterilized	3.5	715 (av 2)	7
		Sterilized	2.4	625 (av 2)	7
99169	St:MA:MMA:MAC from 18:29:9:44 charge modified with 10% VCHO and crosslinked with 1.2% BAM	Sterilized	2.5	720	14
	Crosslinked with 0.6% BAM	Sterilized	2.7	560	8
99178A	Same as 99169	Dry	1.5	6650 (av 6)	-
	Crosslinked with 1.2% BAM	Sterilized	2.3	880 (av 3)	12
	Crosslinked with 1.2% BAM and containing 2% $LiNO_3$	Sterilized	1.8	770 (av 4)	15
	Crosslinked with 0.3% BAM	Sterilized	1.5	640 (av 3)	10
99138B	St:MA:MMA:MAC from 43:25:10:22 charge	Dry	1.4	3400	<3
		Sterilized	3.0	570	4
99129	St:MA:MMA:MAC from 48:25:10:17 charge	Sterilized	3.3	365	43
99158	St:MA:MMA:MAC from 28:20:19:33 charge	Sterilized	2.5	240	385
		Sterilized	2.2	455	80
99115	St:MA:MMA from 33:33:33 charge	Dry	-	5000 (av 2)	3
		Wet after soaking in 40% KOH 1 week	-	1180 (av 4)	<3
99119	St:MA ([n]=4.3)	Dry	-	3750	<3
99130B	St:MA ([n]=1.8)	Wet after soaking in 40% KOH 1 week	-	770	130

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[a] Instron Tensile Tester; "D" Cell; Chart Speed 5 in min^{-1}; Cross-head Speed 2 in min^{-1}; Wet and 0.5 in min^{-} dry; Gage Length 2 3/4 in ± 1/4 in.

[b] MA is maleic anhydride; MMA is methyl methacrylate; St is styrene; MAC is methyl acrylate; CVE is 2-chloroethylvinyl ether; and BAM is bis(4-anilino)-methane

[c] "Sterilized" denotes wet with KOH after exposure to 40% KOH at 135°C for 60 hrs.

Electrical resistivities of the terpolymers were mostly in the range 30 to 60 ohm-in. (Table IV). Reduction of resistivity below this range was prevented by the limitation of the amount of maleic anhydride that could be incorporated into the terpolymers due to the azeotropic effect that is discussed in Section III, D, 5. Therefore, a series of tetrapolymers containing varying amounts of the hydrolyzable acrylate groups were prepared and tested. We found that linear polymers with a high enough content of hydrolyzable anhydride and acrylate groups to give electrical resistivities below 30 ohm-in. had high solubility in 40% KOH. Two of these polymers, prepared from monomer charges of 18:29:19:33 and 28:20:19:33, were therefore modified by crosslinking to reduce solubility. These polymers are described in the following sections.

b. Crosslinked Tetrapolymers

Data describing the mechanical properties of the crosslinked polymers, prepared as described in Section IV, E, are in Table IV. Their electrical properties are given in Table V. These properties of the films made from either unmodified or modified-type polymers crosslinked with diamines were similar. However, as stated in Section IV, E, the modified polymers are preferred as separator materials because they have longer pot lives when crosslinked during film preparation. The results of the tests can be summarized as follows:

- Resistivity of the sterilized films was not markedly affected by the amount of reagent used to crosslink the polymer in the range studied.

- Resistivities of sterilized films were reproducible. For example, thirteen 2 x 6 inch film samples having a 1.2 ± 0.3 mil thickness of polymer 99178, which is modified with 10% vinylcyclohexene oxide, were crosslinked with from 0.3 to 1.2% bis(4-anilino)methane (BAM) and sterilized. Resistivities of these samples were 15 ± 2 ohm-in. Four similar 1.6 ± 0.1 mil films of polymer 99183, which is modified with 10% 2-chloroethyl vinyl ether were crosslinked with 2% BAM and found to have 19 ± 1 ohm-in. resistivity after sterilization. This compares to an average of 21 ohm-in. for films made from duplicate polymer number 99150.

- Tensile strength tests on sterilized films indicate that tensile strength was increased and elongation decreased by using larger amounts of crosslinking reagent [e.g. 99150 with 2 and 1% bis(4-anilino)-methane had strengths of 720 and 300 psi, respectively, and elongations of 6 and 13%]. These results indicated that the degree of crosslinkage was increased by using the larger amount of reagent.

Table V

PROPERTIES OF SEPARATORS MADE FROM CROSSLINKED TETRAPOLYMERS AFTER STERILIZATION IN 40% KOH at 135°C

					Properties After Sterilization[b]		
Reference	Polymer Composition	Crosslinking[a] Modification	Thickness Dry (mils)	Sterilization Time, Hours	Thickness (mils)	Wt. Gain %	ρ (ohm-in)
99146	St:MA:MMA:MAC tetrapolymer from 28:20:19:33 charge modified with 10%CVE	1% BAM by soaking in methanol (105331)	2.3	64	8.0[c]	300	7.1
		2% BAM (105334)	3.2	64	5.3	186	27
		2% BAM (105334)	1.9	64	3.3	171	29
		None	Dissolved during sterilization				
99168	Same as 99146 except modified with 10% VCHO	0.24% MPD (105341A)	1.1	64	3.5	1000	23
		0.5% MPD (105341B)	1.3	64	(2.5-4)	145	~30
99150	St:MA:MMA:MAC from 18:29:9:44 charge modified with 10% CVE	2% BAM by methanol soak(105334)		64	1.8		6.3
		1% BAM (105335-1/2)	0.8	64	2.7	57	7.1
		1% BAM (105335-1/2Δ)[d]	2.1	64	3.5	67	23
		4% BAM (105335-2)[d]	1.2	64	1.7	275	37
		4% BAM (105335-2Δ)[d]	3.5	64	4.5	202	23
		2% BAM (105335-1Δ)[d]	0.8	64	1.5	250	38
		Same as 105335-1	1.6	64	2.5	133	22
			1.4	64	3.0	150	19
		Same as 105335-2	2.1	64	3.8	135	20
			2.6	64	4.5	230	18
99163	Same as 99150 but with no modifications	None	Dissolved during sterilization				
99137	Same as 99163	1% BAM	-	64	2.8	-	18
99183	Same as 99150	2% BAM	1.5	64	2.5	166	16
			1.5	64	2.5	158	20
			1.7	64	3.5	151	20

Table V (Continued)

PROPERTIES OF SEPARATORS MADE FROM CROSSLINKED TETRAPOLYMERS AFTER STERILIZATION IN 40% KOH at 135°C

Reference	Polymer Composition	Crosslinking[a] Modification	Thickness Dry (mils)	Sterilization Time, Hours	Properties After Sterilization[b] Thickness (mils)	Wt. Gain %	ρ (ohm-in)
			1.6	64	3.2	155	19
99153	Same as 99150 except modified with 5% CVE	1% BAM		64	3.3	---	22
			1.5	64	3.7	180	29
		0.5% BAM	---	64	2.7	---	20
			1.2	64	3.2	138	21
99160	Same as 99150 except modified with 5% methyl 3-aminocrotonate	0.5% bis(chloromethyl)mesitylene	0.5	64	Dissolved during sterilization		
		1% " (105337)	2.6	64	Dissolved during sterilization		
99138C	Same as 99163	Films containing 2-methyl anthraquinone exposed to UV light	1.3	64	Dissolved during sterilization		
		Cured with 1% dicumyl peroxide at 115°C for 24hr	1.2	Dissolved during sterilization			
99169	Same as 99150 except modified with 10% VCHO	0.4% TETA(105338)	1.4	64	~8.5[f]	214	~12
		1.2% BAM(105338)	1.2	64	1.5	176	28
			1.2	64	2.2	225	33
		0.6% BAM	1.1	64	2.5	236	24
99178	Same as 99169	1.2% BAM	1.5	64	3.2	148	20
			1.5	64	3.2	158	17
			1.1	64	3.3	171	13
		1.2% BAM at RT	1.0	64	2.5	104	13
			1.1	64	2.5	63	16
		1.2% BAM[e]	1.3	64	3.5	208	14
			1.5	64	3.5	216	15
			1.3	64	3.8	190	17
			1.2	64	3.0	250	15
		0.3% BAM	1.3	64	3.4	163	14
			1.3	64	3.7	244	13
			1.2	64	3.5	138	13
		0.3% BAM at RT	1.0	64	2.5	232	16
110546	Same as 99150	1% BAM		Dissolved during sterilization			

- The crosslinked polymers showed good tear-resistance. Film samples that were fastened to the Teflon frames by Teflon plugs during sterilization did not develop cracks. Elongation of all sterilized films with tensile strengths under 500 psi was greater than 10%.

- Low molecular weight linear polymers require a higher degree of crosslinkage to render them insoluble. Polymer 110546, which had a relative viscosity of only 1.2, dissolved during sterilization when crosslinked with 1% BAM.

B. Film Preparation

1. Laboratory Scale

Small samples of polymer films, approximately 5 by 20 in., were prepared by casting solutions of the polymer onto a flat surface and leveling with a Gardner blade. Special care was taken to minimize dust entrapment and the films were dried at low humidity to avoid film "blush". Detailed conditions used to prepare the different types of films are given in the Experimental section.

2. Pilot Scale

The use of a paper coater was chosen as the most suitable method to scale-up production of film samples of the 31:69 2-vinylpyridine-methyl methacrylate copolymer. The requirements and limitations of the paper coater made it necessary to alter only slightly the conditions used in the laboratory scale preparations described above. The major alterations made were as follows:

- Substrate - Substitute a suitable release paper for polypropylene.

- Concentration of Casting Solution - Increase concentration to 13% solids content to obtain the required film thickness (1.50 ± 0.15 mils) at the maximum roller opening of the paper coater (approximately 18 mils).

- Drying Temperature - Increase drying temperature to complete drying of film during one to three 4-minute passes through the drying ovens.

A total of 100 linear feet of film with 1.4 mil thickness and 19 inch width was prepared in two sessions using a Waldren pilot paper coater and S.D. Warren Transcote AV paper. In the first session 1:3 methanol: benzene was used as solvent. Since it was difficult to control the ovens below 135°F (57°C) at which temperature solutions of the polymer in this solvent started to form bubbles during drying, a 1:4 solvent composition was used in the second session.

We found that changes made in the roller openings at the unusually wide openings needed to make 1.5 mil dry film give erratic changes in film thickness. During the second coating session, A.D. Little Co. had a Beta Gage mounted on the paper coater which enabled us to monitor film thickness at the wet end of the coater. The Beta Gauge reading of the wet coating of our polymer formulation that corresponded to a thickness of 1.4 mil dry film was first determined in a series of trial runs and this reading was maintained during the coating runs. Readings of the Beta Gauge across the coating also showed that the rollers deposited an extremely even coating. Details of these coatings runs are described in the Experimental Section.

In the first session, a total of 40 feet of film, designated Pilot #1, sections R and S, was made. In the second session, over 60 feet of 1.4 mil film, designated Pilot #2, sections G, F, E and D, was made. In addition, about 45 feet of 1.2 mil film was made. However, this film had a pronounced "blush" caused by high humidity of the ambient air during the paper coating operation and was, therefore, discarded.

C. Polymer Preparations

1. 2-Vinylpyridine-Methyl Methacrylate Copolymer

a. Study of Polymerization Conditions

A study of the polymerization conditions was made to increase the molecular weight of the copolymers. Copolymers prepared before (ref. 2) had relative viscosities up to 1.7 in 0.5% solutions of dimethylformamide. Reaction conditions varied in this study were as follows:

a. Temperature (40, 60, 75°C);

b. Amount of catalyst (to give rate of initiation equivalent to 0.02 and 0.005 wt.% at 60°C);

c. Conversion.

The polymerizations were carried out in pressure bottles with a 50g charge of freshly distilled monomers that were flushed with nitrogen in the bottle for 10 min. before sealing the bottle. Properties of polymers prepared in the complete study are detailed in Table VI. The results can be summarized as follows:

Table VI

EFFECT OF VARIATIONS IN POLYMERIZATION CONDITIONS ON PROPERTIES OF 2-VINYLPYRIDINE-METHYL METHACRYLATE COPOLYMER (a)

Reference	Catalyst, (b) g/100g Monomers	Temp °C	Reaction Time Hours	Conversion Wt%	η_R for 0.5%(c) Soln of Polymer	Mole Ratio 2-VP:MMA in Polymer (d)
58019	0.02	60	7	7	1.53	38:62
58024	0.02	60	14	40	1.93	35:65
58021	0.02	60	21	40	2.11	36:64
58022	0.005	60	24	7	1.54	39:61
58038	0.005	60	88	18	1.56	
58027	0.40	40	16	16	1.72	40:60
58036	0.40	40	40	72	2.46	36:64
58037	0.10	40	79	39	2.48	38:62
58039	0.4	40	64	83	4.65	31:69
58040	0.02	60	64	78	3.16	33:67
58042	0.0028	75	20	8	1.51	39:61
58043	0.0028	75	72	10	1.40	38:62
58044(e)	0.4	40	40	16(36)	2.02	39:61
110552A(f)	0.4	40	48	-	2.80	-
110552B	0.4	40	48	63	3.65	-
110555A(f)	0.4	40	64	87	3.12	-
110555B	0.4	40	64	82	3.00	-

(a) Mole ratio monomers charged 2-VP:MMA; 30:70

(b) Azo-bis-isobutyronitrile

(c) In dimethylformamide at $30^{o}C$

(d) Calc. from analysis for pyridine content by perchloric acid titration method

(e) Contained 20% polymer in initial charge

(f) Not shaken

- Significant improvement in molecular weight was obtained by polymerization to high conversion. The viscosity-conversion relationship of this copolymer, shown in Figure 2, is similar to that of some methyl methacrylate homopolymers (ref. 3).
- Polymerizations terminated at less than 40% conversion have slightly higher molecular weights when polymerized at 40°C rather than at higher temperatures;
- The variations in rate of initiation made in runs at 60°C did not affect the molecular weight of the products;
- Polymerizations carried to conversions above 40% require a slight adjustment in monomer charge to maintain constant polymer composition.
- The polymerization is very easily inhibited by trace amounts of oxygen and possibly other unknown impurities also. The sensitivity to impurities is apparently especially high at low catalyst concentrations, since conversions of runs 58042, 59043 and 58038 are abnormally low.

b. Scale-up of Polymerization

Several polymerizations at 40°C using 0.4g azo-bis-isobutyronitrile catalyst for 100g of monomers were run with different batches of distilled monomers in stirred reactive flasks under nitrogen. Conversions were poor even with oxygen-free nitrogen as cover. Therefore, starting in run 99187 the (equivalent) catalyst concentration was doubled and the polymerization was run at 60°C. In these runs, polymers with moderate molecular weight (relative viscosity 2.0 to 2.8 in 0.5% solutions) were obtained (Table VII) in conversions over 50%. Therefore, the large scale polymerizations with 1100g total monomer charge were run under these conditions.

Four runs of this size (110528, 110531, 110533 and 110536 in Table VII) were carried out to obtain enough polymer for preparation of separator film on the pilot paper coater. Conversions and molecular weights of the product polymers were almost identical except 110536 had a slightly lower degree of polymerization. Because of the slightly lower molecular weight of polymer 110536, it was used only in preliminary calibration runs on the paper coater and was not blended into the other polymers.

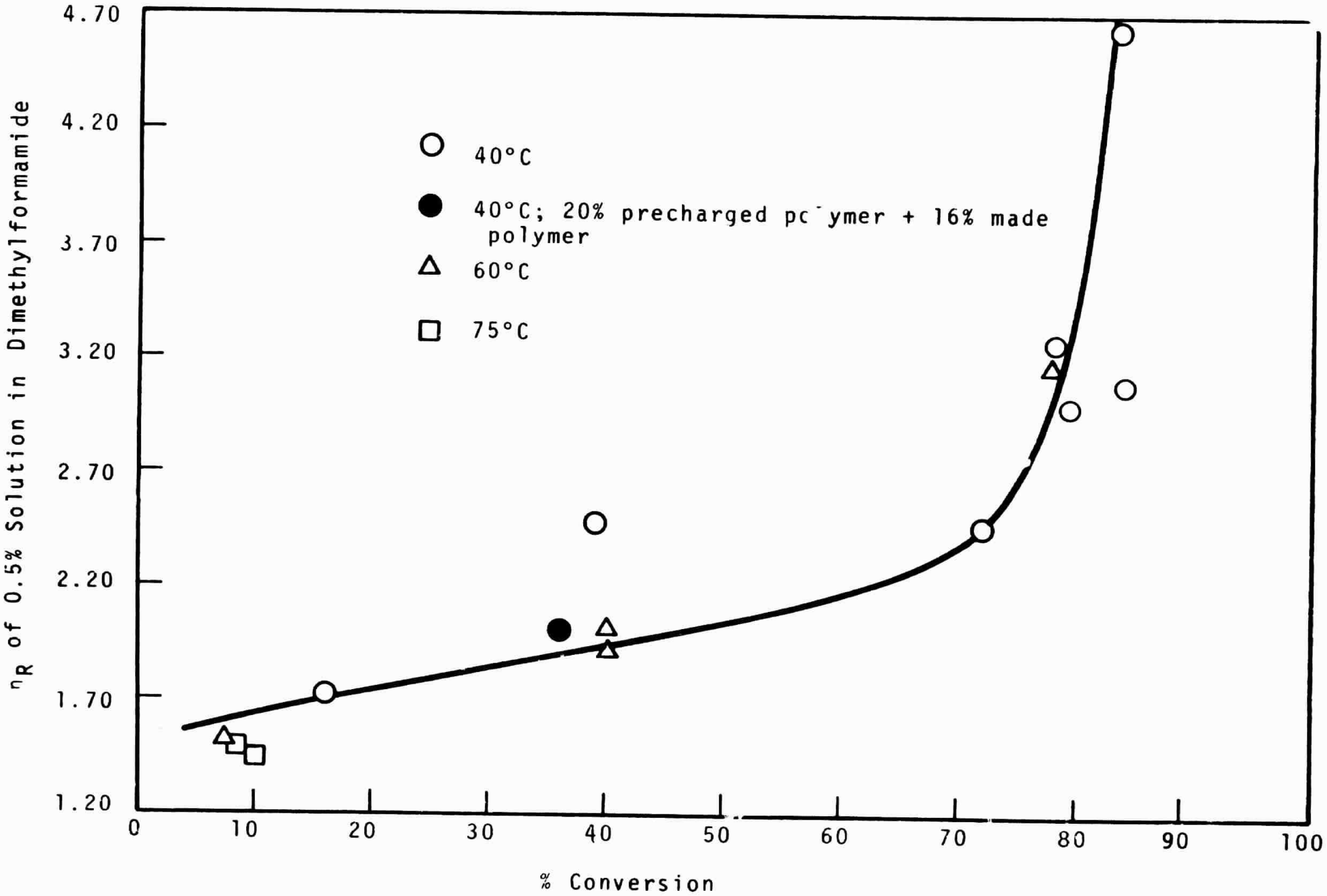

Figure 2. Relationship of Polymer Molecular Weight to Reaction Conversion.

Table VII

PROPERTIES OF 2-VINYLPYRIDINE-METHYL METHACRYLATE COPOLYMERS PREPARED IN REACTION FLASKS

Reference(a)	Special Conditions	Catalyst(b) g/100g Monomer	Temp °C	Reaction Time (hr)	Conversion (wt-%)	η_R for 0.5% Solution	2-Vinylpyridine in Product (wt-%)
99187	---	0.04	60	72	54	2.84	---
99192	---	0.04	60	72	50	2.11	36
99194	---	0.04	60	96	58	2.23	30
110507	0.02g addtl. catalyst added after 45 hrs	0.04	60	90	75	2.11	32
110511	0.02g addtl. catalyst added after 60 hrs	0.04	60	120	76	2.12	33
110513	---	0.04	60	68	74	2.00	31
110518	---	0.04	60	89	60	1.90	---
110524A	---	0.40	40	192	40	1.6	33
110524B	---	0.40	40	288	78	2.1	29
110528	1100g scale	0.04	60	95	54	2.26	30
110531	1100g scale; 0.02% addtl. catalyst added after 45 hrs.	0.04	60	119	60	2.10	32
110533	same as 110531	0.04	60	118	50	2.09	33
110536	same as 110531	0.04	60	119	54	1.88	34

(a) Monomer charge 30:70 2-vinylpyridine:methyl methacrylate

(b) azo-bis-isobutyronitrile

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

A series of these terpolymers was prepared to determine if there existed a terpolymer composition that gave films with usable mechanical properties and that also saponified completely during the standard 60-hour sterilization cycle.

Two terpolymers 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 hydrxide 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 4.7), 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. Styrene-Maleic Anhydride Copolymer

We had found previously (ref. 2) that films of Lytron® 810, styrene-maleic anhydride copolymer, had excellent electrical properties for a battery separator material, but were hard and had low flexibility in dry atmospheres. This copolymer has a molecular weight of about 50,000. Therefore, copolymers with higher molecular weight were prepared to improve these mechanical properties in the styrene-maleic anhydride films. One copolymer was prepared by polymerization of the monomers in methylene chloride solution, following a method developed by Hibbard (ref. 4). The product has an intrinsic viscosity of 4.3 compared to 0.8 for the Lytron 810 resin. Small samples of films prepared from this polymer have much greater flexibility than similar films made from Lytron 810 copolymer. However, it is difficult to prepare films of this polymer with thicknesses over 0.4 mil, because of its low solubility.

Therefore, two polymers with molecular weights intermediate between Lytron 810 copolymer ($[\eta]$ - 0.8) and this high molecular weight copolymer 99119 ($[\eta]$ - 4.3) were prepared by polymerization in methylene chloride containing β-nitrostyrene as chain terminator (Table VIII). Polymers prepared with 0.015 and 0.048% terminator had approximately the same molecular weight ($[\eta]$ - 1.8). These polymers had better film forming properties than polymer 99119, but did not give as flexible films as the tetrapolymers described below in Section II, C, 6.

5. Styrene-Maleic Anhydride-Methyl Methacrylate Terpolymers

A series of polymerizations with the above monomers was run to determine the best reaction conditions for preparation of high molecular weight terpolymers with high maleic anhydride content. Two general reaction procedures were used:

1. Polymerization in bulk at 60°C in nitrogen atmosphere with 0.02 weight % azo-bis-isobutyronitrile catalyst;

2. Polymerization in refluxing 5% methylene chloride solution with either lauroyl peroxide or azo-bis-isobutyronitrile catalyst.

The data obtained are in Table VIII. These data can be summarized as follows:

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Table VIII

COMPOSITION OF STYRENE-MALEIC ANHYDRIDE COPOLYMERS AND STYRENE-MALEIC ANHYDRIDE-METHYL METHACRYLATE TERPOLYMERS

Reference	Mole Ratio Monomers St:MA:MMA	Solvent	Catalyst g/100g Monomer(a)	Temp °C	Reaction Time, Hrs.	Conversion wt-%	η_R for 0.5% Solution	Estimated MA in Polymer wt-%	Estimated Mole Ratio of Monomers in Polymer
99119	50:50:0	MC(b)	0.60 LP	42	20	70	4.51	--	(50:50:0)
99130A	50:50 with 0.015% -nitro-styrene	MC	0.60 LP	42	20	59	2.00	--	(50:50:0)
99130B	50:50 with 0.048% -nitro-styrene	MC	0.60 LP	42	20	56	2.20	--	(50:50:0)
99109A	33:33:33	None	0.02 ABIN	60	1	11	1.08	31	41:32:27
99111C	20:40:40	None	0.02 ABIN	60	1	14	1.04	31	42:32:25
99109B	30:50:20	None	0.02 ABIN	60	1	20	1.08	30	46:31:23
99111D	20:50:30	None	0.02 ABIN	60	1	24	1.03	36	30:37:32
99113A	50:25:25	None	0.02 ABIN	60	1	10	2.65(c)	34	44:35:21
99118	18:50:32	MC	0.60 LP	42	20	19	1.51	32	39:33:28
99115	33:33:33	MC	0.60 LP	42	20	28	1.81	34	
99116	33:33:33	MC	2.0 ABIN	42	26	28	1.27	32	
99117	40:45:15	MC	0.60 LP	42	6	8	1.65	34	40:35:25
99121	50:25:25	MC	0.60 LP	42	19	22	1.86(c)	32	
99122	50:25:25	MC	1.80 ABIN	42	19	22	1.32(c)		
99124	51:24:25	MC	0.30 LP	42	20	14	1.64		
99125	51:24:25	MC	0.90 ABIN	42	40	18	1.36		

(a) ABIN = azobisisobutyronitrile; LP - lauroyl peroxide

(b) MC = methylene chloride

(c) η_R of duplicate composition in bulk preparation was 1.53 (sample 10C24A)

- Variations in the ratio of reactants result in only small changes in polymer composition due to a very marked azeotropic effect;

- Variations in the ratio of reactants markedly effects the rate of polymerization in bulk. For example, increasing the ratio of maleic anhydride to styrene by a factor of 2 1/2 in the charge doubled the rate of reaction;

- Monomer charges with high ratios of maleic anhydride to styrene gave polymers with low degrees of polymerization, in bulk reactions, but gave polymers that have high degrees of polymerization and form usable films, in solution polymerizations in methylene chloride;

- In the solution polymerizations, lauroyl peroxide catalyst consistently yielded polymers with slightly higher molecular weights than those prepared with the azo catalyst.

An attempt was also made to prepare styrene-fumarate-methyl methacrylate terpolymers (Table IX). These monomers saponify to dicarboxylic acids and have copolymerization reactivity ratios with styrene (ref. 5) that should allow production of polymers with appreciable fumarate contents. However, the reactivity of both diethyl fumarate and monoethyl fumarate is extremely low and polymerization in methylene chloride was impracticably slow. Also, a viscosity determination of the terpolymer containing the monoethyl fumarate indicated that its molecular weight was not high enough to give mechanically strong films.

6. Styrene-Maleic Anhydride-Methyl Methacrylate-Methyl Acrylate Tetrapolymers

The styrene-maleic anhydride-methyl methacrylate terpolymers were modified by adding methyl acrylate units to lower electrical resistivity in 40% KOH by increasing the content of hydrolyzable groups. Several polymers with different ratios of the four monomers were prepared by bulk polymerization. Data describing these polymers are in Table IX. Viscosity measurements show that the molecular weights of these polymers are slightly higher than those of the terpolymers.

In our tests of separators made from these polymers (see Section III, A) we found that polymers with high contents of the hydrolyzable anhydride and acrylate groups had high solubility in 40% KOH. Since these polymers have the best electrical properties, they were modified by introduction of sites for crosslinking. These linear polymers were then crosslinked during

Table IX

COMPOSITION OF STYRENE-MALEIC ANHYDRIDE-METHYL METHACRYLATE-METHYL ACRYLATE TETRAPOLYMERS

Reference	Mole Ratio Monomers(a) St:MA:MMA:x	Solvent(b)	Catalyst(c) g/100g Monomer	Temp °C	Reaction Time, Hrs.	Conversion wt-%	η_R for 0.5% Solution
99123	15:0:25:60 DEF	MC	0.70 LP + 0.70 LP	42 42	60 60	under 3	---
99133	19:0:30:51 EF	MC	1.0 LP + 1.0 LP	42 42	25 25	10	1.06
99127	43:25:10:22 MAC	None	0.02 ABIN	60	2	22	2.60
99138B	43:25:10:22 MAC	None	0.02 ABIN	60	2	10	2.76
99128	17:30:20:33 MAC	MC	0.60 LP	42	40	15	1.33
99129	48:25:10:17 MAC	None	0.02 ABIN	60	1.7	22	2.24
99132	28:20:19:33 MAC	None	0.02 ABIN	60	3	over 50	4.8
99137	18:29:9:44 MAC	None	0.02 ABIN	60	2	11	2.59
99138C	18:29:19:33 MAC	None	0.02 ABIN	60	2	12	3.28
99142D	28:20:19:33 MAC	None	0.02 ABIN	60	1.5	10	2.15
99163	28:20:19:33 MAC	None	0.02 ABIN	60	2	12.5	2.24
99171	43:25:10:22 MAC	None	0.02 ABIN	60	1.8	29.5	2.24
99198	18:29:9:44 MAC	None	0.20 ABIN	40	1.5	5.7	1.92
110505	18:29:9:41 MAC	None	0.20 ABIN	40	2.8	7.4	2.36

(a) MAC is methylacrylate, DEF is diethyl fumarate and EF is monoethyl fumarate

(b) MC is methylene chloride

(c) ABIN is azo-bis-isobutyronitrile and LP is lauroyl peroxide film formation to reduce solubility in 40% KOH as described in Section III, D. Two reagents, namely, 2-chloroethyl vinyl ether and vinylcyclohexene oxide were used to modify the polymers. Based on viscosity measurements, vinylcyclohexene oxide and 2-chloroethylvinyl ether lowered the degree of polymerization slightly. However, all the polymers gave mechanically strong films. Data describing the polymers are in Table X.

Two duplicate batches (99183 and 99175) of polymer 99150 and a duplicate batch (99178) of 99169, which have the most promising separator properties, were also prepared on a 200g charge scale for use in testing reproducibility of film properties. These polymerization reactions accelerate and become exothermic at approximately 15% conversion. Better control was obtained at this stage in the larger scale polymerizations at 40°C by using a lower catalyst concentration (0.2%) than in the smaller scale runs. One polymer (110521) was carried to 49% conversion under these conditions.

An attempt was also made to incorporate free amino groups into the tetrapolymers. A polymer with sufficiently high molecular weight to give usable films (99160) was made from a monomer charge containing 5 weight-% methyl 3-aminocrotonate. However, the properties of the polymer indicate that the additive probably entered the polymer mainly as the half-amide of maleic anhydride, rather than by copolymerization of the vinyl group. Sample films of this polymer that were crosslinked by reaction with bis(chloromethyl) mesitylene did not survive sterilization, indicating that permanent crosslinkages were absent.

D. Crosslinking of Tetrapolymers

Methods were developed to crosslink the tetrapolymers during film formation because linear films of this type that had low electrical resistivities after sterilization also had poor mechanical properties due to high solubility in electrolyte. Most of the crosslinking reactions were done with modifications of tetrapolymers prepared from either 28:20:19:33 or 18:29:9:44 styrene-maleic anhydride-methyl methacrylate-methyl acrylate charges, since these linear polymers dissolved in 40% KOH after sterilization. The criteria for a successful crosslinking procedure was taken as the ability of film samples of the crosslinked polymer to remain insoluble and retain mechanical properties after sterilization in 40% KOH. Four types of sites for crosslinking these tetrapolymers were evaluated. The hypothetical crosslinking reactions are shown in Table XI.

Successful crosslinking was first obtained with diamines as the reagent to crosslink modified polymers containing either 2-chloroethyl or cyclohexene oxide sites. The general procedure for reaction was to add the diamine to a solution of polymer just

Table X

COMPOSITION OF MODIFIED STYRENE-MALEIC ANHYDRIDE-METHYL METHACRYLATE-METHYL ACRYLATE TETRAPOLYMERS

Reference	Mole Ratio Monomers St:MA:MMA:MAC	Monomer With Site for Crosslinking(a) Wt-%	Catalyst(b) g/100g Monomer	Temp °C	Reaction Time, Hrs.	Conversion Wt-%	η_R for 0.5% Solution
99142E	28:20:19:33	5 CVE	0.02 ABIN	60	3.5	7.6	1.77
99145	28:20:19:33	5 CVE	0.02 ABIN	60	3.5	27	1.89
99146	28:20:19:33	10 CVE	0.02 ABIN	60	10	18	1.66
99152	50:50:0:0	5 CVE	0.6 LP	42(c)	22	50	1.81
99148	18:29:9:44	5 CVE	0.02 ABIN	60	4	19	1.86
99150	18:29:9:44	10 CVE	0.02 ABIN	60	6	14.5	1.68
99175	18:29:9:44	10 CVE	0.4 ABIN	40	3.5	12	1.73
99183	18:29:9:44	10 CVE	0.2 ABIN	40	5.3	15	1.92
99153	18:29:9:44	5 CVE	0.4 ABIN	40	5	14.5	2.00
99180	18:29:9:44	5 CVE	0.4 ABIN	40	3.5	7	----
99156	18:29:9:44	10 VCH	0.02 ABIN	60	2.5	31.5	1.46
99157	28:20:19:33	10 VCH	0.02 ABIN	60	4	39.5	1.57
99160	18:29:9:44	5 AC	0.8 ABIN	40	4	21	1.39
99168	28:20:19:33	10 VCHO	0.4 ABIN	40	2	15.3	2.63
99169	18:29:9:44	10 VCHO	0.4 ABIN	40	2	10.5	2.59
99178	18:29:9:44	10 VCHO	0.4 ABIN	40	1.3	29	2.81
110521	18:29:9:44	10 CVE	0.2 ABIN	40	6.3	49	1.58
110543	18:29:9:44	10 CVE	0.2 ABIN	40	3.3	33	1.92
110545	18:29:9:44	10 CVE	0.6 LP	42(c)	22	9	1.36
110546	18:29:9:44	10 CVE	0.8 ABIN	42(c)	60	6	1.20
110547	18:29:9:44	10 CVE	0.1 ABIN	60(d)	93	42	1.05

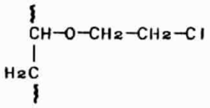
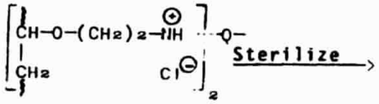
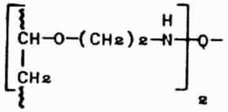
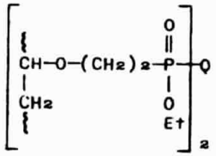
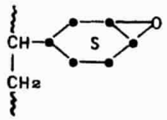
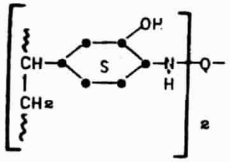
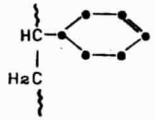
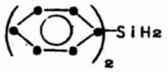
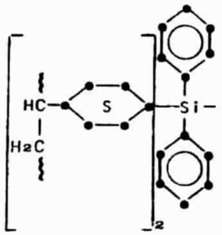
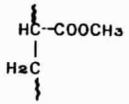
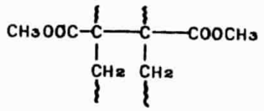
(a) CVE = 2-chloroethylvinyl ether; VCH = 4-vinylcyclohexene; AC = methyl 3-aminocrotonate; VCHO = vinylcyclohexene oxide

(b) LP = lauroyl peroxide; ABIN - azo-bis-isobutyronitrile

(c) in methylene chloride solvent

(d) in acetone solvent; second 0.1 ABIN added after 24 hours

Table XI
CROSSLINKING REACTIONS FOR LIGAND POLYMERS

Type	Crosslinking Site	Reactant*	Crosslinking Bond
IA		$H_2N-Q-NH_2$	 Sterilize 
IB	"	$(EtO)_2P-Q-P(OEt)_2$	
II		$H_2N-Q-NH_2$	
III			
IV		R•	

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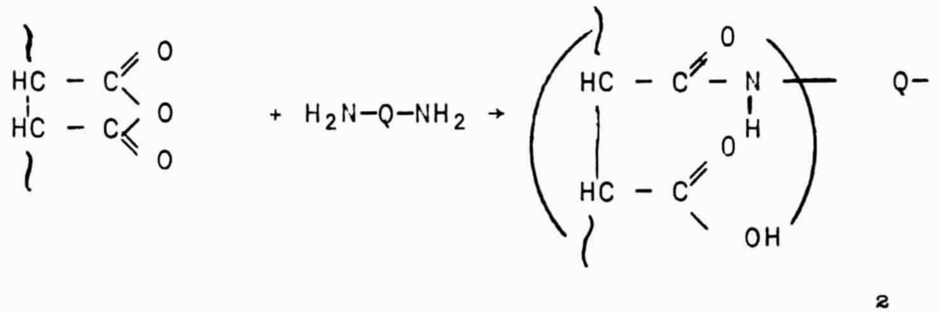
* Q is a connecting linkage such as $-(CH_2)_2-$ or 

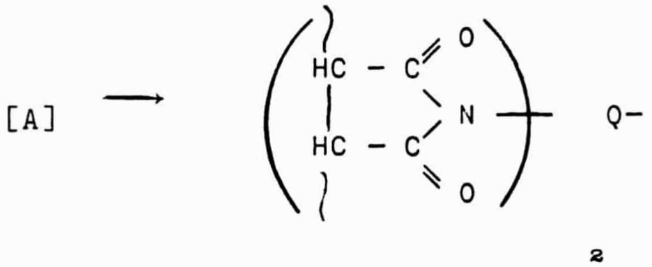
before casting the film. However, alkyl amines caused gel formation under these conditions. With these reagents, better crosslinked films were obtained by soaking preformed films of linear polymer in a methanol solution of the alkyldiamines.

Initially the films made from the epoxide type modification, that were reacted with aromatic diamines, were cured at 80°C overnight, since reaction type II with aromatic amines requires elevated temperatures. However, we found that the 80° cure was not necessary to obtain films that remained insoluble after sterilization. This indicated that by-product amide crosslinks formed by reaction of the diamines with the anhydride groups (ref. 6) were unexpectedly stable to sterilization. This high stability was confirmed with film samples of polymers containing no sites for crosslinkage with the diamines except the anhydride group. It is therefore, highly probably that all polymers of types I and II as well as the unmodified polymers that were reacted with the diamines were crosslinked principally through the anhydride groups in the tetrapolymers as follows, rather than through the other available crosslinking sites.



[A]

Since simple amide bonds such as those in nylons are unstable under sterilization conditions, it is possible that the crosslinkage is stabilized by dehydration of the amide to a cyclic imide during sterilization, as follows



Attempts made to crosslink film samples of an 18:29:19:33 St:MA:MMA:MAC tetrapolymer by direct coupling induced by free radicals were unsuccessful. Films with 3% dicumyl peroxide were cured for 24 hours at 115°C where this peroxide has a half-life of about 15 hours, but the cured samples dissolved during sterilization indicating a low degree of cure. Other samples of this tetrapolymer were cured by using UV light and 2-methylanthraquinone as photosensitizer to generate free radicals. These conditions were developed by Oster (ref. 7) to crosslink acrylate polymers. However, film samples (99163) containing 5 wt. % photosensitizer that were exposed to Black Spectroline X-4 light (366mμ) for periods up to 25 hours dissolved during sterilization.

We also found that *in situ* reaction at 120°C of diphenylsilane with polymers containing vinylcyclohexene groups did not produce a high enough degree of crosslinkage to stabilize the polymer for sterilization.

E. Analysis of Polymers

1. 2-Vinylpyridine-Methyl Methacrylate Copolymer

Composition of these copolymers was readily determined by titration with perchloric acid in acetonitrile-acetic acid solvent. The method developed by Tamikado (ref. 8) was used. Polymers that analyzed 45 and 32 mole % 2-vinylpyridine from elemental nitrogen determinations, analyzed 39.5 ± 1.5 and 29.2 ± 0.4 mole %, respectively, by this titration method.

The use of measures of refractive index of solutions of these polymers as an analytical method was also tried. This method has been used for analysis of styrene-methyl methacrylate copolymers (ref. 9). However, we found that the difference in refractive index between methyl ethyl ketone solutions of 2-vinylpyridine-methyl methacrylate copolymers with 40 and 20 mole % 2-VP was too small to detect the differences in polymer composition.

2. Styrene-Maleic Anhydride-Methyl Methacrylate Terpolymers

The composition of these polymers was determined from their elemental analysis for carbon and hydrogen, together with their neutralization equivalents. The method used to measure neutralization equivalents was described before (ref. 2). Lytron 810 copolymer gave a correct analysis by this method. However, the high molecular weight copolymer 99119 analyzed only 80% of theoretical based on a 1:1 copolymer.

The neutralization equivalents reported in Table VIII are those found from this titration. Values found from elemental analysis also indicate that maleic anhydride contents of the terpolymers are under 40% and that compositions of all polymers are very similar.

Some improvement in the accuracy of this method with the higher molecular weight samples was obtained by adding 1g of sodium chloride to each sample. The presence of the sodium ion made the end point sharper and the accuracy of analysis of copolymer 99130B, assuming 1:1 copolymer composition, was 92%.

Attempts to measure composition of the terpolymers from the absorptions in the infrared of the α-methyl and ester groups of the methyl methacrylate component and the anhydride groups of the maleic anhydride component in terpolymer samples were not successful. Two measures of absorption were determined. The band heights of these absorptions were not reproducible. The band areas give composition values that did not correlate with compositions of polymers that were determined from neutralization equivalents and elemental analysis. Adjacent absorption bands from the styrene component of the terpolymers apparently interfered with this measure.

3. Styrene-Maleic Anhydride-Methyl Methacrylate-Methyl Acrylate Tetrapolymers

Because of the large number of components in these polymers, analysis was limited to determination of hydrolyzable groups. Neutralization equivalents, using the sodium chloride modification of the procedure described above, were determined to measure anhydride content. We also attempted to determine acrylate content from saponification equivalents. The methacrylate groups are considered non-hydrolyzable, since they do not saponify in these polymers under mild saponification conditions.

Samples of the tetrapolymers were saponified by heating overnight at 85°C in standardized 2N NaOH in pressure bottles to convert the anhydride and acrylate groups to their salts. The polymers dissolved during saponification. However, it was not possible to determine reproducible titres by direct titration with acid or back titration with base after acidification because of incomplete reaction near the end point caused by precipitation of the polymer near the neutralization point.

IV. EXPERIMENTAL

A. Preparation of 2-Vinylpyridine-Methyl Methacrylate Copolymers

1. In Pressure Bottles

A 30:70 mole ratio of freshly distilled samples of the above monomers totaling 50g. were charged to a pressure bottle together with azo-bis-isobutyronitrile catalyst. The bottle was flushed with nitrogen, sealed, and shaken in a controlled temperature bath. The product was isolated by precipitation with hexane and purified by three successive reprecipitations using benzene/hexane as the solvent/precipitant combination. Reaction times (conversions) and catalyst concentrations were varied in a series of polymerizations. Data are in Table VI.

2. In Stirred Reaction Flasks

The polymerization procedure was identical to that in the pressure bottles except a stream of oxygen-free nitrogen was passed above the reactants during polymerization. The stirrer stopped when the reaction mass solidified. This was generally after about 7 hours at 60°C.

B. Partial Presaponification of 2-Vinylpyridine-Methyl Methacrylate Copolymers

Partial saponification of polymer 58039 was done by sterilization or by refluxing polymer samples in one of several media, namely, aqueous 10% HCl, 10% HCl in 1:1 methanol:water, or alcoholic sodium hydroxide. The reactions were inhomogeneous and, therefore, rates are probably not reproducible. Specific conditions that were used to prepare samples with 20, 58 and 91% conversions of methacrylate to methacrylic acid are as follows:

20% - 7 hours reflex in 10% HCl in methanol-water or
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.

The acid content was determined directly by titration with standardized tenth normal sodium hydroxide. Absolute methanol was used as solvent.

C. Preparation of Styrene-Maleic Anhydride-Methyl Methacrylate Terpolymers

1. Bulk Polymerization

The reactants were polymerized at 60°C with 0.02% azo-bis-isobutyronitrile catalyst in nitrogen atmosphere. The maleic anhydride had been purified by recrystallization from chloroform; the other two monomers had been freshly distilled. Reactants were stirred during the heating period, the length of which was chosen to give approximately 30% conversion. The polymers were purified by three successive precipitations with hexane from acetone solution and dried in vacuum. Properties of individual polymers are listed in Table VIII.

2. Solution Polymerization

The reactants in 5.5% solution in methylene chloride were heated with stirring to reflux under a blanket of nitrogen. After 15 min., the catalyst was added and the reaction was continued to about 30% conversion. The polymers that precipitated from solution were purified as in Section IV, C, 1.

D. Preparation of Styrene-Maleic Anhydride Copolymer

The procedure of Hibbard (ref. 4) was followed. It is the same as that used for solution preparation of the terpolymers in Section IV, C, 2, except that conversion was carried to about 70%. Data of this preparation are in Table VIII.

E. Preparation of Tetrapolymers

Bulk and solution preparations of the tetrapolymers were done by the same general procedures used for the terpolymers that are described above in Sections IV, C, 1 and IV, C, 2. Polymerizations of the tetrapolymers prepared in bulk generally were stopped when the product became viscous and started to undergo an exotherm. The conversions at this stage were about 10%. Several high conversion tetrapolymers modified with 2-chloroethyl vinyl ether were prepared in bulk at 40°C with low catalyst concentrations or in solution. Data describing these polymers are in Table IX.

F. Preparation of Films

1. General Procedure for 20 by 5 inch Samples

Polymer solutions were strained through layers of cheese cloth and then leveled with a Gardner blade on a flat, smooth polypropylene substrate supported by wooden backing and protected by a dust cover. The resultant leveled castings were about 5 inches wide by 20 inches long. The castings were converted into dry film in an oven maintained at 35°C and 23-25% relative humidity.

An empirical straight-line relationship for optimum casting viscosity was found between the relative viscosity of the polymer and the casting solution concentration. It was found to be 0.35 units of η_R per unit of polymer concentration in weight % for relative viscosities between 1.0 and 3.5 and concentrations between 4 and 14 weight %. This relationship was the same for the tetrapolymers in methyl ethyl ketone solvent and the 2-vinylpyridine-methyl methacrylate copolymers in methanol-benzene solvent. Leveling with Gardner blade heights of 25-35 mils, depending on concentration, gave films with uniform thickness between 1 and 2 mils.

2. Crosslinking of Tetrapolymers During Film Preparation

The aromatic amine crosslinking agents such as bis(4-anilino) methane or m-phenylenediamine were added to the methyl ethyl ketone solution of linear polymer just before casting the film. Viscosity data to determine the pot lives of solutions made from unmodified tetrapolymer (99198) and tetrapolymer modified with 2-chloroethyl vinyl ether (99175) are in Table XII. The solution of polymer 99175 contained 10.5 wt. % polymer and 1 wt. % bis (4-anilino) methane. Corresponding concentrations for polymer 99198 were 5.8% and 1%.

Triethylenetetramine was incorporated into precast films of tetrapolymers by soaking these films for 2 hours in methanol solutions containing about 0.02g triethylenetetramine per gram of polymer in the film.

Table XII

VISCOSITIES OF CROSSLINKED TETRAPOLYMER SOLUTIONS[1]

Time, min.	99198 η,cps	99175 (modified)
0	----	100
1.5	----	200
3	1750	---
4	3200	----
5	5200	---
6	8300	---
8	17200	---
10	----	200
35	----	550

[1] Spindle #3 of Brookfield LVF Viscometer at 6rpm

3. Film Preparation of 2-Vinylpyridine-Methyl Methacrylate Copolymer by Paper Coating Technique

Film was cast on S.D. Warren Transcote AV Patent Paper using the A.D. Little Co.'s Waldren pilot paper coater at a coating speed of 4 feet/min. The roller speeds were decreased to approximately 1 1/2 feet/min. to obtain 1.4 mil dry film with the roller openings at their maximum effective opening, which was about 15 mils. Slightly different conditions were used in the two coating sessions. In the first, a polymer solution with 13% solids content in 1:3 methanol: benzene by weight was used and the films were dried at 120 to 135°F in two passes through the 16 foot ovens. In the second session a 1:4 methanol: benzene solution with 13% solids content was used and the films were dried for 20 minutes at 140°F. This later polymer solution was a blend of polymers 110528, 110531 and 110533 and had viscosity of 1740 cps at 25°C. Beta gauge readings of the wet coating of the blend on the substrate were 298 to 307 for 1.4 mil dry film and about 276 for 1.2 mil film. The substrate reading was 620 to 624.

G. Test Methods

1. Tensile Strength of Membranes

Tensile specimens were prepared by stamping out 1 x 5 in. samples of our polymer films with a steel rule die. These specimens were tested in an Instron-Tensile Tester equipped with one inch "T" grips having sandpaper liner. The grip separation was 2.75 ± 0.25 in. and the crosshead speed was 0.5 in./min. for dry membranes and 2 in./min. for wet membranes unless noted otherwise. Wet thickness was used to calculate strengths of wet membranes. Data are summarized in Table III.

2. Electrical Resistance of Membranes

The general procedure described by Salkind and Kelley (ref. 1) for measuring electrical resistance in 40% KOH was followed. Measurements were made with a Wayne-Kerr Component Bridge, Model B522. The resistance cell is essentially as described in reference 1 but includes the latest improvements made by the ESB personnel. Measurements were made on membranes after soaking overnight in 40% KOH or after sterilization in 40% KOH.

H. Saponification Value for 1.5 mil Copolymer Film

The amount of KOH required to saponify the 31:69 2-vinylpyridine:methyl methacrylate copolymer was calculated to be $2.26 \cdot 10^{-4}$ eq. KOH per in^2 of 1.5 mil film. This number is based on 0.00984 eq/g methacrylate content of the polymer and 0.947 g/cc (15.5 g/in^3) density of the copolymer in film form.

V. REFERENCES

1. A.J. Salkind and J.J. Kelley, "Characteristics of Separators for Alkaline Silver Oxide-Zinc Secondary Batteries", Ed. by J.E. Cooper and A. Fleischer, AF Aero Propulsion Laboratory.

2. J.J. O'Connel et al., "Separator Development for a Heat-Sterilizable Battery", Summary Progress Report, May 1966 to March 1967.

3. M.A. Naylor and F.W. Billmeyer, Jr., J. Am. Chem. Soc., 75, 2181 (1953).

4. B.B. Hibbard, U.S. Patent 2,872,436, Fib. 3, 1959.

5. F.M. Lewis and F.R. Mayo, J. Am. Chem. Soc., 70, 1533 (1948).

6. K.S. Dennis, C.E. Lyons and D.K. Spiekerman, Off. Digest J. Paint Technology and Engineering, 37, 378 (1965).

7. G. Oster, Polymer Letters, 2, 1181 (1964).

8. T. Tamikado, J. Poly. Sci., 43, 489 (1960).

9. J.B. Kinsinger et al., J. Appl. Poly. Sci., 6, 529 (1962).