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SEPARATOR DEVELOPMENT
FOR A HEAT STERILIZABLE BATTERY
Quarterly Summary Progress Report 4

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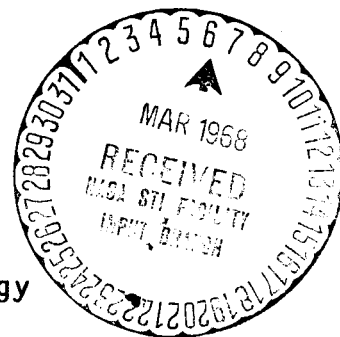
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ABSTRACT

Two ligand-containing polymers were developed and prepared as 1.5 mil flexible films that have satisfactory electrical and mechanical properties as separators for sterilizable silver-zinc cells. One type is a modified styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymer with high content of hydrolyzable anhydride and acrylate groups. Methods were developed to crosslink these polymers with bis(4-anilino)methane during film formation to make them usable separator materials by insolubilizing them in 40% KOH. Tests on duplicate samples from different batches of this type polymer showed good reproducibility.

The second type polymer, 31:69 2-vinylpyridine-methyl methacrylate copolymer, had shown promising electrical properties in our initial program. The mechanical properties of films of this polymer, both before and after sterilization, were improved by increasing its molecular weight.

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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. Complete the study of the effect of reaction parameters on molecular weight of the 40:60 2-vinylpyridine-methyl methacrylate copolymer;
2. Develop methods to crosslink the styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymers during film formation;
3. Determine the degree of crosslinkage necessary to insolubilize tetrapolymers with high maleic anhydride-methyl acrylate contents in 40% KOH;
4. Evaluate the electrical and mechanical properties, before and after sterilization, of films prepared from the modified polymers.

II. SUMMARY

Two types of ligand-containing polymers were improved and developed that meet most of the requirements for a separator material for the sterilizable Ag-ZnO battery. These polymers are the modified styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymers and a 2-vinylpyridine-methyl methacrylate copolymer. The usefulness of the tetrapolymers had been limited before, because the polymers with a high enough content of hydrolyzable anhydride and acrylate groups for low electrical resistivity had some solubility in 40% KOH. These polymers have been crosslinked by reaction with diamines to make them insoluble. Electrical measurements of sterilized films of duplicate samples of different batches of the crosslinked polymers showed excellent reproducibility. A tetrapolymer modified with 2-chloroethylvinyl ether had resistivity of 19 ohm-in after sterilization. Similar films of tetrapolymer modified with vinylcyclohexene oxide had 15 ohm-in resistivity. The electrical properties of these films were not affected by the amount of crosslinking agents used to insolubilize the films. However, tensile strengths of wet sterilized films increased with increases in the degree of crosslinkage. Films with about 2% bis(4-anilino)methane as agent had wet strengths of about 700 psi.

Unmodified tetrapolymers crosslinked with diamines also survived sterilization intact, indicating an unexpected high stability of the amide linkage to hydrolysis in 40% KOH. A comparison of mechanical properties of these films to films of the modified polymers is now being made.

Our study of reaction conditions for preparation of the 2-vinylpyridine-methyl methacrylate copolymer was completed. Polymers with significantly higher molecular weight were obtained by polymerization to high conversions. These polymers formed films that had dry tensile strengths of about 7000 psi and wet tensile strengths after sterilization for 120 hours of about 650 psi. Resistivities of the 31:69 copolymer were under 20 ohm-in. Some films required sterilization times longer than 120 hours for hydrolysis and therefore methods to accelerate wetting and hydrolysis of the films are now being investigated.

III. DISCUSSION OF RESULTS

A. EVALUATION OF SEPARATOR PROPERTIES

1. Modified Styrene:Maleic Anhydride:Methyl Methacrylate:Methyl Acrylate Tetrapolymers

The emphasis in this period was to determine the electrical and mechanical properties of crosslinked polymers derived from polymer modifications of two basic formulations that have the most promising electrical properties. These polymers are made from 28:20:19:33 and 18:29:9:44 St:MA:MMA:MAC monomer charges. Initial tests (Section III, C) to determine the stability to sterilization of the various polymer modifications showed that polymers cross-linked by reaction with diamines were the most stable. Therefore, films of this type containing different amounts of diamine cross-linking agent were sterilized and their electrical properties measured. Preparation of larger film samples made with better quality control, of the most promising combinations, was then done to determine their mechanical as well as electrical properties. Most of these tests were done with polymers modified with either 2-chloroethyl (CVE type) or epoxy (VCHO type) substituents. Testing of unmodified polymers, such as 99137 has just started. The electrical properties measured are summarized in Table 1. Tensile strength determinations are given in Table 2. The results of these tests can be summarized as follows:

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

Table 1

PROPERTIES OF SEPARATORS 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) |
| 99146 | St:MA:MMA:MAC tetra- polymer from 28:20:19:33 charge modified with 10%CVE | 1% BAM by soaking in meth- anol (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 meth- anol soak(105334) | | 64 | 1.8 | | 6.3 |
| | | 1% BAM (105335-1/2) | 0.8 | 64 | 2.7 | 57 | 7.1 |
| | | 1% BAM (105335-1/2) ^d | 2.1 | 64 | 3.5 | 67 | 23 |
| | | 4% BAM (105335-2) ^d | 1.2 | 64 | 1.7 | 275 | 37 |
| | | 4% BAM (105335-2) ^d | 3.5 | 64 | 4.5 | 202 | 23 |
| | | 2% BAM (105335-1) ^d | 0.8 | 64 | 1.5 | 250 | 38 |
| | | Same as 105335-1 | 1.6 | 64 | 2.5 | 133 | 22 |
| | | Same as 105335-2 | 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 modifica- tions | None | Dissolved during sterilization | | | | |
| 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 1 (continued)

PROPERTIES OF SEPARATORS 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 % | (ohm-in) |
| 99153 | Same as 99150 except modified with 5% CVE | 1% BAM | 1.6 | 64 | 3.2 | 155 | 19 |
| | | | 3.3 | --- | 22 | | |
| | | | 1.5 | 64 | 3.7 | 180 | 29 |
| 99160 | Same as 99150 except modified with 5% methyl 3-aminocrotonate | 0.5% BAM | --- | 64 | 2.7 | --- | 20 |
| | | | 1.2 | 64 | 3.2 | 138 | 21 |
| | | | 0.5 | 64 | 3.2 | 138 | 21 |
| 99138C | Same as 99163 | 0.5X bis(chloro- methyl)mesitylene 1X " (105337) Films containing 2-methyl anthra- quinone exposed to UV light | 2.6 | 64 | 3.2 | 138 | 21 |
| | | | 1.3 | 64 | 3.2 | 138 | 21 |
| | | | 1.2 | 64 | 3.2 | 138 | 21 |
| 99169 | Same as 99150 except modified with 10% VCHO | 0.4% TETA(105338) 1.2% BAM(105338) 0.6% BAM 1.2% BAM | 1.4 | 64 | ~8.5 ^f | 214 | ~12 |
| | | | 1.2 | 64 | 1.5 | 176 | 28 |
| | | | 1.2 | 64 | 2.2 | 225 | 33 |
| 99178 | Same as 99169 | 1.2% BAM 1.2% BAM 1.2% BAM ^e | 1.1 | 64 | 2.5 | 236 | 24 |
| | | | 1.5 | 64 | 3.2 | 148 | 20 |
| | | | 1.5 | 64 | 3.2 | 158 | 17 |
| 99169 | Same as 99150 except modified with 10% VCHO | 0.4% TETA(105338) 1.2% BAM(105338) 0.6% BAM 1.2% BAM | 1.1 | 64 | 3.3 | 171 | 13 |
| | | | 1.0 | 64 | 2.5 | 104 | 13 |
| | | | 1.1 | 64 | 2.5 | 63 | 16 |
| 99169 | Same as 99150 except modified with 10% VCHO | 0.4% TETA(105338) 1.2% BAM(105338) 0.6% BAM 1.2% BAM | 1.3 | 64 | 3.5 | 208 | 14 |
| | | | 1.5 | 64 | 3.5 | 216 | 15 |
| | | | 1.3 | 64 | 3.8 | 190 | 17 |
| 99169 | Same as 99150 except modified with 10% VCHO | 0.4% TETA(105338) 1.2% BAM(105338) 0.6% BAM 1.2% BAM | 1.2 | 64 | 3.0 | 250 | 15 |
| | | | 1.3 | 64 | 3.4 | 163 | 14 |
| | | | 1.3 | 64 | 3.7 | 244 | 13 |
| 99169 | Same as 99150 except modified with 10% VCHO | 0.4% TETA(105338) 1.2% BAM(105338) 0.6% BAM 1.2% BAM | 1.2 | 64 | 3.5 | 138 | 13 |
| | | | 1.0 | 64 | 2.5 | 232 | 16 |
| | | | 1.0 | 64 | 2.5 | 232 | 16 |

Table 1 (continued)
 PROPERTIES OF SEPARATORS 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) | Mt. Gain % (ohm-in) |
| 99137 | St:MA:MMA:MAC from 18:29:9:44 charge | 1% BAM | | 64 | 2.8 | 18 |
| 58039 | 31:69 2-VP:MMA copolymer ($n_R = 4.6$) | - | 1.3 | 114 | 2.8 | 283 |
| | | | 1.3 | 120 | 3.2 | 450 |
| | | | 1.5 | 120 | 3.0 | 215 |
| | | | 1.6 | 120 | 3.0 | 173 |
| | | | 1.5 | 120 | 4.2 | --- |
| 58040 | 33:67 2-VP:MMA copolymer ($n_R = 3.2$) | - | 1.5 | 120 | 4.5 | --- |
| | | | --- | 164 | 4.0 | --- |
| | | | 1.0 | 114 | 4.0 | 300 |
| | | | 1.6 | 120 | 3.1 | 127 |
| | | | 1.9 | 120 | 4.5 | 277 |
| 58019 | 38:62 2-VP:MMA copolymer ($n_R = 1.5$) | - | 2.0 | 120 | 4.2 | 217 |
| | | | 1.9 | 120 | 3.3 | 179 |
| | | | 1.1 | 120 | 7 | --- |
| 58027 | 40:60 2-VP:MMA copolymer ($n_R = 1.7$) | - | --- | 164 | 4.5 | --- |
| | | | 2.1 | 120 | 2.8 | 250 |
| 58036 | 36:64 2-VP:MMA copolymer ($n_R = 2.5$) | - | --- | 164 | 2.0 | --- |
| | | | 1.7 | 120 | 2.5 | 240 |

^a BAM is bis(4-anilino)methane; TEIA is triethylenetetramine and MPD is m-phenylenediamine

^b Original area dimensions retained during sterilization by film holder

^c Area dimensions not retained

^d Δ Indicates films were post-cured at 120°C for 16 hours

^e LINO₃ in film, 2 wt-% in tetrapolymers and 5 wt-% in copolymers

^f Rough surface

Table 2

TENSILE STRENGTH OF MEMBRANES^a

| Reference | Polymer Composition ^b | Film State | Thickness mils | Tensile Strength, psi | Elongation at Break % | |
|-----------|---|---------------------------|-------------------------|-----------------------|-----------------------|----|
| 58040 | 33:67 2-VP:MMA | Dry | 1.1 - 1.6 | 7,100(av 10) | <3 | |
| | | Sterilized ^c | 3.2 | 660 | 50 | |
| | | Sterilized ^c | 3.2 | 660 | 60 | |
| 58039 | 31:69 2-VP:MMA | Dry | --- | 7,000(av 7) | -- | |
| | | Sterilized ^c | 2.8 | 640 | 18 | |
| 58036 | 36:64 2-VP:MMA | Sterilized ^c | 3.5 | 2,300 | 9 | |
| 58052B | 36:64 2-VP:MMA ^d | Dry | 1.5 | 8,600 | <3 | |
| 58052A | 40:60 2-VP:MMA ^d | Dry | 2.3 | 6,000 | <3 | |
| 99150 | St:MA:MMA:MAC from 18:29:9:44 charge modified with 10% CVE and crosslinked with 2% BAM | Dry | 1.7 | 6,000 | <3 | |
| | | Sterilized ^e | 3.5 | 720 | 6 | |
| | | Sterilized ^e | 4.0 | 750 | 4 | |
| | | Crosslinked with 1% BAM | Dry | 1.5 | 5,900 | <3 |
| | | Sterilized ^e | 3.0 | 300 | 13 | |
| 99153 | St:MA:MMA:MAC from 18:29:9:44 charge modified with 5% CVE and crosslinked with 1% BAM | Dry | 1.3 | 5,400 | <3 | |
| | | Sterilized ^e | 5.0 | 520 | 7 | |
| | | Sterilized ^e | 3.5 | 500 | 14 | |
| | | Crosslinked with 0.5% BAM | Dry | 1.4 | 4,300 | <3 |
| | | Sterilized ^e | 3.0 | 330 | 14 | |
| 99138B | St:MA:MMA:MAC from 43:25:10:22 charge | Dry | 1.4 | 3,400 | <3 | |
| | | Sterilized ^e | 3.0 | 570 | 4 | |
| | | Sterilized ^e | 3.3 | 365 | 43 | |
| 99129 | St:MA:MMA:MAC from 48:25:10:17 charge | Sterilized ^e | 3.3 | 365 | 43 | |
| | | Sterilized ^e | 2.5 | 240 | 385 | |
| 99158 | St:MA:MMA:MAC from 28:20:19:33 charge | Sterilized ^e | 2.5 | 240 | 385 | |
| | | Sterilized ^e | 2.2 | 455 | 80 | |
| 99169 | St:MA:MMA:MAC from 18:29:9:44 charge modified with 10% VCHO and crosslinked with 1.2% BAM | Sterilized ^e | 2.5 | 720 | 14 | |
| | | Crosslinked with 0.6% BAM | Sterilized ^e | 2.7 | 560 | 8 |
| 99178A | Same as 99169 | Dry | 1.5 | 6,650(av 6) | - | |

^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

^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 and after exposure to 40% KOH for 120 hrs at 135°C

^d LiNO₃ incorporated into film at 5 wt-% of polymer

^e Wet with KOH and after exposure to 40% KOH for 60 hrs at 135°C

that the degree of crosslinkage was increased by using the larger amount of reagent.

- d. 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%.

2. 2-Vinylpyridine-Methyl Methacrylate Copolymers

The polymers evaluated had methyl methacrylate contents ranging from 60 to 69% and had relative viscosities at 0.5% concentration from 1.5 to 4.6. Comparison of these polymers to our earlier polymers, both qualitatively and quantitatively, using our initial tensile strength measurements (Table 2), indicate that the new polymers with higher molecular weight survive sterilization better than lower molecular weight polymers with identical methacrylate contents.

We also found that a higher methacrylate content (67-69%) is apparently needed in the higher molecular weight polymers ($\eta_R \sim 3$) to give resistivities below 60 ohm-in after sterilization (Table 1). Resistivities of samples of polymer 58039, which has a 69% methacrylate content, were under 20 ohm-in.

The minimum time required to saponify these polymers completely under sterilization conditions was not entirely reproducible. Two (of 6) samples of 58039 polymer had resistivities over 50 ohm-in after 120 hours sterilization. Both these samples had been sterilized in the same bomb. The variation in saponification time is probably caused by poor wetting of the films by the electrolyte in the early stages of saponification, since the films in the ester form are extremely hydrophobic. An electrolyte soluble additive, lithium nitrate, was incorporated into two films (58027 and 58036) to aid in electrolyte penetration during saponification. This additive affected electrical properties only very slightly, although it plasticized the film, indicating it was apparently holding water. Other films are now being presoaked in methanol to aid wetting and also possibly accelerate saponification by formation and subsequent reaction of sodium methylete. Initial test samples of presoaked film survived sterilization intact and a test series to determine reproducibility of saponification time is underway.

B. PREPARATION OF POLYMERS

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

Tetrapolymers with high contents of hydrolyzable anhydride and acrylate groups were modified to incorporate sites for cross-linking during film formation. The monomers, 2-chloroethylvinyl ether, 4-vinylcyclohexene or vinylcyclohexene oxide, were used to supply the crosslinking sites. The reaction conditions used to prepare these modified polymers are summarized in Table 3. Based on viscosity measurements, vinylcyclohexene and 2-chloroethylvinyl ether lowered the degree of polymerization slightly. However, all the polymers gave mechanically strong films.

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.

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.

2. 40:60 2-Vinylpyridine-Methyl Methacrylate Copolymer

Our study to increase the molecular weight of this copolymer by improving polymerization conditions was completed. 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.

Table 3

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

| Reference | Mole Ratio Monomers St:MA:MMA:MAC | Monomer With Site for Crosslinking* Wt-% | Catalyst** g/100g Monomer | Temp °C | Reaction Time, Hrs. | Conversion Wt-% | n_D for 0.5% Solution |
|-----------|--------------------------------------|--|------------------------------|------------|------------------------|--------------------|-------------------------------|
| 99152 | 50:50:0:0 | 5 CVE | 0.6 LP | 42*** | 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 |
| 99163 | 28:20:19:33 | ---- | 0.02 ABIN | 60 | 2 | 12.5 | 2.24 |
| 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 |
| 99171 | 43:25:10:22 | ---- | 0.02 ABIN | 60 | 1.8 | 29.5 | 2.24 |

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

** LP = lauroyl peroxide; ABIN - azo-bis-isobutyronitrile

*** in methylene chloride solvent

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 4. The results can be summarized as follows:

- a. Significant improvement in molecular weight was obtained by polymerization to high conversion. The viscosity-conversion relationship of this copolymer, shown in Figure 1, is similar to that of some methyl methacrylate homopolymers (ref. 1).
- b. Polymerizations terminated at less than 40% conversion have slightly higher molecular weights when polymerized at 40°C rather than at higher temperatures;
- c. The variations in rate of initiation made in runs at 60°C did not affect the molecular weight of the products;
- d. Polymerizations carried to conversions above 40% require a slight adjustment in monomer charge to maintain constant polymer composition.

This polymerization is very easily inhibited by trace amounts of oxygen. We found it was necessary to use oxygen-free nitrogen as cover for polymerizations done in resin pots to obtain high molecular weight polymers that were equivalent to the high conversion polymers (e.g. 58039) prepared in pressure bottles.

An attempt to incorporate an amino crosslinking site into the 2-vinylpyridine-methyl methacrylate copolymer was also made. However, the reagent, methyl 3-aminocrotonate, inhibited the polymerization of the standard copolymer charge almost completely when used in 5 weight % concentration at 40°C.

C. CROSSLINKING OF POLYMERS

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 dissolve in 40% KOH after sterilization. The criteria for a successful crosslinking procedure is 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 5.

Table 4

EFFECT OF VARIATIONS IN POLYMERIZATION CONDITIONS ON PROPERTIES OF 40:60
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 |

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

(b) Azo-bis-isobutyronitrile

(c) In dimethylformamide at 30°C

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

(e) Contained 20% polymer in initial charge

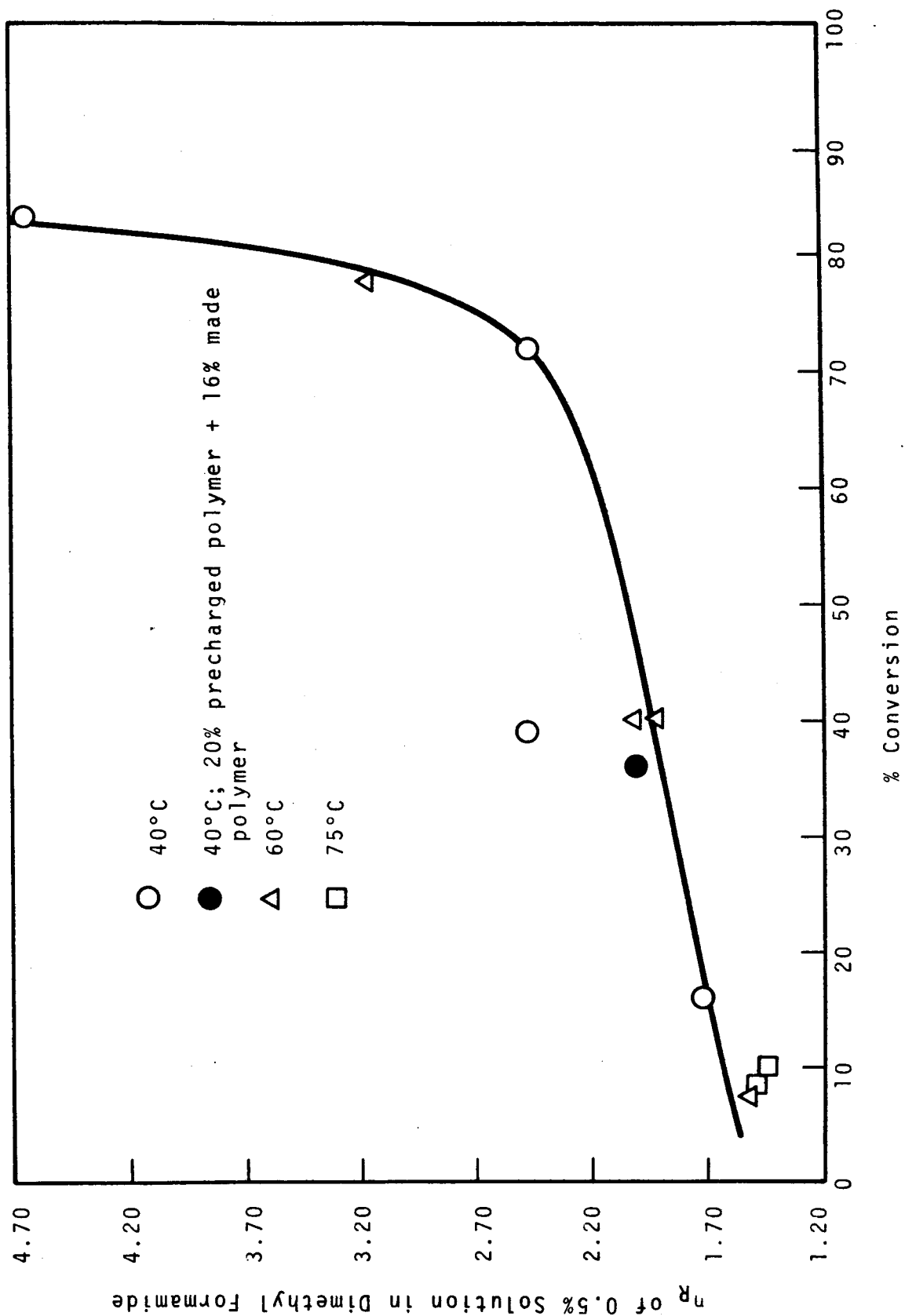
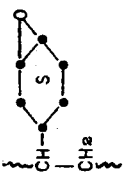
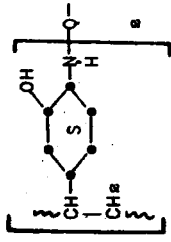
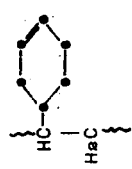

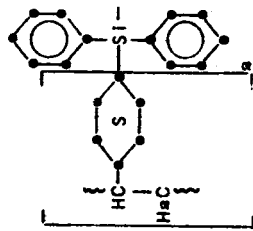
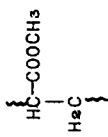
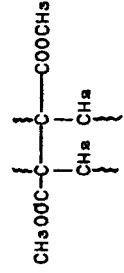



Figure 1. Relationship of Polymer Molecular Weight to Reaction Conversion.

Table 5
CROSSLINKING REACTIONS FOR LIGAND POLYMERS

| Type | Crosslinking Site | Reactant* | Crosslinking Bond |
|------|--|--|---|
| IA | $\begin{array}{c} \text{CH-O-CH}_2\text{-CH}_2\text{-Cl} \\ \\ \text{H}_2\text{C} \end{array}$ | $\text{H}_2\text{N-Q-NH}_2$ | $\left[\begin{array}{c} \text{CH-O-(CH}_2\text{)}_n\text{-NH}_2 \\ \\ \text{CH}_2 \\ \text{Cl}^- \end{array} \right]_2 \xrightarrow{\text{Sterilize}}$ |
| IB | " | $\text{(EtO)}_2\text{P-Q-P(OEt)}_2$ | $\left[\begin{array}{c} \text{CH-O-(CH}_2\text{)}_n\text{-O-} \\ \\ \text{CH}_2 \end{array} \right]_2$ |
| II |  | $\text{H}_2\text{N-Q-NH}_2$ |  |
| III |  |  |  |
| IV |  | R* |  |

* Q is a connecting linkage such as $-(\text{CH}_2)_n-$ or ---  $---$

Successful crosslinking was obtained with diamines as the reagent to crosslink either unmodified polymers or modified polymers containing 2-chloroethyl or cyclohexene oxide sites. The general procedure for reaction was to add the diamine to a solution of polymer just before casting the film. However, alkyl amines caused gel formation under these conditions. Better crosslinked films with these reagents were obtained by soaking preformed films of linear polymer in a methanol solution of the alkyldiamines.

Most of 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°C 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. 2) 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.

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-methylantraquinone as photosensitizer to generate free radicals. These conditions were developed by Oster (ref. 3) to crosslink acrylate polymers. However, film samples (99163) containing 5 wt. % photosensitizer that were exposed to Black Spectroline X-4 light (366 m μ) 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.

D. PREPARATION OF FILMS

Improvements in the quality of our films were made by reducing dust entrapment in the films and by determining better conditions for casting and drying them. Uniform films approximately 5" by 20" with 1 to 2 mil thickness are now being made by leveling strained polymer solutions with a Gardner blade on a flat polypropylene surface protected by a dust cover and drying them 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 wt.% for relative viscosities between 1.0 and 3.5 and concentrations between 4 and 14 wt.%. 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.

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 6. 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 NEXT QUARTER

1. Determine film properties of partially saponified 2-vinylpyridine-methyl methacrylate copolymers.
2. Complete checks on reproducibility of polymer preparations.
3. Prepare batch of polymer selected for scale-up and start arrangements for film preparation.

Table 6

REVISED PROGRAM PLANNING CHART

| <u>Program Phase</u> | <u>Per Cent of Total Research Effort</u> | | | | | | | | | | |
|---|--|------------|-------------|------------|------------|------------|------------|------------|--------------|--------------|------------|
| | <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 |

V. REFERENCES

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