FINAL REPORT

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SILVER-ZINC BATTERY SEPARATOR MATERIAL DEVELOPMENT

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TO
California Institute of Technology
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

DAYTON LABORATORY

DAYTON, OHIO 45407

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ABSTRACT

A project (Contract JPL 951966) has been completed for the development and preparation of ethylene/acrylic acid membranes for application as separators in heat sterilizable silver oxide/zinc secondary batteries. The membranes were made from a precursor copolymer (ethylene/methyl acrylate) by pressing into film, vulcanizing and hydrolyzing. Precursor copolymer was made by copolymerizing ethylene and methyl acrylate at ultra-high pressure.

Membranes of ethylene/acrylic acid (or potassium salt) have been made that are stable in strong caustic during sterilization (140°C, 40% KOH, 60 hours), have low silver and zinc migration (Ag^{110} and Zn^{65} diffusion comparable to acrylic acid grafted on polyethylene), have satisfactory tensile strength for normal handling (500-1700 psi) and satisfactory elongation (120-330%). The acid form of the membranes are stronger and less hygroscopic than the salt form.

One hundred one discs of ethylene/acrylic acid membranes (21 in. x 22 in. minimum), in both acid and salt form were forwarded to JPL which include more than 150 sq. ft. of membrane. The composition of the vulcanized membranes is about 57% ethylene and 43% acrylic acid. A few membranes filled with carbon black (10 wt.%) were also included.

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1. OBJECTIVE

A research and development program was undertaken at Monsanto Research Corporation to develop a membrane material for application as a plate separator in sealed and sterilized silver oxide/zinc secondary batteries. The membranes for this application must be stable in strong caustic during sterilization and operation, have low resistance and have sufficient mechanical stability to allow limited handling and limited shock.

In our experimental work we sought to develop and make membranes of vulcanized ethylene/acrylic acid copolymer for this application by hydrolysis of a precursor copolymer of ethylene/methyl acrylate. The precursor polymer was a necessary intermediate product because acrylic acid does not readily copolymerize directly with ethylene, while the ester does copolymerize.

Some of the properties of the copolymers have been measured and some evaluation tests have been made on the product. Finally, more than 150 sq ft of preferred film has been prepared for the Jet Propulsion Laboratory.

2. SUMMARY

The preparation of battery separator membranes composed of ethylene and acrylic acid involved several logical steps. Since ethylene and acrylic acid do not copolymerize readily, this material was made from a precursor copolymer, namely, ethylene/methyl acrylate (E/MAR). The precursor copolymer was formed into film, vulcanized, and hydrolyzed to give the separator membrane. The work on this project has involved a study of each of these steps and evaluation of the product properties which has governed the development steps for the preparation of suitable membranes.

Typical conditions for copolymerization of ethylene and methyl acrylate were: 85°C, 15,000 psi, 4-5 hours duration, and with 0.03 - 0.04 wt.% benzoyl peroxide initiator (based on total monomer charge). As reaction occurred, additional monomers were added. Monomer ratio in the copolymer product was controlled by the amount of MAR added and the molecular weight was controlled by addition of acetone to the reactants. C and H analysis of E/MAR has been the most precise method for determining monomer ratio of the copolymer. Copolymer with a melt index of >2 (at 150°C, ASTM 1238) has been employed for preparation of most of the membranes.

Thin films of E/MAR have been made by solution casting but most of the membranes (2-5 mil thick) were made by pressing a blend of copolymer and vulcanizing agent in a hydraulic press (20 in. x 20 in. platens, ram force 115 tons) at 140°C. The films were then vulcanized by heating to 150°C for 15 minutes. The desired product was obtained by a two-stage hydrolysis of vulcanized film, in the potassium salt form which is hygroscopic. Acidification of the membranes yields a tougher and non-hygroscopic membrane.

We have chosen a copolymer of about 52/48 E/MAR composition for the preparation of membranes to be made into battery separators. The final hydrolyzed product contains about 43.7% acrylic acid, has a specific resistance of about 10 ohm-in., and seems to have adequate tensile properties for normal handling. The membranes are stable to sterilization (140°C, 40% KOH, 60 hours). Migration of silver and zinc seems to be comparable to published values for membranes of grafted acrylic acid on polyethylene.

Carbon filled membranes and membranes made by polyblending E/MAR with an ethylene/vinyl acetate copolymer have improved handling properties and may have better physical properties. These modifications have not been extensively explored.

To fulfil this contract, 101 discs of membranes amounting to more than 150 sq ft were sent to JPL on 18 June 1968. Most of the membranes contained about 43% acrylic acid and were in the acid form. Some membranes were shipped in the salt form. A few membranes contained carbon black filling (10 wt.%).

3. EXPERIMENTAL WORK

3.1 POLYMERIZATION OF PRECURSOR

Experimental copolymers of ethylene/methyl acrylate (E/MAR) were prepared in a 1 liter SS stirred reactor with a working pressure of 15,000 psi. The initial work on this project was concerned with the optimization of polymerization variables such as initiation concentration, reaction time, temperature, chain transfer agent concentration, and monomer feed rate. A reproducible copolymerization procedure was developed so that polymer could be synthesized with suitable molecular weight and the desired monomer ratio.

3.1.1 INITIATOR LEVEL AND REACTION TEMPERATURE

The initiator level and reaction temperature variables were investigated simultaneously because the two variables are closely related. Early experiments were run using about 0.04 wt.% initiator based on total monomer at 72 to 75°C. Yields were very poor. The initiator level was increased to about 0.14 wt.% and the reaction temperature set at 80°C in the next series of experiments. This change resulted in yields ranging from 10-20%. However, the reactions frequently got out of control, resulting in blowing the rupture disc. Even in runs where the rupture disc was not lost, temperature and pressure control were not good.

In subsequent experiments adjustments were made in initiator level and reaction temperature. Finally, it was found that good yields of E/MAR copolymers were obtained by using from 0.03-0.04 wt.% (based on total monomer charge) initiator at 85°C. These conditions allow a controllable and reproducible copolymerization reaction. These studies are summarized in Table 1.

TABLE 1

VARIABLES INFLUENCING THE E/MAR COPOLYMERIZATION REACTION

Run	Charge: E (Total) moles	Charge: MAR (Total) moles	Monomer[1] Addition Interval (min)	Initiator: g.	Initiator: wt%[4]	Reaction Conditions: Pressure psi x 10^{-3}	Reaction Conditions: Temp. °C	Reaction Conditions: Time (hr)	Acetone: wt%[4]	MI[5]	Yield (g)	Remarks
82957	23.8	0.56	30[2]	0.32	0.04	13-15	72-75	4	0	—	trace	
82961	24.0	0.63	30	1.0	0.14	15-15.6	81-82	2.5	0	--	0	Lost Rupture Disk
82962	24.2	0.62	30	1.0	0.14	14-15	81-82	2.5	0	--	10	Lost Rupture Disk
82965	23.8	0.95	30	1.0	0.13	15-16.2	79-80	3.5	0	0	82.2	
82980	23.8	0.20	15	0.5	0.07	6-15	78-95	2.5	0	0	49.5	Out of Control
82988	23.8	0.48	15	0.5	0.07	9.2-15.4	74-87	3	0	0	41.0	Out of Control
82998	23.8	0.23	15 - 45[3]	0.1	0.01	14.9-15.4	84-86	4	0	0	18.2	
83000	23.8	0.53	15 - 45	0.2	0.03	14.9-15.8	85	6	0	0	39	
83005	19.4	0.34	15 - 45	0.2	0.04	14.9-15.8	85	4.5	1	23	39.3	
83016	19.4	0.20	15 - 45	0.3	0.05	14.1-15.5	80-90	5	1	115	113	Nearly Lost Control
83020	19.4	0.20	15 - 45	0.2	0.04	14.6-15	85	5	1	180	54	
83023	22.7	0.09	15 - 45	0.2	0.03	14.6-15	85	4	0.25	0.2	36	
83026	22.1	0.16	15 - 45	0.2	0.03	14.6-15	85-86	4	0.33	0.8	46	
83028	21.6	0.13	15 - 45	0.2	0.03	14.6-15	85	4	0.5	2.5	59	
83032	21.3	0.17	15 - 45	0.21	0.03	15-15.4	85	4	0.6	4.0	49	

[1]2-15 ml. MAR added at intervals during polymerization; amount added governs monomer ratio in product. E added to 15,000 psig. after MAR addition.

[2]Addition by time interval, not satisfactory

[3]Addition after pressure drop of 400 psig.

[4]Based on total monomer

[5]Melt Index

3.1.2 MONOMER RATIO, MONOMER FEED RATE

The reactivity ratio of ethylene is much smaller than that of methyl acrylate in copolymerization. The feed, therefore, must contain a large excess of ethylene for all copolymers. The working pressure of the autoclave is 15,000 psi. With this restriction, one can use about 19-33 moles of ethylene depending upon the quantitities of other materials present in the reaction mixture.

Early experiments were conducted in such a manner that after charging about 23 moles of E (ethylene) to the autoclave, MAR (methyl acrylate) additions were made on a time interval basis. For example, addition rates of 3 ml every 15 minutes, or perhaps 10 ml every 30 minutes were used. This scheme did not prove to be entirely satisfactory. For example, there were occasions when the pressure was too high to safely make a MAR addition at the scheduled time. In addition, as mentioned above, reactions were sometimes running out of control when an MAR addition was scheduled.

Although the early experiments were not completely satisfactory, the experiments yielded useful information. It was learned that the desired range of copolymer compositions were obtained by MAR additions varying between 2 ml and 12 ml per addition. With the optimum initiator level and reaction temperature, MAR additions on the basis of pressure drop during the reaction were found to be more suitable for obtaining controlled reaction. The charge of initiator, MAR (2-10 ml) and E at 15,000 psi was reacted until the pressure fell to 14,600 psig. Then the desired quantity of MAR was added (about 2 ml for 20% MAR copolymer, about 10 ml for 60% MAR copolymer) and additional E added to restore the pressure to 15,000 psi. By this technique the monomer feed was controlled to give the desired copolymer. Data related to this phase of the work are summarized in Table 1.

3.1.3 REACTION TIME

Reaction time is somewhat arbitrary. At 85°C, the half life of the initiator benzoyl peroxide is about 2 hours 8 minutes (Brochure 30. 30, Lucidol Division, Wallace & Tiernan Company). Therefore, initiation by this material is negligible after about 4 half-life periods (8 hours 32 minutes) and rather slow after about 2 half life periods. Eventually a point is reached at which monomer addition causes a pressure in excess of 15,000 psi. Obviously, it is desirable to prepare as much polymer as possible in each run. Also, because of the unfavorable reactivity ratios of E and MAR, low conversions are desirable to retain control over copolymer composition. From experience with these experiments, we prefer a reaction time of 4-5 hours, which results in a high conversion of MAR (>60%), a low conversion of ethylene (∿15%), and an overall conversion of 20-30% of total monomers. Reactions times are included in the data shown in Table 1.

3.1.4 MOLECULAR WEIGHT CONTROL, CHAIN TRANSFER AGENT

The flow property of a polymer, which is a significant property of polymer to be formed by hot pressing or extrusion, is directly related to the molecular weight of the polymer and it may be assessed by measurement of melt index. The product made in some of the early experiments had molecular weights too high for satisfactory pressing into thin film, and this property was indicated by very low melt index values. Therefore, syntheses were made in which a chain transfer agent, acetone, was included in the polymerization mixture.

A few experiments were conducted with variable concentrations of acetone to determine the amount required to produce E/MAR copolymers having the desirable melt index range. The 150°C melt index, as determined by ASTM 1238, should fall between 2 and 20 for satisfactory

flow at 150°C. The experiments showed that a concentration of about 0.5 wt.% (based on total monomer charge) of acetone will give a product having a melt index in the 1.5 - 7 range. Data related to experiments concerning acetone are included in Table 1.

3.1.5 POLYMERIZATION PROCEDURE

For polymerization, the reactor, containing benzoyl peroxide (0.2 g - 0.3 g) was closed and all lines were then connected to the autoclave. The reactor was evacuated, purged twice with ethylene, and evacuated again. A SS tube (3/32 in. i.d., 1/4 in. o.d.) about 12 inches long was connected to the autoclave through a high pressure valve and was submerged into a graduated cylinder containing a measured quantity of acetone under nitrogen. The valve was opened to admit the acetone to the reactor. Ethylene was pumped into the reactor to a pressure of 8000 psig.

A small amount of MAR was added, heat applied, and the stirrer started. At 85°C, a quantity of MAR equal to the first addition was added. At this time, the total MAR added was equal to that amount predetermined (see above) to give the copolymer with desired monomer ratio, for example, X ml. Additional E was added to increase pressure to 15,000 psi, and the temperature was held at 85°C. As polymerization proceeded, the pressure decreased. At 14,600 psi, X ml MAR was added. After the MAR addition, E was added to make up the difference between the pressure and 15,000 psi. MAR and E additions were continued as the reaction proceeded.

After about 4 hours reaction, the final MAR addition was made. When the pressure fell to 14,800 psi, the heat was turned off, the stirrer was turned off, and the reactor was vented to about 8000 psi. The mixture was allowed to cool to room temperature overnight. The autoclave was then vented to atmospheric pressure and the reactor evacuated

by a vacuum pump. About 800 ml of toluene was introduced into the reactor and the mixture in the reactor was heated at 100-105°C for about 2 hours with stirring. Approximately 400 psig pressure was applied with ethylene and the toluene solution of product was drained into about 1500 ml of boiling hot toluene and a few grams of filter aid (HYFLOW SUPER-CEL). The hot solution was vacuum filtered quickly through a preheated Buchner funnel and washed with hot toluene. The filtrate was poured into 5-6 volumes of methanol with stirring to precipitate the product.

The product was isolated by filtration or decantation. With high MAR copolymers, filtration is not recommended since the product is tacky and tends to adhere to paper. The product is dried in a 40°C vacuum oven for at least 48 hours. The yields have generally been about 40-60 g.

3.1.6 COPOLYMER CHARACTERIZATION

At the outset of this work four analytical methods were considered for polymer characterization, including elemental analysis, density, saponification equivalent, and infrared spectrum. The most useful determinations have been elemental carbon and hydrogen by Dumas Combustion procedure. From these data, oxygen content was calculated by difference. The oxygen content is related to MAR content and a plot of percent oxygen in copolymer vs. percent MAR in copolyner is shown in Figure 1.

Once the compositions of E/MAR copolymers covering the range of low to high MAR had been established by carbon and hydrogen analysis the composition could be related to density. Density measurements are easier and faster than C and H determinations and therefore were used for many of the composition determinations. A plot of density vs. composition is shown in Figure 2. The buoyancy method was used

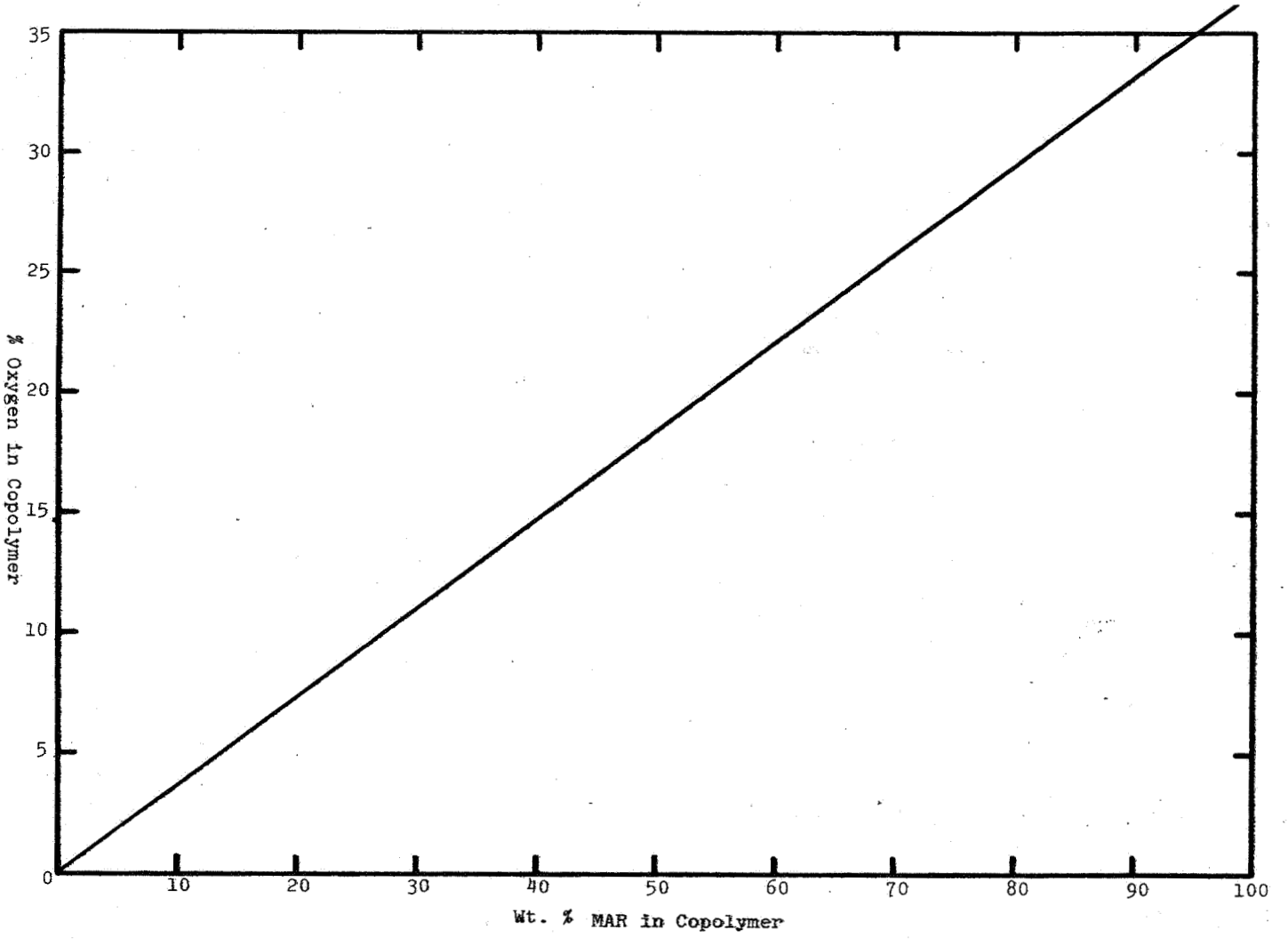

Figure 1. % MAR In Copolymer As A Function Of % O In Copolymer, Calculated.

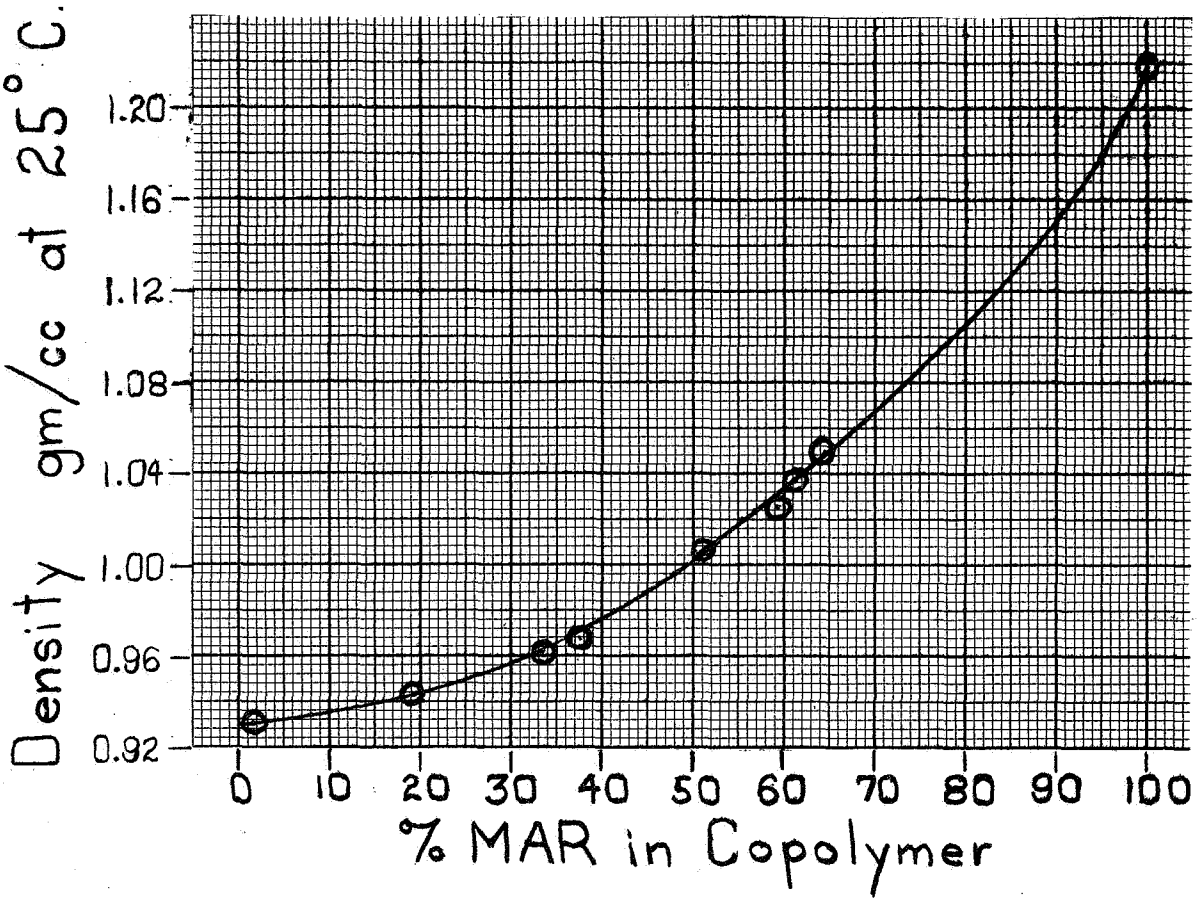

Figure 2. Density VS. Composition.

to determine densities. By this method the sample is weighed in air and in a suitable medium (Dow Corning 200 Fluid) maintained at 25°C. Density of the sample is calculated from the following relationship.

$$\text{Density} = \frac{\text{Wt. of Sample in Air}}{\text{Displacement}} \times \text{Density of Medium}$$

where displacement = sample weight in air minus sample weight in medium.

Theoretically, determination of saponification equivalent should be a good independant method of analysis for E/MAR copolymers. However, several solvent systems were tried for saponification and found to give heterogeneous systems with E/MAR or the hydrolysis product. End points were always uncertain and reproducibility was generally poor. MAR content of copolymers calculated from saponification equivalents generally ran lower than that determined by other methods. The data in Table 2 illustrate this phenomenon. Since the precision of the saponification values was poor, this method appears to be less accurate than carbon-hydrogen measurements for determination of composition and has not been employed as such in this project.

Table 2

SAPONIFICATION EQUIVALENTS OF E/MAR COPOLYMERS

Sample	Saponification Equivalent	% MAR By Sap. Eq.	% MAR By C & H
82998	291	29.4	37.5
83000	205	41.5	51.4
83020	2502	3.4	16.8

The infrared spectrum of E/MAR copolymer film is shown in Figure 3. The ratio of the peak intensities of carbonyl at 5.72 μ to methylene at 6.82 μ increases as MAR content of the copolymer increases. A determination of the ratio of ethylene to methyl acrylate probably may be made from the infrared spectrum by correlation of these peak intensities with the actual composition determined on a few samples by another method. However, this analytical procedure seems to be slower than other determinations (such as by density) and the calibration by infrared spectrum has not been made.

3.2 FILM FORMATION AND VULCANIZATION

During the course of this investigation two methods of film formation were investigated, i.e. casting from solution and hot pressing. Each of these methods has certain advantages and disadvantages, which were compared by exploring both methods. A third method, extrusion, may be useful for making film, but is not amenable to exploratory preparation of film from small samples of polymer and has not been examined or evaluated in this project.

Formation of film and vulcanization are consecutive in all processes examined and often are more or less simultaneous, even though film formation is a physical process and vulcanization is a chemical reaction. Vulcanization is not necessary to the formation of good film, but is necessary to obtain film stability in aqueous caustic.

3.2.1 SOLUTION CASTING

One of the advantages of solution casting is that thin films of uniform thickness may be made. To make film, a warm toluene solution of E/MAR (about 10% solids) and vulcanizing agent, Di-Cup R (dicymyl peroxide recrystallized) was spread evenly on a casting plate with a

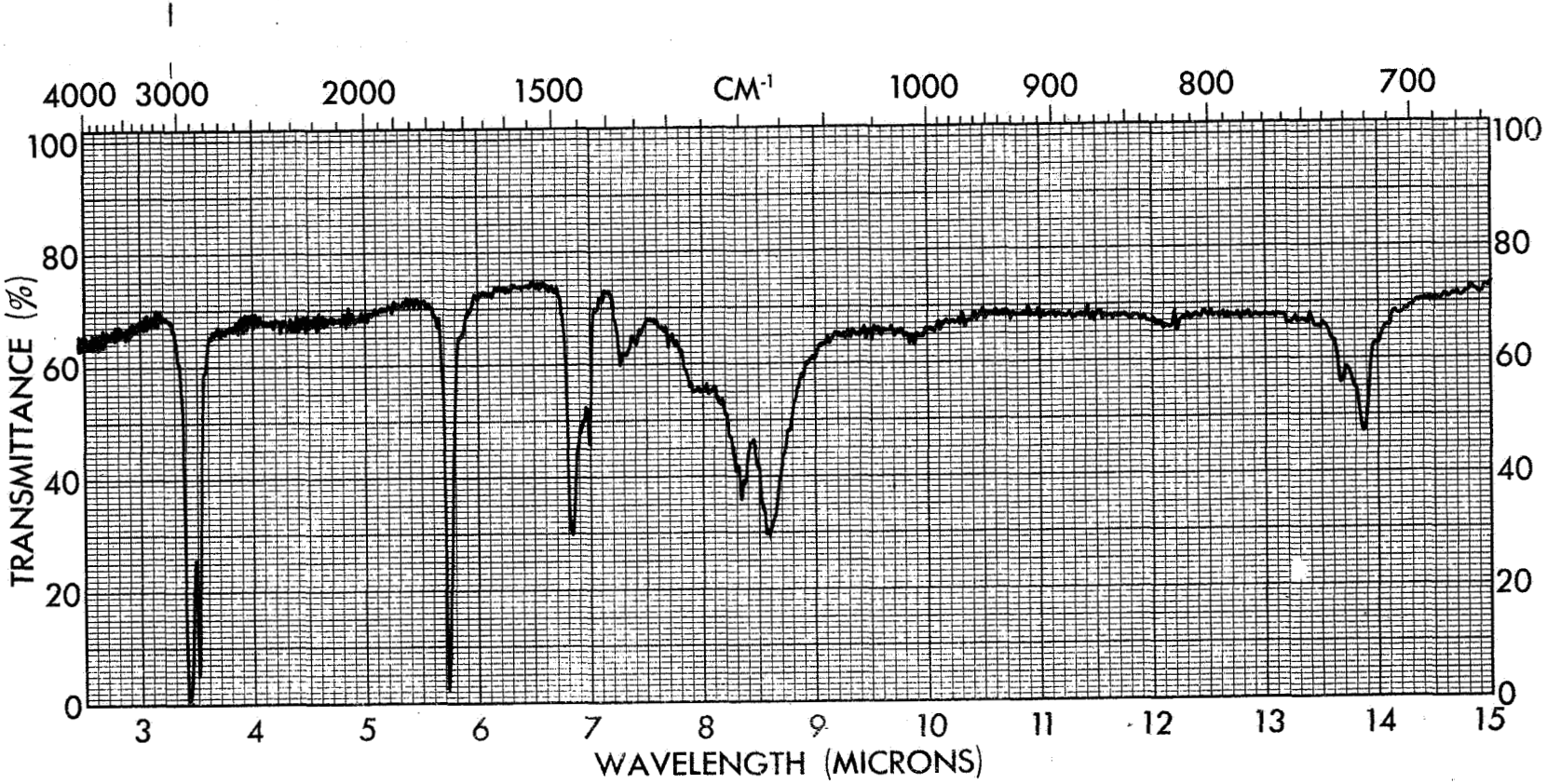

Figure 3. Infrared Spectrum E/MAR.

Doctor blade and the solvent evaporated in air at ambient temperature. The last traces of solvent could be removed by putting the film in a vacuum. The casting plates were usually unscratched glass. The vulcanizing agent amounted to 5 wt.% or less, based on weight of polymer. The blade (Gardner, adjustable) was set to form a liquid layer which when dried gave film of the desired thickness. The dry films could be removed as formed. However, when heated to 150°C for vulcanization, we found that films could not be removed from the plates. A variety of release agents was tried but none was effective. The cast films removed from glass or polished chrome plates before vulcanization generally were not sufficiently self-supporting at 150°C for vulcanization, i.e., polymer flow occurred before extensive vulcanization was accomplished.

It was found that solution cast films on glass plates could be vulcanized in place by exposure to ultraviolet light. The source was a 500-watt Hanovia quartz lamp placed about 6 inches from the film for about 1 hour. Vulcanized films made by this technique were not heated to fusion and could be removed from the glass. However, the degree of vulcanization was apparently rather low. Such films could be hydrolyzed in 2.5 N KOH; they were insoluble in toluene but they did not survive heating for 60 hours in 40% KOH at 140°C.

3.2.2 HOT PRESSING

By this method it is possible to form film and vulcanize it essentially in one step. The polymer was first blended with peroxide catalyst by milling polymer and catalyst on a roll mill at the lowest possible temperature. In the preparation of film that was sent to JPL, two copolymers and the vulcanizing agent were milled between room temperature and 50°C to obtain complete blending.

Two hydraulic presses with heated platens have been used to form and vulcanize film. Many of the exploratory films were made in a Pasadena Press with 12 x 12 in platens and a maximum ram force of 40 tons. The platens were heated electrically, the temperature was controlled by a Brown Pyro-O-Vane controller and subsequently cooled with a stream of tap water through internal coils. The film sent to JPL for conclusion of this contract was made on a French Oil Mill Machine Company hydraulic press with 20 x 20 in platens and a maximum ram force of 115 tons. The platens were heated by steam, and temperature was regulated by a pressure control valve in the steam line. Both the steam and water used for cooling were passed through coils built into the platens. The pressure on the film in these presses was about 555 psi and 575 psi, respectively.

Polymer was formed into film by pressing with the platens heated to about 150°C. At this temperature, unvulcanized polymer of suitable molecular weight (see Section 3.1.4, Molecular Weight Control) flows smoothly and is believed to be in form of film in less than 3 minutes. Vulcanization during this period was not extensive but was complete in 15-30 minutes (half-life of Di-Cup R about 12-13 minutes at 150°C). In some cases, a slightly different time/temperature cycle was used; i.e., polymer was pressed at 140°C for 15 minutes and the temperature was raised to 150°C for 15 minutes (pressure maintained). In this case, very little vulcanization took place during film formation but was complete after film was formed. Somewhat different time/temperature cycles probably may also be used, but the film must be formed before the polymer is extensively vulcanized.

The time/temperature cycle is also governed to some degree by the amount of vulcanizing agent present. The time/temperature cycle given above resulted from evaluating the degree of vulcanization. Specifically, a suitable level of Di-Cup R was determined by extruding

various mixtures of polymer and Di-Cup R through a capillary extrusion rheometer by the method described by Salyer, et. al. [J. Polymer Sci., A, 3, 1911 (1965)]. The extrusion conditions were kept constant and the time (at 150°C) to the appearance of knotty extrudate was measured. The conditions and data are shown in Table 3.

The data shows the "knot" time is a function of Di-Cup R concentration. The appearance of knots in the extrudate indicates extensive vulcanization; the polymer will no longer flow smoothly and no longer is soluble in toluene. The knot time therefore represents the time available for forming film by polymer flow under pressure. Also shown in the table is flake time. At this point vulcanization has proceeded to the point where the extrudate has become brittle and will not flow. The polymer is considered to be over-vulcanized since results obtained later indicate polymer in the flake stage is difficult to hydrolyze (it also has high resistance).

The data in Table 3 show that up to 3% Di-Cup R may be used in a 30-minute cure. This would allow up to 10 minutes flow time for film formation. Actually, a few films containing no peroxide were made to check alignment of the press plates. A flow time of 3 minutes was adequate for making film.

These experiments showed that higher levels of Di-Cup R gave easier-to-handle films. It was also noted that the electrical resistance of films of a given composition increased as the Di-Cup level increased. However, the effect was small at MAR levels above 40%. This effect is discussed in more detail in Section 3.3.

TABLE 3

DEGREE OF VULCANIZATION AS DETERMINED BY EXTRUSION RHEOMETRY

Temperature, 150°C
Piston Rate, 1 in./min.
Orifice, 0.043 in.
Orifice, L/D = 15

Sample	Copolymer Composition[1]	Di-Cup R (wt. %)[2]	Knot Time (min.)	Flake Time (min.)
82877-1	70% E/30% EAR[3]	2.5	9	29
82877-3	70% E/30% EAR[3]	7.5	<5	<5
82877-4	70% E/30% EAR[4]	2.2	9	18
82877-6	70% E/30% EAR[4]	6.6	5.5	10
87665-A	51.8% E/48.2% MAR	3.0	12	25-30
87665-B	51.8% E/48.2% MAR	10.0	5	--
87675-1	81.3% E/18.7% MAR	3.0	10	--
87675-2	81.3% E/18.7% MAR	10.0	<5	9
87680-A	40% E/60% MAR	3.0	9	22
87695-1	78.2% E/21.8% EAR	1.0	10-15	30-35
87695-2	87.6% E/12.4% EAR	1.0	10-13	30-35
87695-3	78.2% E/21.8% EAR	0.5	20-25	>48
87695-4	87.6% E/12.4% EAR	0.5	20-25	>51

[1]E is ethylene, EAR is ethyl acrylate, MAR is methyl acrylate

[2]Dicumyl peroxide, recrystallized

[3]Reported composition

[4]Blend of E/EAR reported to be 20% EAR with homopoly - EAR

As mentioned previously, E/MAR heated to 150°C, becomes fused to metal and other surfaces. With the presses described above, metal sheets were used on either side of the film. But when they were in direct contact with the film, the plates would not separate readily. This problem was eliminated by placing Teflon between metal and polymer during the hot pressing. The films did actually stick to Teflon but could be removed without excessive distortion. The films were pressed between two 20 x 20 in. stainless steel plates. Two 10 mil sheets of Teflon were used above and below the film. Twenty-two grams samples of polymer/Di-Cup blend were cut in a shape resembling a letter "I". These were prepressed at room temperature at 400-lb ram force between 12 x 12 in. Teflon sheets to produce a dumb-bell shape. The dumbbell specimens were then pressed into film and vulcanized in the larger press. Usuable life of the Teflon sheets was markedly increased by the prepressing procedure.

3.3 HYDROLYSIS

Previous work at MRC showed that E/MAR copolymers could be hydrolyzed to the potassium salt of the corresponding acrylic acid copolymer (E/AK). The E/MAR copolymer film was soaked one week at room temperature in 2.5 N alcoholic (equal weight of methanol and isopropanol) KOH and one week in 2.5 N aqueous KOH. During the course of this investigation several films had a high resistance, apparently due to incomplete hydrolysis. This was demonstrated by showing that the area resistance of such films could be made to decrease by additional hydrolysis. Because of this and to reduce the time required, some changes were made in our hydrolysis technique. Films were hydrolyzed for 24-30 hours at 60-70°C, first in alcoholic KOH (2.5 N) and then for a like period at 60 - 70°C in aqueous KOH (2.5 N). The data in Table 4 shows that such treatment

TABLE 4

HYDROLYSIS OF E/EAR FILMS AT 60-70°C

Sample	AA[1] (wt.%)	Hours at 60-70°C in 2.5 N KOH Alcoholic	Aqueous	Wet Thickness[2] (mils)	R_A Ω in.^{2}	r Ω in.
82873	20.7	24	24	1.1	0.75	681
82873	20.7	24	48	1.1	0.70	636
82877-2	10.1	24	24	3.8	2.42	636
82877-2	10.1	24	72	3.9	2.48	635
82877-5	15.9	24	24	4.3	4.15	965
82877-5	15.9	24	72	5.3	3.65	688

[1]Calculated weight percent acrylic acid in hydrolyzed copolymer

[2]Thickness of film used in R_A measurement after conditioning in 40% KOH.

appears to give maximum hydrolysis, which is essentially complete after 24 hours at 60-70°C in each hydrolysis bath. This is indicated by the reasonably small change in area resistance that is noted after additional hydrolysis at 60-70°C in the aqueous bath. This work was actually done with film made from ethylene/ethyl acrylate copolymer (E/EAR). This and other work has indicated E/MAR and E/EAR are interchangeable and react similarly.

3.3.1 HYDROLYSIS IN THE PRESENCE OF A SWELLING AGENT

During the course of this study, highly vulcanized E/MAR's were found to hydrolyze slower and less efficiently than film vulcanized to a lesser degree. This was especially true for films with less than 45-50% acrylate ester. Specifically, E/40% MAR blended with 3 parts Di-Cup R per 100 parts copolymer and vulcanized yielded a product with higher resistance than the product made by blending the same polymer with 0.6 part Di-Cup R per 100 parts of copolymer. The more highly vulcanized film appeared to be preferable, and the addition of toluene to the alcoholic KOH was found to improve the hydrolysis of the highly vulcanized film. A 1:1 dilution of the alcoholic KOH bath with toluene allowed a more complete hydrolysis, as indicated by film resistance measurements. The data in Table 5 illustrate this effect. Apparently, the reason for this effect is that vulcanized E/MAR films are swelled (up to 100%) by toluene more than by alcohol. It is presumed that in the highly swelled state the ester groups are more "exposed" to attack in the hydrolysis medium.

Toluene was not used to hydrolyze films sent to JPL, because since this work, the need for additional swelling resulting from toluene has been reduced or eliminated. Apparently, polyblends made by

TABLE 5

RESISTANCE OF HYDROLYZED E/MAR FILMS AS A FUNCTION OF SWELLING AGENT[1] IN HYDROLYSIS BATH

Polymer	Acr A Wt %	R_A When Hydrolyzed, Ω in.^{2} Standard	R_A When Hydrolyzed, Ω in.^{2} With Toluene	r When Hydrolyzed, Ωin. Standard	r When Hydrolyzed, Ωin. With Toluene
82891-A	20.0[2]	0.0294	0.00393	4.1	0.873
87684-7	27.0	0.164	0.1092	34.9	26.1

[1]2.5 N KOH in 50:50::MeOH:PrOH,
Diluted with an equal volume of toluene

[2]Membrane also contains 26% c-black, from E/MAR with 25% c-black.

blending copolymers with a substantially different monomer ratio hydrolyze more completely than more homogeneous copolymer. The membranes were made for JPL by blending E/66% MAR and E/21.8% EAR, using 3 parts Di-Cup R per 100 parts copolymer, to give a hydrolyzed product containing about 43% acrylic acid and having a low resistance.

3.3.2 FILM HANDLING

As the work progressed and larger films were being made, the mechanical handling became more difficult. Both in the hydrolysis baths and after removal from the baths the films tended to wrinkle and fold upon themselves. They stuck together and were difficult or impossible to unfold without tearing. The simultaneous hydrolysis of several films (a necessity for large scale production) compounded the problem. However, the film entity could be maintained during hydrolysis by supporting the films between layers of polyolefin mesh (5/16 in openings). This caused a slight quilted effect on the films. Therefore, a 324 mesh polypropylene screen support was employed which gave films with relatively smooth surfaces. The best procedure evolved was to build an assembly in which each film to be hydrolyzed was placed between two of the fine polypropylene screens. These were separated from each other by the 5/16 in mesh. A stack of these assemblies containing up to 18 films could be handled. In the preparation of film for JPL, the screen and mesh supports were cut in 24 in circles. The stack of films and supports were placed in a 26 in diameter kettle for hydrolysis. A pan-like lid on the kettle containing chilled water served to prevent loss of solvent and sealed the contents from excessive exposure to CO_2.

3.3.3. ACIDIFICATION OF HYDROLYZED FILMS

There is a dramatic improvement in handling characteristics of hydrolyzed films if they are acidified. The potassium salt form as recovered from the hydrolysis baths, is extremely hygroscopic and easily wrinkled. The

acid form is not hygroscopic and shows much less tendency to wrinkle. Upon being placed in KOH solution, the acid form reverts to the salt form.

Films were acidified by submerging them in a shallow tray containing 95% acetone and 5% water. Enough nitric acid was added to maintain an acidic condition as indicated by pH paper (pH 3 to 4). They were then rinsed in a similar acetone-water bath containing no acid. These films were air dried. Upon drying a deposit of potassium nitrate powder was noted on the surfaces of some of the films. This was easily removed with a barely damp sponge. Films acidified by this method were believed to be still partially in the salt form. They were referred to as "surface acidified" films. Evidence for this was two-fold. First, a piece of such a film gave a basic reaction to pH paper when submerged in water and also showed some swell. Second, a few films that were more completely acidified by soaking in dilute aqueous nitric acid for some time followed by a water wash were not basic in water, did not swell in water, and were more difficult to handle in the dry state than the surface acidified films. Samples of each type were included in the film shipment to JPL.

3.4 AC RESISTANCE

The resistance of battery separators obviously must be low and the resistance of membranes has been measured in this project to screen the products and guide the work. The membranes were mounted in a Lucite resistance cell on loan from JPL, and the resistance was measured with an ESI Impedance Bridge (Model 250). An external variable capacitor was used to balance the impedance of the cell. The external capacitor was a Cornell-Dubilier Decade Capacitor, from 0 to 1.1 microfarad, in 0.01 μf steps, which was connected in the same bridge current circuit as the resistance cell and across the adjacent bridge arm. Adjustment of capacitance more accurately than to the nearest 0.01 μf (with infinitely variable capacitor) did not

appear to improve the measurements significantly. The precision of the bridge with the external capacitor suitably adjusted appeared to be satisfactory; i.e., the null indicator was sensitive to 0.01 ohm change. The best sensitivity was obtained with the detector amplifier at maximum. At this setting, the power across the cell was measured at about 9 milliwatts, maximum, at 1000 cycles, with the oscillator set for maximum output. All measurements were made at this power since the change of resistance with power, if any, was not known.

The resistance measurements in this project have been made with a bridge not previously employed. Additional corroboration of the applicabiluty of this bridge in this measurement thus appeared to be desirable. For this purpose, a sample of film of known area resistance, as measured by the same method using a Wayne-Kerr impedance bridge, has been supplied by JPL. For the test experiment (82866), six pieces of the film about 1/2 in square were cut from different sections of reference film and another piece cut with a center hole larger than the opening thru the resistance cell. All specimens (about 1.2 - 1.5 mil thick) were soaked in 40% KOH for more than 24 hr and the resistance of the six separate pieces of specimen measured. For the determination of the cell resistance, the square "donut" specimen was placed in the cell with none of the membrane in the current path during the resistance measurement. The results are given in Table 6. The external capacitor was set at 0.47 - 0.51 μf for these measurements.

The measured R_A of 0.012 ohm-in^2 agrees well with 0.011 ohm-in^2 value given by Mr. Werner von Hartmann (letter to I. O. Salyer, 28 November 1967). These results indicate that the ESI Impedance Bridge is a satisfactory instrument for these measurements.

TABLE 6

RESISTANCE OF REFERENCE MEMBRANE

ESI Impedance Bridge
1000 Cycle Frequency
Aperture 0.04906 in^2
Electrolyte 40% KOH

Specimen	Elect. Temp. (°C)	Resistance (ohms)	R_A
1	24.7	17.91	--
2	24.8	17.83	--
3	24.9	17.81	--
4	24.9	17.78	--
5	24.9	17.83	--
6	24.9	17.91	--
Avg. of 6 Samples		17.845	--
R, with Spacer	24.9	17.60	0.012 ohm-in^2

It is interesting to note the effect of the plastic washer (or donut) spacer when measuring the resistance of cell alone. The measurement reported in the above table was made with the donut in place, which essentially moves the electrodes farther apart than when the cell is assembled without the donut and separated only by electrolyte. Without the donut the cell resistance was 17.47 ohms. Using this value, the ^{R}A of the reference film is 0.018 ohm-in^2, which is appreciably greater than the ^{R}A of 0.012 ohm-in^2. While a few of the earlier cell measurements were made without a spacer, all pertinent cell resistances were measured with a spacer in place.

The film to be measured was conditioned by soaking in 40% KOH, generally for about 24 hours. The film was mounted in the cell and 40% KOH was introduced on both sides of the film from two separate containers. The 40% KOH served as electrolyte. The resistance was noted by proper balance of the bridge. The electrolyte temperature and external capacitance were also recorded. The film was removed and replaced by film so that the hole between the electrodes was not covered. The cell was assembled and again a resistance measured. The second measurement yielded a cell constant. The difference between the two resistances was taken as the resistance of the film. The area resistance, ^{R}A, was calculated by multiplication of film resistance by 0.04906 (the area in sq in of film exposed during the measurement), in ohm-in^2. Division of ^{R}A by the film thickness, in inches, gave specific resistance, r, in ohm-in.

Table 7 lists some representative resistances of various hydrolyzed E/MAR copolymers as a function of composition.

As expected, there is a decrease in resistance as the acrylic acid content increases. Data of the type shown in Table 7 were used to select the material for the battery separators sent to JPL. On the

TABLE 7

RESISTANCE VS COMPOSITION

Sample	Acr A[1] (%)	Wet Thickness[2] (mils)	R_A ohm-in^2	r ohm-in
87684-7	27.1	4.7	0.164	34.9
87684-11	37.1	4.6	0.0866	18.8
82979	43.7	5.3	0.055	10.5
87680-A	55.6	3.8	0.0103	2.71

[1]%Acr A is the calculated wt.% acrylic acid for hydrolyzed copolymer

[2]Thickness of wet film after conditioning in 40% KOH

basis of resistance alone, the 55.6% acrylic acid membranes would have been chosen. However, films of this composition were extremely difficult to handle. The membrane containing 43.7% acrylic acid is much more manageable and has a specific resistance less than 20 ohm-in, the goal of the work. Thus, the 43.7% acrylic acid composition was chosen on the basis of the best balance of overall characteristics.

3.5 STERILIZATION TESTS

This test is designed to evaluate the stability of separator membranes in strong KOH solution at the temperature that will be used for sterilization and is not described in published literature. Since the sterilization temperature is reported to be 140°C, pressure vessels are necessary for the test. We have made 6 pressure vessels based on a design utilized by Monsanto's Boston Laboratory. The bombs consist of a 316 stainless steel pipe nipple 10 in long x 3 in in diameter enclosed with 316 stainless steel threaded end caps. The bombs are lined with Teflon by means of 16 ounce Teflon bottles with their tops cut off. The threaded caps are sealed with Teflon pipe tape. Experience with these bombs indicate that they can be improved. Specifically, bombs 5-6 in long would be adequate for this test and the bottom closure could conveniently be made by a welded stainless steel plate.

For the test a piece of the membrane is placed inside the bomb and completely covered with 40% KOH solution in water. The bombs are closed and placed in a circulating air oven set at 140°C. After 60 hours, the bombs are removed, cooled, and opened. Films have been evaluated in this work both by measuring the tensile properties and by measuring the electrical resistance. Films with a low degree of vulcanization have been noted that appear to be sufficiently stable for this test, but during the test became crumpled and stuck together in various places. This was prevented by placing the film in a loose roll of Teflon tape. (Caution - Do Not Use Polyethylene).

For convenience, we have used a desk-mounted holder fitted to the bottom of the bombs and a special wrench fitted to the top of the bombs for opening and closing them.

The effects of sterilization on the membrane have been conveniently checked by measuring resistance before and after sterilization. Some results of these tests are shown in Table 8. A number of varieties of film are noted in this table, including one example of a carbon-filled film, one example of a membrane that contains vinyl alcohol in the hydrolyzed product, and some films with resistance too high for use as a battery separator. In a few cases, the resistance actually decreased during sterilization; this is thought to indicate completion of hydrolysis during the sterilization. However, generally the resistance of the film went up slightly during the sterilization, but in a highly vulcanized film, this increase was not significant. Several films had a specific resistance below 10 ohm-in after sterilization. This appears to indicate that membranes of ethylene/acrylic acid are adequately stable during this sterilization test. The effects of sterilization on the tensile properties are shown in Table 9. Both the tensile strength and percent elongation increased slightly during sterilization. However, the effect was slight, and these results seem to indicate this material is adequately stable to sterilization. Some additional results on the effects of sterilization on tensile strength and percent elongation is shown in Table 10. The results are similar.

3.6 SILVER AND ZINC MIGRATION

Methods are described in Chapters 10 and 11 of "Characteristics of Separators for Alkaline Silver Oxide/Zinc Secondary Batteries" for the measurement of diffusion of silver and zinc through membrane

TABLE 8

RESISTANCE OF MEMBRANES BEFORE AND AFTER STERILIZATION[1]

Membrane	Composition[2] E	Acr. A.	C	Film Thick Mils	R_A, ohm-in^2 Before	After	r, ohm-in Before	After	Remarks
87719-1A	44.3	55.7	0	4.2	0.0069	0.0118	1.56	2.80	Highly Vulcanized
87719-2	56.4	43.6	0	5.7	0.0069	0.0368	1.20	6.45	Under Vulcanized
87719-5	83.8	16.2	0	2.8	0.816	1.29	355	461	Insufficient Acr. A.
87719-1B	44.3	55.7	0	4.2	0.0108	0.0127	2.25	3.04	Highly Vulcanized
87719-4	83.0	27.0	0	4.6	0.206	0.281	66.5	61.2	Under Vulcanized Insufficient Acr. A.
87719-6	77.2	22.8	0	6.0	2.21	1.39	395	232	Insufficient Acr. A.
87735A	60.8	31.8	0[3]	5.1	0.0491	0.234	10.09	45.9	
87735B	46.4	27.3	26.3	3.9	0.0090	0.0451	1.75	11.6	

[1]60 hours, 140°C in 40% KOH

[2]All films vulcanized and hydrolyzed. Composition exclusive of di cup residue and Armid O, a release agent. E = ethylene, Acr. A = Acrylic Acid C = statex R (c-black from Columbian Chemical Company).

[3]Also contains ca. 7.5% vinyl alcohol resulting from incorporation of E/41.3% VA in polyblend.

TABLE 9

TENSILE - ELONGATION PROPERTIES OF E/Acr A MEMBRANE BEFORE AND AFTER STERILIZATION*

ASTM D882

Film	% Acr A	% MAR	Tensile (KSI) Before	Tensile (KSI) After	% Elongation Before	% Elongation After
87740-4	26.4	30	1.11 ± 0.17	1.07 ± 0.94	214 ± 33.6	96 ± 49.2
87740-3	35.2	39.3	0.956± 0.100	1.51 ± 0.32	248 ± 54.4	240 ± 50.0
92951-2	40.4	48.2	0.473 ± 0.054	1.60 ± 0.35	159 ± 33.6	317 ± 33.0

*140°C for 60 hours in 40% KOH solution

TABLE 10

TENSILE - ELONGATION OF CARBON-FILLED E/MAR FILMS BEFORE AND AFTER STERILIZATION (1)

Sample	Composition	Tensile, psi (2) Before	Tensile, psi (2) After	% Elongation (2) Before	% Elongation (2) After
92971-8	50% MAR 0% Carbon	392 (4)	700 (4)	124 (4)	150 (4)
92971-6	50% MAR 10% Carbon	522 (5)	648 (3)	111 (5)	160 (3)
92971-3B	60% MAR 10% Carbon	447 (5)	459 (4)	93.3 (5)	139 (4)

(1) Samples of films heated at 140°C in 40% KOH for 112 hours (ran past 60 hours over week-end)

(2) Each value is an average. The number in parenthesis indicates the number of values included in the average. Test conditions were as prescribed in ASTM 882.

materials. The migration of these two metals through a membrane of ethylene/acrylic acid has been measured by slight modification of these methods. Specifically, both measurements were made with radioactive metal solution, Ag^{110} and Zn^{65}. The cell used for both these measurements was that described in Chapter 11 of Reference . The solutions used in both measurements were the same as those described in Chapters 10 and 11. Each side of the cell holds about 200 milliliters and the two sides are separated by the membrane with about 3.32 sq in of film exposed to solution. For these measurements the radioactivity was counted with a NMC scaler, Model DS-1B and using a NMC well, Model US-1B. Aliquot portions of solution were removed from each side of the cell at regular intervals and counted.

The film used in these measurements was from sample 92951-2 and contained 44.4% acrylic acid (calculated) and was made from E/48.2% MAR. Different pieces of the same film were used for the two measurements. The film for the silver measurement was about 3 mils thick, while that for the zinc measurement was about 2.4 mils thick.

A silver solution in 40% KOH was made with about 15.32 µg Ag/g of solution. This solution had 20,976 counts per minute per gram. The results of diffusion of this solution with time are shown in Table 11. These results show that the pick-up of the membrane is considerably less than with cellulosic films and comparable to the acrylic acid grafted on ethylene films as reported in Chapter 10.

Zinc oxide was found to dissolve slowly and incompletely in 40% KOH. Therefore, a 45% KOH solution in which zinc oxide does dissolve readily was used. A solution was made for this test that had about 8438 counts per minute of Zn^{65}. The film for this measurement was 2.4 mils thick. The results are shown in Table 12. The results of this test show that the pick-up of the membrane was about 94.8 milligrams of zinc per hour

TABLE 11

DIFFUSION OF SILVER THROUGH 92951-2
ETHYLENE/ACRYLIC ACID COPOLYMER
3 MILS THICK

Time (hr)	Counts/min/g		Ag Diffusion g/hr/in^2
	Solution A	Solution B	
0	0	20,976	---
1	36	---	---
2	41	---	---
4	51	---	---
6	78	20,637	.00112
22	--	19,369	---
24	183	19,026	.00066

In addition, silver pick-up by the membrane was also noted. The results were:

Area = 2.32 in.^{2}

Total Pick-up = 48.05 ug Ag

$\frac{48.05}{24 \times 2.32}$ = 0.863 ug/hr in.^{2}

TABLE 12

DIFFUSION OF ZINC THROUGH 92951-2
ETHYLENE/ACRYLIC ACID COPOLYMER
2.4 MIL THICK

Time (hr)	Counts/min/g Solution A	Solution B	Zn Diffusion g/hr/in^2
0	8438	29	--
1	8453	148	--
2	8451	156	0.0362
3	8455	156	--
4	8411	157	0.0181
5	8326	157	--
6	8326	160	0.0119

Membrane pick-up - 281 cpm on membrane, Zinc 8438 cpm = 46.84 mg Zn, $\frac{281}{8438} \times 46.84 = 1.28$ mg Zn/2.32 in.^{2}/6 hrs.

Therefore, pick-up = $\frac{1.28}{6 \times 2.32} = 0.0948$ mg Zn hr^{-1} sq. in.$^{-1}$

or 94.8 mg Zn hr^{-1} sq. in.$^{-1}$

per square inch. This is less than the pick-up of the cellulosic film and comparable to the pick-up of acrylic acid grafted on ethylene membrane, as reported in Chapter 11. Using the experimental data, the rate of metal diffusion was calculated by means of the equation shown below.

$$(I) \quad \text{Rate} = \frac{M}{(\Delta t)(A)(M_o)} = \text{grams/hour/sq in film from a molar solution}$$

where M = total increase of metal in dilute cell in grams
Δt = time interval, hours
A = Area of film exposed, sq in
M_o = concentration of metal solution, molarity

By this calculation the rates of diffusion are shown in Tables 10 and 11. However, the rate of diffusion did not reach a steady state and seems to be decreasing as time continues. The final result in each case, however, is comparable to the rate of diffusion of these metals through an ethylene with grafted acrylic acid film as reported in Chapters 10 and 11. The measured rates are substantially less than the rate of diffusion through a cellulosic film as reported in these chapters.

3.7 TENSILE PROPERTIES

In numerous places in this report reference has been made to the product as ethylene/acrylic acid copolymer. Since this copolymer is formed in a caustic solution, a more accurate description would be ethylene/potassium acrylate. The product is generally in the salt form. However, in several cases the salt form of the membranes has been converted to the acid form by acid treatment. The properties of the film differ somewhat, depending on whether the material exists as the acid or the salt form. In most cases, the salt form is the actual item of reference instead of the free acid.

The salt form of the membrane products in this project, that is ethylene/potassium acrylate, is hygroscopic. Therefore, the atmospheric water content was controlled while measuring the physical properties of the materials. For the measurements of tensile strength and elongation, samples of thin film were conditioned for several days in a room that was controlled to 50% RH and about 74°F. The variation of these conditions is expected to be ±2% RH and ±2%F. After equilibration under these conditions, the film (about 3 mils thick) was evaluated as prescribed in ASTM D-882. The results of these tests for some ethylene/potassium acrylate film before and after sterilization are shown in Tables 9 and 10 - given in KSI (1000 lb/in^2). Additional data for films are given in this table for some membranes containing carbon black, both before and after sterilization. A few of the sterilization experiments were run inadvertently for more than 60 hours. This did not seem to have any effect on the results.

All films in this work are stable to the sterilization tests, although films in contact with each other during this test were stuck together somewhat. Sterilization seems to cause a slight increase in the tensile strength. Similar results were found with elongation. Under test conditions, that is, 50% RH and room temperature, these films were moist. Under these conditions the tensile and elongation values indicate these were not strong films. Nevertheless, they did have sufficient tensile strength to withstand moderate shock and to withstand normal handling conditions such as would be incurred during wrapping of the plate.

The effect of carbon black in these membranes is also interesting. The carbon black does not increase the strength of these membranes as is the case with polydiolefin polymers. Instead, the carbon

black causes a slight decrease in the tensile strength and elongation. Again, the carbon-black-containing membranes are not appreciably altered during the sterilization tests, and these films will withstand moderately light shock and normal handling.

3.8 MEMBRANE MODIFICATION

Many ways of modifying polymers are known and some of these methods have been considered as potentially valuable in the modification of membranes for battery separators. A critical examination has been made of a few of these modification methods, one of which (carbon filling) has already been discussed previously.

The effect of carbon black blended into a diolefin or elastomeric polymer is well known, but the effect on the polymers used in this work is not predictable. Several blends of E/MAR copolymers with a carbon black labeled Statex R (from Columbia Carbon Company) were made. Blends of the ethylene copolymer, the carbon black, the vulcanizing agent (Di-Cup R), and a small amount of release agent (0.5 part Armid O per 100 parts resin) were made on a warm roll mill. Films from these blends were suitably made in a hydraulic press with 8 x 8 in platens at 150°C for 30 minutes at a ram force of 20 tons. By this treatment, the film was formed and vulcanized.

Two results were noticed immediately with the carbon-filled film. First, the materials containing carbon were less tacky than those without carbon but of similar composition. Second, the films with carbon black tended to be somewhat thicker than those made with the same polymer without carbon. This was probably due to resistance to flow of the carbon black, making the films form slower and with more difficulty in the press. Some results are shown in Table 13 for carbon-filled films in addition to the data shown previously.

TABLE 13

CARBON FILLED MEMBRANES

EXPERIMENT 87735B

Membrane Composition[1] Weight %				Memb. Thick.	Resistance				
E	MAR	Acr. A.	C	Mils (Wet)	Elect Temp. °C	Ext. Cap. uf	Res. Ohms	R_A Ohm-in.^{2}	r ohm-in.
44	31	0[2]	25	3.5	27.0	0.01	223	10.1	2890
46.4	0	27.3	26.4	5.4	26.1	0.52	17.47	0.0083	1.54
46.4	0	27.3	26.4	5.0	26.1	0.53	17.50	0.0098	1.96
--	--	--	--	none[3]	26.1	0.53	17.30	--	--

[1]Exclusive of Di-Cup residues and Armid O (release agent).

[2]Films conditioned 24 hours in 40% KOH and likely some undetermined amount of hydrolysis occurred, but less hydrolysis than by preferred procedures.

[3]Using spacers, no membrane, to determine cell constant.

The resistance of films filled with carbon is very low. Actually, the resistance of these films is less than would be expected from the same polymer membrane without carbon. This result indicates that the carbon improved the conductance, by a measurable amount. Also shown in Table 13 is the resistance of a carbon filled ethylene/methyl acrylate copolymer film which had not been hydrolyzed. The high resistance of this film indicates that the carbon does not contribute significantly to the electronic conductance of these membranes. In addition, a film was made from polyethylene containing the same amount of carbon black as the film just mentioned. An attempt was made to measure the resistance of this film but it was so high that it could not be accurately measured with our equipment. It has been found in previous work that carbon black in a polymer generally does not contribute to electronic conductance of that polymer when the carbon black is less than 50% of the product. These data indicate that carbon has a beneficial effect on the membrane as far as the resistance is concerned.

Additional data on the carbon-filled membranes in Table 14 indicate that the amount of carbon black in the polymer has an effect on the resistance. However, this effect is small compared to the effect of carbon black vs. no carbon black.

Polyblending is a modification that is thought to be potentially useful for improving the properties of a polymer membrane and for adjusting the monomer ratios of the product to more desirable levels. While composites have been reported for mixtures of copolymers with monomer ratios varying slightly, polyblending as used here refers to mixtures of copolymers with widely variable monomer ratios. Actually, a composite probably is obtained everytime ethylene and methyl acrylate are copolymerized. However, a polyblend is deliberate and might be expected to have somewhat different properties than a more homogeneous polymer or copolymer of the same average composition.

TABLE 14

EFFECT OF CARBON FILLING ON ELECTRICAL RESISTANCE OF VULCANIZED E/Acr A[1] FILMS

Film	%MAR	%EAR	%Acr A[1]	%Statex R	R_A Ω in.^{2}	r Ω in.
87740-4	39.3	---	35.1	0	0.185	57.9
82891A	39.3	---	35.1	25	0.0294	4.1
87700-1	---	21.8	16.7	0	16.89	4960
82891C	---	21.8	16.7	10	6.35	1095
82891B	---	21.8	16.7	25	5.30	1434
87747-2[2]	0	0	0	25	>4,000	>1,250,000

[1]Acr A is the calculated acrylic acid content of the copolymer which would result from complete hydrolysis.

[2]This film made from polyethylene shows that the presence of up to 25% carbon black makes no significant contribution to the conductance of these carbon filled films.

The polyblends discussed here give products that are not simple mixtures. Initially, the copolymers are mixed with a vulcanizing agent, formed into film, and vulcanized. This connects the different small molecules together by chemical bonds into larger molecules. The vulcanized polyblend cannot be extensively separated into the blend components without chemical bond rupture. An obvious reason for polyblending would be to adjust the acrylic acid content of the membrane to a higher level without synthesizing the copolymer. Some experiments to attempt this have been made with Hycar 4021. This commercial polymer is a homopolymer of ethyl acrylate. Some experiments to blend a copolymer of ethylene and ethyl acrylate with the Hycar 4021 are shown in Table 15. The results show that the increase of the acrylate ester into the vulcanized copolymer mixture does indeed lower the resistance or increase the conductance. However, these results were not as expected; that is, resistance was not as low as expected. The reason for this was defined by observing the behavior during the milling of these copolymers to mix them. Specifically, Hycar 4021 does not mill well. This apparently is due to the fact that it is very high molecular weight and thus does not melt readily. A higher proportion of Hycar in these mixtures probably cannot be obtained by milling. Furthermore, the appearance of the films indicates a questionable compatibility of the ethylene-EAR copolymer with Hycar. This also is thought to be a result of the very high molecular weight of Hycar.

The membranes described above in Table 15 were all molded. An additional polyblend with Hycar was made by solution casting which is less sensitive to the molecular weight than molding. In this experiment a polyblend was made which contained a higher acrylate content. The results show that the resistance was indeed much lower. To verify this observation regarding the molecular weight

TABLE 15

POLYBLENDING WITH POLYETHYL ACRYLATE

Experiment	Blend Parts[1]	Blend Comp.[2]	Polymer Av. Comp.	Vulcanization[3]	Acrylic Acid Hyd. Membrane[4]	R_A ohm-in^2	r ohm-in (mils thick)
87706-1	88.4	E/12.4 EAR					
	11.6	H					
	0.5	Di-Cup	E/22.6 EAR	T	17.2	4.5	1353 (3.3)
-2	92.4	E/21.8 EAR					
	7.6	H					
	0.5	Di-Cup	E/27.8 EAR	T	21.7	1.4	342 (4.1)
-3	76.5	E/12.4 EAR					
	23.2	H					
	0.5	Di-Cup	E/32.7 EAR	T	26.0	2.70	600 (4.5)
-4	84.8	E/21.8 EAR					
	15.2	H					
	0.5	Di-Cup	E/33.7 EAR	T	26.8	1.15	261 (4.4)
-5	65.2	E/12.4 EAR					
	34.8	H					
	0.5	Di-Cup	E/42.9 EAR	T	35.1	2.85	634 (4.5)
-6	77.2	E/21.8 EAR					
	22.8	H					
	0.5	Di-Cup	E/39.6 EAR	T	32.2	1.35	329 (4.1)

[1]Normalized to 100 parts copolymer. Blends usually of 20 gram size

[2]E = ethylene; EAR = ethyl acrylate; H = Hycar 4021, polyethyl acrylate; Di-Cup = di cumyl peroxide, vulcanizing agent; AO = Armid O, release agent.

[3]T = Thermal vulcanization @ 150°C, 30 min., during film formation in hot press, 8" x 8" platens, 20 ton ram U.V. = Ultra violet irradiation, 30 min., 6" from 550 watt Hanovia lamp.

[4]All films hydrolyzed 24 hours @ 60-70°C in 2.5 N alc. KOH (1:1 Methanol: Isopropanol) and 24 hours @ 60-70°C in 2.5 N aq. KOH. Value given is calculated proportion of acrylic acid in ethylene copolymer by complete hydrolysis.

of Hycar 4021, the melt index of Hycar was measured. It was found to be 0.1 at 190°C, indicating a very high molecular weight. As has been shown elsewhere, to form films suitably by pressing, a melt index at 150°C of about 2 to 10 is much more desirable.

Polyblending with copolymer of more suitable molecular weight range as indicated by the melt index is shown in Table 16. An advantage to the polyblending became apparent with these films and was subsequently verified. Specifically, polyblending of a low acrylate and a high acrylate copolymer gives a product that generally is less tacky than a homogeneous membrane of similar average acrylate composition. This is a distinct advantage since ethylene copolymers with more than about 35% acrylate are quite tacky and are difficult to handle in thin film form. Polyblends seem to be laminated by the more rigid structure of the low acrylate portion. Membranes made by polyblending have quite suitable low resistance. The data in Table 16 may indicate an advantage of the polyblends over more homogenous copolymers as far as resistance is concerned, but this conclusion does not seem warranted by the number of experiments made to compare such a polymer.

Another type of polyblending is shown in Table 16. A copolymer of ethylene and methyl acrylate was blended with a copolymer of ethylene and vinyl acetate. The well-blended copolymer was vulcanized, making essentially a terpolymer membrane. This mixture is known to be compatible in all ranges of monomer ratios. The film made from this material has a good, low resistance and appeared to be quite suitable for battery separators. An advantage to this type of polyblending was also obvious. This material was less tacky than the copolymer of the acrylate and ethylene alone. The resultant membrane in this case might be expected to have some hydroxyl groups in as much as the vinyl acetate groups would be hydrolyzed during the processing. At this time the effect of the

TABLE 16

POLYBLENDING

Experiment	Blend Parts[1]	Blend Comp.[2]	Polymer Av. Comp.	Vulcanization[3]	% Acrylic Acid Hydrolyzed Membrane[4]	R_A ohm-in^2	r ohm-in (mils thick)
82890A (87735)	80	E/41.3% MAR					
	20	E/41.3% VA					
	6.6	Di-Cup				0.0432	9.38 (4.6)
	0.5	AO	E/8.1 VA/ 35.3 MAR	T	31.8	0.0550	10.8 (5.1)
87716	66.7	E/21.8 EAR					
	33.3	E/67.9 MAR				0.0147	6.69 (2.2)
	5	Di-Cup	E/30% MAR	U.V.	31.9	0.0196	7.00 (2.8)
82880	100	E/41.3 MAR					
	5	Di-Cup					
	0.5	AO	E/41.3 MAR	U.V.	37.0	0.00884	8.84 (1.0)
87680A	33.3	E/67.9% MAR					
	66.7	E/55.7% MAR					
	3	Di-Cup	E/60 MAR	T	50.2	0.0103	2.71 (3.8)

[1]Normalized to 100 parts copolymer. Blends usually of 20 gram size

[2]MAR = methyl acrylate; EAR = ethyl acrylate; VA = vinyl acetate; E = ethylene; Di-Cup R = dicumyl peroxide; AO = Armid O, a mold release agent.

[3]T = Thermal vulcanization @ 150°C, 30 min., during film formation in hot press, 8" x 8" platens, 20 ton ram
U.V. = Ultra violet irradiation, 30 min., 6" from 550 watt Hanovia lamp.

[4]All films hydrolyzed 24 hours @ 60-70°C in 2.5 N alc. KOH (1:1 Methanol: Isopropanol) and 24 hours @ 60-70°C in 2.5 N aq. KOH. Value given is calculated proportion of acrylic acid in ethylene copolymer by complete hydrolysis.

hydroxyl groups is not known. However, we would predict such membranes would have improved water permeation properties.

3.9 RECOMMENDED POLYMER FOR PREPARATION OF PRODUCT

The copolymers of ethylene and acrylic acid that are the object of this project seem to have adequate physical properties at all ranges of monomer ratios and at room temperature. At elevated temperatures such as that used for sterilization of the material (140°C), the material must be stabilized by vulcanization, and the vulcanized product appears to have adequate physical properties for this application at all ratios of monomers studied. There are two other properties we feel are important in considering the optimum ratio of monomers for application as battery separators. First, the resistance of the membrane must be suitably low. As prescribed in our proposal and in this contract, we have made membranes with different ratios of ethylene and acrylic acid. Some examples of this are shown in Table 17. Additional examples similar to this have been reported in our progress reports. The results all indicate that in order to have film with specific resistance below about 20 ohm-in, the membrane should consist of about 40% or more of acrylic acid copolymerized with ethylene. To get this composition in the hydrolyzed polymer, the precursor polymer must contain at least 44% methyl acrylate copolymerized with ethylene. The results all show that the higher acrylate contents have the lower resistances; therefore, even higher acrylate and acrylic acid contents are desirable.

While the tensile properties of the ethylene/acrylic acid copolymer are quite good and the resulting membranes can be readily handled, the tensile properties of the precursor copolymer of ethylene and methyl acrylate are not the same. Specifically, the high acrylate

TABLE 17

RELATION OF E/Acr A COMPOSITION AND SPECIFIC RESISTANCE

Film	% Acr A	Specific Resistance (Ω in.) Before Sterilization	Specific Resistance (Ω in.) After Sterilization
87700-1	15.7	496	---
87719-5	26.4	355	461
87719-4	35.2	66.5	61.2
87665A	40.4	7.1	18.9
87719-1A	55.7	1.56	2.80

ester copolymers are tacky and form rubbery films. Therefore, the second property that has been considered in recommending an optimum concentration has to be the nature of the precursor copolymer. As has been pointed out in several of the monthly reports, an ethylene copolymer containing 60% methyl acrylate is extremely tacky, and so far only small pieces have been manipulated by hand. The preparation of film by hand is more satisfactory with copolymer containing about 50% or less of the methyl acrylate. Therefore, the desirable range of copolymer ratios seems to be an ethylene copolymer with between 44 and 50% methyl acrylate, which will yield a membrane product containing between 40 and about 45% acrylic acid.

The tensile properties and the ease of handling of the precursor can be improved, as mentioned previously, by polyblending. A precursor of E/50% MAR (average composition) made by blending E/70% MAR and E/20% MAR will be easier to handle than a more homogeneous E/50% MAR. These considerations indicate a polyblend to be more desirable than a homogeneous copolymer.

After forming the polymer into film, it must be vulcanized in order to obtain stability in strong caustic up to 140°C. Work has been done which shows that the degree of vulcanization affects the ease of hydrolysis. Specifically, a rather homogeneous copolymer with about 45% MAR cannot be highly vulcanized if the resistance is to be sufficiently low after hydrolysis. At one time, homogeneous copolymers were mixed with about 0.6% by weight of vulcanizing agent (Di-Cup R) to make suitably low resistance membranes but these were hard to handle. Higher levels of vulcanizing agent, which is one of the main ways of controlling the degree of vulcanization, gave membranes that handled better but hydrolyzed with difficulty and often gave film with a high resistance. Since that time two ways have been found of improving the

hydrolysis to obtain membranes with suitably low resistances. For example, the polyblends seem to hydrolyze more readily at high levels of vulcanization than do the more homogeneous polymers. In addition, the addition of toluene to the alcoholic hydrolysis bath also seems to improve the hydrolysis. By making the membranes from a polyblend, up to 3 wt.% of vulcanizing agent (Di-Cup R) can be incorporated in the polymer for vulcanizing. This gives films with good handling properties and with specific resistance of less than 20 ohm-in. Therefore, this level of vulcanizing agent, 3.0 wt.% Di-Cup R, based on weight of polymer, is recommended for use with these membranes in order to obtain a high degree of vulcanization and a high level of stability in caustic solutions at 140°C.

Films of ethylene/methyl acrylate copolymers have been made in two ways: (1) by solution casting and (2) by pressing in a hot press. The films have been thermally vulcanized. This copolymer when heated to around the fusing temperature invariably sticks to a contacting surface. This has created some mechanical problems in handling the material. The best surface found for handling fused E/MAR copolymer is Teflon to which the fused polymer does stick lightly but can be released without serious distortion of the film. The release of the film may be improved by the addition of release agents. Specifically, Armid O (a fatty amine from Armour Chemical Comapny) has been incorporated in the polymer in small proportions (0.5 wt.% of polymer). It is believed to have no effect on the properties of the polymer but does cause improved release from such things as Teflon.

A typical recipe of polymer for the preparation of separator membranes is shown in Table 18. The high acrylate copolymer has been labeled MRC-11-6 and has a melt index of about 10 at 150°C. The

low acrylate copolymer (ethylene plus ethyl acrylate) is labeled Z 1175 and has a melt index of about 4 at 150°C. We calculate the hydrolyzed product will contain about 43% acrylic acid. A few films have also been made from a similar recipe in which the ratio of high to low acrylate copolymer was about 50/50. When hydrolyzed, the material should have about 38% acrylic acid and has been found to have somewhat higher resistance than does the material mentioned in the table.

TABLE 18

POLYMER BLEND FOR SEPARATOR FILM PRODUCTION

Component	Wt. (g)
E/65.8% MAR	60
E/21.8% EAR	40
Di-Cup R (vulcanizing agent)	3
Armid O (release agent)	0.5

The product or copolymer employed in this project is often spoken of as ethylene/acrylic acid copolymer. However, the product from hydrolysis of the precursor copolymer of ethylene/methyl acrylate is recovered from the bath as the potassium salt and the product would be more accurately described as ethylene/potassium acrylate. Films of this material are soft; pliable, and quite hygroscopic. In the prevailing atmosphere of these laboratories, this material will absorb an appreciable amount of moisture from the atmosphere, in which state the membranes tear easier than do dry membranes. However, membranes in the salt form

will be shipped to JPL, hopefully, to arrive in usable form. A more stable form of the membrane may be formed by a light acidification of the membranes as they are removed from the hydrolysis bath. These membranes are made by washing the membrane products in an acetone/acid bath for a short period of time and then air drying them. They are soft and pliable and seem to be quite stable. These films do not absorb moisture from the atmosphere, but occasionally show a white powder on the surface that has been brushed off in all cases. Many of the films will be supplied in this form. More complete acidification of the membranes has also been carried out on some of the film by prolonged soaking in acid solution after removal from the hydrolysis bath. These membranes are somewhat stiff, like parchment paper, and are quite stable. They are less pliable than the surface-acidified form. From this we believe the easiest handled films are the surface acidified or partially acidified forms. The acid used in this acidification was nitric acid and to the best of our ability any excess acid and salt (KNO_3) have been removed from the films by washing and brushing. In general, the acid forms are stable to water while the salt forms are hygroscopic and swell to a considerable degree in water.

4. PROJECT PRODUCT

As a final step in this project, we have made several feet of film of ethylene/acrylic acid copolymer for evaluation by JPL. We have chosen a route for making this film which seems to be most suitable at this time and with this material. All of the materials and processes and products have been described completely elsewhere in this report and at this time, we will briefly outline the specific methods employed to make the material for JPL which is based on our judgement of the most suitable route.

4.1 PROCESS

Precursor copolymer of ethylene and methyl or ethyl acrylate has been made by a high pressure copolymerization. As a result of the work in this project, we have run this copolymerization to give the desired molecular weight range for the material and have developed a means for controlling the monomer ratio of the product in the process. A copolymer product has been analyzed mainly by density determination and then blended to give desirable properties and monomer ratios more closely controlled than is possible in the polymerization.

Film formation and vulcanization has been carried out in a simultaneous step. While extrusion methods may be ideal for making film of this copolymer, this method does not lend itself to small quantities of experimental material. Therefore, exploratory work in this project has been done by hot pressing to give thin membranes. The final product of this project has been made by hot pressing in a hydraulic press (French Oil Mill Manufacturing Company) with 20 x 20 in platens and a ram force of 115 tons. We calculated the

pressure on the membrane to be about 575 psi. A flat disc of the desired polymer mixture, formed by prepressing at room temperature, was placed between Teflon sheets in the press. The film was first formed for 15 minutes at maximum pressure of the press at 140°C where only a little vulcanization occurs. The temperature was then raised to 150°C for 15 minutes which caused vulcanization to occur. The press was then cooled and the pressure released.

For the hydrolysis steps, the films were removed from the Teflon sheet onto a support of polyethylene screen. A stack of films, each separated by at least 2 screens was then placed in a round kettle (26 in diameter) so that the sandwich was completely covered with 2.5 N KOH in methanol. A hot plate beneath the kettle was used to heat the alcohol bath to 60-70°C for hydrolysis over a 24 hour period. At the end of this time, the stack of films was removed from the alcoholic bath and submerged in an aqueous 2.5 N KOH solution for 24 hours at 60-70°C.

The membranes from the hydrolysis bath cannot be water washed because water causes the films to swell some 4-5 times. Therefore, they have been washed in an acetone bath containing up to 5% water to remove excess caustic and water. Some of the films were then dried in the salt stage in air. In some cases, the films were washed in an acetone bath containing a small amount of acid (nitric acid). These were then rinsed a second time in an acetone bath and air dried to give the surface-acidified membrane. Some membranes were washed first in a nitric acid and water bath for complete acidification. These films did not swell in water and were then finally washed a second time in distilled water and air dried.

All films have been placed between two sheets of polyethylene for packaging. All membranes are numbered. The membranes in the salt form, after drying as much as possible in the laboratory atmosphere, were smoothed before placing them between the polyethylene sheets. The acidified membranes were straightened and were brushed and sponged with a damp sponge before placing between polyethylene sheets.

4.2 MEMBRANE PRODUCT

The membranes made in this work are circular or oval in shape because of the method in which they were made, and they are larger than the press platens as a result of swelling during the hydrolysis process. A typical piece is larger than about 20-22 x 21-26 in across the major and minor axes. Therefore, fewer than 100 of these discs would fulfill the requirement for this contract. However, 101 of these discs are supplied to JPL to allow for trimming which will be necessary around the edges and around certain defects inadvertently introduced in the film during the process. Small samples of each film disc have been retained and the resistance of many of these samples has been measured. The value measured here and the description of the form of the particular disc is shown in Table 19. We believe this film more than satisfies the requirements of this contract.

TABLE 19

MEMBRANES FOR BATTERY SEPARATORS

Membrane	Form[1]	Acrylic Acid[2] (Wt.%)	Carbon Black[3] (Wt.%)	AC Resistance		
				Wet Thickness (mils)	R_A ohm-in.^{2}	r ohm-in.
8	S	38	0	4.9	0.400	80.0
9	S	38	0			
10	S	38	0	2.2	0.150	68.0
11	S	38	0	5.5	0.162	29.5
13	S	38	0			
14	S	38	0	4.6	0.150	32.
15	S	43	0	4.7	0.0815	17.3
16	S	43	0	6.1	0.0835	13.7
17	S	43	0	5.1	0.0649	12.7
18	S	43	0	4.3	0.0485	15.2
19	S	43	0	2.7	0.0398	14.7
20	S	43	0	5.0	0.0407	8.15
21	S	38	0	4.5	0.162	36.0
22	S	43	0	5.0	0.0477	9.54
23	S	43	0	2.2	0.0299	13.6
24	S	43	0	5.5	0.0785	14.2
25	S	43	0	3.6	0.0520	14.2
26	S	38	0	3.0	0.159	53.0
27	S	43	0	5.0	0.0860	17.2
28	S	43	0	3.7	0.0486	13.1
29	S	43	0	5.7	0.0987	17.3
30	S	43	0	6.5	0.0914	14.0
31	S	43	0	4.8	0.0392	8.18
32	S	43	0	5.8	0.112	19.3
33	S	43	0	7.6	0.1178	15.5
34	S	43	0	6.7	0.0840	12.5
35	S	43	0	9.5	0.0675	7.07
36	S	43	0	3.9	0.0721	18.5
37	S	43	0	8.8	0.0785	8.93
38	S	43	0	5.2	0.0594	11.4
39	S	43	0	3.2	0.0265	8.28
40	S	43	0	5.6	0.0387	6.93

TABLE 19 CONTINUED

Membrane	Form[1]	Acrylic Acid[2] (Wt.%)	Carbon Black[3] (Wt.%)	AC Resistance		
				Wet Thickness (mils)	R_A ohm-in.^{2}	r ohm-in.
41	S	43	0			
42	SA	43	0	4.0	0.0270	6.75
43	SA	43	0	3.8	0.0535	14.1
44	SA	43	0	5.0	0.0437	8.74
45	SA	43	0	3.0	0.0515	17.2
46	SA	43	0	5.0	0.0422	8.44
47	SA	43	0	4.6	0.0614	13.3
48	SA	43	0	4.0	0.0674	16.8
49	SA	43	0	4.0	0.0614	15.4
50	SA	43	0	4.8	0.0358	7.47
51	S	43	0	3.0	0.0196	6.55
52	SA	43	0	3.4	0.0422	12.4
53	SA	43	0	4.1	0.0402	9.8
54	SA	43	0	2.9	0.0378	13.0
55	SA	43	0	3.6	0.0565	15.7
56	SA	43	0			
57	SA	43	0	4.8	0.0539	11.3
58	SA	43	0			
59	SA	43	0	3.2	0.0575	17.9
60	SA	43	0			
61	SA	43	0	3.5	0.0525	15.0
62	SA	43	0			
63	SA	43	0	3.8	0.0539	14.2
64	SA	43	0			
65	SA	43	0	4.0	0.0750	18.8
66	SA	43	0			
67	SA	43	0	3.8	0.0456	12.0
68	SA	43	0			
69	SA	43	0	3.5	0.0476	13.6
70	SA	43	0			
71	SA	43	0	4.6	0.0839	18.2
72	SA	43	0			
73	A	43	0	6.2	0.0555	8.96
74	A	43	0			
75	A	43	0	3.2	0.0442	13.8

TABLE 19 CONTINUED

Membrane	Form[1]	Acrylic Acid[2] (Wt.%)	Carbon Black[3] (Wt.%)	AC Resistance		
				Wet Thickness (mils)	R_A ohm-in.^{2}	r ohm-in.
76	A	43	0			
77	A	43	0	3.5	0.0344	9.83
78	A	43	0			
79	A	43	0	7.0	0.0354	5.05
80	A	43	10			
81	A	43	10	4.0	0.0344	8.62
82	A	43	10			
85	S	43	10	6.5	0.0446	6.87
86	S	43	10			
87	S	43	10	6.0	0.0417	6.96
88	SA	43	0			
89	SA	43	0	5.2	0.0909	17.5
90	SA	43	0			
91	SA	43	0	5.5	0.0442	8.04
92	SA	43	0			
93	SA	43	0	5.2	0.0510	9.83
94	SA	43	0			
95	SA	43	0	4.6	0.0711	15.4
96	SA	43	0			
97	SA	43	0	3.0	0.0426	14.2
98	SA	43	0			
99	SA	43	0	4.2	0.0466	11.1
100	SA	43	0			
101	SA	43	10	2.5	0.0250	10.0
102	SA	43	10			
103	SA	43	0	3.5	0.0644	18.4
104	SA	43	0			
105	SA	43	0	3.0	0.0595	19.8
106	SA	43	0			
107	SA	43	0	4.2	0.0496	11.8
108	SA	43	0			
109	SA	43	0	3.2	0.0251	7.83
110	SA	43	0			

[1] S = E/K acrylate, no free acid
SA = Surface acidified, partly salt form
A = E/acrylic acid, little salt

[2] Calculated as free acid, exclusive of K^+ and carbon black

[3] Statex R (Columbia Carbon Company) wt.% of polymer

5. RECOMMENDATIONS

On the basis of our tests, the membranes prepared in this project appear to be quite satisfactory. We are looking forward to hearing the results of tests at JPL. The methods we have used to make the membranes appear to us to be satisfactory and perfectly suited for the exploratory type of work being done. However, another process, extrusion, which is not suited to small samples of experimental polymer film, would be more suited for the production of a quantity of film. We believe satisfactory film can be made by this method, since the present work defines the composition of copolymer desirable. Therefore, we recommend extrusion for the preparation of a sizable quantity of film of known composition.

During the course of this project considerable thought has been directed to this material and to the application of the product. It seems to us that more complete encasing of the plate, more effective and firm attachment of separator to plates, and excellent control of separator thickness may be more efficiently and effectively attained by a method other than wrapping the plates with film. Specifically, we believe that dip-coating of the plate prior to vulcanization and hydrolysis may lead to better separators with a monomer ratio not attainable in thin, unsupported film. We suggest future development and research to dip cast plates and make separators more efficient and effective than attainable by film wrapping techniques.