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SILVER-ZINC BATTERY SEPARATOR MATERIAL DEVELOPMENT

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ABSTRACT

Several ethylene/methyl acrylate copolymers have been synthesized in a small batch-operated autoclave at high pressures. By controlling the degree of conversion and incremental monomer addition, the product composition may now be predetermined, despite unfavorable monomer activity ratios. The molecular weight of the polymer product can also be controlled now by incorporating a chain transfer agent so that product with a desirable melt viscosity may be predetermined. The third purpose of the synthesis work - namely, preparing adequate samples of different compositions for subsequent test work - will be accomplished as soon as possible. The copolymer composition currently is calculated from elemental analysis of carbon and hydrogen content; this appears to be the most precise method at the moment. A thin film of polymer (about 1 mil) has not been successfully prepared by hot pressing, but it has been successfully prepared by casting from a warm dope. In the latter process, the film is vulcanized in a separate step. Samples of film for more than test work may be prepared by blow extrusion. The resistance (Ra) of a recently prepared membrane (5.3 mil thick, dry) of ethylene/acrylic acid copolymer was measured as 0.055 ohm-in^2. The bridge employed has been shown to be satisfactory for resistance measurements by means of a reference membrane sample supplied by JPL.

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1. OBJECTIVES

This research and development program is aimed at the preparation of separator membranes for sealed silver-zinc secondary batteries which will function satisfactorily before and after heat sterilization. The program includes synthesis of ethylene/methyl acrylate copolymers by high pressure mass copolymerization, conversion of copolymers to thin film, vulcanization of the thin polymer film, and hydrolysis to thin films of ethylene/acrylic acid. The copolymer characteristics will be determined (especially hydrolytic, thermal and oxidative stability) to establish "optimum" composition. One hundred feet of the best film material will be supplied to JPL at the conclusion of the contract.

2. SUMMARY AND CONCLUSIONS

Considerable time has been spent on the synthesis of copolymers of ethylene/methyl acrylate (E/MAR). Reactions have been made in a one-liter stirred autoclave to controllably synthesize copolymers of different monomer proportions, at about 10-20% conversion of total monomer (methyl acrylate virtually completely converted). The molecular weight of the initial copolymer was too high (i.e., low melt index) and would not flow well in melt extrusion. Addition of controlled amounts of chain transfer agent to the polymerization mixture has produced a lower molecular weight copolymer that is preferable for melt extrusion. The melt viscosity and molecular weight of the copolymer is an inverse function of the "melt index", which is measured readily.

To date, the most precise method of analyzing the copolymers for the ratio of E and MAR has been by elemental carbon and hydrogen determination. From these values, the oxygen content of the copolymer is obtained (by difference), and the MAR content calculated directly. Saponification has generally given appreciably lower values for MAR content than elemental analysis; this appears to be due to incomplete saponification and a nebulous end-point resulting from a heterogeneous system. Infrared absorption spectrum of the copolymers has sharp absorption peaks for carboxyl and methylene groups, but at this time, the quantitative correlation with monomer ratio is not known.

In the past, E/MAR copolymer has been simultaneously hot pressed and vulcanized into sheets thicker than 5 mils. This process is not applicable to making film about 1 mil thick because the polymer film sticks to the mold or press and becomes badly distorted or torn when sufficient force is applied to lossen the film. When sufficient quantity of copolymer becomes available, it is anticipated that thin films can and will be made satisfactorily by blow extrusion.

At the present time, small samples of polymer are on hand and thin films are being made by casting a solution or dope onto smooth plates. The solvent is evaporated at ambient or slightly elevated temperature and the films peeled from the plates. These films are vulcanized in a separate step by heat lamps placed close to the suspended film. Attempts to vulcanize the films in place on the casting plates by heating to 150°C have been unsuccessful, since the heating causes the films to stick to the plates. Methods of vulcanizing films on the casting plates are being investigated further.

A membrane of ethylene/acrylic acid has been made and the resistance measured in the cell on loan from JPL. The Ra for the membrane, which was 5.3 mil thick, was 0.055 ohm-in^2 and indicates that a thinner membrane might be acceptable. The bridge system has been checked by means of a reference film from JPL. The measured Ra of 0.012 ohm-in^2 seems to be in good agreement with the given value of 0.011 ohm-in^2 and indicates that the bridge is satisfactory for this measurement.

Plans for future work include synthesizing additional samples of copolymer, making and vulcanizing thin films with different monomer ratios, and hydrolyzing the thin films. As samples of film become available, test work will be started.

3. EXPERIMENTAL WORK

3.1 Synthesis of Copolymer

Considerable time has been spent synthesizing the copolymer of ethylene (E) and methyl acrylate (MAR). While this copolymer is an insulator, it is a necessary precursor to the desired copolymer of E and acrylic acid (Acr A) because the latter two monomers do not copolymerize readily. Experimental conditions have been defined under which copolymer with different and controllable proportions of comonomers may be made. Specifically, samples of copolymer with about 20% MAR, 30% MAR, 40% MAR, 50% MAR, and 60% MAR, by weight are being synthesized for evaluation in the project.

Details of the copolymerization experiments are given in Table I. [Several experiments in which temperature and pressure control were poor (and/or rupture discs blown) are not included.] From these experiments, a satisfactory level of initiator has been established for obtaining about 10-20% conversion of monomers. Actually, unreacted monomer was virtually all ethylene, and the methyl acrylate was essentially all reacted because of the appreciably different reactivity rates of the two monomers. For the same reason, methyl acrylate was added in small increments during the course of the reaction and when indicated by a pressure drop of about 400 psig. While the ratio of ethylene to methyl acrylate (monomer) in the reactor at any one time was quite high, the molar ratio of total ethylene to total methyl acrylate monomers added to the reactor was varied from about 20 to about 100. This has given the copolymer with different composition ratios shown in Table I.

A possible method for making film for battery separators from the copolymers is by extrusion. From past experience we know the melt viscosity of polymer must be in the range where smooth flow is obtained in order to give satisfactory film by extrusion. The melt viscosity is an inverse function of molecular weight and is generally defined by a melt index (M.I.). The M.I. of several of the polymers in Table I was measured by standard methods at 150°C, since this is the probable temperature for extrusion and vulcanization of film. The copolymers synthesized early in this work had very low M.I. (high molecular weight). Therefore, later experiments were made with a chain transfer agent (CTA) in the polymerization mixture. Adequate control of melt index seems to have been attained, and copolymer with a $M.I._{150}$ of 2-10 will be used to make the separators.

Table I

COPOLYMERIZATION OF ETHYLENE AND METHYL ACRYLATE

	Conditions			Additives		Product		
Run No.	Temp. °C	Pressure psig x 10^{-3}	Time hr	Initiator Wt % (a)	CTA Wt % (b)	Yield Wt % (c)	M.I. (d)	MAR % (e)
82965	79-80	15-16	3.5	0.13	0	11	0	41.3
82998	84-86	15	4	0.01	0	2.7	0	29.4
83000	85	15-15.5	6	0.03	0	5.5	0	41.5
83005	85	15-15.5	4.5	0.04	1	6.9	23	31.1
83007	85	14.6-15	6.0	0.04	1	7.3	1.9	67.9
83011	85	14.6-15.7	5.5	0.04	0.5	3.2	0.3	68.7
83016	80-90	14-15.5	5	0.05	1	20.3	115	9.9
83020	85	14.6-15	5	0.04	1	9.6	180	3.4
83023	85	14.6-15	4	0.03	0.25	5.6	0.2	10.4
83026	85-86	14.6-15	4	0.03	0.33	7.3	0.8	10.8
83028	85	14.6-15	4	0.03	0.5	9.6	2.5	--
83032	85	15-15.4	4	0.03	0.6	8.0	4.0	--

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[a] Wt % initiator, based on total monomer charge
[b] Wt % chain transfer agent (CTA), based on total monomer charge
[c] Wt % yield, based on total monomer charge
[d] Melt Index (M.I.) @ 150°C, ASTM 1238
[e] Methyl acrylate (MAR) in product, based on C and H analysis

The copolymer analysis data given in Table I were obtained from carbon and hydrogen analysis; i.e., the proportion of MAR was calculated from the oxygen content of the copolymer, which is the difference between 100 and the sum of the carbon and hydrogen content. The results by this method have not always given good agreement in repeat analysis, but it still appears to be more precise than the other methods considered. Most of the copolymer samples have been saponified and the proportion of MAR calculated from the saponification equivalent. A comparison of the MAR content calculated by both methods for several copolymers is shown in Table II.

In most cases, the MAR content calculated from the saponification equivalent is appreciably lower than that calculated from elemental analysis (carbon and hydrogen determined, oxygen calculated as difference). This may be due to incomplete saponification and misleading neutralization during titration. Saponification has been carried out in heterogeneous systems of polymer with aqueous or alcoholic caustic, followed by back titration. While small particles of polymer are employed, some polymer may not be readily accessible to the caustic and the end-point may be obscured by the heterogeneous mixture. Therefore, at this time, copolymer distribution determination appears to be more precisely determined by elemental analysis.

The infrared spectrum of thin films of polymer shows characteristic absorption peaks at 5.7μ for the carboxyl group and at 6.8μ for methylene groups. While the absorption peaks appear to be relatively sharp and distinct, quantitative correlation of absorption with copolymer proportion is not readily apparent. A typical spectrum of a copolymer sample, 83032, is shown in Figure 1.

Values labeled "memory" are also shown in Table II. These values indicate the amount of swelling of extruded polymer after leaving the extrusion jet. The values are essentially a function of the orifice diameter and length, extrusion temperature, and polymer molecular weight. The values of about 35-40% for the E/MAR samples indicate the swelling which must be taken into account in extrusion processes for preparing film or other plastic shapes of desired thickness.

Table II

PROPERTIES OF E/MAR COPOLYMERS

	MAR Proportion		Flow Properties		
Run No.	Elemental Analysis	Saponif. Equiv.	M.I.$_{150}$(a)	Nsp(b)	Memory(c) %
82965	49.5	41.3	0	0.088	--
82980	0	--	0	0.317	--
82988	0	--	0	0.258	--
82998	36.0	29.4	0	0.115	--
83000	48.2	41.5	0	0.106	--
83005	37.8	31.1	23.	0.059	83
83007	67.9	60.6	1.9	0.066	69
83011	68.7	59.5	0.3	0.080	55
83016	7.4	9.9	115	--	--
83020	6.2	3.4	180	--	--
83023	8.7	10.4	0.2	0.095	38.5
83026	22.7	10.8	0.8	0.085	57.8
83028	7.2	--	2.5	0.076	31.0
83032	25.0	--	4.0	0.072	32.5

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[a] ASTM 1238, 1260 g load, 89 mil orifice, wt (g) of extrudate in 10 min.

[b] Specific viscosity of 0.1% solution in xylene at 105°C

[c] Extrudate diameter increase as compared to orifice diameter (89 mil)

$$\text{Memory} = \frac{100}{89}[\text{mils extrudate} - 89]$$

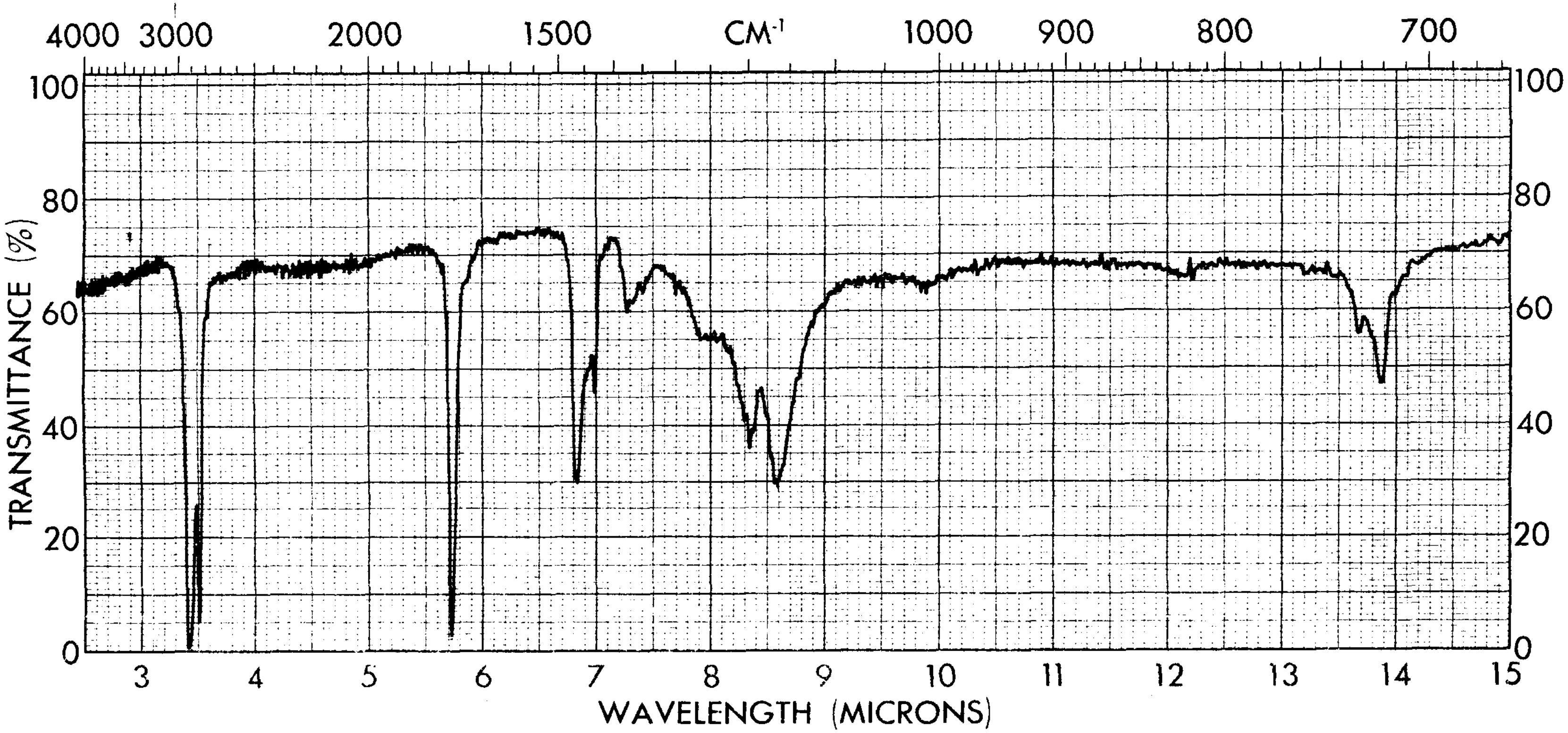

Figure 1. Infra-Red Spectrum
E/MAR 83032
1 mil film
Perkin-Elmer 137

3.2 Film Formation

Thin films of E/MAR may be made by several methods. Quantities of thin film may best be made by blow-extruding, and this method may be used later for preparation of film. However, this method requires polymer samples of appreciable size, which are not yet available. Therefore, other methods of preparing thin films must be used at this time.

In the past, film or sheet has been prepared by hot pressing, a process in which the sheet is formed and vulcanized simultaneously Sheeting 5 mils thick or thicker has been successfully prepared by this method. E/MAR is a rubbery polymer that adheres to solid surfaces after melting. Sheeting that is 5 mils or thicker has sufficient body for support when pulled loose from the mold surfaces. However, 1 mil film adheres just as tightly, and when sufficient force is exerted to remove it from a surface, the film stretches out of shape and tears. Consequently, attempts to make whole and satisfactory film about 1-2 mils thick by this method have not been entirely successful.

Perhaps the most flexible method of making thin films from polymer samples of limited size is casting from a polymer solution or dope. Thin films of about 1 mil thickness have been cast on glass or polished chrome plates from toluene solution. The solutions must be warm, since the cloud temperature (or gel temperature) is above room temperature (homo polyethylene cloud temperature is about 65°C in toluene). A warm solution of polymer (5-10%) is spread evenly on the plate with a Gardner knife and the solvent evaporated. When dry, the films may be peeled from the plates with some stretching, but without excessive distortion and usually without tearing. The films are formed at ambient, or slightly elevated, temperature which is insufficient temperature for vulcanization with the currently employed vulcanizing system.

The cast films must be vulcanized in a separate step. The most successful method for this has been to suspend the free film between two heat lamps placed about 3 in. away from either side of the film for several hours. Small samples of film prepared by this technique are currently being hydrolyzed to E/Acr A film and will be examined further.

Less tedious methods of preparing thin films are also being examined. Faster vulcanization would be effected by heating the film to about 150°C. However, before vulcanization the polymer film is rather weak at this temperature. Therefore, the chrome plates with dried film in place were put in an oven at 150°C. The vulcanized film was found to be tightly stuck to the plates and could not be removed whole. Various release agents have been incorporated into the polymer dopes (82870), and various treatments of the casting plates (82871) have been tried, but to date, none have prevented stocking of the films to the plates. Apparently, the polymer becomes softened when heated to 150°C, and before vulcanization has become extensive, it fuses to the plates. As time permits, other methods of vulcanizing the cast films will be used.'

3.3 AC Resistance of Ion Exchange Membranes

In the first quarterly progress report, the measurement of AC resistnace was discussed. The methods employed in this early work were those developed in previous projects. They were found to be inconsistent with other work on battery separators and were consequently of dubious value. Since then, a resistance-measuring cell has been received on loan from JPL for measuring the AC resistance of thin membranes in an electrolyte. The electrolyte of interest in this work is aqueous KOH, and unless indications are to the contrary, 40% KOH will be employed. The resistance cell is supported on aluminum legs and the electrolyte is kept in plastic bottles connected to the cell by tygon tubing. Actually, each side of the resistance cell is connected to a separate supply of electrolyte.

The measurements have been made with an ESI Impedance Bridge, Model 250, using an external variable capacitor to balance the impedance cell. The external capacitor currently in use is a Cornell-Dubilier Decade Capacitor, from 0 to 1.1 microfarad, in 0.01 uf steps, which is 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 uf (with infinitely variable capacitor) does not appear to improve the measurements significantly. The precision of the bridge with the external capacitor suitably adjusted appears to be satisfactory; i.e., the null indicator is sensitive to 0.01 ohm change. The best sensitivity is obtained with the detector amplifier at maximum, of course. The power across the cell has been measured at about 9 milliwatts, maximum, at 1000 cycles, with the oscillator set for maximum output. All measurements are made at this power since the change of resistance with power output, if any, is not known.

Some film samples made in previous work at Monsanto were retrieved and the AC resistance of the membranes was measured. These samples had been stored for some time without inhibitors. Before the measurements, the samples were soaked for more than 24 hr in 40% KOH solution. The electrolyte employed in the cell also was 40% KOH. The results are shown in Table III.

The data of Table III show these membranes have lower resistance to AC current than some polymers but the measured resistances were somewhat higher than expected. In the calculation of area resistance (Ra) the thickness of the films is not included, although resistance and thickness are directly proportional. An approximate comparison of two films of different thickness may be made from the specific resistance (r), obtained by dividing Ra by film thickness. For example, the specific resistance of 74358-25 is 21.8 ohm-in^2 per inch (.0095 inches thick). Consideration of film thickness in this manner introduces additional uncertainty in the results and therefore the specific resistance has not been calculated in Table III. Specifically, film thickness can only be measured to the nearest 5-10% (less precision for thinner films). The effective thickness of the film is not clearly understood but is thought to differ from the thickness of dry film due to swelling by the electrolyte.

The films mentioned above appear to be stable in the aqueous electrolyte of 40% KOH, but some swelling was noticed. The films were swelled to a much greater extent by soaking in distilled water. The water soaked films also have lower AC resistance, sometimes less than 10% of the resistance of the same film after conditioning in the 40% KOH. Obviously, preconditioning in the electrolyte in which the materials will be employed is necessary for accurate measurements. Without indications to the contrary, 40% KOH will be used in this work.

The resistance of films given in Table III appears to be rather high and not necesarily representative of this copolymer. A film sample has been made from copolymer recently synthesized, i.e., a crosslinked ethylene/acrylic acid copolymer. The sample, 82979, contains 43.6% acrylic acid and is 5.3 mils thick (dry). This sample swells in water and 40% KOH similarly to those discussed above. After conditioning in 40% KOH for more than 24 hr, the resistance of the cell was measured and the Ra calculated to be 0.055 ohm-in^2. A 1-mil film of this material would probably have Ra of about 0.01 - 0.015 ohm-in^2 which is comparable to separator material currently available. This shows the feasibility of making low-resistance separator membranes by the methods employed here.

Table III

AC RESISTANCE OF MEMBRANES

Experiment 82862, 82863
Aperture 0.04906 sq. inches
AC Frequency 1000 cycles
Electrolyte 40% KOH

REFERENCE	COMPOSITION E/MAR[1]	COMPOSITION E/ACrA[2]	DRY FILM MILS	ELECTROLYTE TEMP. °C	Ra[3] OHMS-IN.^{2}
74358-19[4]	54.5/35.5	57.8/31.5	8.5	25.9	0.268
74358-17	45.6/54.4	50/50	5.7	24.8	0.229
74358-17	45.6/54.4	50/50	10	24.1	0.267
74358-24	45.6/54.4	50/50	13.2	25.9	0.405
74358-25	57.5/42.5	61.8/38.2	9.5	23.1	0.207
74358-25B	57.5/42.5	61.8/38.2	15.8	25.0	0.649
74358-26	45.6/54.4	50/50	9	25.8	0.221
74358-27	45.6/54.4	50/50	4.0	26.1	1.328
74358-28	45.6/54.4	50/50	6.1	26.0	0.648

[1] Precursor polymer composition, ethylene/methyl acrylate, crosslinked

[2] Calculated composition of hydrolysed copolymer, ethylene/acrylic acid, exclusive of fillers, when used

[3] Area resistance, i.e. area of exposed membrane (aperture) times difference of cell resistance (OHMS) with and without membrane in place

[4] E/MAR precursor contains 10 wt. % carbon

The conclusions made above are based on measurements with a bridge not previously employed. The bridge appears to be operating satisfactorily and the conclusions appear to be valid. However, additional corroboration of the applicability of this bridge in this measurement appeared 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 IV. The external capacitor was set at 0.47 - 0.51 uf for these measurements.

The measured Ra 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.

It is interesting to note the effect of the plastic washer (or donut) spacer when measuring the resistance of cell alone. The measurement 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 Ra of the reference film calculates to be 0.018 ohm-in^2, which is appreciably greater than the Ra of 0.012 ohm-in^2. Previous measurements of cell resistance have been made with no plastic spacer. In the future cell resistance will be specified as to whether measurements were made with or without a polymeric spacer.

Table IV

RESISTANCE OF REFERENCE MEMBRANE

ESI Impedance Bridge
1000 cycle frequency
Aperture 0.04906 sq. in.
Electrolyte 40% KOH

Specimen	Elect. Temp. °C	Resistance Ohms	Ra
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 Donut	24.9	17.60	0.012 ohm-in^2

4. LIAISON

The project group met with Mr. Werner von Hartmann of JPL on 4 October 1967 at the Dayton Laboratory, to discuss various aspects of the project. A telephone call was received on 24 November 1967 from Mr. von Hartmann to briefly discuss progress on the project and the reference film for checking the resistance measurements. The reference film and a covering letter were received from Mr. von Hartmann on 1 December 1967.

5. FUTURE PLANS

Synthesis of copolymer with different monomer ratios will be continued to produce supplies sufficient for test work.

The copolymers will be characterized.

Thin films will be prepared, vulcanized and hydrolyzed.

Test work on thin films will be started as soon as samples are available.