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GODDARD SPACE FLIGHT CENTER

COVERING

ALKALINE BATTERY SEPARATOR STUDY

MARCH 29 TO JUNE 28, 1964

CONTRACT NAS-5-2860

THE ELECTRIC STORAGE BATTERY COMPANY
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Eighth Quarterly Report
NASA
Goddard Space Flight Center
Contract NAS-5-2860
ESB Report No. 7054.8

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SUMMARY

Screening tests for separators in silver-zinc batteries were developed. They are designed to reduce to a minimum the time consuming battery testing. Three tests yield the most important information: the electrical resistivity, the silver diffusion and the zinc penetration tests. Some potentially useful separator materials and modifications of conventional separators have been prepared. Twenty-five batteries have been built for the evaluation of these separators. Further investigations are recommended in this area.

author

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INTRODUCTION

This is the Eighth Quarterly and Final Report, covering work done under Contract NAS-5-2860, which was awarded to The Electric Storage Battery Company on June 28, 1962.

OBJECTIVES

Before discussing the objectives of this investigation, it may be useful to review the requirements which a separator material for a silver-zinc or silver-cadmium battery should meet. They are:

1. Strong mechanical separation between positive and negative plates.
2. Effective prevention of migration of particles between plates of opposite polarity.
3. Minimum resistance to the flow of electrolyte.
4. Good conductivity in the electrolyte.
5. The separator should be easily wetted by the electrolyte; it should absorb and retain a maximum of electrolyte so that there is always enough electrolyte in contact with both plates to insure an uninterrupted flow of current.
6. The separator should fulfill all these functions over extended periods of time, both under cycling conditions and in prolonged storage. The material must therefore resist, as long as possible, the effects of the battery environment. This entails resistance to the combined effects of hydrolysis in the presence of strong alkali and of oxidation in the presence of the highly oxidative AgO and Ag_2O.
7. Any degradation products of the separator material should not interfere with the proper functioning of the battery.
8. Separators should have sufficient mechanical strength so that they are not damaged in assembling the battery, and withstand reasonable handling of the battery.

9. Separators should also be dimensionally stable, though some degree of swelling due to electrolyte absorption is unavoidable and can be compensated by appropriate cell design.

In the past, the approach to the selection of suitable materials has been largely a pragmatic one; a material that appeared promising was incorporated in a battery and evaluated on the basis of performance under a predetermined set of service conditions. Such tests undoubtedly had merit, but the results were valid only under the particular conditions used, and they were wasteful of time.

The primary objective of this contract was the development of screening tests which would make it possible to choose suitable separator materials without having to subject every potential material to time consuming battery tests.

Another objective was to apply the screening tests in selecting the most promising materials as separators in assembling experimental cells.

Both tasks were completed. The purpose of the present report is to report additional work done in the period March 29 through June 28, 1964, and to review the results obtained since the inception of the contract.

SEPARATOR MATERIALS

The separator materials which were subjected to the screening tests are listed in Table 1. Not all of these materials are commercial products. The manufacture of some of them has been discontinued since this contract went into effect. Others are strictly experimental products; this includes specifically the membranes developed by The Electric Storage Battery Co., either before the inception of the present contract (Nos. 15-21), or developed under the terms of this contract (Nos. 27-29, 32, 34-37).

The Mipor separators (Nos. 18-21) are polyethylene or poly(vinyl chloride) membranes, made microporous by leaching to remove inorganic salts or various starches which have been included as pore formers. The process is covered by several patents(1).

The PMA membranes (Nos. 15-18) are ion-exchange membranes, made by impregnating a "Mipor" polyethylene sheet with methacrylic acid, with a polymerization catalyst (benzoyl peroxide) and divinyl benzene (DVB) as crosslinking agent. The degree of crosslinking is controlled by varying the methacrylic acid: DVB ratio; e.g., PMA 83/17 means a cross-linked poly (methacrylic acid) made by polymerizing 83 parts methacrylic acid and cross-linking with 17 parts DVB. A more detailed description of this patented process was given in the Fifth Quarterly Report (p. 9).

Modifications of these membranes by copolymerizing the methacrylic acid with other monomers led to new, potentially useful separators. These and other developments will be discussed later in this report.

The chemical formulas of membrane materials discussed in this report are shown in Table 1a.

SCREENING TESTS

The following screening tests were used:

1. Hydrolytic resistance to electrolyte
2. Oxidation resistance
3. Tensile strength
4. Dimensional changes in electrolyte
5. Electrolyte absorption and retention
6. Wettability and electrical resistance
7. Porosity and tortuosity
8. Permeability to silver ions
9. Reactivity towards silver ions
10. Resistance to zinc dendrite growth

Special attention was focused on cellophane; it was not only the first material that was chosen as a separator in silver-zinc batteries(2) but it has also remained the most widely used separator material for this purpose.

EFFECTS OF HYDROLYSIS AND OXIDATION ON CELLULOSE

A study be Weltzien and zum Tobel(3) in 1927 showed that some degradation of cellulose occurs by hydrolysis alone in the absence of oxygen (although their description of the experiments leaves some doubt whether oxygen was rigorously excluded). They reached the erroneous conclusion that oxygen played a minor part in the degradation.

Staudinger and Jurisch(4) in 1938 proved conclusively that oxidation, rather than hydrolysis, was the predominant reaction. They demonstrated that the degree of polymerization of cellulose in cuproxam solution was reduced by 6% after 8 days at 20°C in a high vacuum, by 19% after 8 days at 100°C. In the presence of air, the corresponding figures were 62% (at 20°C) and 91% (at 100°C). A better understanding of the degradation of cellulose was obtained by the application of the autoxidation theory, developed in the 1940's by Dr. Bateman's team at the British Rubber Producers Research Association(5). Autoxidation postulates a free radical chain reaction, involving formation of hydroperoxide structures. Peroxide groups have indeed been found in partially oxidized cellulose. Entwistle and his co-workers(6) have shown that oxygen absorption and the appearance of carbonyl groups followed the kinetics of a free radical mechanism. Present concepts, based on Entwistle's work, assume two concurrent processes: oxidation of the terminal aldehyde groups and reduction in DP (degree of polymerization) by depolymerization.

Our experiments with cellophane in KOH solutions were consistent with these findings.

Hydrolysis of cellophane, in the absence of oxygen, was found to lead to a gradual lowering of the molecular weight. When oxygen was present, the pattern became more complicated(7). The effects of degradation were followed by measuring the weight loss, the decay of the tensile strength and of the degree of polymerization; the latter was studied by following the progressive decrease in solution viscosity in a cupriethylene diamine solution(8), as proposed by Battista(9). All three methods indicated, not unexpectedly, that degradation of the cellulose was due to a combination of hydrolysis and oxidation, and that oxidation had the more serious effect on the properties of cellophane.

The oxidation reaction was therefore studied more intensively. The method finally chosen for this purpose was oxidation by potassium permanganate in a weakly alkaline solution, followed by measurement of the weight loss; details of the precedure have been described in an earlier report(10). This method could be used to compare the relative sensitivity of all the separator materials to oxidizing conditions and in a medium which approached the battery environment. The oxidation tests were generally run at 50°C but it was soon found that unprotected cellophane was substantially destroyed in the test; the reaction temperature was therefore reduced to 25°C whenever cellophane samples were tested. It is remarkable that sausage casing behaved differently; it suffered a loss of about 1/3 its original weight at 50°C but it did not disintegrate. The non-cellulosic polymeric materials were far more resistant to oxidation than the cellulosics. Illustrative data are shown in Table 2. In view of these differences between cellulosic and non-cellulosic materials, it appeared desirable to modify the cellulosics in such a way that a better oxidation resistance could be expected. The problem was approached in two ways:

1. Impregnation with known antioxidants

2. Use of chemically modified cellulose

IMPREGNATION

Twenty-five compounds which are known to possess antioxidant activity were used to impregnate cellophane. They include amines, sterically hindered phenols and organic sulfur compounds. In most cases, the results were disappointing: the oxidation resistance of the cellulose was not significantly improved. The exceptions were hydroquinone and p-phenylenediamine. Both reduced the oxidation loss in the $KMnO_4$ screening test (from 60-75%) to the neighborhood of 4 - 5%. Grafting of vinyl monomers onto the cellulose molecule with subsequent polymerization, reduced the oxidation loss, though to a lesser extent. However, the modified cellophane was brittle and the modest protection against oxidation resistance was obtained at the cost of increased electrical resistance.

The oxidation resistance of silver-treated cellophane did not differ sufficiently from that of untreated cellophane to constitute a marked improvement. The reaction rate with dissolved silver is somewhat reduced by the presence of the added silver, though again the effect is not very pronounced.

Impregnation with a diisocyanate (TDI, a mixture of tolylene diisocyanate isomers) had little effect on the oxidation loss of cellophane. However, it was found that the physical structure of the TDI treated cellophane survived the oxidation test, whereas untreated cellophane was largely destroyed under the test conditions.

MODIFIED CELLULOSE

The oxidation resistance of Permion 600 which is reported to be grafted cellulose is improved over that of regular cellophane. Its electrical resistance is appreciably higher and its reaction rate with dissolved silver is lower.

In the course of our investigations, we were able to graft various monomers with olefinic unsaturation on cellulose in the form of cellophane. The monomers which could be grafted to varying degrees were:

acrylonitrile

acrylonitrile + styrene

ethylene imine

methacrylic acid

N, N-diethylaminoethyl methacrylate

N - vinyl - 2 - pyrrolidone

The techniques used have been described in previous reports (IV, 4-6, V, 2-3). The grafting did result in some improvement in the oxidation resistance; however, this protection was gained at the cost of substantially increased electrical resistance and of increasing embrittlement.

TENSILE STRENGTH

Tensile strength tests were used to compare the various classes of separator materials and as a means of comparing the effects of degradation. Measurements were made on both dry and wet materials (wetted by soaking 15 minutes in distilled water). For details of the test, see the Third Quarterly Report, p. 4.

The tensile strengths (dry and wet) of typical separator materials are compared in Table 3. This table shows that the separator materials fall into two distinct classes: the cellulosics, which have dry tensile strength ranging from 13,700 to 20,000 lbs/sq in., and the microporous plastic membranes with tensile strengths which are smaller by an order of magnitude. This pronounced difference is of course partly due to the relatively coarse pore structure of the plastic membranes. The only exception is Polypor WA but here the high tensile strength is due to the supporting fabric (nylon), rather than to the plastic film.

The wet strength of the cellophanes is generally about one third of the dry tensile strength. The tensile strength of the plastic membranes was hardly affected by wetting; this is not surprising because the matrix material does not absorb water; hence the intermolecular forces which account for the tensile strength remain unaffected.

The wet tensile strength of cellophane is increased to 8500 lbs/sq in. by the diisocyanate treatment, an increase of 40%.

ACCELERATED AGING OF CELLOPHANE IN KOH

At the start of this investigation, 3 in. by 2 in. samples of cellophane PUDO 300 were placed individually in glass tubes and covered with 25 ml potassium hydroxide solution; half of the tubes contained 25%, the remaining tubes contained 40% KOH. The tubes were then sealed, leaving approximately 15 ml air above the surface of the solution. The sealed tubes were stored at room temperature (26°C). At the end of the first year, half the tubes in each group were opened; the remaining tubes were opened at the end of the second year. The cellophane samples were used to study the long-range effect of KOH in the presence of a limited amount of air. Two parameters were used to assess the effects of extended storage: degree of polymerization and wet tensile strength.

The degree of polymerization, as determined by the solution viscosity in cupriethylene diamine solution (see First Quarterly Report, p. 5), was initially 520. The results of the solution viscosity tests are shown in the following table:

Time in years	40% KOH	25% KOH
0	520	520
1	480	425
2	420	410

These data show that the initial rate of degradation is faster in 25% KOH than in 40% KOH, presumably due to the stronger swelling in 25% KOH. The final values indicate, however, that the same level is reached eventually because the sample tubes contained the same amount of oxygen, regardless of the KOH concentration.

The wet tensile strength of the cellophane samples in 40% KOH had decayed from the original 12 lbs to 8 lbs after two years storage. Tensile measurements on samples stored in 25% KOH were omitted because the edges of the samples were badly cracked. Samples notched in this way could not be expected to give meaningful tensile values.

A comparison of these results with data obtained in accelerated aging tests (see Table 4) indicates that accelerated aging for 10 days at 90°C in 40 % KOH, in the presence of a limited amount of air, is approximately equivalent to two years storage at room temperature under otherwise similar conditions.

ELECTROLYTE ABSORPTION AND RETENTION

The ability of a separator to absorb and retain as large a volume of electrolyte as possible is an important parameter because good conductance across the separator requires that an adequate supply of electrolyte within the voids of the membrane be available at all times. The electrical resistance of the various separators usually parallels their ability to absorb electrolyte. The cellulosic materials, as a class, exhibit a large absorptive capacity, between 3.6 and 8.4 grams electrolyte per cm^3 of the dry separator material; their specific resistivities are around 10 ohm-cm. The absorptive capacity of most plastic materials was found to be considerably lower - usually from below 1 to 2 grams electrolyte per cm^3 of separator material. The exceptions are:

a) The copolymer of i-propylacrylamide and methacrylic acid on polyethylene. This membrane absorbs 8 g electrolyte per cm^3 and has a low electrical resistivity thus confirming the observation that high absorption and low resistivity go hand in hand. This membrane behaved in both respects more like a cellulosic material.

b) Acropor WA which couples low absorption (1.3 g/cm^3) with low electrical resistivity. The explanation for this unusual combination might be found in the large pore size; the average pore diameter is larger by an order of magnitude than the pore diameters in cellulosic materials. The large pore size might account for the good conductivity despite the poor ability to absorb (and retain) electrolyte.

DIMENSIONAL STABILITY

The effect of prolonged immersion in electrolyte shows wide variations. Cellulosic materials undergo the greatest swelling. The change occurs almost entirely in thickness; length and width remain virtually unchanged. Thickness swelling in cellulosics amounts to something of the order of 200% - usually less at very low temperatures, more at higher temperatures (see Second Quarterly Report, Tables 8 - 10, and subsequent reports). Plastic membranes are dimensionally far more stable. Microporous polyethylene and PVC do not change in length or width, and the thickness swelling reaches a maximum of 25% at 90°C. The crosslinked polymethacrylate membranes increase in all three dimensions by 15 to 30%; the volume swelling amounts to about 80%. Acropor WA increases only in thickness, and this swelling reaches only a maximum of 10%.

The high degree of swelling of cellulosic materials is, of course, due to the high absorption of electrolyte. The absence of any large pore volume in dry cellophane does not afford the space for the adsorption of liquid. Cellophane owes its capacity for the absorption of several times its original volume to its ability to swell to several times its original volume. Our results indicate that this swelling is moderately reduced if the cellophane is impregnated with various agents (Ag, antioxidants, diisocyanate) but always remains substantial.

This dimensional instability is a distinct drawback but it is responsible for the high degree of absorption and consequently for the low electrical resistivity. The problems created by the swelling of the cellophane are generally overcome by appropriate design of the battery.

POROSITY

The method and the equipment used to measure the average pore diameter in separator materials have been described in the Fourth and Fifth Quarterly Reports

(IV, p. 8; V, 15). In later experiments, the reliability of the measurements was improved by the addition of an automatic sensing device ("Therm-O-Watch Electronic Controller", Model L-6, by Instruments for Research & Industry, Cheltenham, Pa.). Its oscillator head is attached to the riser tube, i.e., the burette which contains the electrolyte. The amplifier is connected with the timer. As soon as the meniscus of the electrolyte drops below a predetermined level, the sensing clip activates the relay in the amplifier and stops the timer.

The complete test assembly is shown in Photograph 1.

Porosity data have been given in the Fifth Quarterly Report (p. 24). It remains to add a few more data and to complete the picture by a discussion of tortuosity.

TORTUOSITY

As pointed out in the Fifth Quarterly Report (p. 16), the pore diameter and porosity calculations are based on the assumption that the pores form a system of parallel cylinders, going straight through the matrix, at right angles to its surfaces. Such pores would provide the shortest pathway for ionic migration; their length would be uniform and equal to the measured thickness of the membrane. This is, however, an idealized picture. In reality, the pores are not straight, parallel and perpendicular to the surface but form a complex pattern of inter-connected, randomly bent capillaries of varying lengths and diameters. The length of the capillaries is greater than the thickness of the membrane. Two membranes may therefore have the same average pore cross-sectional area and identical thickness but differ widely in mean path lengths. This will result in different electrical resistivities.

The ratio by which the effective length of the pores exceeds the straight line (= the thickness of the membrane) is termed the Tortuosity Factor:

$$T = \frac{\text{Mean Effective Capillary Length}}{\text{Thickness of the Membrane}} \qquad (1)$$

It is the factor by which the separator thickness must be multiplied to arrive at the actual mean path-length which the ions must travel in diffusing through the separator. The actual path-length will, of course, affect the rate at which ions can travel through the membrane and will therefore influence the conductivity.

The tortuosity factor can be calculated by means of an equation derived by Mackie and Meares$^{(11)}$ and also used by Bergsma and Kruissink$^{(12)}$:

$$T = \frac{1 + V_p}{1 - V_p} \qquad (2)$$

where V_p is the volume fraction of the membrane occupied by the polymer network. To use this equation, the weight and the specific gravity of the dry separator material and the volume swelling of the membrane are required.

From the determinations of electrical resistance and pore size, data were available which made it possible to calculate the tortuosity factor by another equation:

$$T = \sqrt{k \, \frac{A R_O F}{L}} \qquad (3)$$

where k = Spec. conductivity of the electrolyte (31% KOH) = 0.66 $\text{ohm}^{-1}\text{cm}^{-1}$

R_O = Measured resistance of the separator in the electrolyte

A = Cross-sectional area

P = Porosity

L = Apparent path length (i.e. the thickness of the separator)

The term $\frac{R_O A}{L}$ represents the specific resistivity "ρ" of the separator (see Second Quarterly Report, p. 18). The specific conductivity of 31% KOH at 26°C = k = 0.66 $\text{ohm}^{-1}\text{cm}^{-1}$. By the appropriate substitutions, we obtain

$$T = \sqrt{0.66.\rho.F} = 0.8124\sqrt{\rho.F} \qquad (3)$$

The values for the porosity "F" have been calculated in the usual way:

$$F = \frac{B}{L}$$

where B = total pore volume per unit surface area and L is again the thickness of the separator.

The results, obtained by the two methods, are in good agreement. The tortuosity factor of cellophane PUDO-300 was found to be 2.8, based on Equation (2); when using Equation (3), a value of 2.6 was obtained.

The tortuosity data in Table 5 have been calculated by Equation (3). They show wide differences between various separators. Cellulosic materials, cellophane as well as sausage casing, generally have tortuosity factors within a fairly narrow range, from 1.9 to 2.6, i.e., their effective path lengths are about 2 to 2.5 times the thickness of the sheet. These values represent the lowest range of tortuosity factors, coupled with a high degree of porosity (in the swollen state) and low electrical resistivity. Permion 600 has also the high porosity typical of cellulosic materials but its tortuosity factor of 5.5 is more than double the value of unmodified cellophane, presumably due to the grafted sidechain and its electrical resistance is about four times as high as that of the unmodified cellophane.

The plastic separators, the PMA membranes (T = 3.2 - 5.4) and Permion 300 (T = 7.5) have considerably higher tortuosity factors than the cellophanes and their resistivity is also much higher although their porosity is not too different from those of the cellulosic materials. Only the microporous polyethylene membrane Mipor 13 CN and Acropor WA have resistivities which are close to those of the cellulosic separators; in both cases, the average pore size is large while the tortuosity factors are in the range of the cellulosic materials, i.e., in the low range.

Low tortuosity factors,e.g., in the neighborhood of T = 2, are evidently desirable in a separator because low electrical resistance appears to depend on a relatively short path.

Mipor 13 CN and Acropor WA should, on this basis, be very desirable separator materials; both have large pore diameters and low tortuosity factors. Unfortunately, they are deficient in another espect; they are not efficient barriers for dissolved silver.

SILVER REACTIVITY AND SILVER DIFFUSION

In the preceding discussion, we have mentioned repeatedly silver reactivity and silver diffusion. Methods and equipment were described in the Fourth Quarterly Report (p. 6). The data obtained by these methods proved to be among the most valuable parameters for judging the effectiveness of separators. The original expectation had been that the useful lifetime of a separator could be extended if it were possible to protect it against oxidation. Our early efforts were therefore directed towards improving the oxidation resistance by modification of the cellulose or by incorporation of antioxidants. As pointed out above, modified cellophane was defective in some important properties (brittleness, high electrical resistivity). Only a few of the antioxidants had any marked effect on the oxidation resistance of cellophane.

The experiments with tagged silver (Ag^{110}) showed:

1. That silver ions diffuse through a porous material which is reasonably stable to oxidation by Ag_2O.

2. That there is no measurable diffusion through a material which tends to react with dissolved Ag_2O.

Cellophane is typical of materials that are readily oxidized. It reacts with Ag_2O and there is virtually no silver diffusion through a cellophane membrane, up to its capacity to react with Ag_2O. In a diffusion experiment with Ag^{110} and one layer of cellophane PUDO-300, there was no measurable radio-activity in the untagged cell compartment after 100 hours at which time there was still some Ag^{110} left in the tagged compartment. If cellophane is impregnated with an effective antioxidant such as hydroquinone or p-phenylenediamine, its reaction rate with Ag_2O is markedly reduced and its permeability to diffusion by dissolved silver species is increased. Plastic membranes which had proved resistant to alkaline permanganate oxidation were also found to react slowly with Ag_2O but the dissolved Ag ions diffused rapidly through the membranes. These materials could therefore not be considered effective separators.

The inescapable conclusions are:

1. That a useful separator must be capable of preventing diffusion of Ag_2O.

2. That silver diffusion can be stopped only by a separator which can reduce Ag_2O.

In the process, the separator material is oxidized and eventually destroyed.

ZINC DENDRITE GROWTH

The method and apparatus used in the screening tests have been described in the Seventh Quarterly Report (pp. 11-14, Photographs 1-3). A separator area of 1.26 cm^2 was exposed. A solution of 100 g KOH pellets (86.6% KOH) in 100 g water, to which 8 g ZnO were added, served as electrolyte.

Cellophane PUDO-300 was used as reference material against which all other materials were tested. By passing currents from 1 to 50 ma, we established that the ability of cellophane to resist zinc dendrite growth undergoes a reproducible minimum at a current density of 7.9 ma/cm^2. Below this current density, the time to penetration and shorting becomes unduly long. Above 7.9 ma/cm^2, the time increases again because the efficiency of utilization of the current is reduced. This is illustrated in the graph (Figure 1 of this report). All materials were therefore tested by passing a current of 10 ma which corresponds to a current density of 7.9 ma/cm^2.

At least 3 samples of each material were tested simultaneously. Times to shorting due to penetration were recorded. Results are listed in Table 6; column B of the table shows the measured times to penetration, column C shows these times on an equal thickness basis. Taking cellophane as the standard, the results demonstrate that none of the treated cellophanes shows any marked difference. To test the effect of glycerol on the dendrite resistance, DuPont's cellophane PUD 300, containing 20.3% glycerol was used. The results indicate that glycerol has a marked deleterious effect on the resistance of cellophane to dendrite penetration. The time to failure was almost cut in half. The cellophane with glycerol was the least resistant of all cellulosic materials. Of the various plastic materials, microporous polyethylene (Mipor 13 CN), polyvinylchloride (Mipor 34 PN), Acropor, Polypor and various copolymer membranes gave very poor results while highly crosslinked polymethacrylic acid on a polyethylene matrix (PMA 83/17) and Permion 300 (grafted polyethylene) resisted dendrite growth longer than cellophane. A comparison of these results with average pore diameters points clearly to an interdependence; large pore size contributes to early penetration.

By far the best results were obtained with the clear sausage casing; even on an equal thickness basis, it resisted zinc penetration about four times as long as cellophane. Silver treatment of the clear sausage casing did not cause a marked change in the results.

Fibrous sausage casing showed a unique behavior. At first, the times to failure showed a wide scatter. A likely explanation for this irregularity appeared to be the different texture of the two surfaces of the membrane; one side is smooth, the other rough. When all samples in a test run were so arranged that either the rough or the smooth side was facing the cathode, the results were in good agreement. The resistance to dendrite growth was approximately doubled whenever the smooth side of the membrane was facing the Zn electrode. Silver treatment did not substantially change the resistance of fibrous sausage casing to zinc penetration, and the resistance remained higher by a factor of two if the smooth side faced the electrode. It therefore seems advisable to use fibrous sausage casing always in such a way that the smooth side faces the zinc plate.

At best, however, fibrous sausage casing did not come up to the good performance of clear sausage casing. The reason is probably to be found in the delamination which was observed during the test. Under the conditions of our test, the current efficiency is very low. As a result, when a dendrite penetrates the near surface gas bubbles are formed between the laminated layers; these bubbles lead eventually to delamination. In normal battery operation, this is not the case; in a well designed battery, the current utilization is very nearly complete and this kind of phenomenon would not occur. This effect is clearly demonstrated in the accompanying photomicrographs (Figure 3 and 4). The blisters are an indication that delamination has set in. Inside the blisters, zinc deposition has begun; the wall of the membrane has become thinner where delamination has occurred and in several spots, the head of the dendrite has penetrated through the weakened wall.

To sum up the results of the dendrite study, our results indicate that in this area, clear sausage casing is superior to all other materials tested. However, this superiority is not as great as might be desired. Zinc penetration remains a serious limitation on the lifetime of even the best separator materials. None of the limited number of treatments tried in the course of this investigation has resulted in a significant improvement. Unchecked growth of zinc dendrites remains therefore a factor that limits the useful life of the Ag-Zn battery. Indications are that this problem is capable of a solution. T. A. Kryukova(13) reports very substantial improvements (several orders of magnitude) in the ability of regenerated cellulose to resist zinc penetration. In view of the importance of the problem, a thorough investigation appears amply justified.

NEW ION EXCHANGE MEMBRANES

The screening tests have shown that the degree of crosslinking has a marked effect on the electrical resistance of membranes, made by polymerizing methacrylic acid in a matrix of polyethylene. Polar groups in the polymer are eliminated by increased crosslinking. The polymer with the lowest crosslink density (PMA 95/5, i.e., Methacrylic acid: divinyl benzene ratio 95:5) had, as expected, the highest electrolyte absorption and the lowest electrical resistivity. While the electrical resistance was higher than that of cellophane, the difference was comparatively small. Furthermore, our pore size measurements showed that the apparent pore diameter and the tortuosity factor were not too different from the corresponding values for cellophane. Finally, the membranes proved highly resistant to prolonged immersion in battery electrolyte, even at high temperatures; this property should make them very desirable for use in batteries which have to undergo high-temperature sterilization. The only disadvantage is the low tensile strength of these membranes.

It seemed worthwhile to modify the PMA membranes by introducing a co-monomer which should add flexibility to the polymer chain. A major effort was made towards the end of the contract time to develop suitable copolymers. However, there was not enough time left to bring this task anywhere near completion. A copolymer of methacrylic acid (80 parts) and isopropyl acrylamide (20 parts by weight) on a polyethylene matrix had several very desirable properties: electrolyte absorption very close to that of cellophane, electrical resistivity very similar to cellophane (in fact, slightly lower), and chemical resistance on extended immersion in KOH far superior. (This is separator material No. 32 in the tables).

Another means of modifying PMA was copolymerization of methacrylic acid with varying proportions of poly(vinyl acetate) with subsequent hydrolysis of the acetate to hydroxyl groups. The appended tables (No. 7 through 12) show the results of various screening tests. Their dimensional and chemical stabilities in electrolyte are generally good. The electrolyte absorption of the polymer which contains 80% vinyl alcohol units is on the low side and the electrical resistance is about twice as high as that of cellophane. However, the copolymers containing lower VA:MA ratios had satisfactory electrolyte absorption values and their electrical resistivities were near those of the best separators.

A copolymer of methacrylic acid and maleic anhydride (No. 37 in the tables) had similar properties as the vinyl alcohol copolymers. Another variable was introduced in this copolymer. By varying the amount of divinyl benzene, we were able to study the effect of varying crosslink density.

None of the copolymer membranes showed the high reactivity with Ag which characterizes cellophane. However, the appended graphs (Figure 5) show some important differences: the high vinyl alcohol - low methacrylic acid copolymer reacts with Ag_2O about 4 times faster than the copolymer in which the monomer ratio is reversed. An increase in the crosslink density causes a slight drop in the Ag reactivity but the effect is not as pronounced as the effect of changing the monomer ratios.

It would seem very worthwhile to pursue this line of research further.

In a different approach to ion exchange membranes, ion exchange resins were dispersed in a liquid urethane prepolymer which was then cured to an elastomer. The electrical resistance of the resulting membrane was satisfactory, provided a sufficiently high resin: urethane ratio (1:1) was used. Increasing brittleness precluded higher resin proportions. The silver reaction rate of these membranes was very low.

Forming membranes by dip-coating techniques was also attempted (see Seventh Quarterly Report, pp 9-11). The resulting membranes were mechanically weak and their electrical resistivities were generally rather high. No suitable separator was prepared using this technique.

CONCLUSIONS

1. The useful life of silver-zinc batteries is restricted by various causes. An important factor is the limited time during which the separators fulfill their purpose. This limitation is imposed by the hydrolytic degradation which many separator materials undergo in the strongly alkaline battery environment.

2. The purpose of this investigation was a study of the effects of the battery environment on the mechanical and chemical properties of various materials. A series of screening tests were found to be useful for evaluation of these materials without the necessity of time-consuming battery testing.

3. Of all the bench tests, three are expected to yield the most important information about the suitability of a given separator:

Rate of silver reaction and silver diffusion

Rate of zinc dendrite growth

Electrical resistivity

4. The effectiveness of a separator in preventing the diffusion of Ag species was found to be largely a function of its reactivity with Ag. Materials which are resistant to oxidation allow diffusion of silver species; even materials with the smallest pore diameter were found to be unable to prevent diffusion. Only those materials which reacted with the dissolved silver oxides were capable of preventing silver diffusion. Resistance to oxidation can be greatly improved but as oxidative stability is increased, effectiveness as a diffusion barrier decreases.

5. Regenerated cellulose remains the most effective material tested as far as resistance to silver migration is concerned. It functions by arresting this migration though it is consumed in the process.

6. The rate of the reaction of cellulose with dissolved silver oxides can be greatly reduced by treatment with antioxidants though at the cost of some increase in the diffusion rate of these species through the membrane.

7. Five of the batteries which are being delivered to NASA under this contract (see Appendix) contain cellophane which has been impregnated with m-phenylene diamine. Their purpose is to determine whether the presence of an antioxidant results in a satisfactory extension of the useful life of cellophane without an undue increase in the silver diffusion rate.

8. Treatment with diisocyanates can strengthen the physical structure of cellophane without changing, to any marked degree, its electrical resistivity, its rate of reaction with Ag_2O and the rate of diffusion of dissolved Ag species. Five of the batteries which are being supplied under this contract contain tolylene diisocyanate treated cellophane.

9. Pore diameter was found to be less important in regard to silver diffusion than the rate at which a separator material reacts with Ag_2O. However, pore size has a marked effect on the ability of a membrane to resist zinc penetration.

10. Regarding resistance to the growth of zinc dendrites, differences between materials of different composition and of different pore size are comparatively small. Little is known about this aspect.

11. The ability of a membrane to resist the penetration and propagation of a zinc dendrite is no less important than its ability to resist silver diffusion. Comparatively small differences in resistance to dendrite growth were found in the various materials examined, with sausage casing proving to be the most resistant.

RECOMMENDATIONS

1. Some of the co-polymer membranes developed in the latter part of the investigation have properties intermediate between a highly inert separator, such as PMA and Permion 300, and the reactive type, as exemplified by cellophane. An investigation should be pursued in this area to obtain optimum properties (as measured in the screening tests) in such a membrane. Greater resistance to hydrolysis and oxidation than cellophane are obtained while approaching closer to the ability of cellophane to react with dissolved silver.

2. The growth of zinc through the various separator materials was little affected by any of the structures investigated. Cellulosics and the ion exchange membranes with lowest permeabilities gave slightly superior results. A study of the factors governing zinc dendrite growth and of the effect of various organic and inorganic structures on this growth is recommended. A study of means of including or forming effective structures into membranes or separators is also recommended. The zinc penetration test described under this contract can provide a rapid and reliable method of comparing the effectiveness of additives or separator structures in retarding zinc growth.

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Eighth Quarterly Report
NASA
Goddard Space Flight Center
Contract NAS-5-2860
ESB Report No. 7054.8

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Thanks are also expressed to Mr. Howard Wilson who devised the analytical methods used in this work and supervised some phases of the testing; to Messrs. Edward L. Wasser and Edward J. Woytko for their pains-taking test work; and to numerous other colleagues who have contributed to various phases of this study.

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NASA
Goddard Space Flight Center
Contract NAS-5-2860
ESB Report No. 7054.8

ABSTRACT

11631

The objective of this investigation was to develop bench tests which would permit screening of separator materials for Silver Zinc and Silver Cadmium Batteries. These tests were applied to a range of membranes. The experience gained was applied to modify available materials and to develop new membranes of potential use in Ag-Zn batteries. Ability to resist silver diffusion and zinc penetration, and low electrical resistance proved to be the most important parameters. Treatment with some anti-oxidants or with diisocyanates showed promise as a means of improving the resistance of cellophane against degradation by Ag_2O. An ion exchange membrane formed by polymerizing and crosslinking methacrylic acid in a matrix of microporous polyethylene is another potential separator, with improved oxidation resistance. Sausage casings were found to be more resistant to zinc penetration than any other separator material but the improvement is marginal; an intensive investigation of this aspect is recommended.

author

TABLE I

SEPARATOR MATERIALS

The following separator materials were investigated:

1. Cellophane PUDO-300 (duPont)
2. Cellophane PUDO-600 (duPont)
3. Cellophane 140-PUT 76 (Olin)
4. Cellophane, nominal thickness 0.001 in. (Avisco)
5. Cellophane, nominal thickness 0.003 in. (Avisco)

* 6. Cellophane, gel film (laboratory sample, Avisco)

* 7. Sausage Casing (Avisco)

* 8. Fibrous Sausage Casing (Avisco)

* 9. Silvered Sausage Casing (Avisco)

10. Permion 300 (modified polyethylene, Radiation Applications Inc.)
11. Permion 600 (modified cellophane, Radiation Applications Inc.)
12. AMFion C-60 (strongly anionic membrane, Am. Machine & Foundry Co.)
13. AMFion C-103 (weak cationic membrane, Am. Machine & Foundry Co.)

* 14. Polypore WA (Niemand Bros.) a weak acid, acrylic ion exchange resin with nylon backing.

No. 15-17 are microporous polyethylene membranes, impregnated with crosslinked poly(methacrylic acid); they differ in degree of crosslinking:

* 15. PMA 80/20: Methacrylic acid: divinyl benzene ratio = 80:20

Table 1 Cont.

* 16. PMA 83/17: Methacrylic acid: divinyl benzene ratio = 83:17

* 17. PMA 95/5: " " " " " 95:5

* 18. Mipor 12 CN, microporous polyethylene of medium porosity

* 19. Mipor 13 CN, microporous polyethylene of high porosity

* 20. Mipor 34 CN, microporous poly (vinyl chloride) of high porosity and very fine pore size

* 21. Mipor 34 PN, microporous poly (vinyl chloride) of high porosity but a coarser pore size

* 22. Cellophane 111-1 (duPont) and

* 23. Cellophane 111-2 (duPont): both are experimental cellophanes, based on crosslinked cellulose

24. Fibrous Sausage Casing (Visking)

* 25. Cellophane PUDO-300, impregnated with m-phenylene diamine

26. Acropor WA - similar to Polypore WA (see No. 14) but made by Gelman Instrument Co.

* 27. Cellophane PUDO-300, treated with tolylene diisocyanate

* 28. Cellophane PUDO-300, treated with hydroquinone

* 29. Cellophane PUDO-300, treated with zinc chloride

30. C-19-300, a silvered cellophane, submitted by NASA

31. C-19-600, a silvered cellophane, submitted by NASA

* 32. Porous polyethylene, impregnated with a copolymer of methacrylic acid and isopropylacryl amide

33. Permion 1000, a Teflon membrane (Radiation Applications Inc.)

Table 1 Cont.

34-37 Porous polyethylene membranes, impregnated with crosslinked copolymers of:

* 34. Methacrylic acid with vinyl alcohol, monomer ratio 1:4

* 35. Methacrylic acid with vinyl alcohol, monomer ratio 4:1

* 36. Methacrylic acid with vinyl alcohol, monomer ratio 1:1

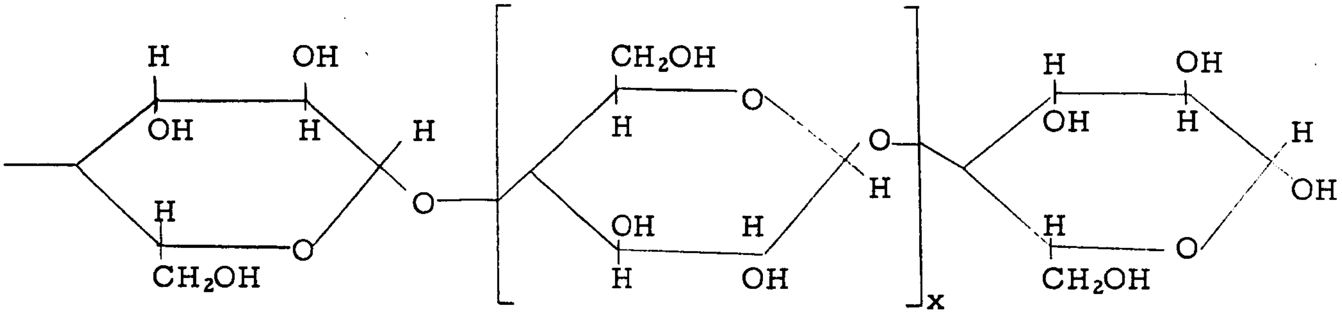
* 37. Methacrylic acid with maleic anhydride, monomer ratio 1:1

* 38. XE-97 Ion Exchange Resin in a matrix of a polyurethane elastomer

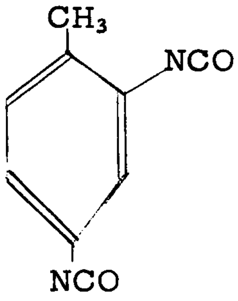
* The items marked with an asterisk are not now in commercial production.

TABLE 1 - A

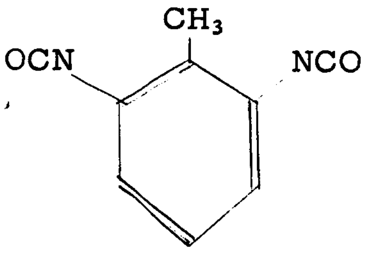
Chemical Formulas of Membrane Materials discussed in this Report



Cellulose



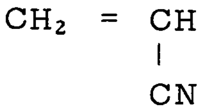
80% 2, 4 -



20% 2, 6 - Tolylene diisocyanate

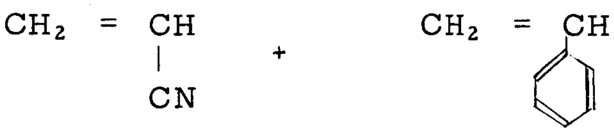
Table 1 A cont'd

Monomers which were Grafted on Cellulose



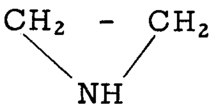
$CH_2 = \underset{\displaystyle CN}{\underset{|}{CH}}$

Acrylonitrile

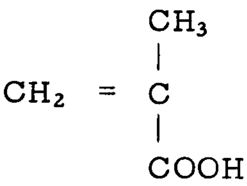


Acrylonitrile

+ Styrene

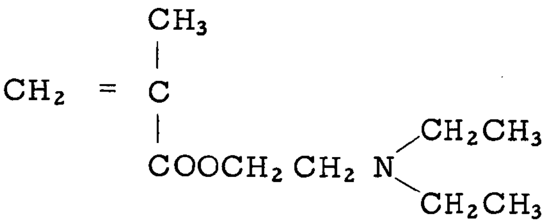


Ethylene imine

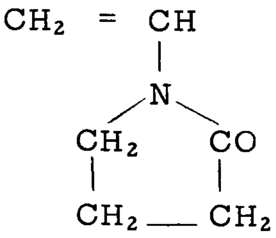


$CH_2 = \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COOH}{\underset{|}{C}}}}$

Methacrylic acid



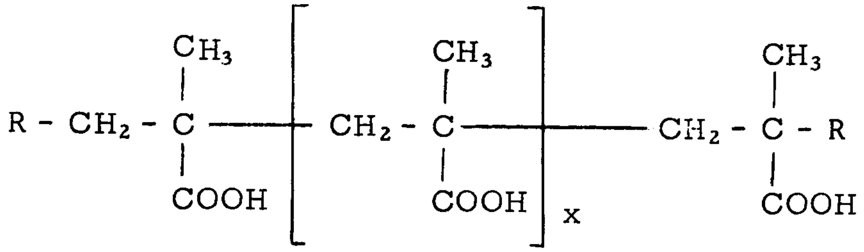
Diethylaminoethyl methacrylate



N - vinyl - 2 - pyrrolidone

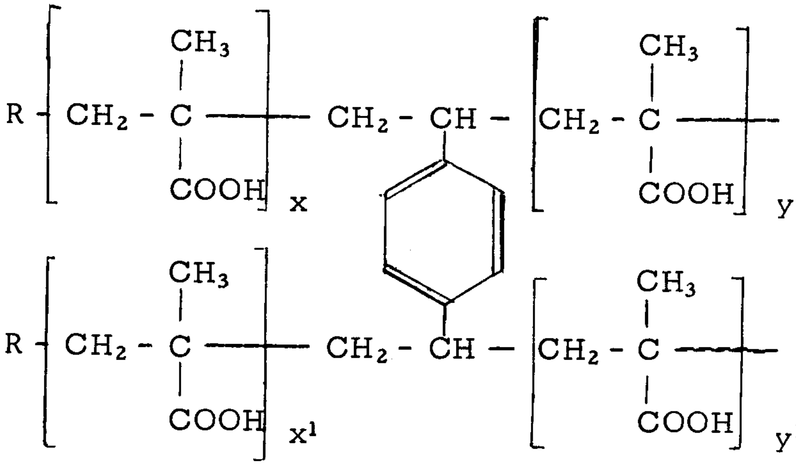
Table 1 A cont'd

Polymeric Membrane Materials

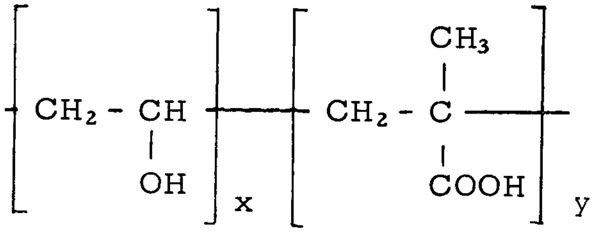


$$R-CH_2-\underset{COOH}{\overset{CH_3}{C}}-\left[CH_2-\underset{COOH}{\overset{CH_3}{C}}\right]_x-CH_2-\underset{COOH}{\overset{CH_3}{C}}-R$$

Polymethacrylic acid



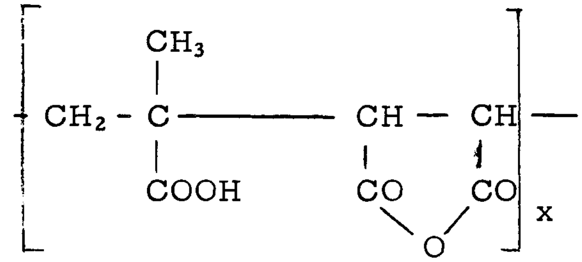
Polymethacrylic acid, crosslinked with divinylbenzene



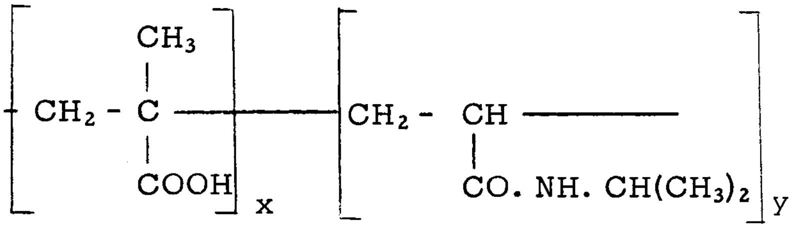
$$\left[CH_2-\underset{OH}{CH}\right]_x\left[CH_2-\underset{COOH}{\overset{CH_3}{C}}\right]_y$$

Copolymer of methacrylic acid and vinyl alcohol

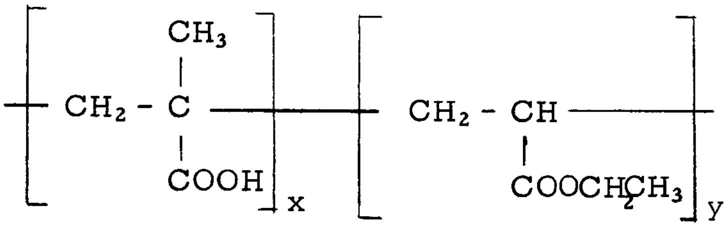
Table 1 A cont'd



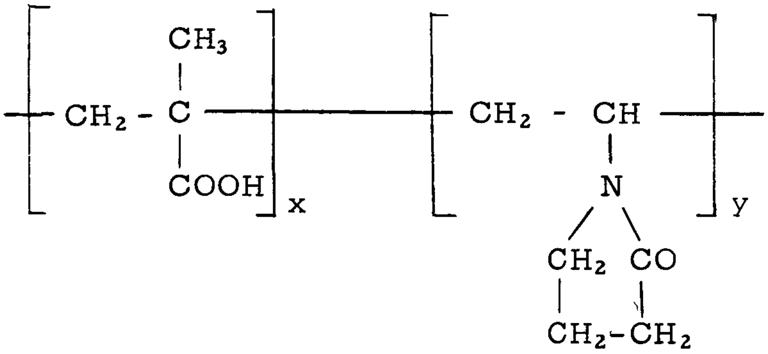
Copolymer of methacrylic acid and maleic anyhdride


$$\left[-CH_2-\underset{COOH}{\overset{CH_3}{C}}- \right]_x \left[-CH_2-\underset{CO.\,NH.\,CH(CH_3)_2}{CH}- \right]_y$$

Copolymer of methacrylic acid and isopropylacrylamide

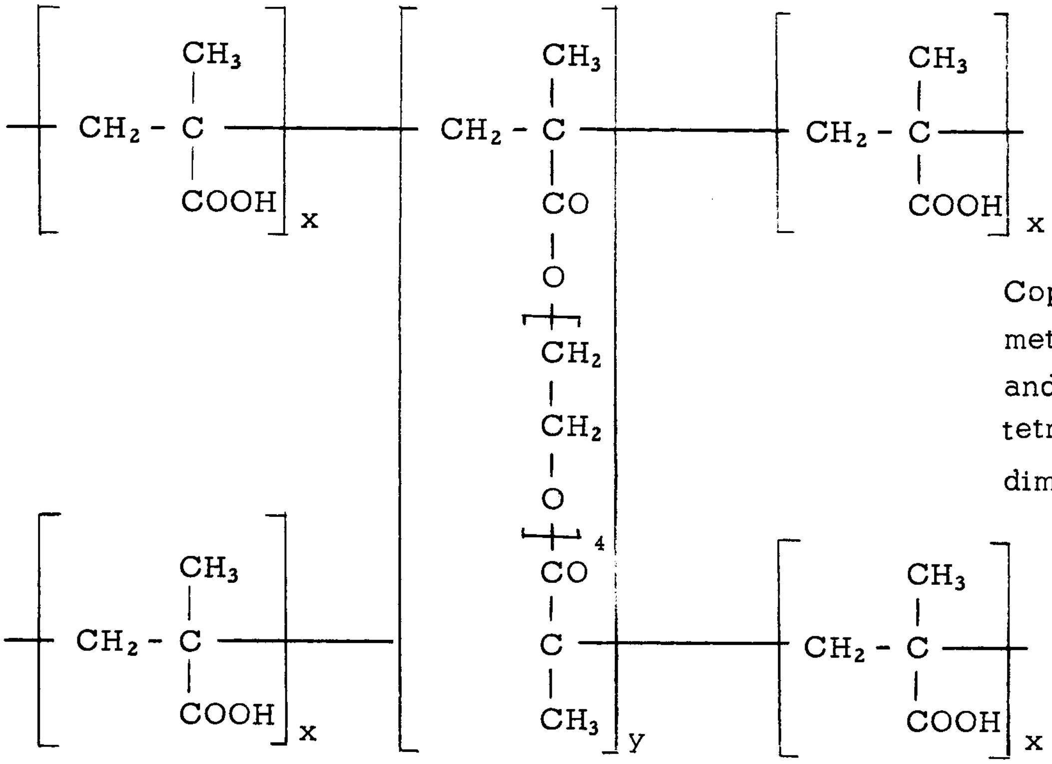

$$\left[-CH_2-\underset{COOH}{\overset{CH_3}{C}}- \right]_x \left[-CH_2-\underset{COOCH_2CH_3}{CH}- \right]_y$$

Copolymer of methacrylic acid and ethylacrylate



Copolymer of methacrylic acid and vinylpyrrolidone

Table 1 A cont'd



Copolymer of
methacrylic acid
and
tetraethylene glycol
dimethacrylate

TABLE 2

Oxidation Losses in $KMnO_4$

Material	% Weight Loss	
Cellulosics	at 25°C	at 50°C
Cellophane PUDO-300	69	-
Cellophane PUDO-600	63	75
Cellophane 111 -1 (crosslinked)	32	-
Cellophane 111 -2 (crosslinked)	60	-
Fibrous Sausage Casing	-	38
Silvered Sausage Casing	-	31
Permion 600	-	41
Non-Cellulosics		
Permion 300 (modig. polyethyl.)	-	23
Permion 1000 - 15 m Ω	-	19
Permion 1000 - 40 m Ω	-	8
Mipor 12 CN	-	1.2
Mipor 13 CN	-	0.8
Mipor 34 CN	-	1.5
Mipor 34 PN	-	0.9
Acropor WA	-	0
PMA (all levels of crosslinking)	-	10

TABLE 3

TENSILE STRENGTHS

Material	Dry Thickness in.	Tensile Strength lbs/sq in.	
		Dry	Wet
Cellophane PUDO-300	0.0010	20,000	6,000
Cellophane PUDO-600	0.0016	17,500	5,300
Cellophane 111-1	0.0012	17,920	7,080
Cellophane 111-2	0.0012	20,000	6,670
Fibrous Sausage Casing	0.0035	14,570	6,800
Silvered Sausage Casing	0.0031	17,750	9,350
Permion 600	0.0015	12,330	6,300
Permion 300	0.0011	9,550	5,430
Mipor 12 CN	0.0048	840	840
Mipor 13 CN	0.0048	520	520
Mipor 34 CN	0.0038	1,180	1,180
Mipor 34 PN	0.0060	1,330	1,330
Polypor WA	0.0031	15,660	12,750

TABLE 4

Degree of Polymerization of Cellophane vs. Time in 40% KOH at 90°C

Days	D.P.
0	525
1	472
2	463
3	463
4	454
5	449
6	447
7	449
8	441
9	432
10	418

TABLE 5a

Resistivity, Pore Diameter and Tortuosity of Cellulosic Materials

Sample No.		Spec. Resistivity [ohm-cm]	Average Pore Diameter [Ångstrom]	Tortuosity Factor
1	Cellophane PUDO-300	8.5	200	2.6
2	Cellophane PUDO-600	8.4	400	2.5
7	Clear Sausage Casing	7.4	450	2.1
9	Clear Sausage Casing silvered	5.9	200	1.9
8	Fibr. Sausage Casing	7.6	300	1.9
24	Fibr. Sausage Casing	8.2	450	2.1
23	Exper. Celloph. 111-2	10.0	240	2.6
25	Cellophane PUDO-300 + m-phenylenediamine	7.8	110	2.4
11	Permion 600 (modified cellulose)	38.6	80	5.5
30	C-19-300 (Silvered Cello.)	8.3	460	2.8
31	C-19-600 (Silvered Cello.)	8.5	400	2.6

TABLE 5b

Resistivity, Pore Diameter and Tortuosity of Non-Cellulosic Materials

Sample No.	Spec. Resistivity [ohm-cm]	Pore Dia. [Ångstrom]	Tortuosity Factor
19 Permion 300 (modif. polyethylene)	34.8	75	7.5
19 Mipor (polyethylene)	12.8	2300	2.1
26 Acropor WA	11.0	3200	2.7
15 PMA 80/20	63.5	300	4.7
16 PMA 83/17	39.6	350	5.4
17 PMA 95/5	22.3	300	3.2

TABLE 6

	(A) Wet Thickness [cm x 10^{-4}]	(B) Time to penetration [minutes]	(C) Ratio $\frac{B}{A}$ [min/cm x 10^{-4}]
Cellophane PUDO-300	71	117	1.6
Cellophane PUDO-300 + ethyleneimine	101	114	1.1
Cellophane PUDO-300 + $ZnCl_2$	79	139	1.8
Cellophane PUDO-300 + i-eugenol	76	150	2.0
Cellophane PUDO-300 + TDI	97	118	1.2
Cellophane PUDO-300 + m-phenylene-diamine	64	135	2.1
Cellophane PUDO-300 + p-phenylene-diamine	64	115	1.8
Cellophane PUDO-300 + hydroquionone	79	120	1.5
Cellophane PUDO-300 Ag treated (NASA C-19-300)	79	153	1.9
Cellophane PUDO-600 treated with triethanolamine + epichlorohydrin	89	126	1.4
Cellophane PUDO-600	102	158	1.6

Table 6, Cont.	(A)	(B)	(C)
Cellophane PUDO-600 Ag treated (NASA C-19-600)	112	310	2.8
Cellophane PUD 300 (20.3% glycerol)	58	63	1.1
Permion 600 (modif. cello.)	79	158	2.0
Cellophane 111-2 (exper.)	76	261	3.4
Clear Sausage Casing	216	1336	6.2
Clear Sausage Casing Ag Treated	214	1242	5.8
Fibrous Sausage Casing			
rough side facing Zn	178	207	1.1
smooth side facing Zn	178	425	2.4
Fibr. Saus. Casing, Ag treated			
rough side facing Zn	185	242	1.3
smooth side facing Zn	185	415	2.2

Table 6, Cont.	(A)	(B)	(C)
Permion 300 Modified) polyethylene	36	117	3.2
Permion 1000 (modified polytetrafluoroethylene)	76	84	1.1
Mipor 34 PN (microporous polyvinylchloride)	147	64	0.4
Acropor WA	127	16	0.1
Polymethacrylic acid/polyethylene:			
PMA 90/10 (low crosslink)	191	190	1.0
PMA 83/17 (high crosslink)	152	367	2.4
Copolymers:			
Methacryl acid: vinyl alcohol	168	43	0.2
Methacryl acid: maleic anh.	135	35	0.3
Methacryl acid: i-propyl acrylamide	152	47	0.3

TABLE 7

Electrolyte Absorption and Retention at 26°C

Sample No.	Dry weight grams	Thickness cm x 10^{-4}		Volume cm^3 x 10^{-4}		Absorption		Retention	
		Dry	Wet	Dry	Wet	g	g/cc	g	g/cc
34	.1954	127	127	2458	2458	.487	1.983	.2313	.941
35	.2588	135	178	2613	3445	1.065	4.078	.5682	1.649
36	.2065	127	140	2458	2710	.680	2.769	.3654	1.348
37	.2175	114	127	2206	2458	.703	3.189	.3203	1.452

TABLE 8

Electrical Resistance (Ohms) in 31% KOH at 26°C After Different Soaking Times

Sample No.	Material	5 min	10 min	20 min	1 hr	24 hrs
34	Methacryl ac. + vinyl alc., 1:4	0.517	0.403	0.327	0.338	0.242
35	Methacryl ac. + vinyl alc., 4:1	0.191	0.175	0.162	0.155	0.155
36	Methacryl ac. + vinyl alc., 1:1	0.193	0.168	0.157	0.141	0.137
37	Methacryl ac. + maleic anh. 1:1	0.170	0.163	0.166	0.163	0.162

TABLE 9

Electrical Resistance in 31% KOH in 31% KOH at 26°C

		R_0 [ohm]	Wet Thickness [in. x 10^{-4}]	[cm. 10^{-4}]	R_1 ohm-in^2	ρ ohm-cm
34	Methacr. ac.-vinyl alc. (1:4)	0.242	45	114	0.036	20.3
35	Methacr. ac.-vinyl alc. (4:1)	0.155	66	168	0.023	9.0
36	Methacr. ac.-vinyl alc. (1:1)	0.137	57	145	0.021	9.2
37	Methacr. ac.-maleic anh.(1:1)	0.162	53	135	0.024	12.5

R_0 = observed resistance values after 24 hrs soaking,
exposed separator area = 0.15 in^2

R_1 = resistance at actual wet thickness

ρ = specific resistivity

TABLE 10

Dimensional Changes in 31% KOH at -26°C

Sample No.	Copolymer	70 hrs			7 days		
		Length	Width	Thickness	Length	Width	Thickness
34	Methacr. ac. vinyl alc. (4:1)	+ 4	9	-2	+ 4	+ 9	-2
35	Methacr. ac. vinyl alc. (1:4)	+ 10	+ 23	+ 30	+ 11	+ 23	+ 40
36	Methacr. ac. vinyl alc. (1:1)	+ 7	17	+ 10	+ 7	+ 17	+ 17
37	Methacr. ac. maleic anh.	+ 2	+ 9	+ 20	+ 2	+ 9	+ 24

Sample No.	14 days			21 days			28 days		
	Length	Width	Thickness	Length	Width	Thickness	Length	Width	Thickness
34	+ 4	+ 0	0	+ 4	+ 9	9	+ 5	+ 9	0
35	+ 10	+ 23	+ 40	+ 10	+ 23	+ 40	+ 10	+ 23	+ 40
36	+ 7	+ 17	+ 17	+ 7	+ 17	+ 20	+ 7	+ 17	+ 20
37	+ 3	+ 10	+ 28	+ 3	+ 9	+ 33	+ 2	+ 11	+ 31

TABLE 11

Dimensional Changes in 31% KOH at + 26°C

Sample No.	Copolymer	70 hrs			7 days		
		Length	Width	Thickness	Length	Width	Thickness
34	Methacr. ac. vinyl alc. (1:4)	+5	+10	-5	+6	+9	-4
35	Methacr. ac. vinyl alc. (4:1)	+12	+26	+34	+12	+27	+37
36	Methacr. ac. vinyl alc. (1:1)	+6	+18	+5	+6	+18	+8
37	Methacr. ac. vinyl anh. (1:1)	+10	+12	+23	+9	+12	+50

Sample No.	14 days			21 days			28 days		
	Length	Width	Thickness	Length	Width	Thickness	Length	Width	Thickness
34	+6	+10	0	+6	+10	0	+5	+10	0
35	+12	+27	+50	+12	+27	+50	+12	+28	+50
36	+6	+18	+14	+6	+18	+14	+6	+18	+14
37	+10	+12	+46	+10	+12	+49	+10	+12	+45

TABLE 12

Dimensional Changes in 31% KOH at + 90°C

Sample No.	Copolymer	70 hrs			7 days		
		Length	Width	Thickness	Length	Width	Thickness
34	Methacr. ac. vinyl alc. (1:4)	+6	+10	-15	+6	+11	-10
35	Methacr. ac. vinyl alc. (4:1)	+13	+32	+25	+13	+32	+32
36	Methacr. ac. vinyl alc. (1:1)	+3	+25	+3	+12	+25	+15
37	Methacr. ac.	+13	+18	+27	+13	+18	+40

Sample No.	14 days			21 days			28 days		
	Length	Width	Thickness	Length	Width	Thickness	Length	Width	Thickness
34	+4	+10	-10	+4	+10	-8	+5	+10	-8
35	+14	+31	+25	+13	+32	+36	+13	+32	+36
36	+8	+18	+15	+12	+25	+15	+12	+25	+15
37	+10	+18	+40	+16	+25	+40	+16	+25	+43

Figure 2

Zinc Penetration in Cellophane PUDO-300
as a Function of Current x Time

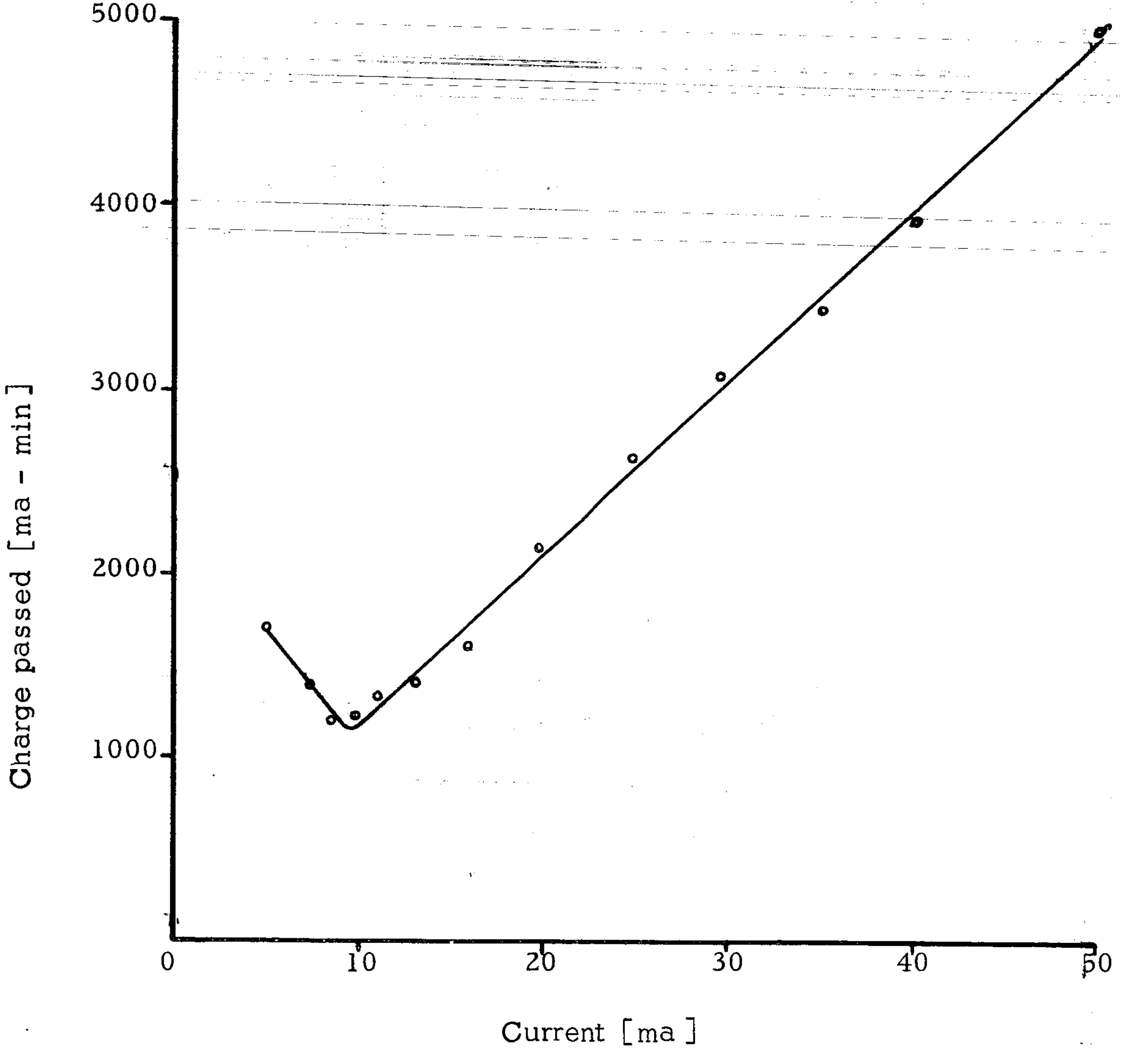
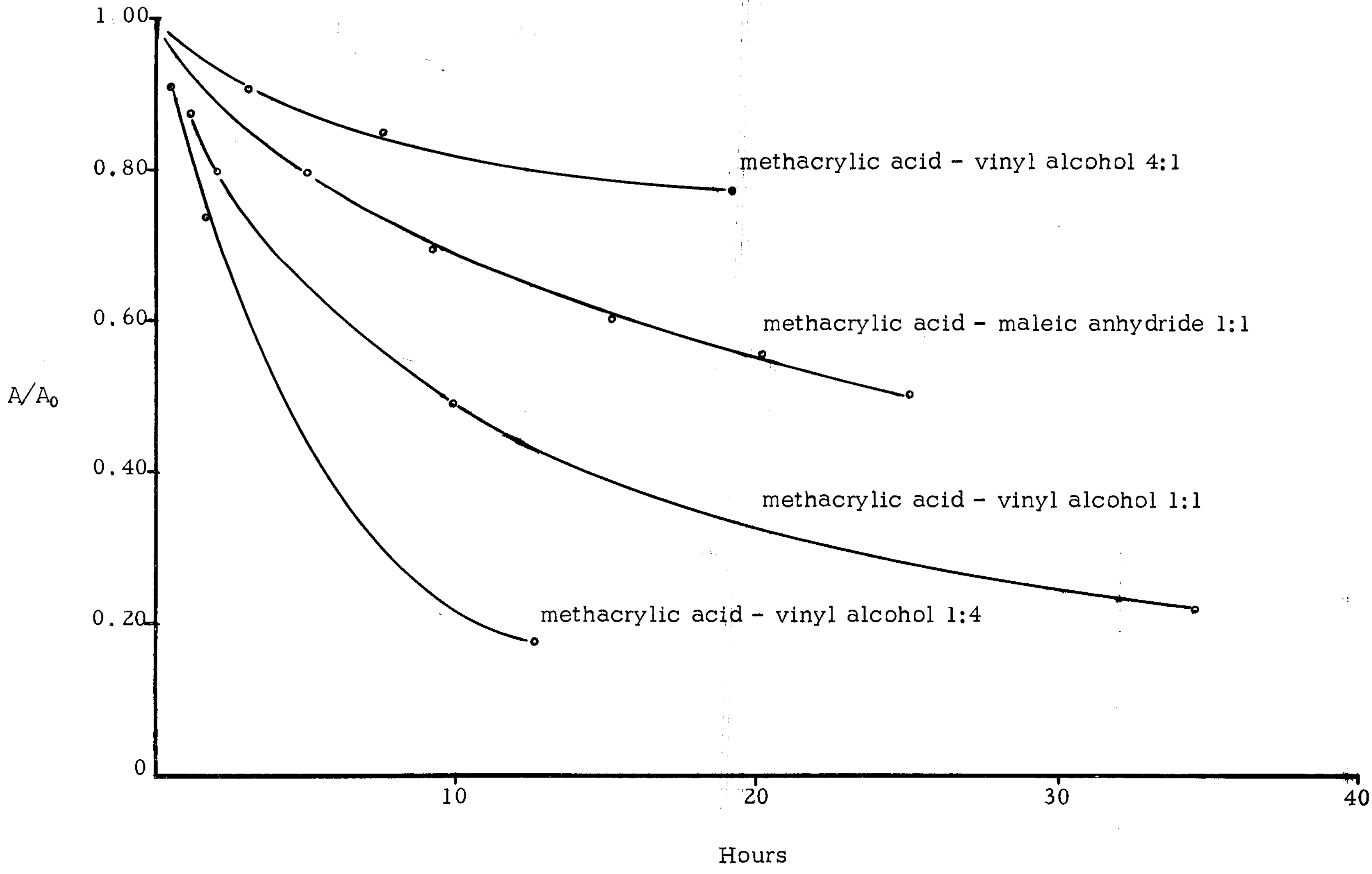


Figure 5

Ag reaction of Ion Exchange Co-Polymers



APPENDIX

Cell Tests

1. Test Cell Design

Twenty-five cells were delivered to Goddard Space Flight Center for test purposes Each cell contains 5 positive and 6 negative plates, with a rated capacity of 24 amp hrs The cell stack has been so designed that a constant free space ratio was maintained among the five separator systems used.

Each negative plate was wrapped in one layer of Viskon, 0.035 in. thick. Each positive plate was wrapped in one layer of Dynel EM 309 non-woven fabric.

Five separator systems were used:

a) Five cells (Nos. 1 - 5): 8 layers of Cellophane PUD-O-300.
b) Five cells (Nos. 6 - 10):

   1. Three layers of Cellophane PUD-O-300, treated with tolylene diisocyanate - nearest to the positive - followed by

   2. Five layers of Cellophane PUD-O-300 (untreated).

c) Five cells (Nos. 11 - 15):

   1. Two layers Permion 300 - 40/30
   2. Two layers Cellophane PUD-O-300
   3. Two layers Fibrous Sausage Casing

d) Five cells (Nos. 16 - 20):

   1. One layer PMA 83/17
   2. One layer Cellophane PUD-O-300
   3. Two layers Fibrous Sausage Casing

e) Five cells (Nos. 21 - 25):

   1. Three layers Cellophane PUD-O-300, treated with m-phenylene diamine.

   2. Two layers Fibrous Sausage Casing

II. Test Program

Electric Storage Battery Cells with Modified Cellophane

Capacity (C) = 24 ampere hours

1. Electrolyte addition, potassium hydroxide, 40%
2. Add 65 cc to each cell, vacuum fill
   Allow to stand 72 hours
3. Conditioning cycles:
   a. Sixty (60) hour CP charge, current limit at 1.0 ampere and voltage limit at 1.97 per cell
   b. Level electrolyte to top of plates (add or subtract)
   c. Discharge at C/5 to 1.3 volts per cell
   d. Recharge to C/20 for 24 hours
   e. Discharge at C/5 to 1.3 volts. After 12 ampere hours have been removed, pulse at C/3 rate for 5 seconds and the C rate for 5 seconds.
4. Life test cycles
   a. Start after the two conditioning cycles
   b. Charge at C/20 amperes to give an input of 120% of the previous discharge
   c. Stand in the charged state for 16 hours
   d. Discharge at C/5 amperes to 1.3 volts per cell
   e. Stand in the discharged state 1 to 5 hours
   f. Repeat b through e.

   Cycle until the output of 60% of C or less

During the cycle tests, add ESB supplied 20% KOH as needed, with the cells in the charged state, to bring the electrolyte level up to the top of the plates. Measure amount of electrolyte added and time of addition.

Photograph 1

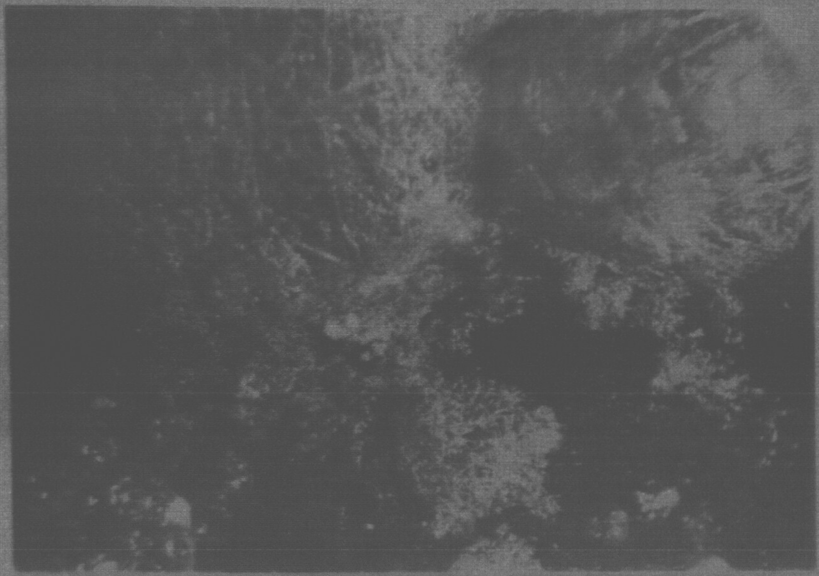


FIGURE 3 X7

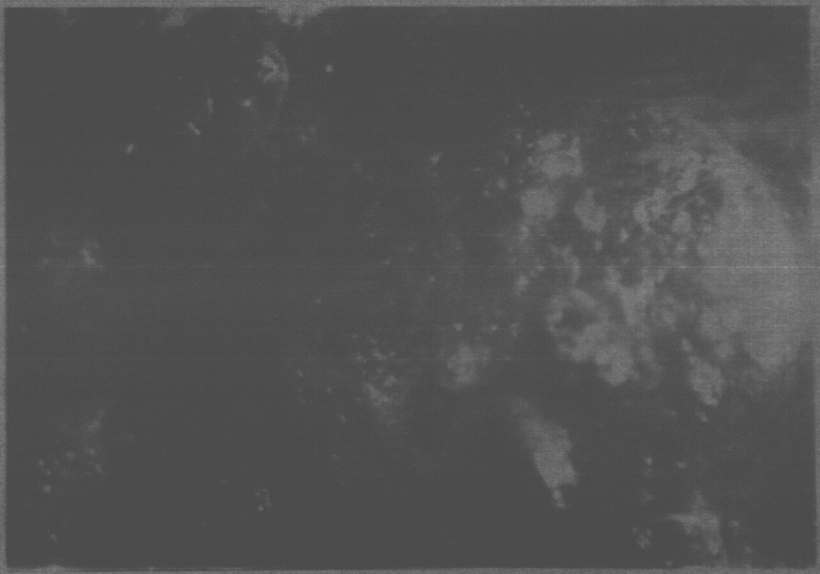


FIGURE 4 X7