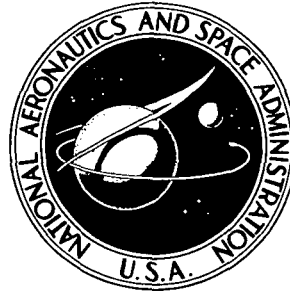


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**FUNCTIONING OF INORGANIC/ORGANIC BATTERY  
SEPARATORS IN SILVER-ZINC CELLS**

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16. Abstract <p>The results of three experimental studies related to the inorganic/organic battery separator operating mechanism are described: saponification of the plasticizer, resistivity of the simulated separators, and zincate diffusion through the separators. The inorganic/organic (I/O) separator appears to be a particular example of a general class of ionic conducting films composed of inorganic fillers and/or substrates bonded together by an organic polymer containing an incompatible plasticizer that may be leached by the electrolyte. The I/O separator functions as a microporous film of varying tortuosity with essentially no specific chemical inhibition to zincate diffusion.</p>			
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# FUNCTIONING OF INORGANIC/ORGANIC BATTERY SEPARATORS IN SILVER-ZINC CELLS

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## SUMMARY

This report presents the results of three experimental studies on inorganic/organic (I/O) separators and their components. Experiments concerned saponification of the plasticizer, ionic resistivity of simulated I/O separators, and zincate diffusion through various I/O separators.

The I/O separator used in the NASA Lewis silver-zinc cells appears to be a particular example of a general class of ionic conducting films composed of inorganic fillers and/or substrates bonded together by an organic polymer containing an incompatible plasticizer that may be leached by the electrolyte. This I/O separator is a microporous film of varying tortuosity with essentially no specific inhibition to zincate diffusion.

## INTRODUCTION

Separators used in silver-zinc (Ag-Zn) alkaline secondary batteries are often made from regenerated cellulose. Cells using regenerated cellulose separators usually fail because the separator deteriorates through oxidation of the cellulose by soluble silver species present in the concentrated aqueous potassium hydroxide (KOH) electrolyte. Efforts at the Astropower Company in the early 1960's to fabricate a better separator, in terms of resistance to chemical attack, led to the development of a separator fabricated from inorganic and organic components (ref. 1). This type of separator (Astropower I/O separator) is used at present in NASA Lewis Ag-Zn cells. It is made by coating pretreated asbestos sheet with a slurry composed of specially treated, calcia-stabilized zirconium dioxide ( $ZrO_2$ ) and pigmentary potassium titanate (PKT) suspended in a chloroform solution of polyphenylene oxide (PPO) and Plastolein P-9750,<sup>1</sup> a plasticizer. The resultant separator consists of an asbestos sheet covered on one side with a

<sup>1</sup>Emery Industries, Cincinnati, Ohio.

semiflexible surface coating. A more detailed procedure for slurry preparation and coating method is given by Sheibley in a recent report (ref. 2). This type of separator gives a much longer lifetime to a Ag-Zn cell than regenerated cellulose. The primary failure mode of Ag-Zn cells that use the I/O separator is internal short circuiting caused by zinc nodule growth.

The success of the Astropower I/O separator in Ag-Zn cell service has led to interest in its physical structure and mechanism of ionic conduction. Bozek (ref. 3) investigated the physical structure of the separator with a scanning electron microscope. The surface is described as a very thin membrane or skin of organic material. Micrometer-size holes numbering about  $10^5$  to  $10^6$  per square centimeter of the surface area penetrate this skin. Under the skin is a porous region composed of the specially treated, calcia-stabilized  $ZrO_2$  and PKT particles bonded with an organic polymer. Bozek (ref. 3) studied PPO films (cast on glass) containing the various components of the I/O slurry composition. He reports that the presence of both plasticizer and inorganic fillers is necessary for good ionic conductivity in 45 percent aqueous KOH.

Our investigation of the I/O separator was conducted to gain a fundamental understanding of those separator characteristics that are pertinent to its successful use in alkaline Ag-Zn secondary batteries. The report presents the results of three different studies with this aim in mind: saponification of the plasticizer, resistivity of simulated I/O separators, and zincate diffusion rates through the separators. By these studies we have determined some of the fundamental factors in the formulation of an I/O separator and postulated a mechanism for its ionic conduction. Finally, we discuss possible reasons for the good performance of the Astropower I/O separator.

The experimental details are given in the appendix.

## SAPONIFICATION OF PLASTICIZER

In the formulation of the Astropower I/O separator, a relatively large proportion of P-9750 plasticizer is used; the weight ratio of polymer (PPO) to P-9750 is about 1:1 (ref. 2). This is an anomaly from the normal art of polymer film making. Cast films made from chloroform solutions of equal parts of PPO and P-9750 are somewhat translucent, indicating that the P-9750 and PPO are not completely miscible. In this report, such immiscibility between polymer and plasticizer is referred to as incompatibility.

### Saponification Products

Plastolein P-9750 is a viscous polyester of the condensation polymer type that readily saponifies in aqueous KOH. Our analysis of these saponification products shows

them to be the potassium salt of azelaic acid ( $\text{HOOC}(\text{CH}_2)_7\text{COOH}$ ) and 1,2 propanediol ( $\text{CH}_3\text{CHOHCH}_2\text{OH}$ ) with minor amounts of a low-melting organic acid impurity, probably pelargonic acid.

### Saponification in Cast Films and Inorganic/Organic Separator

Although P-9750 saponifies readily in aqueous KOH, we found that at room temperature it does not saponify when incorporated into cast films of I/O separators. The measurements were made by means of both transmission and multiple-internal-reflection infrared spectroscopy. This lack of saponification was evident even after long exposures (300 hr) to 45 percent KOH at room temperature.

At  $100^\circ\text{C}$ , however, saponification of the plasticizer in the cast film did take place (determined by transmission infrared spectroscopy (IR)) but at a relatively slow rate. This is shown by the solid curve in figure 1, which is a plot of the ratio of unsaponified P-9750 to PPO in the cast film as a function of exposure time in 45 percent aqueous KOH at  $100^\circ\text{C}$ . The other data in figure 1 (obtained by multiple-internal-reflection spectroscopy (MIR)) illustrate the saponification in the surface region of both the cast film and the I/O separator. Both sets of data can be fit by the same dashed curve. The saponification in the I/O separator could not be studied by transmission IR because of its opaqueness. However, in that the rate of P-9750 saponification in the bulk of the film is slower than on the surface, the saponification rate in the bulk of the I/O separator may be slower than that observed for the surface of the separator.

There is a sharp decline in the ratio of unsaponified P-9750 to PPO for all the curves (fig. 1) during the first 200 minutes of exposure to the hot KOH solution followed by a flat portion of the curve beyond this time. Thus, practically all saponification occurs during the first 200 minutes of exposure. A correlation can now be made between saponification of the P-9750 and the ionic conductivity of the separator by reference to Sheibley's findings on the conductivity of conditioned I/O separators (unpublished work by D. W. Sheibley of Lewis). Sheibley found that the ionic conductivity of the separator approached a maximum and constant value after about 3 hours of conditioning in 45 percent aqueous KOH at  $100^\circ\text{C}$ . It is reasonable to assume that the conductivity arises as a result of the saponification process.

Figure 1 also shows that even after 1440 minutes, some of the P-9750 in both the cast film and the I/O separator remained unsaponified. At the same time, some potassium azelate was detected (by IR); thus, it appears that some of the saponification product remained unleached.

## Apparent Loss of Plasticizer

The data in figure 1 show that for both the untreated (zero time) I/O separator and the untreated cast film, the ratio of P-9750 to PPO is somewhat less than the 1:1 ratio used in the original formulation (i. e. , about 0.6:1). This implies that some P-9750 is lost during fabrication. In the case of the cast film, some P-9750 remained on the glass during casting. In the case of the separator, the P-9750 (being a liquid) may have diffused through the asbestos more quickly than did the PPO. Indeed, the presence of P-9750 was detected on the back uncoated side of the asbestos substrate, while no increase in PPO was found. In both cases P-9750 appears to be readily adsorbed on inorganic solids.

## CONDUCTIVITY OF SIMULATED INORGANIC/ORGANIC SEPARATORS

Previous investigations at Lewis (refs. 2 and 3) and the results of our study of P-9750 chemistry suggest that high conductivity is not unique for a specific polymer (PPO), plasticizer (P-9750), and filler composition (PKT + treated calcia-stabilized  $ZrO_2$ ). Rather it involves the general properties of a polymer-plasticizer-filler system. Thus, a separator composed of another polymer, plasticizer, and filler could exhibit conductivity characteristics similar to those of the Astropower I/O separator. As indicated in the subsequent discussion, resistivity measurements on films comprising a variety of polymers, plasticizers, and fillers support this idea.

### Effect of Additives Other Than Plastolein P-9750

Table I gives the area resistivity, in 45 percent KOH electrolyte, of cast films and asbestos impregnates made from PPO and various additives with varying solubility properties in the PPO and the electrolyte. All of the purely organic cast films (including those with no additive) were highly resistive ( $R_1$  and  $R_2$ ) in KOH electrolyte regardless of the additive. However, certain asbestos impregnates exhibited low ionic resistance ( $R_3$  and  $R_4$ ) in this medium. This agrees with earlier work (ref. 3) that implies that an inorganic filler, as well as the proper organic additive, is requisite for good ionic conductivity.

The additives were selected to have varying solubility in the final PPO cast film and in the electrolyte. Insolubility in the PPO was denoted by the partial translucence of the film. Cast films containing Plastolein P-9750, 1,2-propanediol, and azelaic acid were somewhat translucent, indicating insolubility (incompatibility) with the polymer: Asbes-

tos impregnates involving these additives, particularly when conditioned in 45 percent KOH at 100° C for 24 hours, were good conductors ( $R_4$ ). In contrast, the cast films obtained with PPO and dibenzylether or 1-butanol were transparent, indicating complete solubility of the PPO and the additive components. The asbestos impregnates involving these additives were poor conductors. Thus, an apparent criterion for good ionic conductivity, at least in the impregnates, seems to be the use of an additive that is insoluble in the polymer.

When the impregnated asbestos sample containing P-9750 was not conditioned at 100° C in 45 percent KOH, it was not a good conductor. This is undoubtedly associated with our finding that P-9750 does not saponify to any extent at room temperature when incorporated with PPO in cast films or in the I/O separator. At elevated temperatures, saponification does occur and one saponification product, 1,2-propanediol, is soluble in 45 percent KOH; the other product, potassium azelate is perhaps slightly soluble. (Potassium azelate is readily soluble in water, but its solubility decreases in concentrated KOH solution.) The other incompatible additives tested, 1,2-propanediol and azelaic acid, are likewise somewhat soluble without saponification in 45 percent KOH. Thus, solubility of the additive or its saponification product in the electrolyte appears to be another requirement for conduction.

The idea that high conductivity of PPO films is related to the solubility of the additive in the electrolyte was previously demonstrated by Sheibley's work (ref. 2) on the resistivity of fiberglass-supported PPO films containing several polyester plasticizers derived from adipic acid. After conditioning the films in hot aqueous KOH, Sheibley found that the resistivity was lowest for those films containing ester plasticizers that saponify in KOH solution to short-chain, water-soluble glycols (e. g., 1,2-propanediol and ethylene glycol; ref. 2, table IV).

#### Effect of Various Fillers

Table II gives the area resistivity of membranes cast from slurries comprising a solution of PPO and 1,2-propanediol in chloroform with various insoluble fillers suspended in the solution. About the same volume ratio of filler to PPO (~0.35) was used for each filler incorporated into the casting slurry. Good conducting films in 45 percent aqueous KOH electrolyte were obtained for all inorganic fillers tested. In contrast the film containing polyethylene powder exhibited high resistivity. Thus, the data indicate that the formation of a membrane with good conduction requires a polar filler.

## Effect of Another Polymer

Table III shows that a polymer other than PPO can be used to fabricate ionic conducting films. Polymethylmethacrylate (PMM), a polymeric material of different molecular structure than PPO, results in even lower resistance. As can be seen in table III, the same additive solubility properties (insoluble in the polymer but soluble in the electrolyte) also apply for PMM films. For cast films the difference in resistivity between films containing an insoluble additive (1,2 propanediol) and those containing a soluble additive (1-butanol) is significant but not as impressive as in PPO films. Nevertheless with PMM films and especially in PMM-impregnated asbestos, the need for the proper additive is apparent for good conducting separators. When no additive is used, the area resistivity of the PMM asbestos impregnate in 45 percent aqueous KOH is at least 20 times that for a similar sample involving the additive 1,2-propanediol.

## ZINCATE DIFFUSION THROUGH SEPARATORS

Our next experiments were aimed to find out if some of the success of the Astropower I/O separator in Ag-Zn batteries could be due to the separator inhibiting the diffusion of zincate. In other words, we wanted to know if the ratio of zincate diffusion rate to conductivity for the I/O separator was the same as for cellulose. Along with this work, we determined the zincate diffusion rate and the conductivity of several PPO cast films containing various fillers. The constant ratio of zincate diffusion rate ( $r$ ) to conductivity ( $1/\rho$ ) should yield a straight line with a slope of -1 if  $\log r$  is plotted against  $\log (1/\rho)$ , because

$$r = \frac{K}{\rho}$$

or

$$\log r = - \log \rho + \log K$$

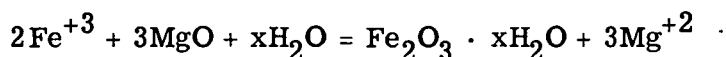
where  $K$  is a proportionality constant and  $\rho$  is the area resistivity.

In figure 2 we have drawn such a line; the position of the line is based on the average proportionality constant  $K$  calculated from the data points (except  $\nabla 13A$ ). The average deviation of  $K$  is 38 percent. We can attribute much of this to variation within an individual sample batch. The line in figure 2 shows that all separators and films tested have essentially the same ratio of zincate diffusion rate to conductivity. Thus,



the I/O separator, as well as all cast films tested, is no more or no less specific to the zincate ion than is cellulose. The performance of the I/O separator can therefore not be attributed to any appreciable interaction with the zincate ion. Moreover, figure 2 indicates that, by changing fillers or using thicker films, the zincate diffusion rate may be decreased but at the expense of a proportionally lower conductivity.

Basically, none of the fillers used are more specific to the zincate ion than any of the other fillers tested. However, this does not imply that a reactive filler or additive in an I/O-type separator could not inhibit the diffusion of a particular ion. In fact, we have demonstrated this for the diffusion of ferric ion (in 0.1 molar  $\text{Fe}(\text{NO}_3)_3$  and 0.05 molar  $\text{HNO}_3$ ) through an I/O-type film containing MgO of the same composition as film 4 of figure 2. For this case, the initial ferric ion diffusion rate was roughly three orders of magnitude less than that for films containing unreactive fillers (i. e. , magnesium silicate, mullite,  $\text{ZrO}_2$ , and PKT) with similar conductivities. After exposure of the membrane to a solution containing ferric ion for several hours, a brown deposit (probably hydrated ferric oxide) was observed in the film. Thus, there was an ion exchange between the ferric ion in solution and the divalent magnesium in the membrane according to the reaction



This suggests that the filler particle must be in contact with the ferric nitrate solution. It is logical, then, to assume that for the I/O separator in aqueous 45 percent KOH, the filler particle is likewise exposed to the electrolyte.

## GENERAL DISCUSSION

### Criteria for Conductivity in Inorganic/Organic Separators

Based on the results of the present investigation as well as other studies sponsored by Lewis (refs. 2 to 4), we believe that the Astropower inorganic/organic (I/O) separator, as far as conduction mechanism is concerned, represents one specific example of a broad general class of ionic conducting separator systems. The fabrication of this general type of membrane involves the following:

- (1) A volatile solvent (e. g. , chloroform)
- (2) A polymeric material (e. g. , polyphenylene oxide (PPO)) that is soluble in the solvent and stable in the electrolyte used (e. g. , 45 percent potassium hydroxide (KOH))
- (3) An inorganic polar filler or substrate that is insoluble in the solvent and polymer

- (e. g. , pigmentary potassium titanate (PKT), asbestos,  $ZrO_2$ ).
- (4) An additive (termed a plasticizer in the Astropower I/O separator; e. g. , Plastolein P-9750) that is soluble in the solvent. In the quantity used, a significant proportion of the additive must be insoluble in the polymeric material following evaporation of the solvent. The additive or its reaction products with the electrolyte must be soluble in the electrolyte.

### Mechanism of Conductivity

In order to account for the ionic conductivity of the Astropower I/O separator in terms of our summarized criteria, we have postulated a simplified mechanism. We will begin by discussing the glass cast film and then apply our reasoning to the Astropower I/O separator. It is first necessary to visualize the formation of a cast film from a suspension of an inorganic filler in a solution of a polymer and a suitable additive in a volatile solvent. After casting the film on glass, the solvent evaporates and this causes the additive to precipitate because of its insolubility in the polymer. Based on our observation that some additives (Plastolein P-9750 and 1,2 propanediol) adhere to the glass, we speculate that they also adhere to the inorganic filler in the polymer matrix. The deposition of the additive around the filler is illustrated in figure 3. We attribute the adherence to adsorption of the additive on the filler; this is to be expected because of the polar functional groups (e. g. , hydroxyl (-OH), carboxyl (-COOH), and ester (-COOR)) present on the organic additive molecule.

When the cast film is exposed to the electrolyte, the additive, if soluble in the electrolyte, dissolves and is eventually replaced by the electrolyte. When P-9750 or other polyesters are used, any dissolution must be preceded by saponification. This results in electrolyte channels comparable in size with the filler particles, which are of micrometer size. The random placement of the filler particles leads to varying tortuosity of the conducting channels. In that the coating on the Astropower I/O separator can be considered analogous to a cast film, we postulate that the ionic conductivity of the Astropower separator involves the same mechanism.

### Effectiveness of Inorganic/Organic Separators

There appears to be no significant hindrance to zincate diffusion through the I/O separator when compared with cellulose and with films containing a variety of fillers. The success of the I/O separator may still be attributable to its good durability in concentrated KOH electrolyte, its chemical stability to silver ion attack, its low resistivity,

and its good homogeneity with respect to conductivity. This last property, uniform conductivity, is considered to be important in retarding zinc penetration. Zinc dendrite formation is generally thought to arise at local regions of high current density. Such a local region would be a small area of the separator that had a relatively low resistance with respect to the separator as a whole. A low-resistance area may be a defect or pin hole in the film. It is known that the presence of treated, crystalline, calcia-stabilized  $ZrO_2$  in the I/O separator retards zinc penetration (ref. 2).

A better understanding of the functioning of I/O-type separators should lead to improvements in existing formulation and fabrication methods. However, with the exception of the initial additive (plasticizer) saponification reaction, the operation of I/O-type films and separators appears to be physical in nature rather than a chemical phenomenon.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, November 20, 1975,  
506-16.

## APPENDIX - EXPERIMENTAL DETAILS

### Fabrication of Films and Asbestos Impregnates

The first step in preparing cast films was to dissolve the specified amount of solid powdered polymeric material (generally, polyphenylene oxide (PPO)) in chloroform. The plasticizer was then added and the mixture was stirred until all components went into solution. For films containing fillers, the chloroform solution and then the desired amount of filler were poured into a ball mill. The mixture was then milled for about 24 hours. The resulting slurry was made into films by casting on smooth glass with a Gardner blade and allowing the chloroform to evaporate. The milling operation was omitted in making films with no filler.

The asbestos impregnates were made by immersing 5-centimeter by 5-centimeter (2-in. by 2-in.) sheets overnight in the polymer solution or in the milled slurry. The following day the slurry was stirred occasionally over a 2-hour period, excess liquid was drained off, and the impregnated sheets were suspended on clips to air dry at room temperature.

The regenerated cellulose used in these experiments was a commercial product, and I/O separator samples were cut from completed pockets made for use in Lewis Research Center battery projects. Plastolein P-9750, calcia-stabilized zirconium dioxide, pigmentary potassium titanate, and polyphenylene oxide powder were also materials normally used at Lewis for the fabrication of I/O separators. All other materials used in separators and films were in general high-quality, commercial-grade products.

### Resistance Measurements

The procedure and apparatus used in our direct-current resistance measurements of films and asbestos impregnates are described in an Air Force Aero Propulsion Laboratory publication on screening methods for battery separators (ref. 5).

### Hydrolysis Experiments on the Plasticizer Plastolein P-9750

Hydrolysis experiments were performed on the I/O separator and glass cast films containing a 1:1 weight ratio of Plastolein P-9750 to PPO. The percentage of P-9750 saponification was determined by transmission infrared spectroscopy (IR) for the film and by multiple-internal-reflection infrared spectroscopy (MIR) with a 30° KRS5 prism for the surfaces of both the film and the I/O separator. The peak at about 1725 centimeters<sup>-1</sup> (carbonyl stretching) was used as a measure of the P-9750 content, and the

peak at 1595 centimeters<sup>-1</sup> (a readily measureable peak) was used as a measure of the PPO content. The results are reported in terms of the weight ratio of P-9750 to PPO. Conversion of peak height ratio to weight ratio was accomplished by calibration using known ratios of P-9750 to PPO in potassium bromide (KBr) pellets. In the MIR determinations, the measured intensity of the 1595-centimeters<sup>-1</sup> band had to be decreased by 8 percent because of the 8 percent greater penetration at 1595 centimeters<sup>-1</sup> than at 1725 centimeters<sup>-1</sup> (ref. 6, p. 30).

Specimens were always used in pairs (one about 50 mm by 19 mm and the other 47 mm by 19 mm; these dimensions were dictated by the size of the KRS5 prism used). Following the initial IR measurements of the specimens, the specimens were treated for 10 minutes in 45 percent aqueous KOH at 100<sup>o</sup> C, rinsed in 1 molar hydrochloric acid (HCl) at room temperature for 2 minutes, then rinsed for several seconds in distilled water, and finally allowed to dry in air for a day. The IR measurements were then made on the treated samples. The treatments and measurements were repeated at selected time intervals on the same sample for a total of 24 hours exposure to the hot KOH solution. The acid treatment of the sample was required to prevent interference from carbonate in the IR spectrum. Auxiliary experiments without HCl treatment indicated that the HCl had no significant effect on the hydrolysis of the P-9750.

#### Determination of Zincate Diffusion Rates through Membranes and Separators

The zincate diffusion rates through membranes and separators were determined by a modification of a standard method based on a concentration cell technique (ref. 5, p. 115). A drawing of our disassembled apparatus is shown in figure 4. One of the modifications was the use of a small diffusate compartment. Its purpose was to yield higher concentration changes of zincate per unit time than would the standard method. Thus, it was possible to determine the low rate of diffusion exhibited by some of the films investigated. The use of a small diffusate compartment, however, prevented stirring. This may have, in turn, caused errors in each measurement. But any error is probably somewhat proportional to the rate measured, so comparison of values is meaningful.

Prior to the test, the zinc electrodes were amalgamated by placing them in a saturated mercuric chloride solution for 2 minutes. They were then rinsed with distilled water and dried. Platinum contacts were used because of the brittleness of the amalgamated zinc electrode. The separator sample to be tested was used to separate the two compartments. After the cell was assembled, 45 percent aqueous KOH was introduced into one half-cell compartment; and an aqueous solution, 1.25 molar in zincate ion and 45 percent KOH, was introduced into the other half-cell compartment. Solutions

were introduced by means of a hypodermic syringe. The volume of each compartment was 0.9 centimeter ( $\pm 5$  percent); the diffusion area was 2.8 square centimeters. Voltages were measured with either a strip-chart recorder or a digital recorder printout system over a period of several hours for each film.

Our modified method of using the zincate source compartment as one of the half cells lends itself to a simple mathematical treatment as compared with the standard method, as follows:

$$E = \left( \frac{-RT}{2F} \right) \left( \ln \frac{C}{C_s} \right) \quad (A1)$$

and

$$C = \left( \frac{Art}{V} \right) + C_0 \quad (A2)$$

where

E voltage between electrodes, volts

R universal gas constant (8.313 J/mol/K)

T absolute temperature, K

F Faraday (96 500 coulombs)

C zincate ion concentration in diffusate compartment, moles/cm<sup>3</sup>

C<sub>s</sub> zincate ion concentration in source compartment (assumed constant), moles/cm<sup>3</sup>

A diffusion area, cm<sup>2</sup>

r diffusion rate, moles/cm<sup>2</sup>/min

t time, min

V volume of diffusate compartment, cm<sup>3</sup>

C<sub>0</sub> initial value of C, moles/cm<sup>3</sup>

From equation (A1)

$$e^{-2EF/RT} = \frac{C}{C_s} \quad (A3)$$

Substitution of equation (A2) and rearrangement yield

$$rt = \left( \frac{VC_s}{A} \right) e^{-2EF/RT} + \frac{VC_0}{A} \quad (A4)$$

By means of equation (A4), values of  $r$  were calculated by least-squares fit of  $e^{-2EF/RT}$  against  $t$ . Correlation coefficients were usually about 0.995. The value obtained for cellulose is comparable with literature values. Our diffusion rates were also compared with values we obtained by using atomic absorption spectroscopy on the diffusate compartment; agreement was within 20 percent.

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TABLE I. - RESISTIVITY OF FILMS AND COATED ASBESTOS MADE FROM  
POLYPHENYLENE OXIDE (PPO) AND A VARIETY OF ADDITIVES

[Formulation (solution): 150 milliliters chloroform, 20 g PPO, and 5 g additive; electrolyte: 45 percent aqueous KOH at 20° C.]

Additive	Cast films			Asbestos impregnate	
	Appearance of cast films	Not conditioned, <sup>a</sup>	Conditioned, <sup>b</sup>	Not conditioned, <sup>a</sup>	Conditioned, <sup>b</sup>
		R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
Resistance, ohm-cm <sup>2</sup>					
Plastolein P-9750	Translucent	1250	1180	240	1.7
1,2-Propanediol	Translucent	790	790	7.9	3.3
Azelaic acid	Translucent	(c)	(c)	12	6.3
Dibenzylether	Clear	1020	(c)	790	126
1-Butanol	Clear	1500	1200	390	157
No additive	Clear	2600	1350	710	314

<sup>a</sup>Specimen exposed to 45 percent aqueous KOH at 20° C for 24 hr prior to test.

<sup>b</sup>Specimen exposed to 45 percent aqueous KOH at 100° C for 24 hr prior to test.

<sup>c</sup>No film.

TABLE II. - RESISTIVITY OF GLASS CAST FILMS OF POLYPHENYLENE  
OXIDE (PPO) CONTAINING A VARIETY OF FILLERS

[Formulation: 150 milliliters CHCl<sub>3</sub>, 20 g PPO, 5 g 1,2-propanediol, and filler (volume ratio of filler to PPO = 0.35); film wet thickness: 0.051 cm (20 mil); electrolyte: 45 percent KOH at 20° C; film exposure: 45 percent KOH at 20° C for 24 hr prior to test.]

Filler	Resistivity, ohm-cm <sup>2</sup>
Magnesium oxide . . . . .	5.4
Zirconium dioxide . . . . .	11.5
Magnesium silicate . . . . .	2.7
Mullite . . . . .	1.0
Potassium titanate . . . . .	2.9
Potassium azelate . . . . .	2.0
Polyethylene powder . . . . .	<sup>a</sup> 400
No filler . . . . .	<sup>b</sup> 790

<sup>a</sup>Considerable variation in resistivity. Individual values varied from 200 to 600 ohm-cm<sup>2</sup>.

<sup>b</sup>Taken from R1 of table I.

TABLE III. - RESISTIVITY OF FILMS AND ASBESTOS IMPREGNATES BASED  
ON POLYMETHYLMETHACRYLATE (PMM) AND THOSE  
BASED ON POLYPHENYLENE OXIDE (PPO)

[Formulation: 150 milliliters  $\text{CHCl}_3$ , 20 g PMM or PPO, and 5 g additive;  
electrolyte: 45 percent aqueous KOH at 20° C; specimen exposure:  
45 percent KOH at 20° C for 24 hr prior to test.]

Specimen	No additive	Soluble additive 1-butanol <sup>a</sup>	Insoluble additive 1, 2-propanediol <sup>b</sup>
	Resistivity, ohm-cm <sup>2</sup>		
Asbestos impregnated with PPO formulation (see headnote)	710	390	7.9
Asbestos impregnated with PPM formulation (see headnote)	58	20	2.7
PPO cast film with 0.051-cm (20-mil) wet thickness; formu- lation (see headnote) + 30-g- MgO filler	---	47	3.2
PPM cast film with 0.051-cm (20-mil) wet thickness; formu- lation (see headnote) + 30-g- MgO filler	---	8.2	1.4

<sup>a</sup>Solubility of 1-butanol with polymer is indicated by transparency of cast film without filler.

<sup>b</sup>Insolubility of 1, 2-propanediol with polymer is indicated by translucency of cast film without filler.

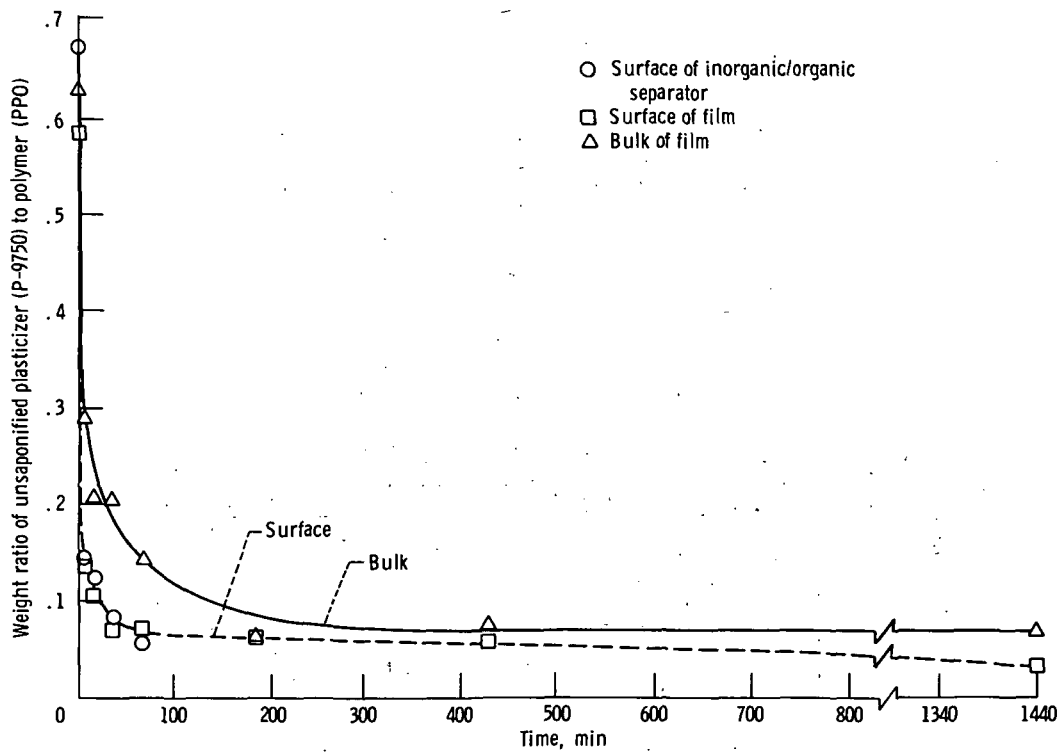


Figure 1. - Hydrolysis of Plastolein P-9750 in films exposed to 45 percent potassium hydroxide (KOH) electrolyte at 100° C. 1:1 PPO/P-9750 used in formulation.

- ▽ Conditioned at least 24 hr in 45 percent aqueous KOH at room temperature
- △ Conditioned at least 12 hr in 45 percent aqueous KOH at 100° C

- A Dry thickness of film, 70 μm
- B Dry thickness of film, 35 μm

- 1 Regenerated cellulose 90 μm thick
- 2 Complete Astropower I/O separator
- 3 20 g mullite
- 4 23 g magnesium oxide
- 5 20 g magnesium silicate
- 6 37 g treated calcia-stabilized zirconium dioxide (material used in I/O separator)
- 7 37 g zirconium dioxide (unstabilized)
- 8 21 g pigmentary potassium titanate (PKT)
- 9 30 g PKT
- 10 15 g polyethylene powder
- 11 15 g polyethylene powder and 15 g PKT
- 12 15 g potassium azelate
- 13 150 milliliters chloroform; 20 g PPO; 5 g P-9750; and 30 g PKT
- 14 150 milliliters chloroform; 20 g PPO; and 21 g potassium azelate

Films cast on glass and having following formulation: 150 milliliters chloroform; 20 g PPO; 5 g 1, 2 propanediol; plus fillers indicated

Films cast on glass with these formulations

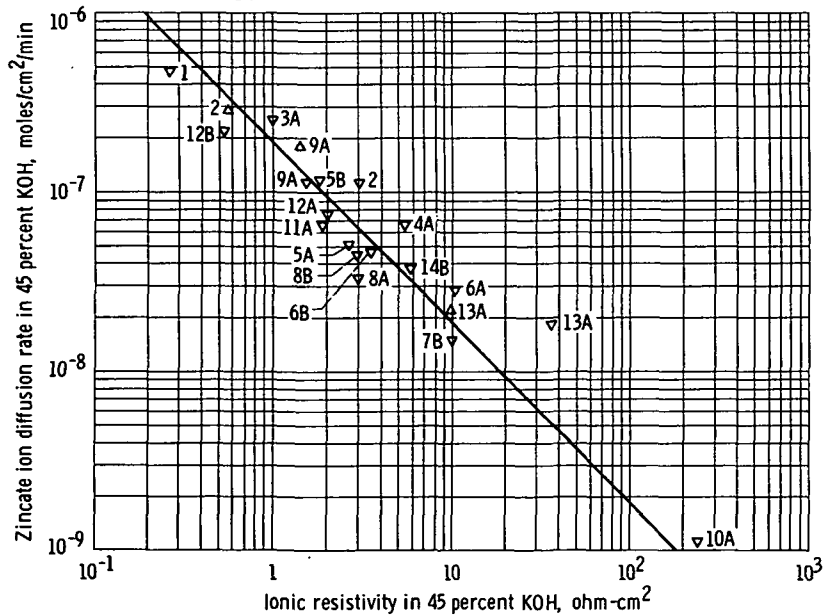


Figure 2. - Correlation of ionic resistivity with zincate ion diffusion rate for various separators in 45 percent aqueous potassium hydroxide (KOH) electrolyte.

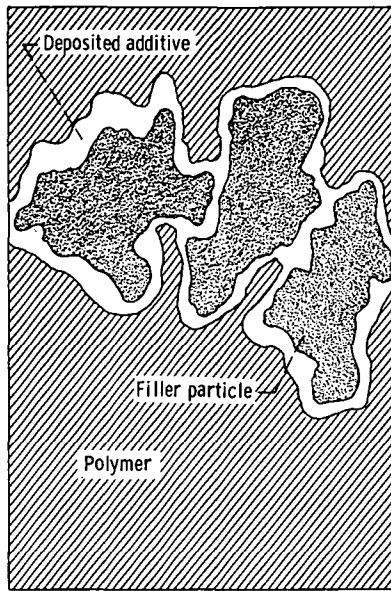
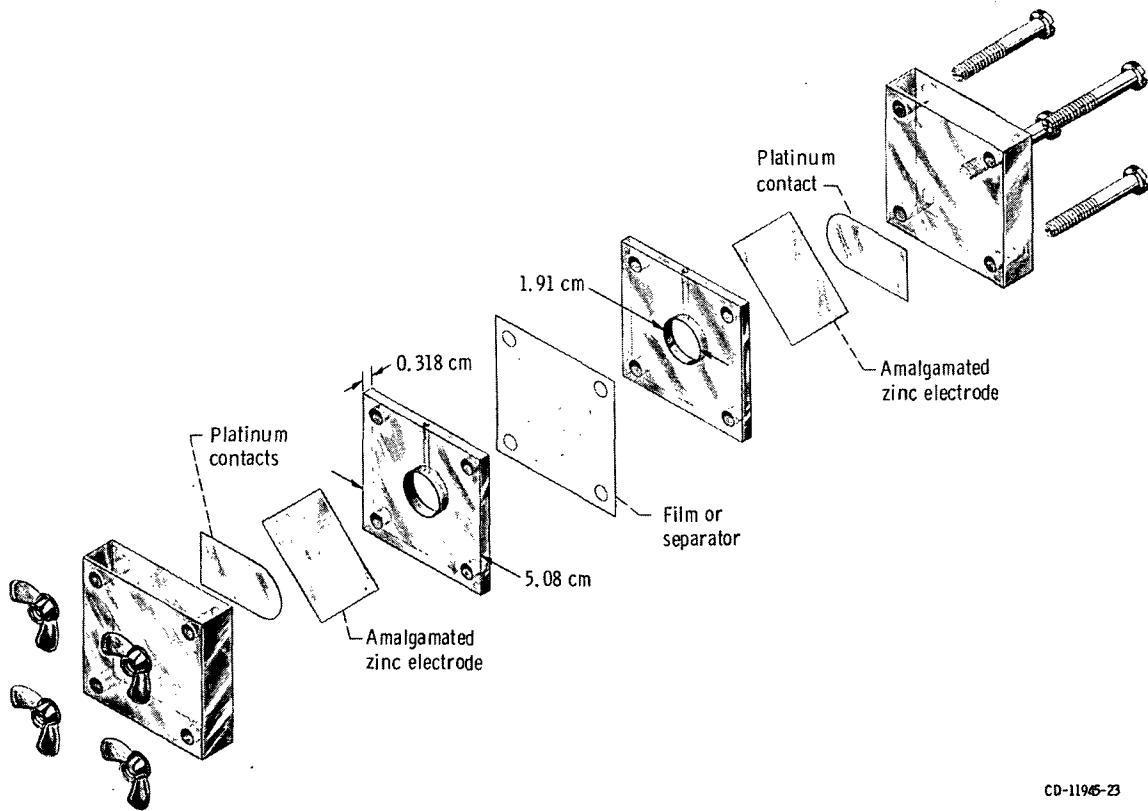


Figure 3. - Simplified ionic conduction model.



CD-1196-Z3

Figure 4. - Disassembled zinc diffusion cell.



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