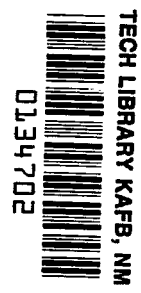


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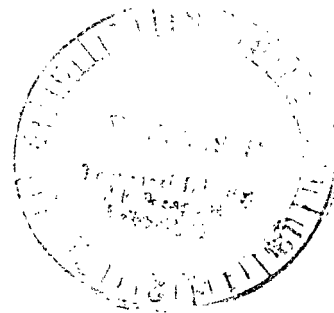


Improved, Low-Cost Inorganic-Organic Separators for Rechargeable Silver-Zinc Batteries

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Improved, Low-Cost Inorganic- Organic Separators for Rechargeable Silver-Zinc Batteries

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and Space Administration

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SUMMARY

A separator development program was started in 1973 at the NASA Lewis Research Center to produce a flexible, low-cost improved-performance separator for sealed rechargeable silver-zinc batteries. Several separators have been developed that apparently meet these goals. Test results were compared with the performance of the Astropower separator made either by a hand-dipping process or on continuous-production equipment. The new separators were more flexible than the Astropower separator; cost about one-fourth as much; and gave equivalent operating performance, a more uniform current density, and a cycle life improvement of 30 to 60 percent.

The Astropower Corp. developed the original inorganic-organic separator. NASA tested and evaluated it in secondary silver-zinc cells and later obtained a license for its fabrication and government use. This standard separator was made by hand dipping a preformed asbestos bag in a slurry coating. A method of applying the slurry coating to the asbestos on continuous-production equipment has been developed by NASA to produce separator materials in large quantity. These continuous-production materials are designated "I/O separators." The Astropower I/O separator costs about \$13.50 per square meter (\$1.25/ft²). The cycle life of cells using the Astropower I/O separator is about 150 cycles, based on 50-percent depth of discharge of 8-ampere-hour cells three times per day (6 hr charge and 2 hr discharge).

Unfortunately, the continuous-production Astropower material is brittle and hard to work with in cell construction, as was the case with the hand-dipped material. Because of this, development work was begun on new, flexible separators to replace the Astropower I/O separator. These new separators are flexible and can be produced on continuous-production equipment for about \$3.80 per square meter (\$0.35/ft²). The better separators exhibited cycle lives of over 200 cycles under the same test regime used for the I/O separator.

All the I/O separators exhibited a microporous structure under scanning electron microscope examination. The Astropower I/O separator has a rather nonuniform structure of voids and particles, and the surface contains numerous defects. The new, flexible, low-cost separators also appeared to be microporous but had more uniform cellular structure that seemed to produce a more uniform current density. Although the cycle lives of these flexible separators probably depend on the uniformity of the microporous structure, chemical factors related to the various fillers used may also be involved. This is undergoing further evaluation.

INTRODUCTION

A separator development program for alkaline batteries was undertaken at the NASA Lewis Research Center in 1973. The program was intended to develop flexible, low-cost separators with extended cycle life to replace the standard inorganic-organic separator used by Lewis for silver-zinc (Ag-Zn) secondary batteries. This inorganic-organic separator was initially developed and patented (ref. 1) by Astropower Corp. Under contract, NASA tested and evaluated the separator in Ag-Zn cells and later obtained a license for the fabrication and government use of the separator in alkaline batteries.

Briefly, the Astropower separator is an envelope constructed from 0.0254-centimeter- (10-mil-) thick, fuel-cell-grade asbestos impregnated with 2-weight-percent polyphenylene oxide (PPO) and manually dip-coated twice on the outside with a slurry. (The fuel-cell-grade asbestos sheet consists of four layers of asbestos sheet that have been calendered into a single sheet.) The slurry consists of a PPO-chloroform solution containing an organic additive (a polyester of a diol) and inorganic fillers (pigmentary potassium titanate and calcia-doped zirconia). The coated asbestos, when dry, has a thickness of 0.038 centimeter (15 mils). The filler content of the dry coating is about 60 percent by weight. The preparation, physical properties, and other characteristics of the Astropower separator are described in detail in references 2 and 3. The advantages of this separator are that it resists hot-shorts, does not degrade with time, and has a wet stand life in the discharged state of more than 7 years. The advantages and disadvantages of the Astropower separator are discussed more fully in the appendix.

In an effort to reduce costs and to implement transfer of this separator technology to commercial application, a continuous-production process for making the Astropower separator material on factory equipment was devised by Lewis. The term "I/O separator" is used to designate separator materials (either the Astropower separator or the new, flexible, low-cost separators) made by machine coating rather than by hand dipping. The I/O separator bags are made by glueing together two pieces of separator material (coated side out).

The basic formulas used to make the improved, flexible, low-cost I/O separators are described in reference 2. The composition of these separators includes a polymer, an organic additive (polymeric polyester), and a combination of fillers. The filler combination includes one that reacts with the electrolyte (a pore former) and another that is inert to the electrolyte.

The I/O separators - both the Astropower and the improved, flexible, low-cost separators - exhibited a microporous structure under scanning electron microscope

(SEM) examination. The cycle lives of these separators appear to be related to the uniformity of size and distribution of the micropores.

This report documents the performance trends of these improved, flexible, low-cost separator materials, as compared with the performance of the Astropower I/O separator, in Ag-Zn test cells constructed at Lewis. Separator coating formulas are discussed first, along with application methods. Details characterizing the microstructure are given. The test cell construction and cycle testing are then described. Cycle life data are presented for the Astropower I/O separator and several improved, flexible, low-cost I/O separators. Finally, the variability in cycle life is discussed in terms of coating and substrate defects; and the reasons for the greater flexibility and fewer flaws of the improved, flexible, low-cost separators are discussed generally.

EXPERIMENTAL PROCEDURE

SEPARATOR FORMULAS

Two separator formulas were used in this study: the standard Astropower coating, both hand dipped and applied by factory machinery; and the improved, flexible, low-cost separator coatings applied by factory machinery.

Standard Astropower Coating

The standard Astropower coating (hand dipped) is the same as the Astropower I/O coating (machine applied) except that chloroform is used as the solvent in the standard coating and trichloroethylene is used as the solvent in the I/O coating. Table I summarizes the coating compositions, both wet and dry.

The hand-dipping process starts with a preformed asbestos bag made from a fuel-cell-grade asbestos sheet impregnated with 2-weight-percent PPO (thickness, 0.025 cm). The two sides and the bottom edge of the bag are sealed with a neoprene cement. The bag contains a dummy electrode. The bag is dipped twice into a well-stirred slurry (no vortex) for 15 seconds each time and allowed to drain dry in the solvent vapors over the slurry. The temperature of the slurry during the dipping process is usually 22° to 25° C. When the coated bag has dried, the dummy electrode is removed and replaced with an actual electrode.

The machine-coating process uses commercial coating equipment made available under contract with Duracote Corp., Ravenna, Ohio. It is a continuous-production process capable of producing thousands of square meters of coated separator per day.

In the process a knife blade is set at a fixed height above the substrate, which is moving beneath the blade. The slurry or coating is poured into a trough attached to the knife blade. The substrate material (asbestos) that exits from under the blade contains a wet coating of slurry (fig. 1). The coating dries at room temperature. This coating process has been used to apply both the Astropower slurry and the improved, low-cost slurries to asbestos and to other substrates.

Two wet coats, each 0.0254 centimeter (10 mils) thick, are applied to asbestos sheet of the same thickness. The dry film thickness is 0.0762 to 0.1016 centimeter (3 to 4 mils), giving an overall thickness of 0.0330 to 0.0355 centimeter (13 to 14 mils) to the finished separator sheet.

Improved, Flexible, Low-Cost Coatings

Three types of formulas have been developed to replace the Astropower formula. Two types, A and B, are described in reference 2. Each of these three formulas contain two fillers, one reactive with the electrolyte and one unreactive with, or inert to, the electrolyte. The ingredients of the three types are shown in table II. Type A consists of polyphenylene oxide (PPO), a polyester plasticizer, reprecipitated calcium silicate (Silene EF, PPG Industries, Pittsburgh, Pa.) as the reactive filler, and an inert filler. Type B is similar except that silicon dioxide (Cab-O-Sil, Cabot Corp., Boston, Mass.) is used as the reactive filler. Type C contains an inert filler: Cab-O-Sil as the reactive filler; and a natural calcium silicate (wollastonite), which is mostly unreactive with the electrolyte.

To reduce costs, the inert fillers were chosen from appropriate inexpensive materials to replace the calcia-doped zirconia and the pigmentary potassium titanate (no longer commercially available) used in the Astropower formula (table I). In all cases, the filler volume content was kept below 40 percent, that is, below the critical pigment volume concentration (CPVC). The CPVC is usually from 40 to 45 volume percent for well-dispersed fillers (ref. 4). The fillers evaluated are listed in table III. All fillers were incorporated in type A formulas, some in type B, and several in type C. All the coatings were applied to asbestos in the manner described in the preceding section. Table III also contains information on the material supplier, the total filler volume content (in type A), which type A formulas were tested in cells, and which other formulas incorporated the fillers.

PHYSICAL CHARACTERIZATION

Flexibility

Separator materials were evaluated for flexibility by a simple bend test. Bending through 180° and flattening or bending over mandrels of various diameters from 0.3 to 1.9 centimeters. Details of this test are given in reference 2.

Characterization of Microstructure

Scanning electron microscopy (SEM) examination. - Separator materials were examined for microporous structure with a scanning electron microscope. Small separator samples were prepared for observation by depositing gold in vacuo. Typical scans were taken of the surface ($\times 100$) and edge (cross section) ($\times 300$, $\times 1000$, and $\times 3000$). The surface was sometimes examined at a 40° tilt ($\times 300$ and $\times 1000$) to give a better picture of surface roughness and defects.

Average-pore-radii determination. - Average pore radii were measured by means of water permeability, as described by Cooke and Lander (ref. 5). Porosity and thickness were first determined. Porosity was estimated by measuring the weight of liquid retained by the separator material after it was heated at 90° C overnight in 45-weight-percent KOH, drained for 15 minutes at an angle of 30° to 45° , and then pressed between several sheets of filter paper for 30 seconds under a 1-kilogram weight. Wet thickness was measured on a thickness gage that had a 0.9-centimeter-diameter foot under a weight of 100 grams. The wet separator was placed between two pieces of 0.0013-centimeter- (1/2-mil-) thick Saran wrap during the thickness measurement to keep the asbestos from being pushed aside and to protect the instrument. This procedure gave the most reproducible results without undue effort. The results for asbestos agreed with those of other investigators. The separator specimen was then placed in the water permeation cell and the procedure of reference 5 (ch. 5a) followed. The diameter of the sample exposed to the water flow was 5.1 centimeters.

TEST CELL CONSTRUCTION

The cells used in this work were constructed with three plates (two negative and one positive) with a 3.5 negative-to-positive capacity ratio designed to deliver 8 ampere-hours. The silver and zinc electrodes were obtained from commercial sources. Lucite shims were used in the cells to provide close to identical pack pressure in the cell cases (made of polysulfone) irrespective of thickness variations in the cell components. This was done in an attempt to control the many variables involved

in cell assembly so that the cell used for evaluating separators would be a uniform test article. The area of each electrode face was 68.6 square centimeters (7.3 cm by 9.4 cm).

Separator bags were made by cutting the machine-coated separator approximately 1 centimeter wider and 1 centimeter longer than the electrode. The bag was made by placing the electrode between two pieces of the cut separator (coated side out) and filling the space between the separator pieces with epoxy cement. Several applications of epoxy cement were usually needed to completely seal the edge (free of defects). To prevent delamination of the four asbestos layers, the edges of the cut pieces were dipped several times into a diluted epoxy solution and dried, before the bag-edge sealing operation began. The finished bags were heated to 90° C overnight to cure the epoxy cement. A newer method of sealing the separator bags is presently being evaluated. This method uses polyethylene foam tape with acrylic adhesive on both sides. Preliminary evaluation of this method shows it to be at least as satisfactory with regard to cell cycle life as the epoxy cement method used for the cells in this study. Significantly, it requires about one-third of the manhours to use and may lend itself to automated bag-edge sealing.

Assembled cells were filled with electrolyte (45-wt % KOH) to within 1 centimeter of the top of the separator bag. Initially, 40 cubic centimeters of electrolyte were added. The cells were placed in a bell jar that was then evacuated for 15 minutes to remove air from the cell interior in order to ensure good wetting of the separator and the electrodes. The cells were then sealed and heated overnight at 100° C to activate the separator (the electrolyte reaction with plasticizer and fillers). Usually 5 cubic centimeters more electrolyte was needed to reestablish the desired electrolyte level. These cells would be considered "flooded."

TEST CELL FORMATION

Cells were formed by charging for 30 hours at 280 milliamperes and discharging at 1 ampere to 1.2 volts. After several formation cycles, an ampere-hour efficiency of 90 percent or greater was achieved. Cells were then charged and given a higher rate discharge (usually C/2) before being placed into the cycle testing equipment.

CYCLE TESTING

The cycle testing regime was the same for all cells tested and included three 8-hour cycles per day (6 hr charge and 1.9 hr discharge) at 50-percent depth of discharge based on the nominal 8-ampere-hour capacity. Current densities were about

5 and 15 milliamperes per square centimeter on charge and discharge, respectively. Cycle testing was done on automatic cycling equipment. Cell voltage and current were monitored three times per hour by a scanner, and the data were fed to the NASA Lewis IBM-360 computer for processing. Data were returned showing voltage, current, and accumulated ampere-hours, along with occasional voltage-time plots.

Since the testing was to evaluate separators, no upper voltage cutoff was used. The only restriction imposed was to minimize overcharge. Charge currents were set to maintain ampere-hour input at 4.0 to 4.1 ampere-hours. When voltage before the end of the discharge time reached 1 volt, the cell was checked for shorts. Some cells exhibited a charge condition wherein the silver electrode would not charge to the second plateau. Cycle life was determined to be the point where shorting occurred or where the cell failed to charge above 1.72 volts.

POST-TEST EXAMINATION

The following were procedures used for analysis of failed cells:

- (1) Cells were weighed after a complete discharge through a 1-ohm resistor.
- (2) Small holes were drilled through the cell case top in diagonal corners. Free electrolyte was poured out, its volume was measured, and it was then analyzed for OH^- , $\text{CO}_3^{=}$, and $\text{Zn(OH)}_4^{=}$.
- (3) The cell case was carefully cut open with a band saw to remove the cell-case face. Then the terminal straps were snipped off and the top of the cell case was removed.
- (4) The electrode pack was removed. The separators were carefully examined for zinc dendrites or nodules and for coating defects (cracks). Then the separators were removed from the electrodes. The electrodes were visually examined for warping and dimensional changes. The zinc electrodes were evaluated for washout, redistribution, dryness, color, and densification. Photographs were usually taken of the electrodes and the separators. A brief written description of the cell condition was made. The components were then placed in polyethylene bags and heat sealed until further tests - such as resistivity, pore size, and silver content - could be performed on the separators as required.

RESISTIVITY MEASUREMENTS

Volume resistivities were measured with a test apparatus and procedure based on those described by Salkind and Kelley (ref. 5, ch. 6b). In most cases, resistivities were measured on at least two samples (3.8 cm by 3.8 cm) to establish precision.

Resistivity measurements were made in approximately 45-weight-percent KOH at room temperature. At least two samples of each separator were pretreated by soaking in 45-weight-percent KOH overnight at 90^o to 100^o C. The test area in the conductivity cell was 0.95 square centimeter. The dry thickness of the separator was used in calculating volume resistivity because it was difficult to measure the wet separator thickness once the separator was positioned in the resistivity cell and the cell halves were tightened together. The wet thickness of some separators has been found to be up to 25 percent greater than the dry thickness in a uncompressed state.

RESULTS AND DISCUSSION

ASTROPOWER SEPARATORS

Astropower separators are brittle and crack when bent over a mandrel with a diameter of less than 1.9 centimeters. Two Ag-Zn cells containing hand-dipped Astropower separators failed at 161 and 109 cycles, respectively, for a mean and standard deviation of 135±37. Eight Ag-Zn cells containing the most recent Astropower separator material made with continuous-production equipment failed at 102, 138, 218, 108, 181, 279, 139, and 167 cycles, respectively, for a mean and standard deviation of 166±59. In both sets of tests the failure mode was identical, namely, zinc nodule and dendrite shorting with little or no redistribution or shape change in the zinc electrode. These mean values of cycles to failure provide a baseline for comparison with the newer formulas and illustrate the typical data scatter experienced for a given batch of separator material. Similar scatter was observed among different batches of separator material of identical composition. This scatter is consistent with the presence of defects in the Astropower coatings that were caused by high filler volume content (>45 vol %) and application to a porous, nonhomogenous substrate. Other production variables, such as relative humidity and difference in drying rate due to variable room temperature, can also affect separator porosity and hence cycle life. This is discussed in some depth in a later section.

IMPROVED, FLEXIBLE, LOW-COST I/O SEPARATORS

Regardless of the inert filler used, all the improved separator materials passed a bend test over a 0.63-centimeter-diameter mandrel. Most passed a bend test over an 0.32-centimeter-diameter mandrel. Some could even be bent through 180^o and flattened without cracking. It is clear that the brittleness problem has been resolved by keeping the filler volume content below the CPVC.

The data summarized in table IV are the mean cycle life and cycles to failure for the typical flexible, low-cost formulas evaluated. The data cover the three types of formulas - A, B, and C. These data are presented to show several features in the evolution of improved separators. Formulas CX47W and CX47W1 contain a natural calcium silicate (wollastonite) rather than the reprecipitated material (Silene EF) used in the usual type A formula (AX47). Formula CX47W1 is a further modification to reduce the resistivity of CX47W by adding reactive Cab-O-Sil. The addition of the Cab-O-Sil increased the filler volume content from 29 volume percent for CX47W to 31 volume percent for CX47W1. Separator CX47W1 operated satisfactorily (above 1.25 V) at the C/2 discharge rate, but separator CX47W operated at this load voltage only at discharge rates of C/4 and lower. Table IV also contains a qualitative description of separator resistivity as related to cell performance under load.

Area resistivity for these I/O separators ranged from 0.5 to 1 $\Omega\text{-cm}^2$. Volume resistivity ranged typically from 10 to 30 $\Omega\text{-cm}$. Separators with area resistivities above 1 $\Omega\text{-cm}^2$ and volume resistivities above 30 $\Omega\text{-cm}$ usually are considered "too resistive." Separators with volume resistivities from 0.7 to 1.0 $\Omega\text{-cm}$ are considered "somewhat resistive." Separators with area resistivities less than 0.7 $\Omega\text{-cm}^2$ would be considered "acceptable." In terms of performance criteria, resistivity is usually reflected in the cell operating voltage during charge and discharge. If we use the Astropower I/O separator as the performance standard (20 $\Omega\text{-cm}$, 0.7 $\Omega\text{-cm}^2$) the upper limit on charge voltage is 2.04 volts. The discharge (midpoint) voltage at the C/8 rate (1 A) is ~1.45 volts, and at the C/2 rate (4 A) it is about 1.3 volts. These are "acceptable" performance standards.

The data in table IV are significant for several reasons. First, within experimental error, all formulas have a mean cycle life to failure that equals or exceeds the mean cycle life to failure of the machine-coated Astropower I/O separator (166±59). Second, as shown in figure 2, the charge-discharge performance (at 50-percent depth of discharge) of separators BX40 and CX47W1 at ~200 cycles is similar to the performance of the machine-coated Astropower I/O separator at approximately 150 cycles. (This separator failed after 167 cycles by a nodule shorting.) All cells in table IV except AX47 and CX47W performed acceptably at the standard C/12 charge rate and at the C/4 discharge rate at 50-percent depth of discharge.

Figure 2 gives voltage-time curves for the BX40, CX47W1, and Astropower I/O separators. Figure 3 gives voltage - ampere-hour curves for these separators. The Astropower I/O separator (6D0575) had midpoint voltages of 1.47 volts at the C/8 discharge rate and 1.31 volts at the C/2 rate. The BX40 separator had midpoint voltages of 1.46 volts at the C/8 discharge rate and 1.30 volts at the C/2 rate. The CX47W1 separator had midpoint voltages of 1.43 volts at the C/8 discharge rate and 1.25 volts at the C/2 rate. However, the capacity of CX47W1 at both rates was superior to that

of the Astropower I/O, and the capacity of BX40 was somewhat better at the lower rate and somewhat worse at the higher rate than that of the Astropower I/O. Separator BX40 exhibited voltages under load that were equal to the standard. Although separator CX47W1 also showed comparable resistivity to the standard under load conditions, the voltages were somewhat depressed. As the formulas were refined both by proper selection of inert fillers and inert filler - reactive filler combinations, the failure mode changed characteristically from one caused by one or several nodule shorts to one caused by very fine, uniformly dispersed dendrites. This latter failure mode indicates a separator of more uniform microcellular structure that in turn produces a more uniform current density over the electrode face. None of the zinc electrodes represented by table IV data showed any shape change or redistribution.

Separator BX40 contained calcium zirconate as the inert filler. The volume resistivity ($\sim 20 \Omega\text{-cm}$) in 45-weight-percent KOH was equivalent to that of the Astropower I/O separator. Cycle life (206 ± 31) was marginally better than that of the Astropower I/O separator (166 ± 59). The BX40 data shown in table IV came from two different batches of the same formula that were machine coated on different days. The purpose was to evaluate the effects of batch-to-batch differences. The batch effect appears to be minimal. Separator BX118 contained nickel titanate as the inert filler. The BX118 material is no longer under consideration because of a price increase in nickel titanate from \$4.95 per kilogram to \$13.75 per kilogram (\$2.25/lb to \$6.25/lb). Separator AX107 contained 100-mesh wood flour as the "inert" filler. However, this separator was dropped because of the unknown long-term stability of wood flour in KOH and the presence of nodules as a failure mode.

Costs of these separators produced on factory equipment ranged from \$2.70 to \$3.80 per square meter (\$0.25 to \$0.35/ft²), as compared with \$13.50 per square meter (\$1.25/ft²) for the Astropower I/O separator. Of this cost, the PPO-impregnated, fuel-cell-grade asbestos sheet accounted for \$1.62 per square meter (\$0.15/ft²). These costs are within reason for commercial products. The costs quoted per square meter include raw materials, impregnated fuel-cell-grade asbestos, labor, and machine rental time. These costs in no way represent a minimum cost since the methods of making the asbestos substrate and the impregnation of the substrate have not been optimized. Much handling and labor are included in the \$1.62-per-square-meter (\$0.15/ft²) cost. The machine coating was performed to demonstrate feasibility and does not represent an optimum condition for application.

VARIABILITY IN CYCLE LIFE

The causes of the data scatter have been carefully examined as a guide producing a uniform, commercial separator. Since data scatter greater than 20 percent persisted even after the coatings were reformulated, the next logical causes would be either the application method or the substrate itself. The cycle test data showed greater scatter for laboratory-machine-coated materials than for similar materials produced on factory equipment. The scatter for the hand-dipped Astropower material was generally the same as that for the machine-coated Astropower material. Hence, the asbestos substrate was suspect. Under inspection, the asbestos sheet was found to be markedly inhomogeneous with respect to thickness and the presence of fiber clumps. The fiber clumps produced high spots in the asbestos substrate. These high spots caused almost all machine shutdowns because of substrate tearing during continuous production. High spots and variations in substrate thickness resulted in a dry, coated asbestos substrate of the same thickness that was not uniform with respect to asbestos thickness and coating thickness. Presently, methods of reconstituting the asbestos and forming the mat in one step with the binder present are being investigated.

MICROSTRUCTURE OF COATINGS AND MECHANISM OF SEPARATOR ACTION

The Astropower I/O separator and the improved, flexible, low-cost separators exhibited a Astropower microporous structure under the scanning electron microscope (SEM). The Astropower I/O separator, produced on automated factory equipment, had a rather nonuniform structure of voids and particles, and the surface contained many defects.

Figure 4 is a cross section ($\times 300$) of the Astropower I/O separator with various features designated. Figure 5 is a $\times 1000$ cross section of the same Astropower I/O separator. Figure 6 is a similar view of the CX47W1 separator. Examination of figures 5 and 6 reveals that the CX47W1 separator had a finer more uniform honeycomb structure than the structure shown in figure 5 for the Astropower I/O separator. The water permeability tests on these CX47W1 specimens soaked overnight at 100° C in 45-weight-percent KOH gave average pore diameters of 10 to 15 nanometers (100 to 150 angstroms). (Laboratory-made materials had pore diameters about three times larger.) Because of the presence of KOH reaction products (gels) in the pores, this result was not unexpected and perhaps represented the effective pore dimensions in an operating Ag-Zn cell. The surfaces of the factory-produced materials contained relatively few defects, and SEM showed a thin layer of polymer present on the coating.

J. M. Parry of A. D. Little, Inc., in a private communication suggested that this film influences hydroxyl and zincate ion diffusion as well as osmotic pressure across the separator.

The difference in the packing effect of the filler particles is probably exhibited in the apparently superior cycle lives for the CX47W and CX47W1 separators over that of the AX47 separator. As noted previously, formula AX47 contained a reprecipitated, hydrated calcium silicate (Silene EF). Formula CX47W contained a natural calcium silicate mineral (wollastonite). This wollastonite had an average particle diameter of 4.6 micrometers; Silene EF had a much smaller particle diameter (only 0.03 μm). Both were formulated with 29-volume-percent filler.¹ Formula CX47W1 is the same as CX47W with Cab-O-Sil added, bringing the filler volume content to 31 volume percent. Formula AX47 combined an inert filler (magnesium titanate) of 1.7-micrometer particle diameter with the reprecipitated calcium silicate filler of 0.03-micrometer particle diameter. Formula CX47W combined the magnesium titanate inert filler with wollastonite, which had a larger mean particle diameter (4.6 μm) but also a greater range of diameters (<1 μm to 10 μm). When the larger particles were combined with smaller particles of about the same magnitude, the dispersion consisted of a mixture with the smaller particles in the spaces between the larger ones. This resulted in an interaction wherein less polymer was required to coat or cover the particles. This interaction led to more favorable effects in the film, such as greater durability and less permeability (ref. 4), and hence better cycles-to-failure results.

The generally greater cycle life of the factory-produced separators appears at this time (based on unpublished data and the work of Philipp and May, ref. 6, fig. 2) to be related mostly to the influence of the more uniform microporous structure.

CONCLUDING REMARKS

The cell performance and cycle life test results presented and discussed in this report document achievement of the goal of developing separators for Ag-Zn batteries that are flexible, lower in cost than the Astropower separator, and at least equal to it in cycle life capability.

These advances were achieved by formulating a separator based on an understanding, which has developed over a period of time, of the operating mechanism. Coating materials were formulated that contained fillers and organic additives reactive with the potassium hydroxide electrolyte and fillers inert or nonreactive with the electrolyte. The reactions of the electrolyte with the reactive fillers and organic additives

¹(Filler volume)/(Filler volume + Polymer volume) = Volume percent.

yielded some products that improved conductivity and others that served as sites for adsorption or possible precipitation of zincate ion. The inert fillers served as physical barriers that increased the tortuosity of the separator. The inert filler particles and flocculent precipitates resulting from filler reaction with the electrolyte reduced the diameter of the unobstructed pathway that zincate ion must traverse to move across the separator. These fillers included low-cost materials such as calcium silicate (wollastonite), silicon dioxide, various titanates, and mixed silicates. Different filler combinations gave variations in pore size, volume resistivity, zinc dendrite penetration rate, and cell cycle life. The relationship between the separator-characterization test results and the cycle lives in test cells is still obscure.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 14, 1979,
506-23.

APPENDIX - ADVANTAGES AND DISADVANTAGES OF ASTROPOWER

INORGANIC-ORGANIC SEPARATORS

Using a coated asbestos separator in Ag-Zn cells has several advantages:

- (1) The zinc electrode does not display the traditional life-limiting aspects of slumping and shape change.
- (2) The migration of soluble silver species in the electrolyte is reduced through reaction with the PPO in the asbestos and in the coating.
- (3) The hand-dipped separator has a demonstrated wet stand life of over 7 years.
- (4) The separator can be produced in quantity on continuous-production factory equipment, thereby reducing labor costs.
- (5) The separator is not subject to degradation or to an increase in resistance that occurs with organic polymer separators.

Astropower hand-dipped separator material used in 40-ampere-hour Ag-Zn cells has so far demonstrated a wet stand life of 7 years. Recently unpublished test results of cells that were constructed and initially formed with 40-ampere-hour capacity in December 1969 showed a 100-percent retention of capacity after three formation cycles in March 1977. These cells had been stored at 0° C during the 8-year wet stand period. They represent a backup cell design that incorporated an extra piece of separator material between the silver and zinc electrode bags.

In addition to the advantages cited, the Air Force has identified the Astropower I/O separator as a superior separator for use in alkaline silver-hydrogen (Ag-H₂) cells. The report (ref. 7) states that "of four membranes tested . . . , only the NASA separator was found suitable for use in practical Ag/H₂ cells." Advantages cited were electrolyte equilibration via "backwicking," electrolyte capacity, and the pore size and pore-size distribution of the absorber layer (asbestos). The asbestos layer thickness was found to have the greatest influence on capacity retention. In Ag-H₂ cell tests with Astropower I/O separators in 20-ampere-hour cells, more than 600 charge-discharge cycles at 70-percent depth of discharge have been achieved.

Unfortunately, there are several disadvantages of the Astropower formula whether it is applied by hand dipping the 0.0254-centimeter- (10-mil-) thick asbestos impregnated with 2-percent polyphenylene oxide or coated by automatic factory equipment (I/O separator). One disadvantage is the cost (\$11.90 to \$13.50 per m², \$1.10 to \$1.25 per ft²), which is mainly due to the use of calcium-doped zirconia (\$18.25/kg, \$8.25/lb) as the ceramic filler.

Some other disadvantages relate to the separator constituents and the way the coating slurry is formulated. In particular, the high filler volume content of 60 percent

(based on dry film), which is well above the critical pigment volume concentration (CPVC) of 40 to 50 percent for well-dispersed fillers (ref. 4), results in a very brittle coating whose surface and interior contain numerous defects. Also, one ingredient, pigmentary potassium titanate (PKT), is no longer available commercially (Fybex L, DuPont de Nemours). The brittleness has been further aggravated by switching the solvent from chloroform to trichloroethylene to meet Occupational Safety and Health Administration (OSHA) requirements in the factory coating operation. Trichloroethylene imparts greater brittleness because its slower evaporation leads to higher crystallinity in the PPO. More recently, trichloroethylene has been classed as a carcinogen.

In addition, both fillers, the zirconia and PKT fibers, have large ($>1 \mu\text{m}$) particle diameters, exceed the CPVC, and do not represent an optimum filler packing condition. A larger quantity of polymer (PPO) would be necessary to completely wet filler particles. The CPVC is assumed to represent the tightest possible packing of the filler particles compatible with the minimum amount of polymer needed to provide the adsorption layer on the filler particles and to fill the interstices between the wetted particles. If, as for the Astropower separator, the amount of binder is insufficient to fill the interstices, the coating will show greater permeability and other inferior properties. Applying this polymer-deficient coating to a porous substrate (asbestos) further increases the filler volume concentration and results in a coating whose surface shows a wide range of porosity. The SEM work on the I/O separator published by Bozek (ref. 3) shows this porosity variation in both the coating surface and interior. This coating porosity variation results in uneven current density over the electrode area. The resulting higher current density at defect points promotes zinc dendrite and nodule growth and ultimately leads to cell shorting.

Table V summarizes the advantages and disadvantages of the Astropower hand-dipped separator and the Astropower I/O separator. The improved, flexible, low-cost I/O separators are compared with the Astropower separators.

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TABLE I. - ASTROPOWER SLURRY COATING FORMULA

Component	Weight, g	Dry weight, wt %	Dry volume, vol %
PPO (binder)	47	10	27.7
Solvent ^a	360	--	----
P-9750 (plasticizer)	47	10	27.7
Solvent ^a	60	--	----
PKT (filler)	10	4	3.1
ZrO ₂ (filler) treated (calcium stabilized)	356	76	41.5

^aHand-dipping process uses chloroform; machine-coating process uses trichloroethylene (C₂HCl₃).

TABLE II. - INGREDIENTS OF NASA IMPROVED, FLEXIBLE, LOW-COST I/O SEPARATORS

[Apply two wet coats (0.0254 cm (10 mils) thick) to asbestos sheet; dry film thickness, 0.0762 to 0.1016 cm (3 to 5 mils); asbestos thickness, 0.0254 cm (10 mils); separator thickness, 0.0330 to 0.0355 cm (13 to 14 mils.)]

Type A	Type B	Type C
PPO	PPO	PPO
Polyester plasticizer	Polyester plasticizer	Polyester plasticizer
Calcium silicate (reprecipitated)	Silicon dioxide (Cab-O-Sil ^a)	Calcium silicate (natural)
Inert filler	Inert filler	Inert filler
20- to 30-vol % fillers in PPO	30- to 40-vol % fillers in PPO	Silicon dioxide (Cab-O-Sil ^a) 30- to 35-vol % fillers in PPO

^aCabot Corp., Boston, Mass.

TABLE III. - INERT FILLERS TESTED IN TYPE A SEPARATORS ON

0.0254-cm- (10-mil-) THICK ASBESTOS SHEET

Coating formula	Inert fillers	Supplier	Filler volume content, vol %	Tested in cells	Used in other type of formula
X-10	Calcia-doped zirconia	Proprietary process	26.3	Yes	B
X-24	Calcium titanate	TAM Products Division, NL Industries, Hightstown, N.J.	29.1	No	----
X-47	Magnesium titanate	↓	30.9	Yes	B, C
X-55	Lead titanate		23.9	Yes	B, C
X-68	Lead titanate (2X)		29.8	No	----
X-56	Zinc magnesium titanate		28.6	No	----
X-64	Magnesium zirconate		28.8	No	----
X-65	Calcium zirconium silicate		28.4	Yes	B
X-66	Magnesium zirconium silicate		28.1	No	----
X-67	Zinc zirconium silicate		27.3	No	----
X-92	Magnesium aluminosilicate	Baroid Division, NL Industries, Houston, Tex.	29.2	Yes	----
X-101	Magnesium silicate, synthetic	Baroid Division, NL Industries, Houston, Tex.	29.0	No	----
X-98	Magnesium silicate (Microtalc)	Minerals, Pigments Div., Pfizer, Inc., New York, N.Y.	29.0	Yes	----
X-70	Magnesium silicate	Whittaker, Clark & Daniels, Inc., Plainfield, N.J.	29.0	No	----
X-103	Aluminum silicate (kaolin)	Georgia Kaolin, Elizabeth, N.J.	29.3	No	----
X-104	Nickel titanate	TAM Products Division, NL Industries, Hightstown, N.J.	29.1	Yes	B
X-114	White pine wood flour, 100 mesh	Wood Flour, Inc., Winchester, N.H.	34.1	Yes	----
X-116	Lignin, Kraft process	Westvaco, North Charleston, S.C.	29.0	Yes	B
X-120	Lead zirconium titanate	TAM Products Division, NL Industries, Hightstown, N.J.	26.8	No	B
X-113	Titanium dioxide	Degussa, New York, N.Y.	28	No	----

TABLE IV. - CYCLE TEST RESULTS WITH NASA IMPROVED, FLEXIBLE, LOW-COST SEPARATORS

	Formula					
	X47	X107	X118	^a X40	X47W	X47W1
	Type					
	A	A	B	B	C	C
Inert filler	Magnesium titanate ^b	Wood flour ^c	Nickel titanate ^b	Calcium zirconate ^b	Magnesium titanate ^b	Magnesium titanate ^b
Mean cycle life	149±11	260±56	212±34	206±31	293±94	233±41
Actual cycles to failure	137	220	173	173	204	253
	155	300	227	219	284	259
	156		236	219	392	186
				173		
				199		
				252		
Remarks	Too resistive	Somewhat resistive	Somewhat resistive	Acceptably resistive	Too resistive	Acceptably resistive
Maximum discharge rate above 1.25 V	C/4	C/2	C/2	C/2	C/4	C/2
Failure mode	Numerous Zn dendrites; nodule in one cell	Nodules	Zn dendrites; ZnO found outside of separator bag	Fine dendrites; small nodules	Fine dendrites along bottom 1/3 of electrodes	Very fine, uniformly dispersed dendrites

^aContains cycle life data from two batches of separator material, each produced on a different day.

^bTAM Products Division, NL Industries, Hightstown, N.J. 08520

^cWood Flour, Inc., Winchester, N.H. 03470

TABLE V. - COMPARISON OF ADVANTAGES AND DISADVANTAGES OF ASTROPOWER SEPARATOR
AND NASA IMPROVED, FLEXIBLE, LOW-COST I/O SEPARATORS

	Astropower hand-dipped separator	Astropower machine-coated separator (I/O)	NASA improved I/O separators
Wet stand life	Demonstrated wet stand life longer than 7 years	Wet stand life not yet determined	Wet stand life not yet determined
Quantity production	Cannot readily be produced in quantity	Can be produced in continuous-production factory equipment	Produced on continuous-production equipment; more uniform, less expensive product
Flexibility	High filler content (60 vol %), greater than CPVC, leads to brittleness and defects	Brittleness aggravated by use of trichloroethylene	Lower filler content (30 to 40 vol %) gives greater flexibility and fewer defects and flaws
Filler packing effect	Size of fillers precludes achieving optimum packing effect	Size of fillers precludes achieving optimum packing effect	Better filler packing leads to fewer defects and more uniform cellular structure
Silver migration	Less migration of soluble silver than with polymeric separator; degradation reduced and resistance stable	Less migration of soluble silver than with polymeric separator; degradation reduced and resistance stable	Less migration of soluble silver than with polymeric separator; degradation reduced and resistance stable
Zinc electrode changes	Little slumping and shape change	Little slumping and shape change	Little slumping and shape change
Zinc dendrite and nodule shorting	Less dendrite and nodule formation than with traditional organic separators	Less dendrite and nodule formation than with traditional organic separators	Still less dendrite and nodule formation because of fewer flaws
Cost of coating materials	High because calcia-doped zirconia used; pigmentary potassium titanate no longer available	High because calcia-doped zirconia used; pigmentary potassium titanate no longer available	Use of inexpensive, commercially available fillers reduced cost

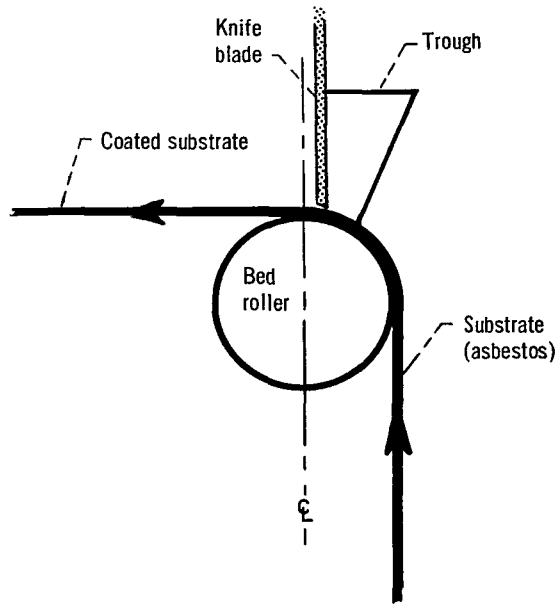


Figure 1. - Sketch of continuous-production coating process using a fixed blade over a roller.

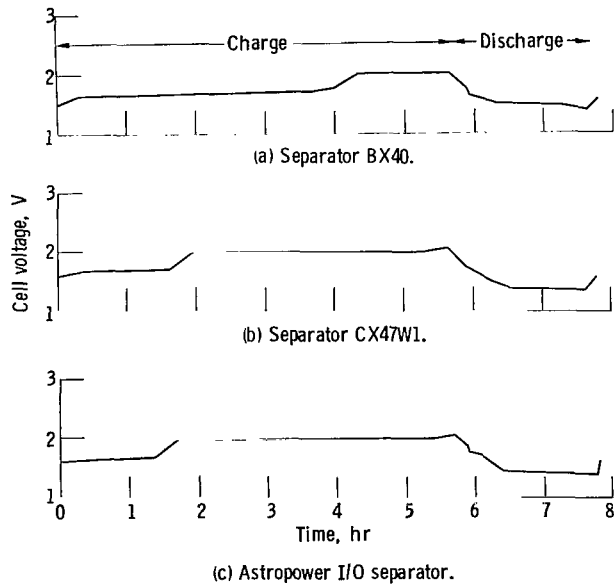


Figure 2. - Charge-discharge behavior of BX40, CX47W1, and Astropower I/O separators.

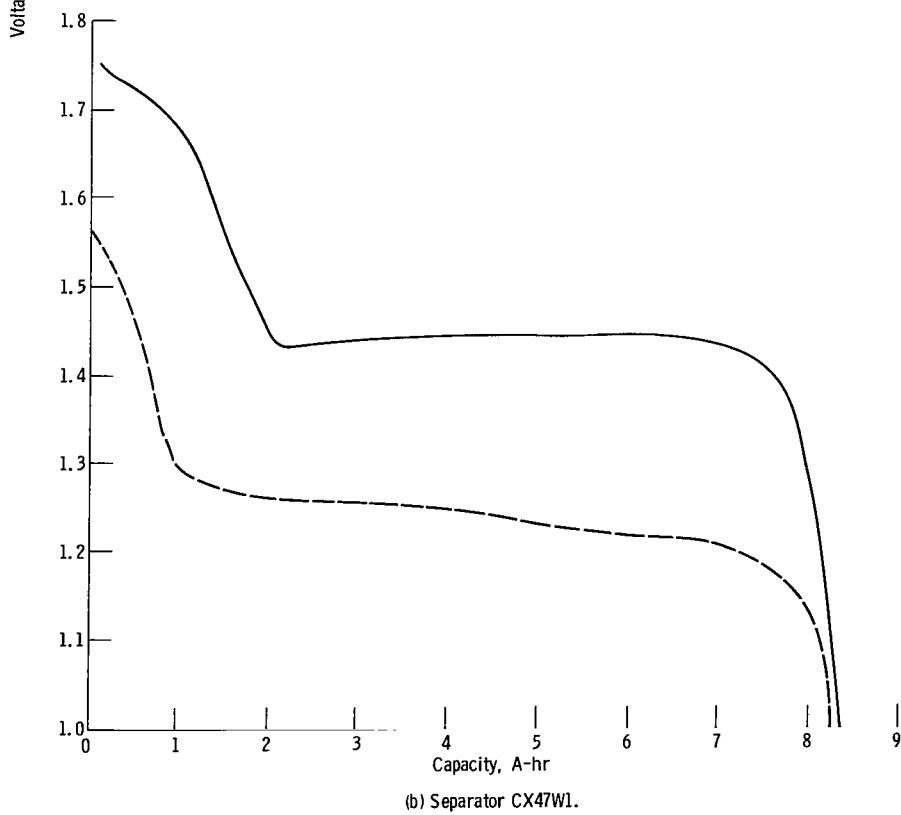
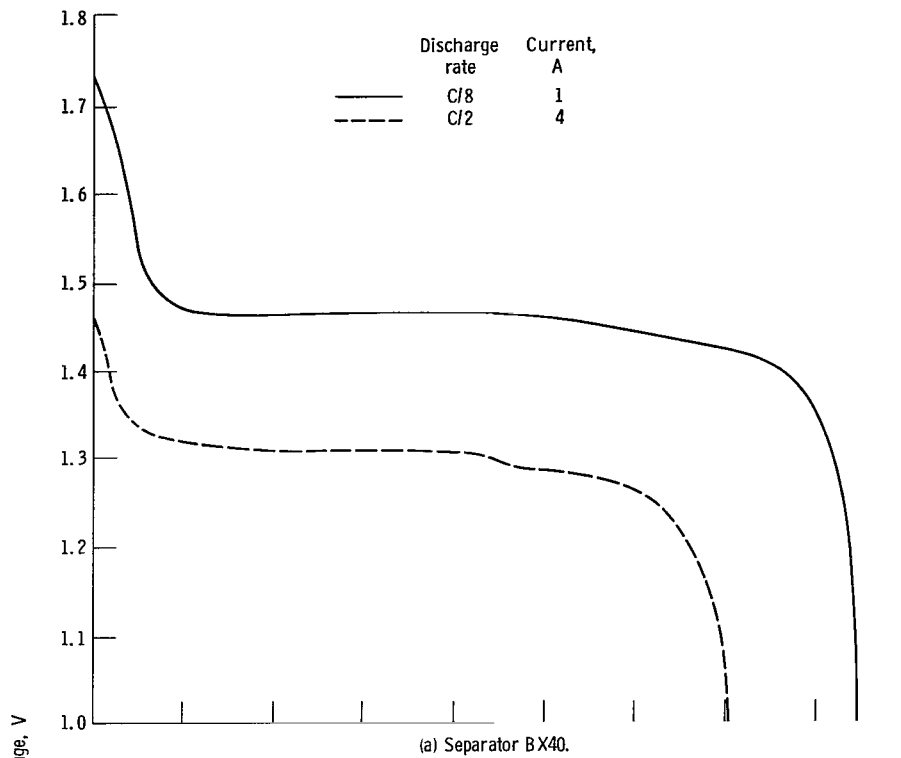
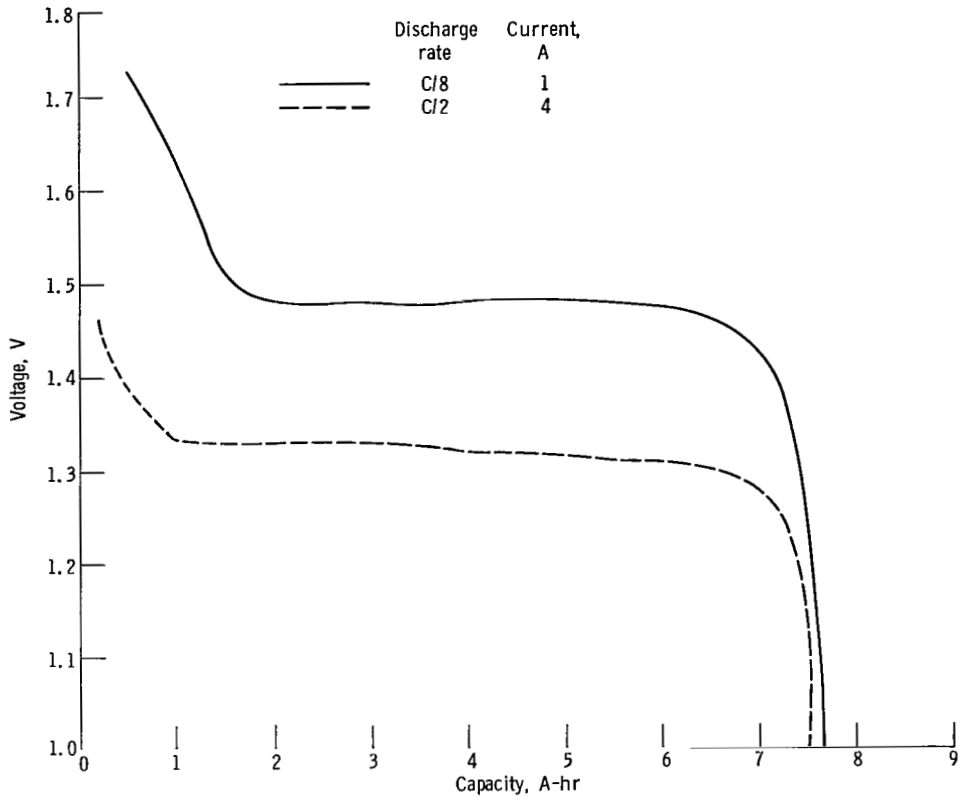


Figure 3. - Capacity of BX40, CX47W1, and Astropower I/O separators.



(c) Astropower I/O separator.

Figure 3. - Concluded.

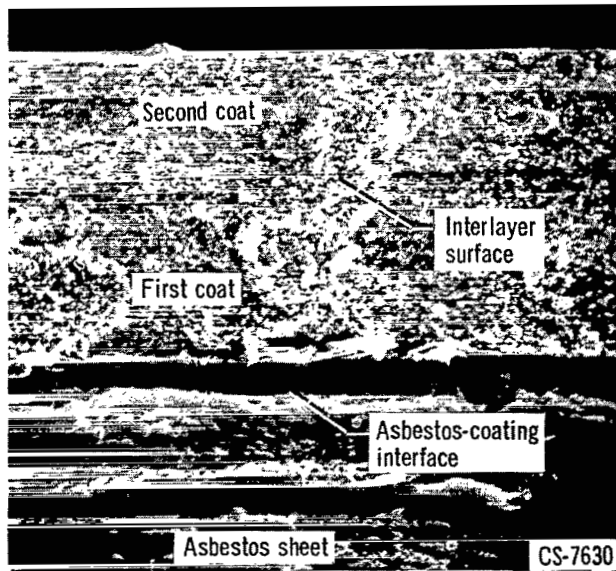


Figure 4. - Cross section of Astropower I/O separator. $\times 300$.

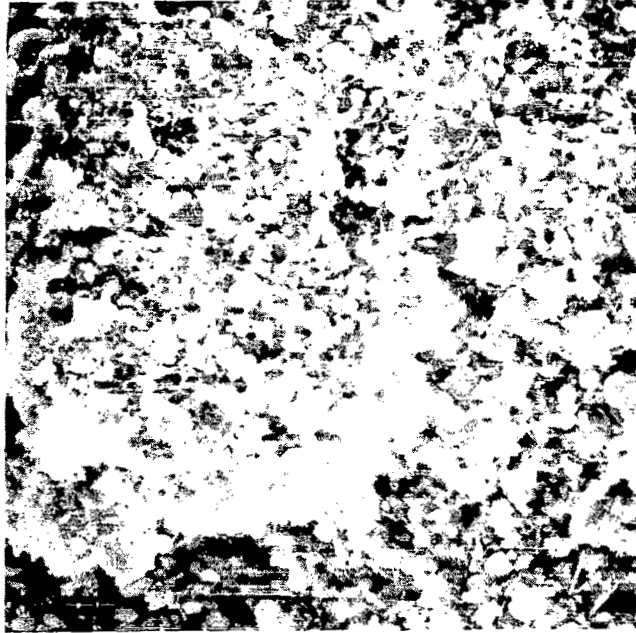


Figure 5. - Cross section of Astropower I/O separator. $\times 1000$.

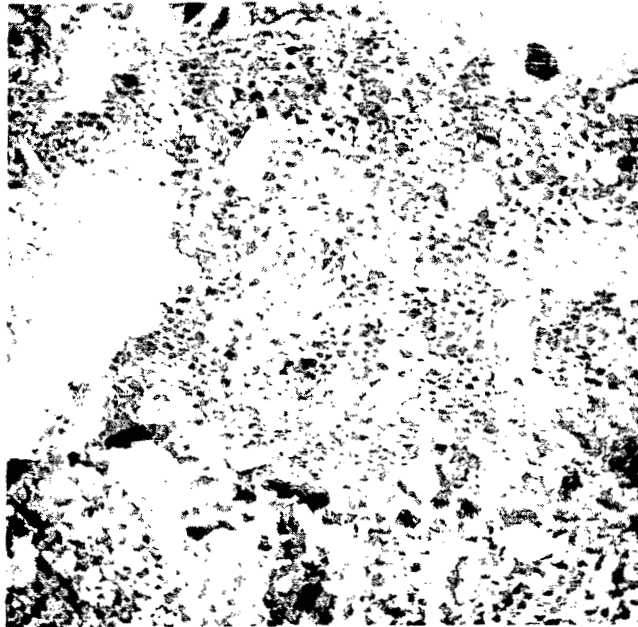


Figure 6. - Cross section of CX47W1 I/O separator. $\times 1000$.

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16. Abstract A program was started in 1973 to develop a flexible, low-cost inorganic-organic separator with performance characteristics and cycle life equal to, or better than, the Lewis Research Center Astropower separator. Several separators have been developed that meet this goal. These new separators can be made on continuous-production equipment at about one-fourth the cost of the Astropower separator produced the same way. In test cells, these new separators have demonstrated cycle life improvement, acceptable operating characteristics, and uniform current density. Details of the various separator formulas, test cell construction, and data analysis are described.		
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