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Evaluation of Production Version of the NASA Improved Inorganic-Organic Separator

Dean Sheibley
Lewis Research Center
Cleveland, Ohio

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EVALUATION OF PRODUCTION VERSION OF THE NASA IMPROVED INORGANIC-ORGANIC SEPARATOR

Dean Sheibley

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

As a result of a successful in-house effort at NASA Lewis Research Center to develop the technology of an inorganic-organic (I/O) separator, which demonstrated improved flexibility, reduced cost, production feasibility and improved cycle life, it was decided to transfer the improved I/O separator technology to an industrial supplier. A cost-sharing contract with Munising Paper Division of Kimberly-Clark Corporation was negotiated. The primary goals were to evolve other substrates to replace asbestos and to define water-based separator coatings to replace the solvent-based coatings. Secondary goals were to develop an improved fuel cell grade asbestos sheet and to demonstrate a large-scale production capability for the NASA solvent-based I/O separator.

Most of the goals of the cost-sharing contract between NASA and Kimberly-Clark Corporation have been achieved:

(1) A cellulose-based substrate and a nonwoven polypropylene fiber substrate have been successfully evaluated as replacements for the asbestos. Both the cellulose and polypropylene substrates have been coated with solvent-based and water-based coatings to produce a modified I/O separator.

(2) The solvent-based coatings have been modified to produce aqueous separator coatings with acceptable separator properties.

(3) A single-ply fuel cell grade asbestos with a binder (BTA) was produced. It has shown to be an acceptable substrate for the solvent- and water-based separator coatings, an acceptable absorber for alkaline cells, and an acceptable matrix for alkaline fuel cells.

(4) The original NASA solvent-based separator (K19W1), using asbestos as a substrate, was prepared by Kimberly-Clark using production methods. However, its resistance was unacceptably high. The Kimberly-Clark modified version of NASA K168T was commercially produced on the BTA substrate and was superior to K19W1 in all measured properties.

The separator materials prepared on industrial equipment generally behaved in the following manner:

(1) Measured separator properties were improved when compared with the original NASA solvent-based separators, with resistivity being significantly improved.

(2) Cycle life of 8-A-hr nickel-zinc cells appeared to be dependent upon substrate regardless of the type of coating, composition, or solvent. Cycle life decreased in the following order of substrates: asbestos > cellulose paper > nonwoven polypropylene. Only coated asbestos separators achieved cycle life in excess of the NASA K19W1 standard.

(3) Solvent-based coatings showed better cycle life than water-based coatings in nickel-zinc cells.

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INTRODUCTION

The NASA inorganic-organic (I/O) separator (ref. 1) was developed inhouse at the Lewis Research Center from 1973 through 1978. The development effort had several goals: to improve the flexibility of the separator, reduce the cost, and demonstrate production capability. This effort was driven primarily by the NASA Lewis program to improve separators (matrices) for metal-hydrogen batteries, alkaline fuel cells, and alkaline batteries with zinc electrodes (Ni/Zn, Ag/Zn).

The NASA Astropower I/O separator (refs. 2 and 3), which had demonstrated acceptable life and performance in heat sterilizable, sealed silver-zinc (Ag/Zn) cells, and in silver-hydrogen (Ag/H_2) cells (ref. 4) proved to be unsatisfactory in nickel-zinc (Ni/Zn) cells because of brittleness, high cost, and difficulty to produce in quantity.

With the success of improving flexibility, reducing cost, and demonstrating production feasibility, coupled with promising performance and cycle life in alkaline Ni/Zn cells, NASA decided to transfer the improved I/O separator technology to an industrial supplier. To this end, NASA entered into a cost-sharing contract (ref. 5) with the Munising Paper Division of Kimberly-Clark Corporation in 1976. Mindful of regulatory requirements for the work place and environment, the primary contract goals were to develop other substrates as replacement for asbestos, and modify the solvent-based separator coating formulations for compatibility with aqueous systems. Secondary goals of the contract were to develop an improved single-ply fuel cell grade asbestos sheet containing a binder and to produce the solvent-based NASA-improved I/O separator.

The initial effort resulted in evaluation of handsheet samples of four NASA solvent-based coatings on several substrates and water-based versions of the same substrates. With the results of the evaluation of these materials, the focus of the effort was directed to pilot plant production of samples in an effort to identify production-related problems. During the course of this development work, the solvent and several fillers in the coatings were designated by OSHA and EPA as contributing to health problems. In response to the regulatory requirements, other materials were evaluated and substituted into the separator production process. Substitution of the solvent affected the drying rate and the coating rheology. As a result, application of these modified coatings to several substrates required further formulation changes.

However by 1980 most of the problems were solved. Kimberly-Clark produced quantities of the modified solvent-and water-based separators on industrial production equipment. The development of the substrates and coatings and the application of the coatings to the substrates are described in reference 6, the contract report. (Some data on performance and cycle life are also included.)

The purpose of this report is to provide details and results of the evaluation of these production-version separators based upon cell and separator screening tests conducted at NASA Lewis.

EXPERIMENTAL

The experimental details are divided into two categories: laboratory screening tests to measure separator properties and in-cell testing to measure the effect of the separator on cell performance and cycle life.

Laboratory screening tests. - The measured separator properties were resistivity, pore size, porosity, zincate diffusivity, hydroxyl diffusivity, and zinc-dendrite penetration rate. The procedures used to measure these properties are outlined in the Air Force manual on screening methods, edited by Cooper and Fleischer (ref. 7). The d.c. method of measuring resistivity was used.

Cell testing. - The effect of separator properties on cell performance and cycle life were measured by comparing differences in cell performance and cycle life between the NASA I/O separator and the Kimberly-Clark production separator. Testing in Ni/Zn cells was performed in a standard 8-A-hr test cell where the separator and absorber materials could be varied from cell to cell.

Test cell construction: The zinc electrodes were enclosed in a separator bag (coated side out) which was constructed using the technique described in the Appendix of reference 6. The Ni/Zn cells had an absorber bag of beater-treated asbestos (BTA, the Kimberly-Clark 7-mil single-ply fuel cell grade-binder impregnated asbestos sheet) on the nickel electrode. Thirty-five-weight percent KOH solution was used as the electrolyte in the Ni/Zn cells. Electrode sizes were 7.3 cm by 9.4 cm with thickness ranging from 0.075 cm for the nickel electrodes to 0.22 cm for the zinc-oxide electrodes. The Ni/Zn cell electrode configuration was Ni/Zn/2Ni/Zn/Ni. Ampere-hour efficiencies reached 95 percent or greater after three formation cycles. Overcharge was limited to 10 percent in Ni/Zn cells.

Performance characterization: Performance was characterized at discharge rates of C/8 (the rate at which the nominal cell capacity is discharged in 8 hr), C/4, C/2, C, and 2C. Midpoint voltage (the cell voltage when 1/2 the nominal cell capacity has been discharged: for an 8-A-hr cell, voltage is at 4 A-hr) was recorded as was the ampere-hour capacity above 1 V.

Cycle testing: Cycle testing consisted of 8-hr cycles (6 hr of charge - C/12 rate and 2 hr discharge - C/4 rate). The discharge current density was about 7.5 mA/cm^2 at the C/4 rate. The testing was continuous; that is, 3 cycles/day, 7 days/week. Depth of discharge was 50 percent based on nominal cell capacity. Cell failure was determined to occur when the cell would no longer deliver 50 percent nominal capacity above 1 V for three consecutive cycles. The method of cell-discharge testing was changed from discharge through a constant load resistor to discharge at constant current. This resulted from a change in the automatic cycling test equipment in October 1980. As a result, most of the cycle test data on the Kimberly-Clark production separators was obtained at constant current charge and discharge while the data on the NASA standard separators was based on discharge through a constant load resistor. All performance characterization was obtained by constant current discharge. The relationship between cycle life obtained using both discharge methods was obtained experimentally for the Ni/Zn cell. The relationship shows that cycles at constant current discharge (CCD) must be multiplied by 1.80 to be equivalent to cycles obtained by constant load discharge (CCD): CLD = 1.80 (CCD).

Measurement of cell capacity: Part of the cycle-life testing included measuring the cell capacity from time to time. The procedure involved removing the cells from the cycle-test equipment at the end of the charge portion of the cycle. The cells were then discharged at the C/4 rate (CCD) on laboratory bench equipment to measure the capacity to 1 V. The cells were then charged to ~8.5 A-hr over a 16 to 17 hr period, then deep-discharged to 1 V at the C/4 rate (2 A). This process was repeated. Usually the capacities measured were reasonably close and an average value was obtained. If not, the deep-discharge cycle was repeated a third time to establish an average value. The cells were then recharged and returned to the cycle-test equipment for further testing.

RESULTS AND DISCUSSION

The contract effort with Kimberly-Clark was initially based upon modification of four NASA solvent-based separators developed for Ni/Zn and Ag/Zn cells. The formulation of these separators and the identification are shown in table 1. The K19W1 was the original flexible, machine-made separator used by NASA in early Ni/Zn cell tests for electric vehicles. This separator was widely distributed to the battery industry. The K19W2 was a variation of K19W1 formulated to reduce resistivity. The X40 and X47W1 formulations were developed for, and displayed acceptable performance and cycle life in Ag/Zn cells (ref. 8). Cycle testing in Ni/Zn cells also produced cycle life exceeding that of the K19W1 formulation.

While evaluation of these separators and their water-based homologs on several substrates was proceeding under the contract with Kimberly-Clark, the in-house development effort at The Lewis Research Center continued. Several new formulations, K143 and K144, were developed which showed lower resistivity and twice the cycle life of K19W1. These two separators were modifications of the X40 formula, but used the Kraton G binder and other less expensive inert fillers in place of the polypropylene-oxide binder and the calcium-zirconate filler shown in table I. The two separators plus an advanced I/O separator, identified as K158, were introduced to the development program at Kimberly-Clark. Table II identified the NASA formulations and filler compositions to which the Kimberly-Clark production separators are most closely related.

SOLVENT-BASED SEPARATOR PRODUCTION

Kimberly-Clark demonstrated its ability to produce the K19W1 on their 7-mil fuel cell grade asbestos sheet (BTA) and several commercial electrical grades of asbestos in 1978. However, the effort on K19W1 was discontinued because the formulation consistently exhibited undesirably high-volume resistivity values (30 to 60 Ω-cm). Data comparing the properties of the NASA machine-made I/O separators (K19W1, K158) with pilot-plant materials made by Kimberly-Clark are shown in table III. The results reflect some improvements of the K158 design over the K19W1 separator such as lower resistivity, smaller pore size, lower zinc-dendrite penetration rate, and greater cycle life.The formulation of K158 is shown in table IV.

The Kimberly-Clark production separators (table II) represent formulations which were compromises between good separator performance and their ability to produce a separator within the constraints of OSHA and EPA regulations. Because of personnel hazards associated with asbestos, organic solvents, and several fillers, other materials were evaluated and substituted into the separator-production process. The problems encountered are described in reference 6. The Kimberly-Clark production versions of the I/O separators (table II) were produced (Mar. 1980) on three substrates: BTA, cellulose, and a permanently wettable nonwoven polypropylene. NASA formulations for the machine coatings are shown in table V. Necessary modifications of these formulas to compensate for changes in coating rheology and three substrates are described in reference 6. Results of the laboratory screening tests to evaluate the separator properties of Kimberly-Clark solvent-based materials are shown in table VI. Test results on two commercial alkaline battery separators, cellophane and Celgard 3401, are included in table VI for comparison purposes.

Some explanation of the information in table VI is required. The table contains information on the NASA machine-made solvent-based separators, K143, K144 and K158. In the coating column the Kimberly-Clark designations ending in "P" represent modified versions of the solvent-based formulations shown in table V. The K172 on substrate N and G represent the unmodified NASA solvent-coating formulation, which was used as a control to determine the effect of formula modifications.

The substrate column identifies substrates by letters, as described in the table VI footnotes. The designation K172N identifies the K172 coating on the cellulose substrate; K177PG identifies the Kimberly-Clark version of K177 on the BTA.

WATER-BASED SEPARATOR PRODUCTION

The results of laboratory screening tests on water-based separators produced by Kimberly-Clark are presented in table VII. Problems encountered with modifying the solvent coatings were more easily resolved than with aqueous coatings. Working within the constraints of program dollars and declining interest for the Ni/Zn application, and evaluation effort on water-based separators was restricted to one NASA coating formula and a low-cost coating suggested by Kimberly-Clark.

The original coating systems based on the butyl rubber (K40, K40A and K40C in table VII) performed with reasonable success as separators but exhibited blocking (a tendency for the material to adhere to itself when rolled upon itself). The blocking problem could be overcome by using a release liner during product roll-up, but this results in higher production costs. The C47972 formulation on the cellulose substrate has the butyl-rubber binder. Its formulation can be found in table XV of reference 6. To eliminate the blocking problems, the modified Kraton G binder was emulsified and used as the binder for the water-based systems. Formulations for the water-based K172 and the low-cost NYAD coatings are given in table XVII of reference 6.

Some general comparisons are made between the Kimberly-Clark solvent and water-based separators and the commercial separators, cellophane and Celgard 3401:

(1) The Kimberly-Clark solvent and water-based separators (except K173PR) exhibit much lower resistivities than the two commercial separators.

(2) Zincate diffusivity values are 1/4 to 1/2 of the values of the two commercial products.

(3) Many of the pore-size values of solvent-based separators are close to the 90 A value of Celgard 3401.

(4) The hydroxyl diffusion rate is only 1/4 to 1/3 the value of the commercial separators.

SEPARATOR CHARACTERIZATION

Characterization of the separators produced by Kimberly-Clark using production equipment is divided into two sets of data: the laboratory screening tests used to evaluate properties of separator materials and in-cell tests used to characterize performance and measure cycle life. The following general statements are true for both the solvent and water-based coated separators. There are some exceptions which will be pointed out during the specific discussion of results.

(1) Characteristics of the separators were examined to determine whether the particular coating of substrate affected the measured separator properties. Resistivity and porosity seemed to be more strongly influenced by substrate. Zinc-dendrite penetration and hydroxyl diffusion rates appeared more affected by coating formula. Zincate diffusivity and pore size did not appear related to either substrate or coating.

(2) Data taken from cell tests include performance characterization (voltage decreased as a function of increased discharge rate), cycle life, and rate of capacity loss. Cycle life appeared to be affected mostly by substrate for a given coating; whereas, performance characteristics and capacity loss did not appear related to either coating or substrate. Further distinction can be drawn between solvent and water-based coated separators. Solvent-based separators produced greater cycle life and a lower rate of capacity loss than aqueous coatings. However, aqueous-coated separators showed better performance characteristics.

RESISTIVITY

For comparison, separator resistivity was grouped according to substrate (see fig. 1). The K173P coating produced the highest resistivity in each substrate group. As a substrate group, the coatings on polypropylene (S49024) (R) showed higher resistivities than either cellulose (N) or BTA (G). There was no clearcut difference between cellulose and BTA.

The resistivity data of the aqueous coatings (K172 and NYAD), shown in figure 2, are similar to the solvent coatings where the coated polypropylene gave a higher resistivity. However with the K172 aqueous coating, the BTA has a somewhat higher resistivity than the S49024 polypropylene.

POROSITY

Porosity is a measure of the void volume of the separator which reflects the separator's ability to hold electrolyte. For both the solvent and water-based coatings, BTA substrate porosity values ranged from 55 to 62 percent, cellulose ranged from 42 to 52 percent, while the coated polypropylene separators ranged from 18 to 28 percent. Results are displayed in figures 3 and 4 for comparison.

PORE SIZE

Pore size of solvent-based separators are compared by grouping according to substrate (fig. 5). The coated BTA pore size ranges from ~70 to 100 Å, coated polypropylene substrates range from ~90 to 150 Å, and coated cellulose ranges from ~110 to ~250 Å. The aqueous-coated separators show a similar relationship between BTA and polypropylenes but with a much greater difference (see fig. 6).

The relationship of the water-based, NYAD-coated cellulose and polypropylene is reversed from the solvent-coated relationship.

ZINCATE DIFFUSIVITY

There is no obvious relationship for the solvent-based coatings when results are grouped by either substrate or coating. Measurements on aqueous-coated separators show that the polypropylene substrate has a somewhat lower zincate diffusion rate than cellulose for the NYAD coating, but a higher zincate diffusion rate than BTA for the aqueous K172 coating. Again no obvious relationship exists.

ZINC DENDRITE PENETRATION RATE

When the zinc-dendrite penetration rate measurements of the solvent-based separators are grouped according to coating in figure 7, the K173P and K177P coatings appear to be superior (lower penetration rate) to the K172P and K168P coatings. When the results of the aqueous separators are grouped by substrate, as shown in figure 8, the NYAD-coated polypropylene substrate showed a higher dendrite penetration rate than the NYAD-coated cellulose; the K172 coating on BTA had the lowest dendrite penetration rate.

HYDROXYL DIFFUSION RATE

When hydroxyl diffusion rate measurements are group according to the solvent-based coatings (as shown in fig. 9), the K168P coating exhibits the highest hydroxyl diffusion rate of the solvent-coated separators regardless of substrate. The water-based coatings show generally greater hydroxyl diffusion than the solvent-based coatings except for K168P. The water-based K172P on BTA and polypropylene has a hydroxyl diffusion rate about twice that of the similar K172P solvent-coated substrate.

COMPARISON OF SOLVENT AND WATER-BASED COATED K172

K172 was coated as the modified (K172P) and unmodified (K172) solvent-based formulation as well as the water-based modified formulation (K172P). As a result, the difference between the three coating materials can be evaluated on several substrates. From the data in table VIII an obvious order emerges. Considering resistivity to be the inverse of ionic conductivity, the seven values of ionic conductivity, hydroxyl diffusivity, zincate diffusity (two exceptions), pore size (one exception), and zinc dendrite penetration rate (one exception) all increase in the following order: solvent to modified solvent to water base, regardless of substrate. With the limited data sample, there is an apparent inverse relationship between volume resistivity and hydroxyl diffusivity.

CELL TEST RESULTS

The true evaluation of a separator material comes from its performance in test cells under different load conditions (discharge rates) and cycle-life testing to failure.

The solvent and water-based separators were extensively cell-tested to identify the differences in performance and life.

Table IX contains results of cell tests of both the NASA I/O solvent-based separators and the Kimberly-Clark solvent and water-based separator materials. Table IX also includes data on the test cells containing commercially available cellophane and Celgard separator materials. In table IX coating and substrate are identified in column 2. Midpoint voltages (at 2.0-A hr capacity discharged) are shown in column 3 for the C/4 and 2C discharge rates, the rate (linear slope) at which the midpoint voltage decreases as a function of discharge rate between the C/8 and 2C, rates is shown in column 4. With the data in columns C/4 and 2C, a linear curve of midpoint voltage versus dicharge rate can be drawn since correlation coefficients were > -0.985 in all cases. The column on cycle life contains three types of information. The subheading CCD (Constant Current Discharge) lists the three cycles used to compute the mean values under the subheading Mean Cycle Life (in some cases only two values were used with the other dropped). The ± value represents the standard deviation (1 δ) about the mean. The values appearing under Mean Cycle Life and having no values under the CCD subheading were earlier data, obtained using discharge through a constant load resistor. The values shown under the subheading Mean x 1.8 represents estimates of cycle life which would be obtained under constant load discharge.

Only those values which are shown in the column Mean x 1.8 are within the mean value and standard deviation of K19W1 (257 ± 10 cycles) or exceed it . The estimated values of cellophane and Celgard cycle life are shown at the bottom of the column. The last column provides the value for the rate of capacity loss versus cycles for 8-A-hr test cells. This information was obtained by measuring the cell capacity after a deep discharge cycle at various times during the cycle life. Data are shown for separators where three or more measurements of cell capacity were made during cycle testing. The data can be used for further comparison between separator coatings and substrates.

PERFORMANCE CHARACTERIZATION

Midpoint voltages are important since they represent the expected plateau voltage a cell will exhibit under a load condition. Data on midpoint voltage at the C/4 and 2C discharge rates are shown in table IX. For the most part, the rate of voltage drop is linear with increasing discharge rate. The greatest deviation from linear behavior occurred with the K143 and K144 NASA I/O separators at the higher rates (C, 2C). Based on the relatively higher resistivity (30 to 40 Ω-cm) and the lower hydroxyl diffusion rate data ($1\text{-}5\times10^{-5}$ moles/cm^2-min) shown in table VI, this behavior is expected. Voltage losses for K143 and K144 are compared with Celgard and cellophane in figure 10. The two commercial separators showed the lowest rates of loss. This is consistent with their use in high-rate batteries.

The slopes for K143 and K144, -0.606 and -0.629, shown in table XI are based on a linear regression analysis which predicts the values at the 2C rate, shown in parentheses. Figure 11 compares the drop in midpoint voltage versus discharge rate for the solvent-based K172, K172P, and K172P water-based formulas on the BTA substrate. The water-based K172P exhibits the least rate of voltage loss.

Other significant comparisons of voltage loss with increasing discharge rate are:

(1) The lowest (best) rate of voltage drop for a solvent-based separator was K143C on polypropylene substrate (-0.194).

(2) The K177TP coating exhibited nearly the same rate for all three substrates (-0.210 to -0.212).

(3) The lowest rate was shown by the water-based coating C-47972 on cellulose (-0.175). This is shown in figure 12 along with the NYAD coating on cellulose and PP.

The C47972 separator (cellulose substrate) has a plateau or operating voltage closest to the operating voltage of cellophane and Celgard separators. These I/O separators were not designed to be solely high-rate separators. The goal was to design a separator which exhibits good performance along with good cycle life and low production cost.

A typical set of discharge voltage versus ampere-hours-capacity curves are shown in figure 4. The data show that the Kimberly-Clark production separator K172PG (BTA substrate) has about 35 mV higher operating voltage at the C/2 rate (4 A) than the NASA K19W1F and K144F separators. Although the cellophane showed better voltage performance at the start and near the end of discharge, the midpoint voltage was ~ 20 mV lower than the K172P. The formula modifications made by Kimberly-Clark to achieve a production separator have resulted in separators possessing better performancé characteristics than the NASA production materials and the commercial separators (except at high rates).

CYCLE LIFE

The results of cycle-life testing based on the cycling regime described in the "Experimental" section are shown in table IX. Those estimates which equal or exceed the cycle life of K19W1F are shown in figure 14 along with data on the NASA separators, K19W1F, K143F, K144F and K158F. Figure 14 also contains cycle-life data on commercial and developmental separators, which were also evaluated at Lewis so that work on the I/O separator materials would remain in perspective and represent an improved technology. The shaded areas on certain bars represent the estimated cycle life as a result of multiplying cycle life results by 1.8 for comparison with earlier cycle-life data. The separator designations with the o preceeding indicate the water-based separators. The substrate letter code is inserted before the formula number to avoid confusion between water and solvent-based separator designations. Details of cell construction are given in table X.

Data on the Kimberly-Clark production separator show that almost all of the materials which were equal to or exceeded the cycle life of K19W1F have an asbestos substrate. The only exceptions are the K177TP solvent coating on the cellulose (N) and polypropylene (R) substrates.

The only water-based coating which exceeded the cycle life of K19W1 was the K172P, also on asbestos. Cycle life results on the water-based K40A on asbestos and cellulose substrate are included since they were reasonably close to K19W1.

Further examination of the data in table IX shows that, except for the K177TP coating, the cycle life decreases with substrate from asbestos to cellulose to polypropylene. The result is true for water-based coatings as well. The production version of a K168PG separator made for a Ni/Zn wheelchair battery demonstration program by the NASA Headquarters Technology Utilization Office approaches the cycle life of K143F and K144F. The general conclusion that can be drawn from cycle life data in figure 14 is that the Kimberly-Clark production version of separators shown here exhibit better cycle life in small Ni/Zn cells than most commercially available separators. Further, the cycle life of K168PG and K172G approach the cycle life of the best NASA production batch separators, K143F, K144F, and K158F.

RATE OF CAPACITY LOSS

As a group, those separators based on the NASA K143 separator (K173P, K143B, and K143C) have higher capacity rate losses than any other group. The exception was the K143BR which has a low value of -0.010 A-hr/cycle. However, the K143BR cells did not attain many cycles and failed by dendritic shorting, which was characteristic of the polypropylene-based separators. The group based on the NASA K144 separator (K172 and K172P) showed the lowest rate of loss for the K172 and K172P formulations. Only the K172N and the water-based KR172P had rate values above -0.012 A-hr/cycle. The group based on NASA 158 (K177TP and K168P) cover a range. The best rate value belongs to K168PG. The worst values belong to K177TPN and K168PN, both on cellulose substrate. The worst group for rate of capacity loss was the low-cost NYAD formulations (water-based coating) on cellulose and polypropylene. The rate of capacity loss with cellophane was well above most of the Kimberly-Clark production separators.

Some of the capacity loss data versus cycle life are plotted in figure 15. Whereas cellophane would predict a 50 percent capacity (4 A-hr) at ~250 cycles, the others extrapolate to 1/2 capacity at 300 to 350 cycles. Differences between the extrapolated values and the actual cycle-life values in table IX probably result from correlating the data to a linear model since the correlation coefficients ranged from -0.778 to -0.999. The effort to measure the rate of capacity loss in Ni/Zn cells showed that occasional deep-discharge reconditioning was beneficial for the cells. In most cases, the cell capacity displayed during the cycle testing just before deep-discharge reconditioning was improved by 20 to 50 percent as a result of the deepdischarge treatment. As the cells aged, the improvement in capacity was not long retained once the cycle test resumed.

CONCLUDING REMARKS

The effort to produce improved versions of the NASA inorganic-organic separator materials on commercial production equipment was moderately successful. However from the standpoint of producing a commercial product, the use of asbestos in the separator was unacceptable to the Kimberly-Clark Corporation. This consideration when coupled with the requirement of a solvent-recovering system necessary for a volume-production facility for a solvent-based separator severely limits the production potential of the separator.

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TABLE I. - SOLVENT-BASED NASA COATING FORMULATION[1].

	K19W1	K19W2	X40	X47W1
Kraton GX7050	40	40	-	-
Trichloroethylene	500	500	-	-
PPO	-	-	47	47
Chloroform	-	-	410	410
Paraplex G62	16	16	-	-
Plastolein 9750	-	-	47	47
Cab-O-Sil	3.2	6.4	4.8	2
Lead Titanate	20	20	-	-
Wollastonite P-15	55.2	55.2	-	26.2
Magnesium Titanate	-	-	-	36
Calcium Zirconate	-	-	142	-

[1] Parts by weight.

TABLE II. - FILLER COMPOSITION OF NASA SEPARATORS; RELATIONSHIP TO KIMBERLY-CLARK SEPARATORS.

NASA formulation	Kimberly-Clark production	Filler composition of NASA formulations
K19W1	K19W1	calcium silicate, silica, lead titanate
K143	K173P, K143B, K143C	wood flour silica (fine particle)
K144	K172P	calcium zirconate silicate silica (fine particle)
K158	K168P, K177P K158	titania aluminum silicate titanate-zirconate

TABLE III. - COMPARISON OF NASA MACHINE-MADE I/O SEPERATORS WITH KIMBERLY-CLARK TRIAL PRODUCTION BATCH SEPARATOR MATERIALS.

Produced by	Coating	Substrate	Vol-res, Ω -CM	Zn-dendrite pen. rate, cm/min	Pore size, Å	Porosity, percent	Cycle life to <1 V, end of discharge; mean ± std. dev.
NASA	K19W1	F	40	5.5×10^{-4}	120	65	257 ± 10
KC	K19W1	G	33	8.7×10^{-4}	195	62	162 ± 36
KC	K19W1	FF	64	19.0×10^{-4}	135	43	364 ± 13
NASA	K158	F	30	3.9×10^{-4}	90	54	317 ± 34
KC	K158	HH	22	6.9×10^{-4}	23	55	231 ± 35
KC	K158	FF	28	1.1×10^{-4}	54	52	231 ± 14

F - 2 percent PPO impregnated fuel cell grade asbestos - 10-mil - 4-ply - NASA standard.

G - Single-ply - 7-mil - beater-treated binder impregnated fuel cell grade asbestos.

FF - 7-mil electrical grade asbestos (MANNITEMP 111).

HH - 7-mil commercial grade asbestos - 10 percent cellulose (MANNITEMP 170).

TABLE IV. - K158 FORMULATION[1].

Kraton G1650	40
Toluene	300
Plastolein 9750	20
Hydrite UF	26.3
Unitane O-110	36
Lead Titanate	22.5
P-25 Titanium Dioxise	16

[1] Parts by weight.

TABLE V. - NASA FORMULATIONS FOR MACHINE COATING[1].

	K168T	K172	K173	K177	K143B	K143C
Kraton G1650	40	40	40	40	40	40
Plastelein 9750	20	16	16	20	-	-
Toluene	350	350	350	350	350	350
Hydrite UF	26.3	-	-	26.3	-	-
Unitane O-110	36	-	-	36	-	-
P-25 TiO_2	16	20	20	16	-	20
Lead Zirconium Titanate	15.2	-	-	-	-	-
Calcium Zirconium Silicate	-	116.3	-	12.9	-	-
Wood Flour	-	-	24	-	24	24
Cab-o-Sil (M5)	-	-	-	-	4.8	-
Rhoplex HA-16	-	-	-	-	35.2	35.2

[1] Parts by weight.

TABLE VI. - COMPARISON OF NASA MACHINE-MADE I/O SEPARATOR WITH KIMBERLY-CLARK PRODUCTION VERSIONS (SOLVENT BASE).

Produced by	Coating	Substrate[a]	Vol-res, Ω -cm	Zn-dendrite penetration cm/min rate	Zincate diffusion, moles/cm^2-min	Hydroxyl diffusion, mole/cm^2-min	Pore size, Å	Porosity, percent
NASA	K143	F	17.6	5.8x10^{-4}	1.43x10^{-7}	4.9x10^{-5}	480	58
KC	K173P	N	11.3	34.0	4.8	5.7	240	50
	K173P	R	26.9	5.2	1.5	3.5	90	26
	K173P	G	11.6	6.0	3.3	5.7	80	54
	K143B	R	3.3	28.0	8.1	15.6	-	37
	K143C	R	4.9	12.0	4.8	5.9	90	37
NASA	K144	F	26.1	7.7	4.2	1.9	280	63
KC	K172P	N	5.2	12.5	5.4	5.5	130	45
	K172P	R	18.5	7.3	4.3	5.6	120	22
	K172P	G	8.0	11.0	4.4	5.1	70	60
	K172	N	14.6	7.4	5.4	3.2	150	45
	K172	G	22	3.5	2.2	2.9	50	50
NASA	K158	F	30.0	3.9	3.4	2.1	90	54
KC	K177P	N	6.4	7.1	2.9	6.5	110	53
	K177P	R	13.9	5.7	3.7	6.4	130	17
	K177P	G	6.0	4.3	8.3	7.8	60	55
	K168P	N	3.2	12.6	3.6	8.5	210	42
	K168P	R	13.3	8.4	7.1	15.2	140	18
	K168P	G	6.9	10.8	5.1	13.2	100	62
	K168P*	G	5.6	1.6	0.4	10.6	100	66
DUPONT	CELLOPHANE	-	20	0.37	22.9	22.7	15	52
CELANESE	CELGARD 3401	-	31	8.5	29.4	24.1	90	23

[a] F - 2-percent, PPO impregnated fuel cell grade asbestos - 10 mil - 4 ply - NASA standard.
[a] N - KC cellulose saturating base.
[a] R - 45-g/m^2 permanently wettable polyproplyene - S49024.
[a] G - Single-ply 7-mil beater-treated binder impregnated fuel cell asbestos.
* - Production batch for wheelchair battery demonstration.

TABLE VII. - KIMBERLY-CLARK WATER-BASED PRODUCTION SEPARATORS.

Produced by	Coating	Substrate[a]	Vol-res, Ω -cm	Zn-dendrite penetration cm/min rate	Zincate diffusion, moles/cm^2-min	Hydroxyl diffusion, moles/cm^2-min	Pore size, Å	Porosity, percent
KC	K40	G	15	9.2×10^{-4}	-	-	780	52
	K40A	N	13	13.4	-	-	11430	26
	K40C	FF	14	15.3	-	-	130	60
	K172P	G	6.8	8.8	3.1×10^{-7}	11×10^{-5}	130	53
	K172P	R	8.7	11.3	11.3	10	300	19
	NYAD	N	6.0	10.2	8.4	6.6	610	34
	NYAD	R	18	20.8	6.7	10	890	17
	C47972	N	12	6.7	-	-	5600	32

G - Single-ply 7-mil beater-treated binder impregnated fuel cell asbestos.
N - KC cellulose saturating base.
R - 45-g/m^2 permanently wettable nonwoven polypropylene
FF - 7-mil electrical grade asbestos (MANNITEMP 111).

TABLE VIII. - COMPARISON OF K172 FORMULATIONS - SOLVENT AND WATER BASE.

Solvent(S) or water base (A)	Coating	Substrate*	Vol-res, -cm	Zn-dendrite pen. rate, cm/min	Zincate diffusion, moles/cm^2-min	Hydroxyl diffusion, moles/cm^{2}min	Pore size, Å	Porosity, percent
S	K172	G	22	$3.5\text{x}10^{-4}$	$2.2\text{x}10^{-7}$	$2.9\text{x}10^{-5}$	50	50
S	K172P	G	8.0	11.0	4.4	5.1	70	60
A	K172P	G	6.8	8.8	3.1	11.0	130	53
S	K172P	R	18.5	7.3	4.3	5.6	120	22
A	K172P	R	8.7	11.3	11.3	10.0	300	19
S	K172	N	14.6	7.4	5.4	3.2	150	45
S	K172P	N	5.2	12.5	5.4	5.5	130	45

*G - Single-ply 7-mil beater-treated binder impregnated fuel cell asbestos.
R - 45-g/m^2 permanently wettable polypropylene.
N - KC cellulose saturating base.

TABLE IX.
CELL TEST PERFORMANCE AND CYCLE LIFE RESULTS

Product by	Coating	Sub-strate	Midpoint voltages at discharge rate		Midpoint voltage loss as a function of discharge rate, V/c/x	Cycle life; C/4 discharge to 1 V at end of discharge			Rate of A-hr capacity loss as a function of cycles,
			C/4	2C		CCD	MEAN cycle life	MEAN X1.8	(A-hr/cycle)
NASA	K143	F	1.56	(0.51)	-0.606	----------	441±44	---	-----
KC	K173P	G	1.59	1.19	-0.229	176,23,48	------	---	-0.0196
	K173P	N	1.60	1.16	-0.246	156,69,44	------	---	-0.0198
	K173P	R	1.58	1.14	-0.252	24,45,161	------	---	-----
	K143B	R	1.57	1.08	-0.281	98,121,126	------	---	-0.0100
	K143C	R	1.59	1.26	-0.194	90,93,85	------	---	-0.0132
NASA	K144	F	1.56	(0.46)	-0.629	----------	483±82	---	-0.0118
KC	K172	G	1.57	1.06	-0.288	213,165,196	191±24	344	-0.0117
	K172P	G	1.59	1.16	-0.235	167,162,71	164±4	296	-0.0101
	K172	N	1.58	1.08	-0.284	23,162,169	165±5	298	-0.0097
	K172P	N	1.59	1.20	-0.224	160,125,89	-----	---	-0.016
	K172P	R	1.59	1.22	-0.213	47,76,46	-----	---	-----
o	K172P	G	1.59	1.25	-0.193	126,153,130	136±15	245	-0.0114
o	K172P	R	1.58	1.22	-0.209	59,64,86	-----	---	-0.0144
NASA	K158	F	1.55	0.99	-0.314	340,275,336	317±34	570	-0.0071
KC	K177TP	G	1.59	1.22	-0.210	160,153,165	159±6	287	-0.0142
	K177TP	N	1.59	1.22	-0.212	142,161,166	156±12	281	-0.020
	K177TP	R	1.58	1.21	-0.212	99,161,144	152±12	274	-0.013
	K168P	G	1.59	1.22	-0.210	82,147,175	161±20	290	-----
	K168P*	G	1.58	1.13	-0.256	209,233,226	222±12	400	-0.0106
	K168P	N	1.58	1.10	-0.273	46,119,53	-----	---	-0.021
	K168P	R	1.57	1.13	-0.219	69,86,71	-----	---	-----
NASA	X40	F	---	---	----	----------	337±150	---	-----
KC o	K40A	N	1.60	1.25	-0.201	----------	226±6	---	-----
o	K40A	G	1.60	1.26	-0.196	----------	230±20	---	-----
o	K40C	FF	1.56	1.24	-0.189	----------	243±29	---	-----
o	NYAD	N	1.56	1.15	-0.238	75,116,87	------	---	-0.025
o	NYAD	R	1.59	1.25	-0.194	50,79,74	------	---	-0.024
o	C47972	N	1.61	1.30	-0.175	98,198,84	------	---	-----
DUPONT	CELLOPHANE-		1.58	1.33	-0.143	131	------	238	-0.0181
CELANESE	CELGARD 3401 -		1.58	1.37	-0.133	82	------	147	-0.0109

o Water-base separator.
* Production batch for wheelchair demonstration batteries.
F - 10-mil 4-ply cell grade asbestos impregnated with 2 wt. percent polyphenelyene oxide.
G - 7-mil single-ply fuel cell grade asbestos impregnated with 5 wt. percent butyl rubber binder.
N - Kimberly-Clark cellulose saturating base.
R - 45-g/m^2 permanently wettable polypropylene (S49024).

TABLE X. - Ni/Zn CELL CONSTRUCTION (fig. 14).

Material	Ni electrode	Zn electrode	Supplier
DLSP	BTA	DALKASEP (1 layer)	W. R. Grace
DARMC	BTA	DURAMIC (1 layer)	W. R. Grace
P1010	BTA	P1010 (2 wraps)	RAI
SAC 2016	BTA	EATH 2016 (2 wraps)	SAC Membrance Products
CG STD	BTA	Celgard 3400 (2 wraps)	Celanese Research
C-19 STD	Pellon (5 mil)	Cellophane (5 wraps)	Yardney Electric
K168 PG	BTA	K168 (solvent) on BTA (Bag)	Kimberly-Clark
K172G	BTA	K172 (solvent) on BTA (Bag)	Kimberly-Clark
K172PG	BTA	K172P (solvent) on BTA (Bag)	Kimberly-Clark
KG172	BTA	K172 (aqueous) on BTA (Bag)	Kimberly-Clark
K177TPN	BTA	K177TP (solvent) on (Bag) cellulose	Kimberly-Clark
K177TPR	BTA	K177TP (solvent) on Polypropylene (S-49024) (Bag)	Kimberly-Clark
K19W1F	Asbestos - 2% PPO	K19W1 (solvent) on asbestos (2% PPO) (Bag)	NASA
K143F	Asbestos - 2% PPO	K143 (solvent) on asbestos (2% PPO) (Bag)	NASA
1258F	Asbestos - 2% PPO	K158 (solvent) on asbestos (2% PPO) (Bag)	NASA

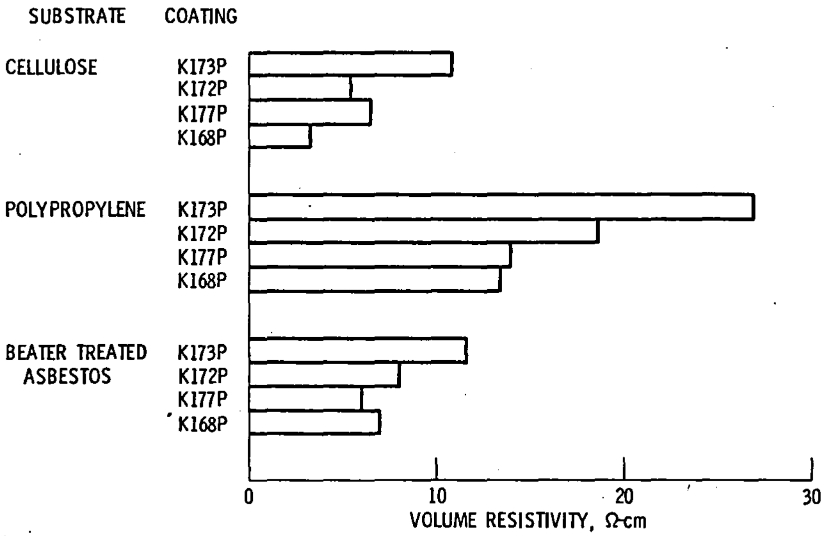

Figure 1. - Separator resistivity compared by substrate grouping.

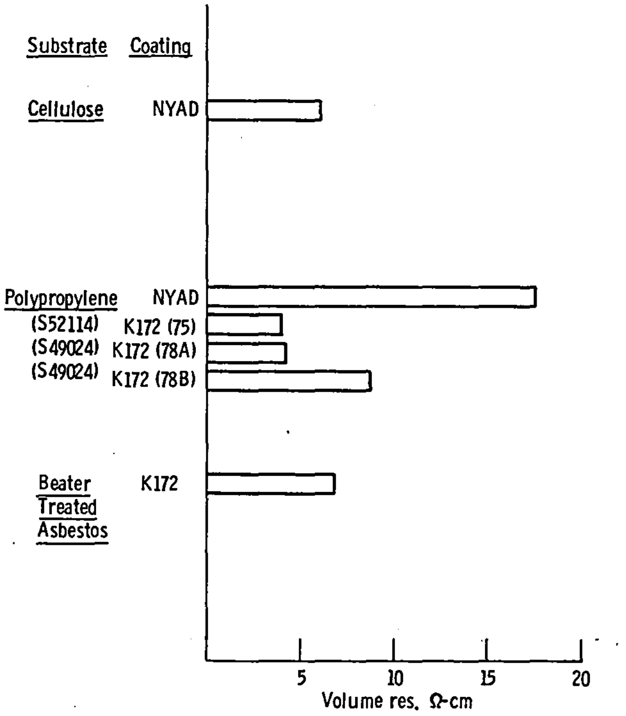

Figure 2. - Comparison of volume resistivity based on substrate; water base coatings.

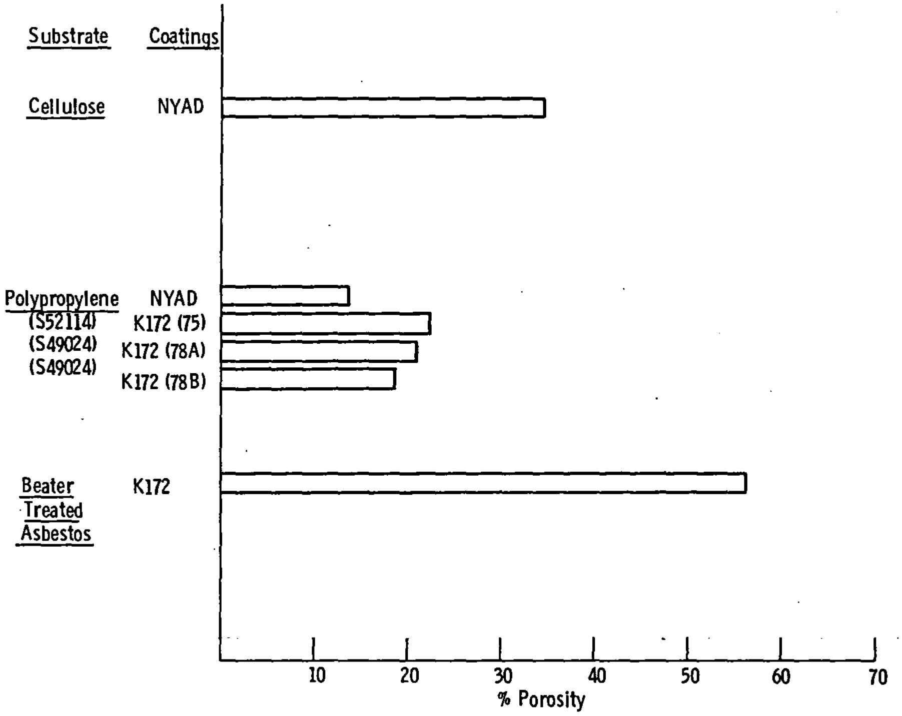

Figure 4. - Comparison of porosity according to substrate; water base coatings.

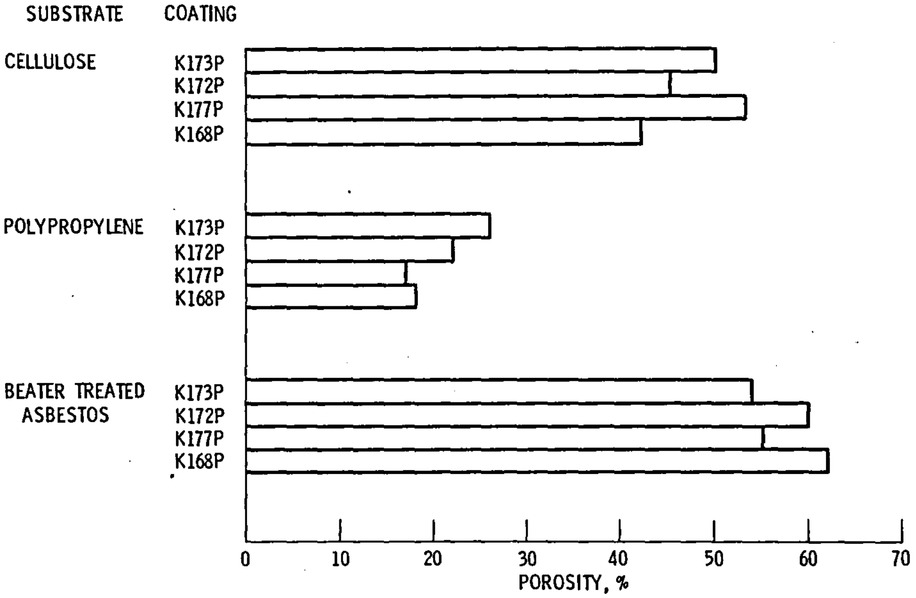

Figure 3. - Separator porosity compared by substrate grouping.

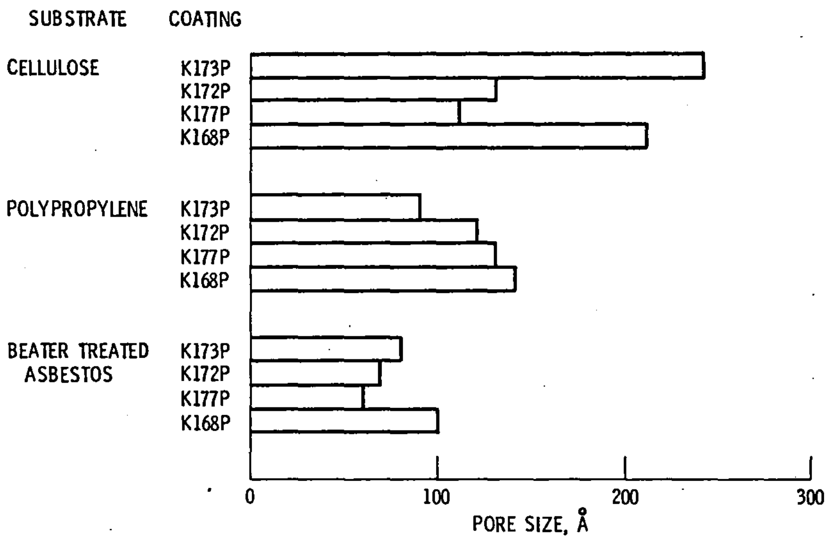

Figure 5. - Separator pore size compared by substrate grouping.

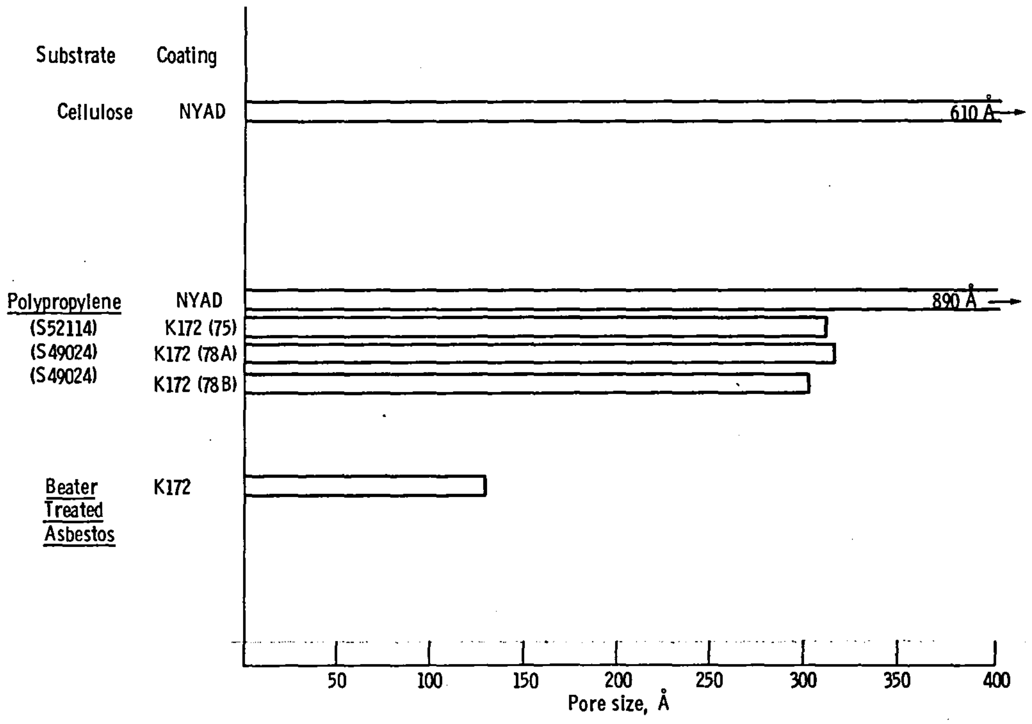

Figure 6. - Comparison of pore size according to substrate; waterbase coatings.

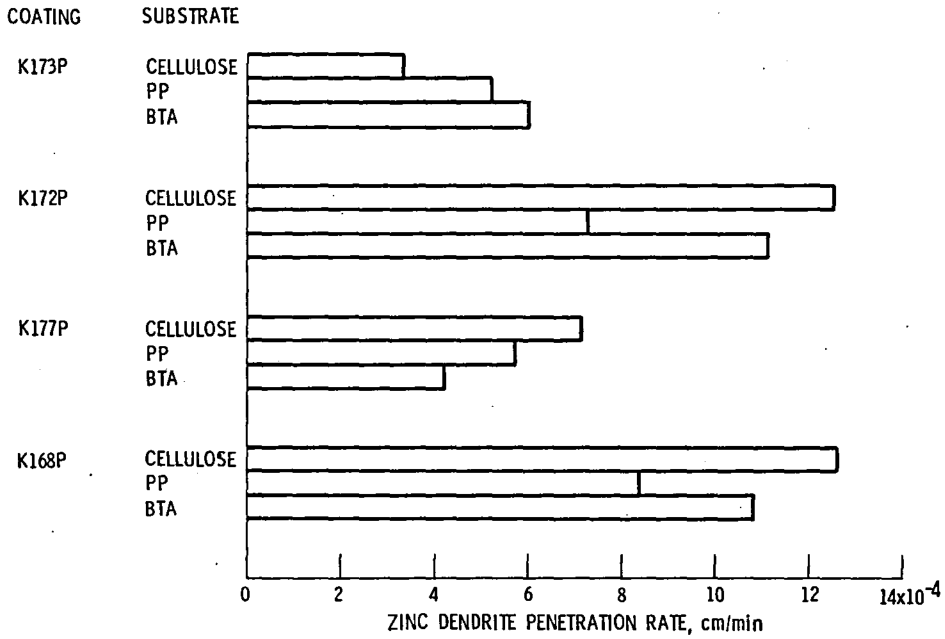

Figure 7. - Zinc dendrite penetration rate compared by coating grouping.

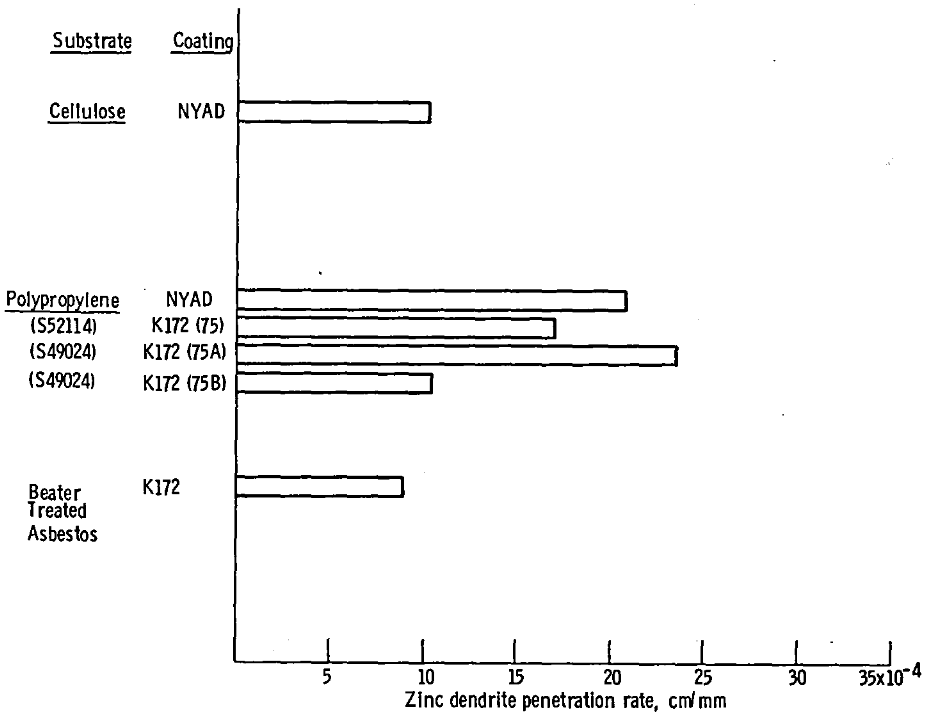

Figure 8. - Comparison of zinc dendrite penetration rate according to substrate; water base coatings.

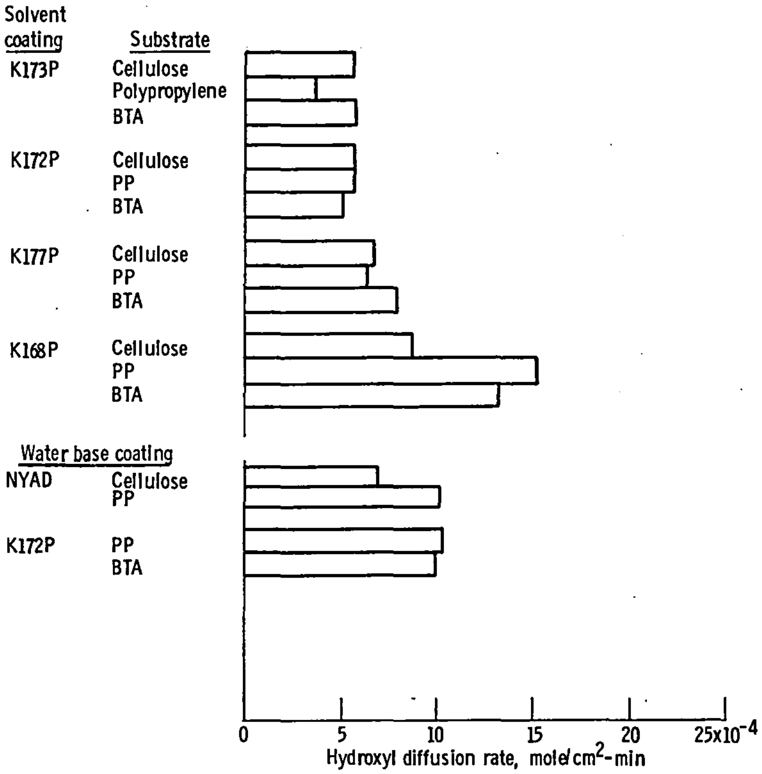

Figure 9. - Hydroxyl diffusion rate compared by coating.

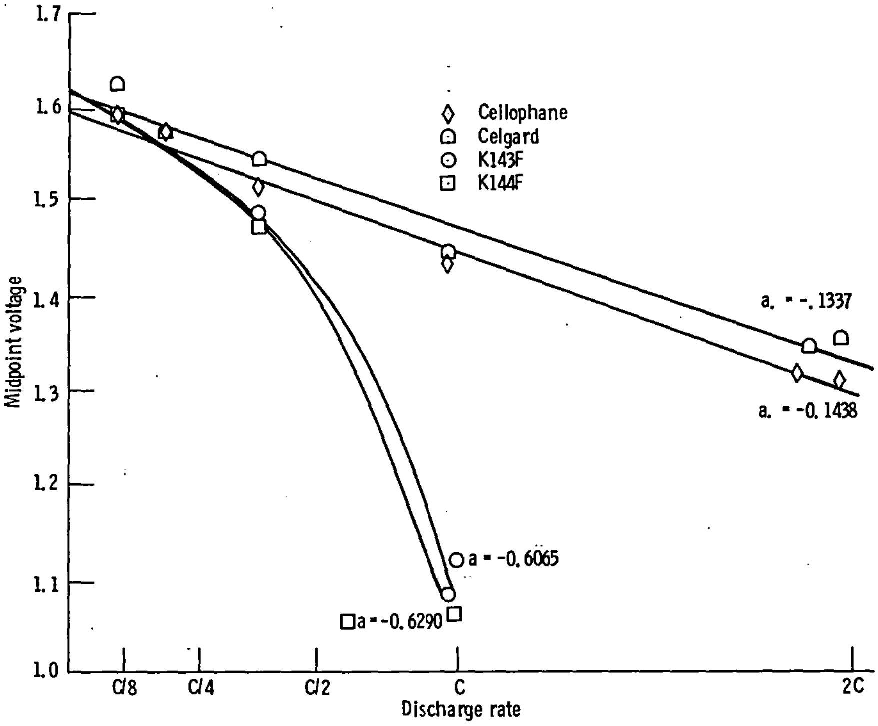

Figure 10. - Midpoint voltage versus discharge rate.

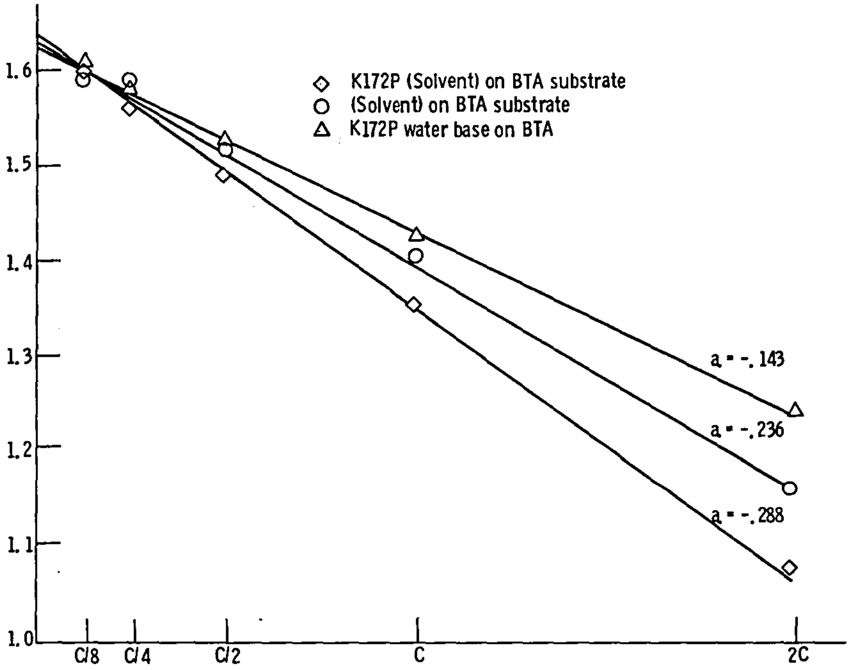

Figure 11. - Midpoint voltage versus discharge rate for K172.

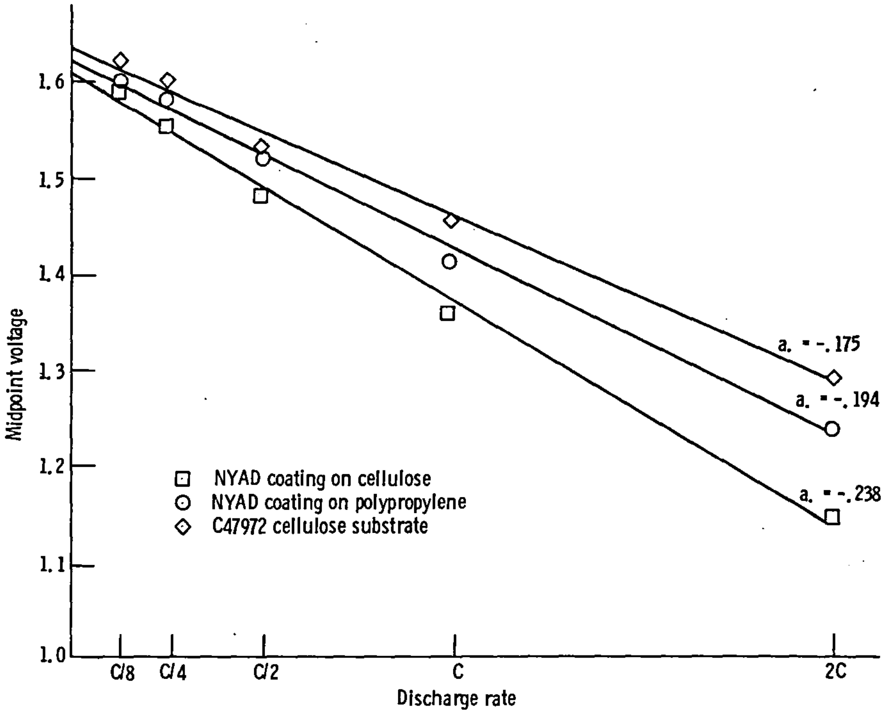

Figure 12. - Midpoint voltage versus discharge rate; water base coatings.

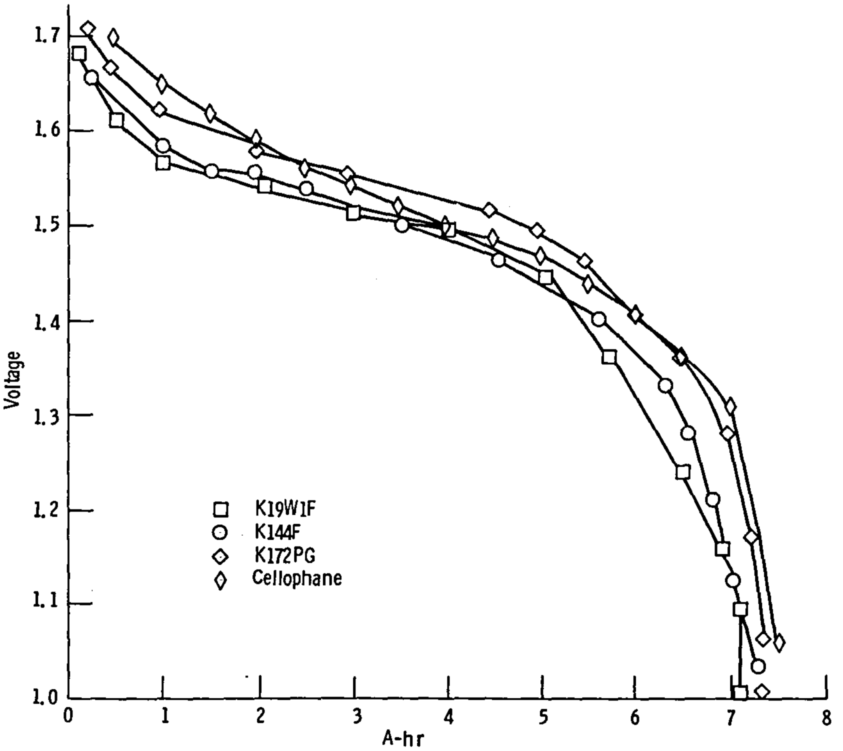

Figure 13. - Comparison of voltage (C/2 discharge rate) of Kimberly-Clark production separators with NASA separators and cellophane.

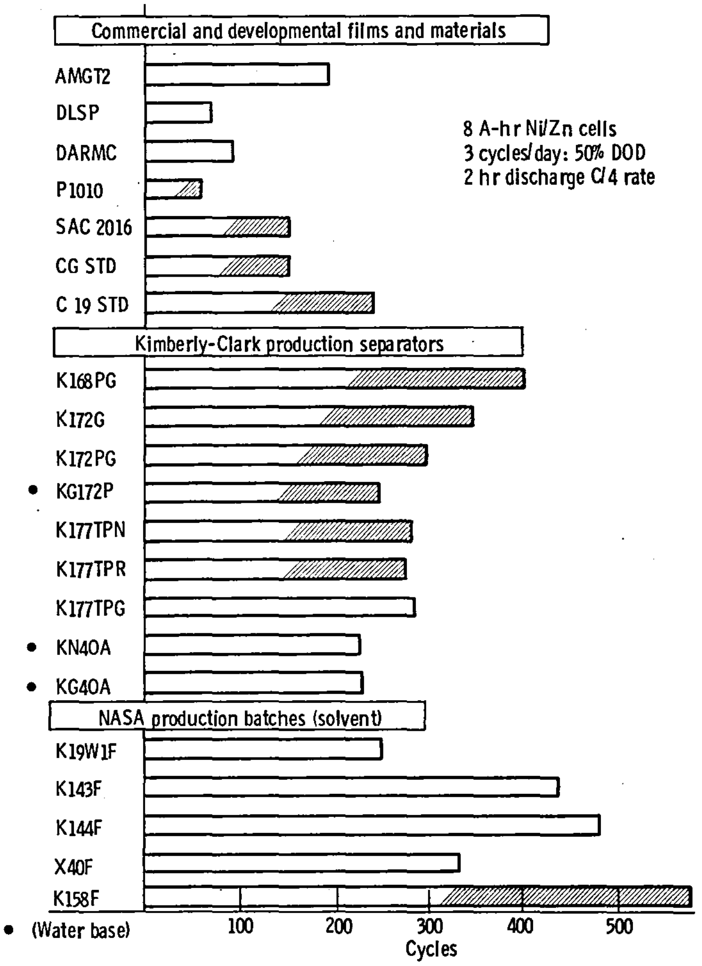

Figure 14. - Cycle life comparisons of commerical and developmental separators, Kimberly-Clark production runs, and NASA production batches.

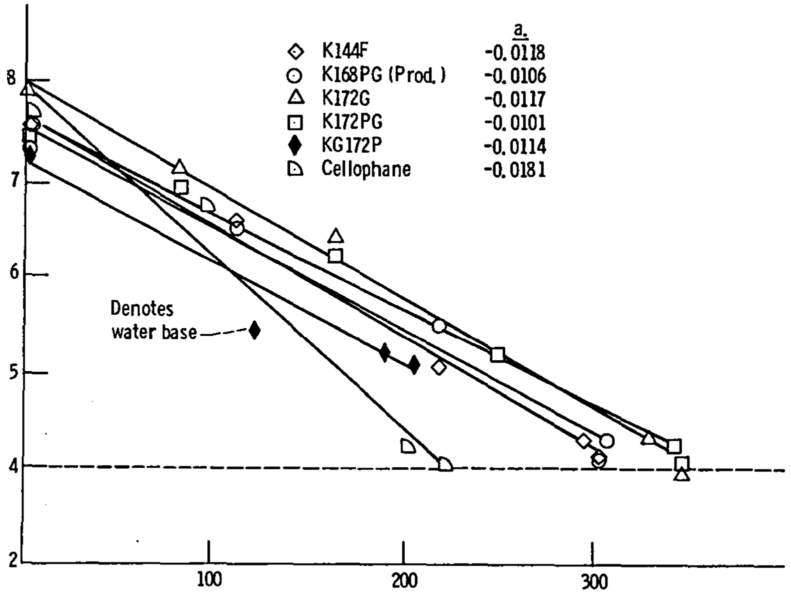

Figure 15. - Ampere-hr capacity loss vs. cycle life.

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16. Abstract

As a result of successful in-house effort at NASA Lewis Research Center to develop the technology of an inorganic-organic (I/O) separator, which demonstrated improved flexibility, reduced cost, production feasibility and improved cycle life, it was decided to transfer the improved I/O separator technology to an industrial supplier. A cost-sharing contract with Munising Paper Division of Kimberly-Clark Corporation was negotiated. The primary goals were to evolve other substrates to replace asbestos and to define water-based separator coatings to replace the solvent-based coatings. Secondary goals were to develop an improved fuel cell grade asbestos sheet and to demonstrate a large-scale production capability for the NASA solvent-based I/O separator. Most of the goals of the cost-sharing contract between NASA and Kimberly-Clark Corporation have been achieved: (1) A cellulose-based substrate and a nonwoven polypropylene fiber substrate have been successfully evaluated as replacements for the asbestos. Both the cellulose and polypropylene substrates have been coated with solvent-based and water-based coatings to produce a modified I/O separator. (2) The solvent-based coatings have been modified to produce aqueous separator coatings with acceptable separator properties. (3) A single-ply fuel cell grade asbestos with a binder (BTA) was produced. It has shown to be an acceptable substrate for the solvent- and water-based separator coatings, an acceptable absorber for alkaline cells, and an acceptable matrix for alkaline fuel cells. (4) The original NASA solvent-based separator (K19W1), using asbestos as a substrate, was prepared by Kimberly-Clark using production methods. However, its resistance was unacceptably high. The Kimberly-Clark modified version of NASA K168T was commercially produced on the BTA substrate and was superior to K19W1 in all measured properties. The separator materials prepared on industrial equipment generally behaved in the following manner: (1) measured separator properties were improved when compared with the original NASA solvent-based separators with resistivity being significantly improved. (2) Cycle life of 8-A-hr nickel-zinc cells appeared to be dependent upon substrate regardless of the type of coating, composition, or solvent. Cycle life decreased in the following order of substrates: Asbestos cellulose paper nonwoven polypropylene. Only coated asbestos separators achieved cycle life in excess of the NASA K19W1 standard. (3) Solvent-based coatings showed better cycle life than water-based coatings in nickel-zinc cells.

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