INVESTIGATION OF STERILIZATION OF SECONDARY BATTERIES

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ABSTRACT

This is the final report of an 8-month study to develop a nickel-cadmium cell that can be thermally sterilized at 145°C, and yield a power density and cycle life approaching that of present state-of-the-art nickel-cadmium cells. A number of existing separator systems are evaluated; the more sterilization resistant types being incorporated into cells. Two asbestos and one polypropylene separator systems appears the most promising. Tests indicate that the nickel plate contributes to the capacity loss while the negative plate limits the overcharge capability following thermal sterilization. X-ray spectrographs of the nickel-plate before and after sterilization are shown.

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INTRODUCTION

This report covers an eight month study to develop a nickel-cadmium cell which when subjected to a thermal sterilization procedure at 145°C will give a power density and cycle life approaching that of the present state-of-the-art nickel-cadmium cell. This investigation was undertaken principally to provide a thermally sterilizable secondary cell for service on long life planetary landers. Although a great deal of effort was being expended to develop a high energy density cell of the primary type, very little was being done to provide a secondary type cell. Standard components and commercially available materials were employed for all testing to ascertain the present capability of the nickel-cadmium cell.

The first phase of this investigation was to evaluate existing separator materials. The procedure was to subject the test pieces to the environment that the cells would be required to experience.

The second phase was to incorporate the more promising separators into cells. After the cell characteristics had been determined, they were subjected to sterilization as given by the Test Approval procedure.

The third phase is concerned with a detailed evaluation of the effects that the sterilization has on individual components when incorporated into cells.

Finally, batteries fabricated with suitable sterilizable materials are to be delivered to NASA Langley.

FACTUAL DATA

Separators and Separator Testing

The first part of this program was concerned with screening various materials to be employed as separators in nickel-cadmium cells. Below is a description of the test methods employed and the results that were observed.

Experimental Methods - The separator test employed was designed to determine the effect of the elevated temperature on the various samples. The Test Approval Procedure specifies that the components will be heated to 145°C while immersed in a solution of potassium hydroxide and will be maintained at this temperature for 36 hours in a sealed container. Three such exposures are required. Prior to each exposure, one hour is allowed for temperature stabilization. The total time was 111 hours.

The particular test that was employed for the separators was as follows. The sample in question was cut. The length and width were measured to the nearest 1/64 of an inch. In addition, the direction in which the separator was wound was noted. For the purposes of clarity, the designation "direction of roll" is the direction perpendicular to the axis of the mandrel on which the separator was rolled.

The thickness was measured at random locations along the sample with a Starret micrometer and read to the nearest 0.0001 inch. The first click of the ratchet was used as the stop. Finally, each separator was weighed on an analytical balance.

The pressure vessel consisted of a can, cover, and a gasket. The can was fabricated from 304L stainless steel. The interior of the can was passivated with a dilute nitric acid solution. A flange, made also of 304L stainless steel, was welded to the top lip of the can. The outside periphery of the flange was drilled and tapped. The cover was of 1/8 inch cold rolled steel plate. Holes were line bored with those in the flange. The gasket was a sheet of Teflon 20 mils thick. The film was laid on the flange and sealing was accomplished when the cover was bolted securely. The Teflon film was continuous, and consequently, the cover was protected from the cell atmosphere.

The separator was then placed in the can. A 5 mil Teflon sheet was placed between the interior of the can and the separator. Sufficient 34% potassium hydroxide was added to submerge the sample. The can was then sealed and placed in the oven which was maintained at 145°C. After a minimum of 111 hours, the vessels were taken out of the oven. The vessels were opened. The separators were removed and washed free of potassium hydroxide.

After drying, the sample was measured and reweighed. Visual changes were noted, and an estimate was made of the mechanical strength. These data are tabulated in Table II. The suppliers of all the samples are listed in Table I.

Test Results From the First Sterilization - The results of the first sterilization are given below.

a. Asbestos Cloth Type 7410 - Very little change in length or width was observed. However, there was a large decrease in separator weight and thickness. The material was lighter in color and more brittle after the test.

This asbestos cloth was also evaluated with 45% potassium hydroxide. The same type of results were obtained as in 34% KOH.

b. Polypropylene SM91 - There was considerable shrinkage in both the length and width. The change in weight was negligible. There was, however, a large increase in thickness. No visual change was apparent.

c. Polypropylene EM476 - There was considerable shrinkage in both length and width. There was a noticeable weight change. However, a large increase in thickness was evident. No visual change was noticed in color or consistency.

d. Polypropylene - Nylon SM124.3 - As in the case of the above polypropylene separators, there was a significant degree of shrinkage in both the length and width of the material. A large weight change was observed. The thickness showed a typically large decrease. When the separator was removed from the can, and rinsed with water, a milky substance was leached out of the separator.

e. Non-woven Nylon 2505ML - The material disintegrated in the electrolyte.

f. Asbestos Paper - This material disintegrated in the electrolyte to pulp.

g. Aluminum Oxide Paper 970AH - This sample was a felted "paper" composed of refractory aluminum oxide and a binder. After treatment, the material was reduced to a pulp in the electrolyte.

h. Special Filter Paper - This sample was composed of Teflon deposited on a fiberglass base. After exposure to the heat sterilization test, there was considerable shrinkage in both directions. There was also a large decrease in weight and thickness. With the very thin separator that resulted, there was no further interest in this material. It should be noted that after the test, the filter paper was still continuous and pliable.

i. Fuel Cell Asbestos Board (10 mil) - A sample of 10 mil fuel cell asbestos board was received from Johns Manville and subjected to the sterilization routine according to the procedure described above. The sample deteriorated to a pulpy mass, making extraction from the pressure vessel difficult. The color of the material was unchanged and the asbestos fibers appeared to be intact.

j. Fuel Cell Asbestos Board (15 mil) - A sample of 15 mil fuel cell asbestos board was also received from Johns Manville and subjected to the heat sterilization routine as above. This sample also deteriorated to a pulpy mass. The extent of the loss of physical integrity was nearly that of the 10 mil board. As with the previous material, the color did not change.

k. High Temperature Nylon - Samples of a high temperature nylon (trade name NOMEX) was received from DuPont. A sample of this material, type 25062, was subjected to the sterilization routine. The material disintegrated completely. No attempt was made to test similar samples with the same base composition.

l. Pure Asbestos - Two asbestos materials were received from the Raybestos Corporation. These materials, designated as 7301 and 7401, are pure asbestos cloths. The type 7401 contains a small percentage of binder. The type 7301 is a pyrolized version of 7401.

Both samples were subjected to the heat sterilization routine. The results, shown in Table II indicate that the overall shrinkage was slight. The type 7301 asbestos showed smaller dimensional and weight changes than the type 7401 except for thickness. The difference in results is not very large.

Test Results from the Second Sterilization - The results of the second sterilization are given below.

a. Polypropylene and Polypropylene-Nylon Separators - Several separators notably the polypropylene and polypropylene-nylon show considerable shrinkage in length. This means that they should not be employed for wrapping cells, since the resulting change in length would cause the separators to tear or produce weak areas. In order to determine if the sterilization was merely allowing these separators to attain a stable state, a second heat sterilization was conducted. The results which are shown in Table III indicate that further changes are sufficiently small so that they could be employed to wrap cells.

The first heat sterilization will then be employed as a pre-treatment. After wrapping, the second sterilization would correspond to what the cell is expected to encounter in operation.

b. Types 7301 and 7401 Asbestos - A second sterilization was conducted on the 7301 and 7401 asbestos. The results shown in Table IV illustrate that the changes during the second sterilization are less than the first sterilization. Therefore, we again can employ the first sterilization as a pre-treatment for the asbestos separator. In addition to this type, 7301 shows less dimensional changes. Consequently, it was chosen for future evaluation..

CELL OPERATION

The more promising materials were incorporated into cells to determine what type of operation would result.

Cells With the Washed Asbestos Separator - It was noted that the type 7410 asbestos cloth separator contains a high percentage of fiberglass. To eliminate the impurity, the separator was soaked in a 34% potassium hydroxide solution for five days and then rinsed and dried.

Five cell packs were wrapped with the washed separator. The standard VO-6HS components having the two isolated terminals were utilized. Before inserting the pack into the can, it was surrounded with an insulating envelope made from 5 mil Teflon sheet. This assembly was placed into the can and heliarc welded. It was then leak tested on the Veeco mass spectrometer.

In addition, two control cells were fabricated in the identical manner except that the standard non-woven nylon separator was employed to wrap the electrode packs.

The cells were filled with a restricted quantity of electrolyte, 34% potassium hydroxide. After a formation charge of C/10, 600ma, for 16 hours, they were discharged at C/2 (3.0 amperes) to 1.0 volt. The cells with the asbestos separator gave slightly lower capacities, average of 5.90 AH. After charging and discharging again in the same manner without equalization, the capacities of the cells with the asbestos separator and those with the standard separator decreased. The low end of charge pressures, average of 5.8 psia, indicated that an insufficient quantity of electrolyte was available. The volume of 34% potassium hydroxide was raised to 15.5 cc in all cells. A C/10 charge for 16 hours followed by a C/2 discharge showed that the capacities were again lower.

All cells were equalized with one ohm resistors and a similar manual charge and discharge was conducted. The capacity of the cells with the standard separator rose 20% while the capacity of the cells with the asbestos separator dropped 50%. On the discharge the can was employed as an indicating electrode. The electrode that exhausted first and limited the capacities was the negative.

The cells with the asbestos separator were given a vented, saturation charge to ascertain if the capacities could be reclaimed. The subsequent discharge gave very low capacities. Obviously the type 7410 asbestos separator is unsuitable for use in these cells, and all work with this material was discontinued.

Cells With Polypropylene and Polypropylene-Nylon Separators - Two polypropylene and one polypropylene-nylon separator were described in the previous section. Three groups of five cells each were fabricated with each group having one of the above heat treated separators. The components and methods of assembly were identical to the cells with asbestos separator.

Sealed nickel-cadmium cells usually contain 1 layer of type 2505 nylon which is 8 mils thick. For these cells polypropylene type 476 which is 4 mils thick and polypropylene-nylon type 124.3 which is 6 mils thick were thin enough to make the cells with 2 layers of separators. Propylene type SM91 is nearly as thick as the usual material, 7 mils, so that only one layer was used.

The first charge consisted of a vented formation charge followed by a discharge at C/2. The second charge was conducted for 19.5 hours. The discharge indicated that an insufficient quantity of electrolyte was available. The end of charge voltages and pressure as well as the capacities are shown in Table V. Small increments of 34% potassium hydroxide was added until 18cc was reached.

Prior to insertion into the sterilization chamber the cells were discharged to 1.0 volt. Table VI shows the average capacity of the cells with the various separator systems. The average capacity of standard cells are also included.

To remove the residual capacity, one ohm resistors were placed across the cells overnight. Three cells of each group were placed in the oven for 37 hours. The oven temperature was maintained at 145°C.

In addition to the above cells, a "standard" was also inserted in the oven. This consisted of a welded case and cover assembly to which a pressure gauge was attached. No components were inside the cell, but 15.0cc of 34% potassium hydroxide was added. The purpose of this device was to observe the pressure in the cell, due to the vapor pressure of the electrolyte.

The cells were placed in the oven. Periodically during the total immersion time of 37 hours, the individual pressures were monitored. Table VII shows the individual pressures at the end of the 37 hour period. As can be seen, there was no abnormal rise in pressure of the test cells. Maximum pressures were about 5 psi greater and occured about 5 hours prior to removal from the chamber.

A total of three sterilization routines were conducted. Of the five cells that were fabricated, the two not placed in the chamber were used as controls. In the case of the group containing the SM124.3 polypropylene-nylon separator where only four cells were available, one cell was used as a control. Prior to, and after each sterilization routine, the cells were charged and discharged in series. The charging time, however, had to be reduced to 16 hours rather than 19.5 hours in order to keep the pressures tolerable. To ascertain the effect due to the sterilization, the data given in Table VIII shows the capacities compared to the respective control cells in each group which were not placed in the oven.

In addition to the drop in capacity, the plateau voltages decreased after the sterilization routines. This means that the effective internal resistance of the cells had increased. The fifth column of Table VIII indicates the drop in voltage compared to an unsterilized cell. As an indication of the useful output, the last column gives the actual average capacities of the cells that were subjected to 3 cycles of heat sterilization. It is obvious that the

that the capacities of the SM91 and EM476 polypropylene are lower than the nominal six ampere-hours. The pressures obtained in the cells on charge after 3 sterilization cycles, were slightly higher, about 5 psi, than obtained prior to sterilization.

In an attempt to determine whether cells can be sterilized in the fully charged state by maintaining a trickle charge while they are in the oven, fully charged cells were placed in the oven and trickle charged at 100ma initially. The cells used for this had already been thermally cycled. They contained the SM124.3, EM476 and SM91 separator systems. The charging rate was gradually increased to 250ma and maintained at this rate for 30 of the 37 hours sterilization period. The following discharge at the C/2 rate, (3.0 amperes) yielded very little capacity.

Two cells with SM124.3 polypropylene shorted and are not included in the data in Table IX. Several facts are evident from Table IX. First, approximately 4 atmospheres of pressure were developed in the cells. The pressure during trickle charge was the same as that observed on thermal treatment of these cells in the discharged condition. Second, the cells were not in overcharge according to the voltages. The question of the charge efficiency of the positives and the self-discharge is not solved, but what is clear is that the negative electrode can recombine at a rate corresponding to 250ma.

In order to determine if the capacity was irreversibly lost, the cells were charged at C/10 for 16 hours. At the end of charge, the voltages were very high. These voltage values are shown in Table X. Because of the high voltages hydrogen was formed. On discharge low capacities were evident. After allowing the oxygen to recombine, the cell atmosphere was evacuated and oxygen at 50 psi was added to each cell so that the charged capacity of the negative electrodes were reduced 0.6AH. Two additional charges and discharges were conducted with the result that the capacities increased markedly. The data are shown in Table X. The capacity of these cells after the third discharge is higher than the capacity after the third sterilization routine. While it appears possible to recover nearly all of the capacity, the formation of hydrogen gas in the cell requires operation at higher pressures. As a consequence, cells would have to be designed for this operation or scavenger electrodes would have to be included.

The cells exhibiting the high voltage were opened and flooded. A thin strip of positive electrode was charged and placed in the top of the cell for use as a reference electrode. Upon charging the cell, it was found that the high cell voltages could be associated with the positive electrode.

An x-ray diffraction pattern was taken of positive plates prior to sterilization in a cell and of other plates after sterilization while being trickle charged. The patterns did not permit conclusive information. Figure 1 shows the unsterilized electrode x-ray pattern while Figure 2 shows the sterilized electrode. In each case the sample was scanned from 10^{o} - 80^{o} at a chart speed of 2^{o} per minute.

Cells With the Type 7301 Asbestos Separator - The first tests were made with five plate cells to determine if good capacities could be obtained. This cell consisted of two positive electrodes and three negative electrodes. A normal VO-6HS has ten negative electrodes and nine positive electrodes. Two layers of pre-sterilized type 7301 asbestos was placed between each positive and negative electrode. Pressure was maintained on the pack with lucite pressure jackets and the entire assembly flooded in 34% potassium hydroxide. Nine charges and discharges were conducted. The expected capacity from these cells was 1.65 AH. The data shown in Table XI illustrated that satisfactory capacities were obtained. In addition, no degradation in performance was caused by the asbestos. During the discharge, the voltages were those normally encountered in nickel-cadmium cells, indicating that no high internal resistance was observed.

Sealed cells were made employing the 7301 separator. The standard VO-6HS case, cover assembly and stack assembly was employed. The pack was wrapped with two layers of the pre-sterilized type 7301 separator and a Teflon sheet was employed to insulate the pack from the can. Five cells were fabricated in this manner.

A restricted quantity of electrolyte, 12cc, was added to the cells. After charging and discharging, incremental increases of electrolyte were added until the correct quantity was obtained. The amount determined was 18cc.

In each case the cells were charged at C/10 for 16 hours followed by a 3.0 amperes discharge. When the capacity became stabilized, the cells were placed in the oven in the discharged state. No abnormal rise in pressure was observed during the 37 hour immersion period. After the sterilization, the cells were charged at C/10 for 16 hours three times, each followed by a C/2 discharge. On the third charge, high pressures developed in two cells. The high pressure was removed and the charging rate reduced to 14 hours. On the subsequent charge, the end-of-charge voltages and pressures were lower. This information is given in Table III.

The cells that were sterilized lost 5% of capacity while the controls lost 3%. The end-of-charge voltage was higher for the cells that were sterilized. When the length of charge time was dropped to 14 hours, the capacities of the sterilized cells did not drop while there was a small (3%) drop in the capacities of the contral cells. During the 14 hour charge the sterilized cells showed a lowered end-of-charge voltage

(though still higher than the controls) and very low pressure. In fact, the pressures were lower than the control cells. This suggests that there is a change in operating characteristics of the positives, which do not gas until late in the charge. If the charge of these sterilized cells is continued after 14 hours, the hydrogen free capacity of the negative is exceeded, and hydrogen is formed.

These cells were sterilized three times in a discharged state. After the third sterilization, they were charged at 600ma for 14 hours. High pressures and voltages were observed in two cells. This is shown in Table XIII. Subsequent charging after the removal of the cell atmosphere showed no formation of hydrogen. Apparently, temporary passivation of the negative electrode occurred.

This problem of sensitivity of cells to charging time was evident in the cells with the polypropylene separators as well as the cells with the type 7301 asbestos separator. During the early (pre-sterilization) charging of the cells with the polypropylene separators, 19.5 hours of charge at the C/10 rate could be absorbed. After sterilization a maximum of 16 hours could be tolerated without the generation of excessive quantities of gas.

In the case of the cells with the type 7301 separator, 16 hours of charge was employed prior to sterilization. After sterilization, the maximum time was 14 hours or less.

CELLS WITH THE INDIVIDUALLY STERILIZED COMPONENTS

A number of cells were made with various individually sterilized components. The method of sterilizing the individual components is identical to the separator screening test. That is, the component is placed in a pressure vessel and immersed in 34% potassium hydroxide. After sealing, the vessel was placed in an oven which was maintained at 145°C for a period of 112 hours. The components were removed from the container, rinsed free of electrolyte, and dried. The outline for the fabrication of the test cells is shown in Table XIV. Each group below contained 4 cells each, except groups 4 and 5, which had 2 cells each.

Group 1. - The cells in this group contain unsterilized positives, sterilized negatives, and fresh electrolyte. The separator employed was the type 7301 asbestos and was pre-treated by subjecting it to the heat sterilization routine mentioned in the initial section of the report.

Initially, these sealed cells were charged at C/10 for 16 hours. High pressures developed, and on discharge residual pressures were observed as shown in Table XV. The cell atmospheres were evacuated. The subsequent charge was limited to 13.7 hours with the result that on discharge the pressures were in vacuum. Another charge was conducted and after the 13.7 hour charging period the charging rate was reduced in increments. After two hours of charging at C/40 there was a rise of 2 pounds gauge (average gauge pressure 4p.s.i.g.) indicating that these cells will not accept an overcharge. The negative had clearly influenced the characteristics of the cell. The capacity on the subsequent discharge shows good capacity, indicating that the negative did not reduce the useful capacity.

Group 2. - The cells in this group contain the sterilized positives, the unsterilized negatives and fresh electrolyte.

On the initial charge of the sealed cells at the C/10 rate, the pressures after 16 hours were normal. On discharge the capacities were low but the pressures dropped into vacuum. When the cells on overcharge were dropped to a C/24 rate the pressures decreased. On discharge the plateau voltages were lowered 20mv. In addition, the capacities were reduced.

Group 3. - The cells in this group contain the sterilized positives and sterilized negatives and fresh electrolyte.

On the initial charge of the sealed cells at the C/10 rate, the pressures after 16 hours were low. On discharge the capacities were very low (average 3.52 AH). On subsequent charges no high pressures were developed, and low capacities were observed. No satisfactory explanation can be rendered at this point.

Groups 4 and 5. - These two groups were very similar. They contained unsterilized positives and negatives. The difference lay in the fact that Group 4 contained electrolyte that was obtained when the positives were sterilized. Group 5 contained electrolyte which was obtained when the negatives were sterilized. As expected, these cells behaved normally after the first cycle and gave a final capacity of 6.85AH.

ADDITIONAL DEVELOPMENTS

Positive Electrodes Without Cobalt Additives

Cells were made with different positives. These positives employed a very similar sinter and did not contain any cobalt as do the standard positives used for the testing that has been mentioned. The remaining components were the standard VO-6HS equipment. In all these cells the two polypropylene and one polypropylene-nylon separators were tested in parallel with the previous cells of this type. The cells gave equal or better capacity to those with the standard positive electrode. However, after the first 36 hour sterilization routine, a large decrease in capacity and an increase in internal resistance was observed in all cells.

In order to determine the cause for this abnormal behavior, an unsterilized electrode, and one that had been exposed to the heat sterilization while in the discharged state in the cell were subjected to an x-ray analysis. The plates were scanned from 10^{o} to 80^{o} at a chart speed of 2^{o} per minute. Figure 3 shows the diffraction pattern of the unsterilized plate while Figure 4 shows the diffraction pattern of the sterilized plate. The results show that the ratio of nickel hydroxide peaks, compared to the nickel peaks are much higher for the sterilized plate than the unsterilized plate. One possible explanation is that the heat sterilization routine and testing allowed the nickel hydroxide to recrystallize. This results in making some of the nickel hydroxide less available for electrical utilization because the centers of the crystals are not intimately in contact with the nickel sites which act as current collectors. Secondly, a layer of the material on the surface of the plates leads to partial passivation.

Modified Asbestos Separator

We have found that it is possible to treat the asbestos with a suitable binder so that it retains its physical integrity for a much longer period of time in boiling 34% potassium hydroxide. A sample of 10 mil fuel cell asbestos board, and a sample of the same material which was modified, were placed in individual beakers of boiling 34% potassium hydroxide. The sample of standard asbestos showed considerable disintegration after three minutes of boiling. The sample of modified asbestos was boiled for 50 minutes without any physical disintegration. Because of this finding, additional work was initiated. A three plate flooded cell was made having one positive and two negative electrodes. Pressure was maintained on the pack by lucite plates, and 34% potassium hydroxide was employed as electrolyte. Four charges and discharges were conducted. The data on Table XVI indicate that no loss of capacity is observed, but slightly lower plateau voltage are obtained.

Several cells using VO-6HS components were made employing this separator. The cells were charged at C/10 for 14 hours followed by a discharge at 3.0 amps to 1.0 volt and this information is shown in Table XVII. The results show that the cell can operate sealed and give useful capacity. The separator that was employed is thicker than normally used and may be a significant contributing factor to the 40 mohm increase in internal resistance.

CONCLUSIONS

1. Two polypropylene and one polypropylene-nylon separator was found to have excellent thermal stability. When incorporated into cells, the nominal capacity is obtained and the cell will operate in a sealed condition.

2. A commercial asbestos has been found that can withstand the sterilization routine. When incorporated into cells, the nominal capacity is met and the cell is able to operate in a sealed condition.

3. A process has been developed where various asbestos materials can be modified so that it is more resistant at elevated temperatures in a 34% potassium hydroxide solution.

4. At this time we do not have enough information to justify the making a decision as to the direction of further study (i.e. asbestos or polypropylene separator).

5. When subjected to the Test Approval Procedure the modified asbestos cells develop a high electrical resistance which is evidenced as lowered voltages on discharge and increased voltages on charge.

6. The increased internal resistance was found to be caused by the positive electrode.

7. When subjected to the Test Approval Procedure, the hydrogen free capacity of the negative electrode is reduced not permitting extensive overcharge of the cell.

8. When positive electrodes, similar to those used in the sealed cells, were subjected to the Test Approval Procedure and then x-rayed, the diffraction pattern showed that the nickel hydroxide recrystallized into a more defined crystal and migrated to the surface of the electrode.

9. The cells could not be maintained in a charged state at 145°C with a charge rate of 250 ma during the 37 hours at that temperature.

10. After charging the cells in the oven, the capacity lost can be reclaimed but not without the generation of hydrogen, even at reduced charging current.

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TABLE I. SEPARATOR MATERIALS AND SUPPLIER

MATERIAL	SUPPLIER
Asbestos Cloth Type 7410	RAYBESTOS MANHATTAN
Polypropylene SM91	KENDALL MILLS
Polypropylene EM476	KENDALL MILLS
Polypropylene-Nylon 124.3	KENDALL MILLS
Non-Woven Nylon 2505 ML	PELLON CORP.
Asbestos Paper	CRANE COMPANY
Aluminum Oxide Paper 970 AH	CARBORUNDUM CO.
Special Filter Paper	ACE SCIENTIFIC
Fuel Cell Asbestos Board (10 Mil)	JOHNS MANVILLE
Fuel Cell Asbestos Board (15 mil)	JOHNS MANVILLE
High Temperature Nylon	DU PONT
Type 7301 Asbestos	RAYBESTOS MANHATTAN
Type 7401 Asbestos	RAYBESTOS MANHATTAN

TABLE II

RESULTS OF SEPARATOR SCREENING TESTS

MATERIAL	KOH Conc.	SAMPLE	LENGTH		WIDTH		THICKNESS		WEIGHT	
			% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av. %
Asbestos Cloth Type 7410	34%	1	-0.4	-0.4	+1.6	+2.0*	-23.8	-29.4	-41.2	-42.4
		2	-0.3		+0.4		-34.9		-43.5	
Asbestos Cloth Type 7410	45%	1	-0.3	-0.5	+4.0	+4.0*	-29.3	-32.5	-45.4	-45.4
		2	-0.6		+4.0		-35.7		-45.4	
Polypropylene SM 91	34%	1	-9.4	-10.0	-7.1	-7.5*	+40.3	+40.2	-0.9	-1.6
		2	-10.6		-7.9		+40.0		-2.4	
Polypropylene EM 476	34%	1	-10.7	-9.5	-7.4	-5.9*	+37.4	+36.8	-4.0	-3.6
		2	-8.3		-4.3		+36.1		-3.2	
Polypropylene - Nylon SM 124.3	34%	1	-11.1	-11.4	-9.8	-10.4*	-8.9	-8.5	-53.6	-53.6
		2	-11.7		-11.0		-8.1		-53.5	
Non-Woven Nylon 2505 ML	34%	1	DISINTEGRATED IN KOH							
		2								
Asbestos Paper	34%	1	DISINTEGRATED IN KOH							
		2								
Aluminum Oxide Paper 970 AH	34%	1	DISINTEGRATED IN KOH							
		2								
Special Filter Paper	34%	1	-3.3	-3.8	-3.8	-4.0	-50.1	-46.7	-34.1	-30.7
		2	-4.3		-4.1		-43.3		-27.2	

* Direction of Roll

TABLE II (CONTINUED)

RESULTS OF SEPARATOR SCREENING TESTS

MATERIAL	KOH Conc.	SAMPLE	LENGTH		WIDTH		THICKNESS		WEIGHT	
			% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av. %
Fuel Cell Asbestos Board (10 mil)	34%	1	DETERIORATED IN KOH							
		2								
Fuel Cell Asbestos Board (15 mil)	34%	1	DETERIORATED IN KOH							
		2								
High Temperature Nylon (NOMEX)	34%	1	DISINTEGRATED IN KOH							
		2								
Asbestos Type 7301	34%	1	-0.3	-0.3	+1.6	+1.3*	-8.1	-9.1	-4.9	-5.1
		2	-0.3		+1.0		-10.1		-5.3	
Asbestos Type 7401	34%	1	-0.7	-0.8	+2.0	+2.0*	-8.5	-7.9	-7.0	-7.3
		2	-0.8		+2.0		-7.3		-7.5	

Limits of Accuracy for Asbestos Cloth:

Length	±0.05%
Width	±0.2%
Thickness	±1%
Weight	±0.01%

Limits of Accuracy for all other Samples:

Length	±0.1%
Width	±0.2%
Thickness	±1%
Weight	±0.01%

* Direction of Roll

TABLE III

SECOND STERILIZATION OF THE POLYPROPYLENE
AND
POLYPROPYLENE-NYLON SEPARATORS

MATERIAL	KOH Conc.	SAMPLE	LENGTH		WIDTH		THICKNESS		WEIGHT	
			% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av. %
Polypropylene (SM91)	34%	1	-0.2	-0.2	-0.4	-1.6	-5.0	-0.2	+0.4	+0.4
		2	-0.2		+0.9		+4.7		+0.4	
Polypropylene (EM476)	34%	1	-0.3	-1.2	+0.9	+0.3	+2.9	+2.5	+0.7	+0.7
		2	-2.1		-0.4		+2.1		+0.6	
Polypropylene-Nylon (SM124.3)	34%	1	-0.3	-0.3	-0.4	-0.2	+3.9	+3.4	+0.2	-0.1
		2	-0.3		0.0		+2.8		-0.4	

TABLE IV

EFFECT OF THE SECOND STERILIZATION ROUTINE

ON THE ASBESTOS SEPARATORS

MATERIAL	KOH Conc.	SAMPLE	LENGTH		WIDTH		THICKNESS		WEIGHT	
			% CHANGE	Av. %	% CHANGE	Av. %	% CHANGE	Av.	% CHANGE	Av. %
Type 7301	34%	1	+0.2	+0.1	+0.4	+0.2	-1.2	-1.0	-1.2	-1.4
		2	-0.03		-0.15		-0.8		-1.6	
Type 7401	34%	1	+.15	+0.1	-0.4	-0.2	-3.7	-5.1	-1.8	-2.1
		2	+.10		0.0		-6.5		-2.4	

Limits of accuracy on length ±0.1%

Limits of accuracy on width ±0.2%

Limits of accuracy on thickness ±1%

Limits of accuracy on weight ±0.01%

TABLE V

SECOND CHARGE AND DISCHARGE OF CELLS WITH THE POLYPROPYLENE AND POLYPROPYLENE-NYLON SEPARATORS

CELL	MATERIAL	NO. OF LAYERS OF SEPARATORS	END OF CHARGE VOLTAGE	END OF CHARGE PRESSURE	CAPACITY
P-1	Polypropylene SM91	1	1.46 volts	18.5 p.s.i.a.	4.50 AH
P-2	Polypropylene SM91	1	1.44 volts	16.0	5.37
P-3	Polypropylene SM91	1	1.44 volts	16.0	5.30
P-4	Polypropylene SM91	1	1.50 volts	17.0	5.30
P-5	Polypropylene SM91	1	1.49 volts	21.0	4.95
P-6	Polypropylene EM476	2	1.49 volts	22.5 p.s.i.a.	5.55 AH
P-7	Polypropylene EM476	2	1.45 volts	22.5	5.35
P-8	Polypropylene EM476	2	1.45 volts	19.0	5.35
P-9	Polypropylene EM476	2	1.44 volts	22.5	5.45
P-10	Polypropylene EM476	2	1.49 volts	16.0	5.55
P-11	Polypropylene SM124.3	2	1.47 volts	20 p.s.i.a.	5.70 AH
P-12	Polypropylene SM124.3	2	1.43 volts	20.5	6.10
P-13	Polypropylene SM124.3	2	1.47 volts	21.5	5.85
P-14	Polypropylene SM124.3	2	1.44 volts	12.0	5.70

Charge C/10 for 19.5 hours

Discharge C/2 (3.0 amps) to 1.0 volts

TABLE VI

CAPACITIES OF CELLS PRIOR TO INSERTION IN THE STERILIZING CHAMBER

CELL GROUP	SEPARATOR SYSTEM	NO. OF CELLS PER GROUP	CAPACITY TO 1.0V*
1	SM91 Polypropylene	5	6.65 AH
2	EM476 Polypropylene	5	6.55
3	SM124.3 Polypropylene-Nylon	4	6.76
4	Standard Pellon Separator System**	2	7.28

* Discharge rate 3.0 amp.

** Not placed in Chamber.

TABLE VII

CELL PRESSURE DURING FIRST STERILIZATION

CELL GROUP	SEPARATOR SYSTEM	AVER. PRESSURE IN OVEN LBS. GAUGE
1	SM91 Polypropylene	51.7
2	EM476 Polypropylene	54.3
3	SM124.3 Polypropylene-Nylon	49.8
4	Standard Pellon Separator System	----
Control*	----------	47.0

* Sealed cell case containing only 15 cc of 34% KOH.

TABLE VIII

COMPARISON IN CAPACITY BETWEEN CONTROL CELLS
AND THOSE CELLS THAT HAVE UNDERGONE THE STERILIZATION PROCEDURES

	PERCENT CHANGE COMPARED TO CONTROL CELLS					
SEPARATOR SYSTEM	Prior To Steril.	After 1st Steril.	After 2nd Steril.	After 3rd Steril.	Voltage Diff.	Actual* Cap.
Polypropylene-Nylon SM124.3	0%	+4.5%	-2.8%	-14.6%	-40 mv	5.85AH
Polypropylene EM476	+2.3%	+5.2%	-0.8%	-0.8%	-40 mv	5.16AH
Polypropylene SM91	+7.0%	+7.9%	+0.6%	+0.6%	-60 mv	5.80AH

Cells charged at 600 mA for 16 hours
Cells discharged at 3.0 amperes
*Cells that were subjected to the sterilization routine

TABLE IX

CELL PRESSURES DURING STERILIZATION OF CHARGED CELLS
AND CAPACITY AFTER STERILIZATION

SEPARATOR SYSTEM	NO. OF CELLS PER GROUP	AVERAGE PRESSURE*	AVG. CELL VOLTAGE	VOLTAGE SPREAD
Polypropylene-Nylon SM124.3	1	54psig	1.14 V.	----------
Polypropylene EM476	3	53	1.19	1.14-1.24V
Polypropylene SM91	3	54	1.22	1.19-1.24V
Control**	1	41	----	

* At end of 37 hour period. Charging rate 250 mA for last 30 hours.

** Sealed cell case containing only 15 cc of 34% KOH.

TABLE X

ELECTRICAL OPERATION OF CELLS AFTER STERILIZATION
WITH TRICKLE CHARGING

	1ST CHARGE & DISCHARGE			2ND CHG. & DISCHG.	3RD CHARGE & DISCHARGE		
SEPARATOR SYSTEM	AVG. CHARGE VOLTAGE	VOLTAGE SPREAD	AVERAGE CAPACITY	AVERAGE CAPACITY	AVG. CHG. VOLTAGE	VOLTAGE SPREAD	AVERAGE CAPACITY
Polypropylene-Nylon SM124.3	1.66V	---*	4.95AH	5.65AH	1.58V	---*	6.20AH
Polypropylene EM476	1.67	1.61-1.71	4.13	4.98	1.60	1.60-1.60	5.73AH
Polypropylene SM91	1.66	1.65-1.66	4.80	5.57	1.60	1.60-1.60	6.22

Charge Rate 600 mA

Discharge Rate 3.0 Amperes

* One Cell in Group

TABLE XI

CAPACITIES OF FLOODED FIVE-PLATE CELLS WITH TYPE 7301 ASBESTOS SEPARATOR

CYCLE	CAPACITY TO 1.0 VOLT *
1	1.57 AH
2	1.64
3	1.74
4	1.64
5	1.65
6	---
7	1.68
8	1.65
9	1.58
Av.	1.64

* Discharge Rate 0.75 A, Charge Rate 140 mA

TABLE XII

CHARACTERISTICS OF CELLS WITH THE TYPE 7301 ASBESTOS SEPARATOR

PRIOR TO AND AFTER 1ST STERILIZATION

	PRIOR TO STERILIZATION			AFTER 1ST STERILIZATION					
	16 HOURS OF CHARGE			16 HOURS OF CHARGE			14 HOURS OF CHARGE		
CELLS	END OF CHG. VOLTAGE	END OF CHG. PRESSURE	CAPACITY	END OF CHG. VOLTAGE	END OF CHG. PRESSURE	CAPACITY	END OF CHG. VOLTAGE	END OF CHG. PRESSURE	CAPACITY
1 Sterilized	1.50V	38 psig	6.35AH	1.59V	15.5 psig	6.09AH	1.49V	7.0 psig	6.13AH
2 Sterilized	1.50V	12	6.70	1.59	65	6.05	1.49	1.5	6.23
4 Sterilized	1.50V	30	6.25	1.54	-1	6.15	1.50	0.0	6.05
3 Not Sterilized	1.49V	45	6.25	1.48	---	5.95	1.47	31.0	5.79
5 " "	1.49V	34	6.65	1.50	---	6.56	1.47	24.5	6.30

Charge Rate 600 ma .

Discharge Rate 3.0 amperes to 1.0 volts.

TABLE XIII

CHARACTERISTICS OF CELLS WITH TYPE 7301 ASBESTOS SEPARATOR

AFTER THE THIRD STERILIZATION

	AFTER 14 HRS OF CHARGE		DISCHARGE	
HISTORY	VOLTAGE	PRESSURE	CAPACITY	END OF DISCHARGE PRESSURE
Sterilized	1.65 V	180 psia	5.61 AH	165 psia
Sterilized	1.65	190	5.61	182
Sterilized	1.52	9.5	5.46	9.
Control	1.46	4.	6.45	2.
Control	1.44	4	6.39	3.5

Charge Rate 600 ma

Discharge Rate 3.0 amps

TABLE XIV

CONSTRUCTION OUTLINE FOR CELLS

WITH INDIVIDUALLY STERILIZED COMPONENTS

	UNSTERILIZED COMPONENTS			STERILIZED COMPONENTS				
GROUP	POS.	NEG.	ELECTRO-LYTE	POS.	NEG.	SEPARATOR*	ELECTRO-LYTE FROM POSITIVE	ELECTRO-LYTE FROM NEGATIVE
1	X		X		X	X		
2		X	X	X		X		
3			X	X	X	X		
4	X	X				X	X	
5	X	X				X		X

* Separator type 7301 Asbestos. This separator is pre-sterilized before use.

TABLE XV

CHARACTERISTICS OF CELLS WITH INDIVIDUALLY STERILIZED COMPONENTS

GROUP	AVERAGE END OF CHARGE PRESSURE AFTER 16 HOURS	AVERAGE CAPACITY	AVERAGE RESIDUAL PRESSURE AFTER DISCHARGE	AVERAGE END OF CHARGE PRESSURE AFTER 14 HOURS	AVERAGE FINAL CAPACITY
1	88 psia	6.59AH	24 psia	51 psia	6.69AH
2	46	5.67	3	13	5.85
3	40	3.52	3	8	4.51

TABLE XVI

CELL VOLTAGE AND CAPACITIES OF THREE PLATE, FLOODED CELLS CONTAINING MODIFIED ASBESTOS SEPARATORS

CYCLE	VOLTAGE*	CAPACITY
1	1.14	0.810 AH
2	----	0.788
3	1.19	0.865
4	1.22	0.870

Charge 1 to 3 Rate 60 ma
Charge 4 Rate 60 ma for 17.7 hours then 90 ma
Discharge Rate 333 ma to 1.0V

* Voltage taken after 60 minutes.

TABLE XVII

CHARGE AND DISCHARGE OF CELLS

WITH THE MODIFIED ASBESTOS SEPARATOR

END OF CHARGE PRESSURE	AVERAGE CAPACITY
17 psia	5.08 AH

Charge Rate C/10 600 ma for 14 hours.

Discharge Rate 3.0 amps to 1.0 volts.

TABLE XVIII

SUMMARY

SEPARATOR TYPE	NO.OF CELLS	REMARKS
ASBESTOS TYPE 7410	10	Poor capacity before sterilization. Discontinued investigation.
POLYPROPYLENE SM91	10	Good capacity before and after sterilization.
POLYPROPYLENE EM476	10	Had to reduce charging time after sterilization to prevent high pressures.
POLYPROPYLENE-NYLON SM124.3	9	
ASBESTOS TYPE 7301	25	Good capacity before and after sterilization. Had to reduce charge time after sterilization to prevent high pressures.
MODIFIED ASBESTOS	8	Good capacity before and after sterilization. Had to reduce charging time after sterilization to prevent high pressures.