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INVESTIGATION OF STERILIZATION OF SECONDARY BATTERIES

By John Liska

FIRST QUARTERLY PROGRESS REPORT

COVERING THE PERIOD

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TABLE OF CONTENTS

I. INTRODUCTION

This report covers the first quarter of an eight month study to develop a nickel-cadmium cell which, after being sterilized according to the Test Approval Procedure, will give a power density and cycle life approaching a standard nickel-cadmium cell.

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

The second phase of this study will incorporate the more promising separator materials in cells. After the cell characteristics have been determined, they will be subjected to the Test Approval procedure.

The third phase of this program will go through a more detailed evaluation of the effect of test environment on the individual cell components.

II. FACTUAL DATA

A. SEPARATOR SCREENING TESTS

1. Procedure

The first part of this program was concerned with screening various separators. 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 304 L 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. This data is tabulated in Table II. The suppliers of all the samples are listed in Table I.

2. Test Results

a. Asbestos Cloth - 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.

The asbestos cloth was also evaluated with 45% potassium hydroxide. The same type of results were obtained as in 34% KOH. There was a layer expansion in width, the thickness decrease was more pronounced, 26.3% to 32.5%, and the weight loss was slightly more pronounced, 42.4% to 45.4%.

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 124.3 - 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 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.

The resulting shrinkages in the polypropylene and polypropylene-nylon separators are sufficiently pronounced to prevent wrapping of the packs prior to heat sterilization. The resulting change in dimensions during the sterilization procedure may cause the separator to rip or give

weak spots. The possibility does exist that the sterilization procedure will allow the materials to attain a more stable state, and consequently, subjecting the separator to another high temperature exposure will result in no significant changes.

The two polypropylene and the polypropylene-nylon materials were given a second sterilization treatment. The results shown in Table III illustrate that the changes are very small. Therefore, a sterilization procedure can be employed as a pre-treatment for these separators prior to wrapping the cells.

B. FABRICATION AND TESTING OF CELLS

1. Cells with Asbestos Separator

It was known that the asbestos cloth separator under test contains large amounts of fiberglass. By leaching out the fiberglass, it was assumed that the material would be suitable for use. The asbestos was soaked in 34% potassium hydroxide for 5 days, and then rinsed and dried. Five packs were fabricated using this separator.

The packs were welded to the standard VO-6HS cover assemblies having the two isolated terminals. The cans were the standard VO-6HS containers. After wrapping with the separator, the pack was surrounded with an insulating envelope made from 5 mil Teflon sheet. This assembly was placed into the can and heliarc welded. The cell was then leak tested on the Veeco mass spectrometer.

Two control cells were fabricated in the identical manner except that the standard separator system was employed to wrap the electrode packs.

The cells with the experimental separator were filled with 12.0 cc of 34% potassium hydroxide. This was a restricted quantity of electrolyte.

The correct amount will be determined by adding small increments and observing the resulting capacities, internal cell resistance, and the overcharge pressures. Figure 1 shows how the capacities of standard cells vary with electrolyte volume. The apparent dropoff is probably due to an aging phenomenon. Figure 2 shows the variation in cell pressure during overcharge as a function of electrolyte volume. Note that there is a relatively narrow range in the desirable quantity of electrolyte.

One of the control cells was filled with 12 cc of electrolyte. The other was filled with 15.5 cc, the next increment to give an indication of the incremental increase in capacity.

After the formation charge, the cells were discharged at C/2, 3.0 amperes to 1.0 volt. The results are shown in Table IV. The cells were then charged again at C/10 for 16 hours and discharged at C/2. The end of charge pressures and the capacity of the cells are given in Table V. All cells gave lower capacity on the second cycle. With the low pressures during overcharge, the cells generally indicate low electrolyte content. Sufficient electrolyte was added to each cell to bring the electrolyte content to 15.5 cc.

Further testing of these cells is now in progress.

2. Cells With The Polypropylene and Polypropylene-nylon Separators

The polypropylene and polypropylene-nylon separators were pretested as described in the previous section. The components and method of fabrication were identical to those employed for the cells with the asbestos separator. As indicated in Table III, one polypropylene and the polypropylene-nylon separator are relatively thin. Therefore, layers of these materials were wrapped between the electrodes.

After the formation charge, the cells were discharged at C/2, 3.0 amperes. The results are shown in Table VI. Two cells showed low capacities. A small increment of electrolyte will be added in an attempt to increase the capacities of the cells.

III. FUTURE WORK

A. PLANS FOR WORK DURING NEXT REPORT PERIOD

1. Separator Testing

The testing of the cells having the asbestos cloth as the separator will continue. The correct quantity of electrolyte will be determined. In addition, voltages and pressures during overcharge, and cell capacities on discharge, will be determined. After this phase, the cells will be subjected to the Test Approval Procedure as specified in the Work Statement.

In order to determine what the characteristics of pure asbestos separators would be, several samples have been ordered; as of this writing, they have not been received.

The cells with the polypropylene and the polypropylene-nylon separators are undergoing the same testing as the cells with the asbestos separator.

Two samples of polypropylene separator have been received from the Pellon Corporation and are undergoing screening.

2. Determination of Resulting Degradation

At the completion of the 3rd sterilization procedure, the components of the cells will be removed and tested to determine whether there is any degradation as a result of the exposure to the heat sterilization cycle.

3. Sterilization of Components

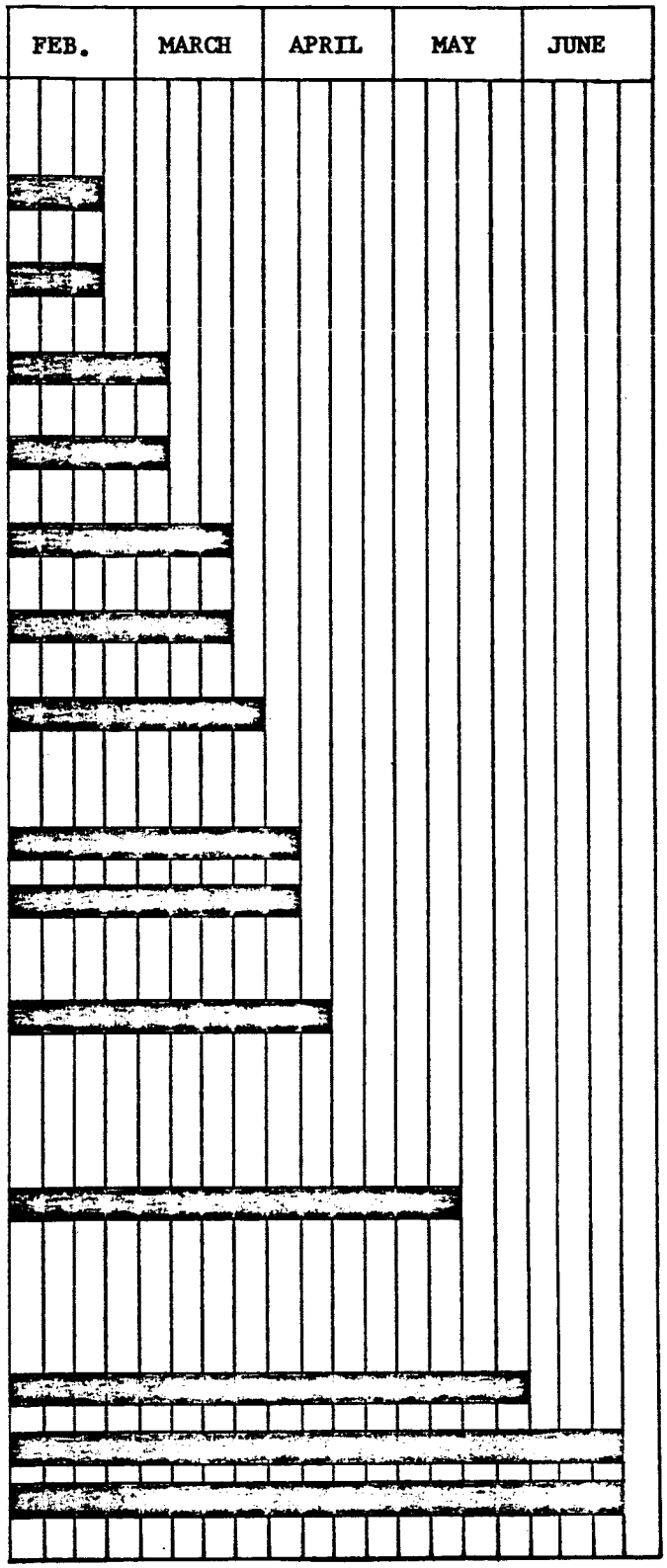
Packs fabricated at the present time will be subjected to the Test Approval Procedure.

4. Fabrication of Cells With The Combinations of Heat-Treated and Untreated Cell Components

Special laboratory cells have been ordered and are scheduled to be received by the 3rd week of February. These vessels are made from VO-6HS cans which have a stainless steel flange welded flush with the top edge. The cover is being fabricated to accept two isolated terminals and a pressure gauge assembly. These vessels will be employed to fabricate cells which have the various combinations of heat-treated and untreated cell components.

B. SCHEDULE OF REMAINING ACTIVITIES

ESTIMATED COMPLETION DATE



TASK NO. 1

1. 1st Sterilization of Cells With Asbestos Separator
2. 1st Sterilization of Cells With Polypropylene Sep.
3. 2nd Sterilization of Cells With Asbestos Separator
4. 2nd Sterilization of Cells With Polypropylene Sep.
5. 3rd Sterilization of Cells With Asbestos Separator
6. 3rd Sterilization of Cells With Polypropylene Sep.
7. Determination of Degradation

TASK NO. 2

1. Sterilize Electrodes
2. Sterilize Separators
3. Fabricate Cells With 3 Combinations of Treated & Untreated Electrodes, Separators, & Solutions From Treated Components
4. Test Cells With Combinations of Cells With Treated & Untreated Electrodes, Separators, & Solutions From Treated Components

TASK NO. 3

OPERATIONAL SCHEMES

MAKE DELIVERABLE ITEMS

FINAL REPORT

TABLE I. SEPARATOR MATERIALS AND SUPPLIER

MATERIAL	SUPPLIER
Asbestos Cloth	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 CO.
Aluminum Oxide Paper 970 AH	CARBORUNDUM CO.
Special Filter Paper	ACE SCIENTIFIC

TABLE II.

RESULTS OF SEPARATOR SCREENING TEST

MATERIAL	KOH Conc.	SAMPLE	LENGTH		WIDTH		THICKNESS		WEIGHT	
			% Change	Av %	% Change	Av %	% Change	Av %	% Change	Av %
Asbestos Cloth	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	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 EM 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	

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 (EM124.3)	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

CAPACITIES OF CELLS WITH ASBESTOS SEPARATORS ON FIRST DISCHARGE

CELL NO.	SEPARATOR SYSTEM	AM'T. ELECTROLYTE	CAPACITY TO 1.0V
1	Asbestos	12.0 cc	6.15 AH
2	Asbestos	12.0 cc	5.80 AH
3	Asbestos	12.0 cc	5.80 AH
4	Asbestos	12.0 cc	5.75 AH
5	Asbestos	12.0 cc	6.00 AH
C-1	Non-woven Nylon	12.0 cc	6.85 AH
C-2	Non-woven Nylon	15.5 cc	7.55 AH

TABLE V

END OF CHARGE PRESSURES AND AH CAPACITIES OF CELLS WITH THE ASBESTOS SEPARATORS

CELL NO.	SEPARATOR SYSTEM	END OF CHARGE PRESSURES	CAPACITY TO 1.0V
1	Asbestos	4.0 psia	4.56 AH
2	Asbestos	4.0 psia	4.29 AH
3	Asbestos	5.5 psia	4.26 AH
4	Asbestos	4.5 psia	4.20 AH
5	Asbestos	6.5 psia	5.41 AH
C-1	Non-woven Nylon	6.5 psia	4.50 AH
C-2	Non-woven Nylon	9.5 psia	5.25 AH

TABLE VI

CAPACITIES OF CELLS WITH THE POLYPROPYLENE AND POLYPROPYLENE-NYLON SEPARATORS

CELL NO.	SEPARATOR SYSTEM	NO. OF LAYERS	CAPACITY TO 1.0V
P-1	SM91	1	6.60 AH
P-2	SM91	1	6.50 AH
P-3	SM91	1	7.10 AH
P-4	SM91	1	6.85 AH
P-5	SM91	1	7.00 AH
P-6	EM476	2	7.25 AH
P-7	EM476	2	7.35 AH
P-8	EM476	2	7.55 AH
P-9	EM476	2	7.20 AH
P-10	EM476	2	7.05 AH
P-11	EM124.3	2	4.55 AH
P-12	EM124.3	2	7.25 AH
P-13	EM124.3	2	7.50 AH
P-14	EM124.3	2	5.30 AH
P-15	EM124.3	2	7.50 AH

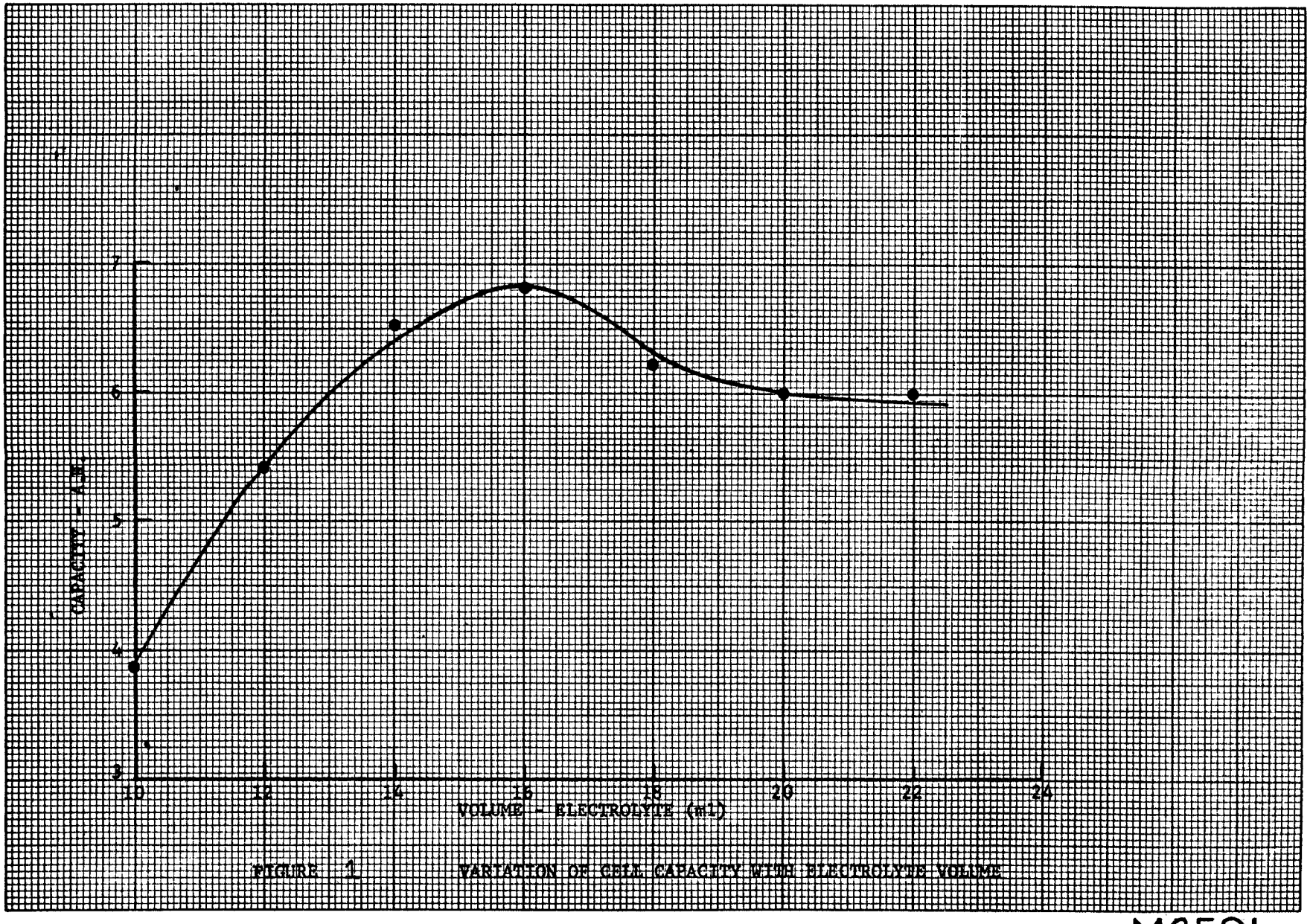


FIGURE 1 VARIATION OF CELL CAPACITY WITH ELECTROLYTE VOLUME

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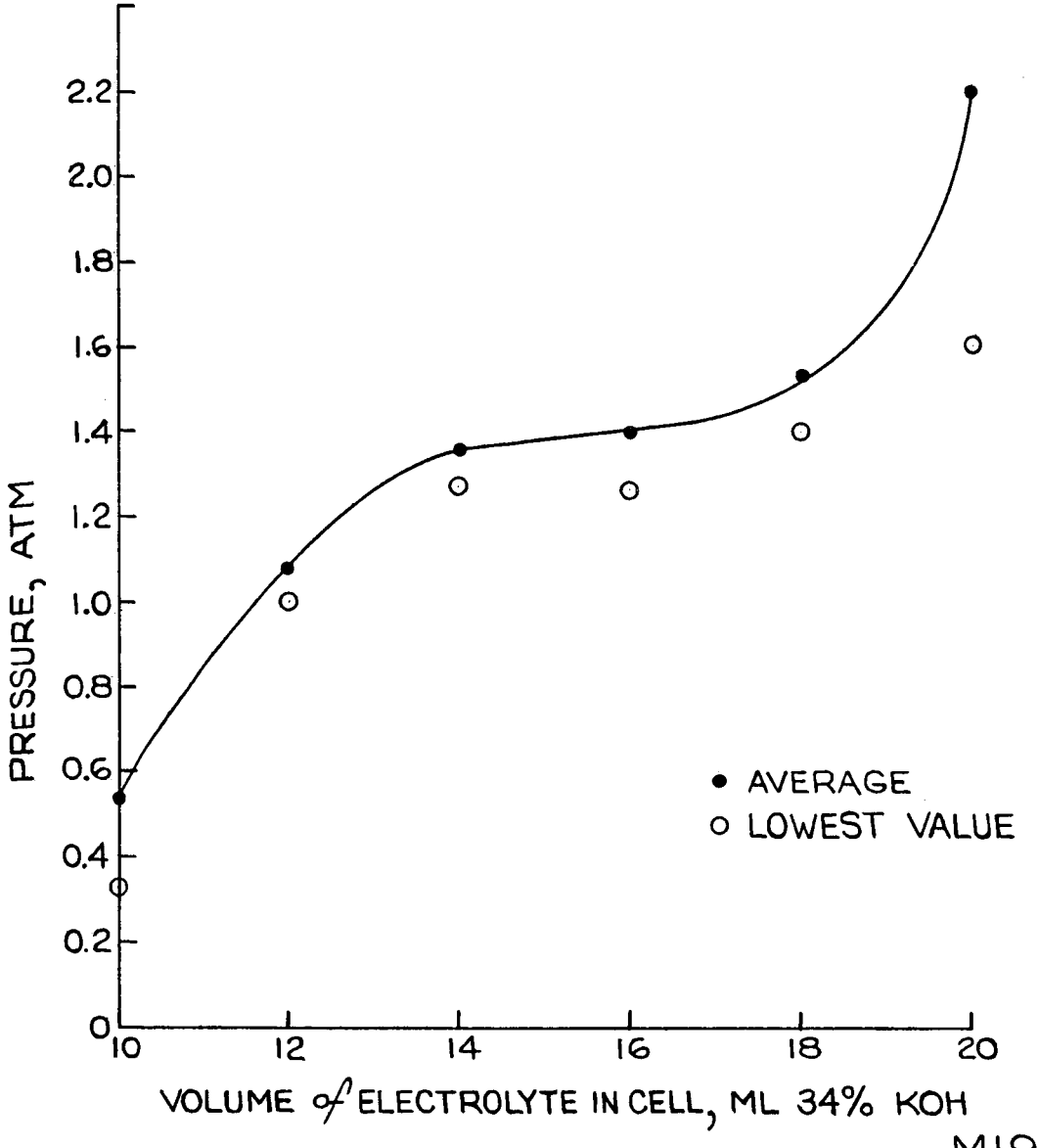

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FIG. 2 PRESSURE CHANGES WITH ELECTROLYTE VOLUME DURING OVERCHARGE of SEALED NICKEL-CADMIUM CELLS

NASA-Langley, 1966 CR-66105