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DEVELOPMENT OF MAGNESIUM WAFER CELLS

Fourth Quarterly Report

by

LLOYD W. EATON

October 1967

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CONTRACT NO. DA 28043 AMC 02135 (E)

BURGESS BATTERY COMPANY
DIVISION OF SERVEL, INC.
FREEPORT, ILLINOIS 61032

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TECHNICAL REPORT ECOM 02135-4 October 1967

DEVELOPMENT OF MAGNESIUM WAFER CELLS

Fourth Quarterly Report
Period Covered
1 February 1967 to 30 April 1967

Report No. 4

Contract No. DA28-043 AMC 02135 (E)
DA Project No. 1C6-22001-A053, Task 02, Subtask 38

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Abstract

Contract No. Da28 043 AMC 02135 (E)

Battery units have been made that survive two weeks storage at 160°F. Battery units stored one month at 160°F. suffered a complete degradation of the cell wrap necessitating a review of the construction with respect to materials and assembly to protect the cell wrap and anode moisture barrier contact.

The most likely material changes that will produce early results are use of Dow Chemical Company Experimental Plastic Film PZ-2000.03 or PZ-2000.21 as cell wrap or the replacement of the rolled tin plated steel vapor barrier with a copper foil vapor barrier. The addition of a polyester film separator between the moisture barrier and cell wrap on the anode side is also to be considered even though the complexity of the cell is greatly increased.

Publications, Lectures, Reports and Conferences

Publications: None

Reports: None

Lectures: None

Conferences:

1. 1 February 1967, outlined progress to date and objectives. Held at ECOM, Fort Monmouth, New Jersey, attended by John J. Murphy, Donald B. Wood, and Harry L. Williams of the U. S. Army Electronic Command and Howard J. Strauss and Terry G. Messing of Burgess.

2. 14 March 1967 outlined progress and objectives. Held at Burgess Battery Co., Freeport, Illinois. Attended by Donald B. Wood of the U. S. Army Electronic Command and Joseph J. Coleman, Howard J. Strauss, Milton E. Wilke, Lloyd W. Eaton, Terry Messing, and Roger Woodworth of Burgess.

CELL AND BATTERY CONSTRUCTION

The basic flaw in the intercell connection between the cathode material of one cell and the magnesium anode of the next cell, described in the Third Quarterly Report, was overcome by the cell designs noted as Fig. 2 and 3 in that report and included, for reference, as Fig. 1 and 2 in this report. This basic flaw had masked a number of material problems that subsequently became apparent. The following list of cell and battery parts, in the order of appearance in the investigation, required alteration in either material, process, or design:

1. Separator -- Changed from plain Kraft to methylcellulose coated Kraft.
2. Cathode mix - Wetter content reduced and process changed to produce a drier cake.
3. Addition of adhesive ring to protect weld of vapor shield to anode.
4. Cell wrap - Addition of a polyester film shield to protect the rubber hydrochloride cell wrap between the vapor shield and anode or replacement of rubber hydrochloride film with another material.

Separator

A series of 1/2 A_2 sections of the BA-4386/PRC-25 containing nine (9) cells with plain Kraft paper separators were made and stored one week at 160°F. The units would survive the storage period and have an acceptable voltage when placed on load but a high percentage would drop below the 10 volt end point within the next six hours. The units would frequently recover voltage and run a reasonable period of time to 10 volts. Typical examples of this characteristic are noted in the following table:

Voltage on Load Cycle

Unit No.	Voltage Reading at Hourly Points									Capacity
	0	1	2	3	4	5	6	7	8	
1	14.6	13.2	--	--	9.8	--	10.6	--	--	80 hrs.
2	14.2	--	12.6	--	--	7.0	--	--	10.7	55 hrs.
3	14.0	--	12.2	--	9.2	--	11.1	11.0	11.2	58 hrs.
4	13.7	--	12.1	--	9.8	--	10.2	10.4	10.8	63 hrs.
5	--	--	11.7	9.0	9.6	10.1	--	--	10.2	57 hrs.
6	--	--	11.9	--	10.6	9.4	9.7	--	10.4	60 hrs.
7	--	--	12.2	9.7	7.6	8.05	8.0	10.0	--	60 hrs.

The fact that these units would recover voltage after six to eight hours indicated loss of contact and the normal expectation would be the intercell contact failed partially or loss of compression resulted from storage. Repeated disassembly of units showing this characteristic indicated that the intercell resistance remained low and did not cause this voltage drop. A series of units were made with the compressed length of the cell stack reduced, to remove any chance of compression loss during storage, without any improvement in discharge characteristic and considerable increase in difficulty with the cathode mix cake. It was finally concluded that a separation between the separator and anode was occurring, probably due to gas formation, and that a separator that would produce a gel would be required.

As an experiment a series of ten $\frac{1}{2}$ A_2 batteries were made using Webril as the separator. The results were uniformly poor and the severe drop in voltage in the early hours of discharge still occurred in eight of the units. The early hour voltage readings are given in the following table:

Unit No.	Hourly Voltages 0	1	2	3	4	5	Cap. to 10 volts after recovery
1	13.0	--	--	10.6	--	10.9	15 hrs.
2	13.2	--	--	6.0	--	11.2	19 hrs.
3	12.9	--	--	6.9	--	9.8	22 hrs.
4	13.4	--	--	11.9	--	11.6	24 hrs.
5	12.6	--	--	4.6	--	10.8	16 hrs.
6	13.8	10.7	8.5	7.2	10.8	--	16 hrs.
7	14.2	10.0	8.2	8.1	11.9	--	31 hrs.
8	14.1	10.8	8.6	12.2	12.1	--	23 hrs.
9	14.4	0	0	0	--	--	--
10	13.6	6.2	11.6	11.4	--	--	19 hrs.

The use of plain Kraft paper coated with methylcellulose appears to correct this early hour discharge failure as indicated in the following table:

Unit No.	Hourly Voltages 0	1	2	3	4	5	160°F Storage	Capacity to 10 Volts
1	13.8	13.6	12.6	12.0	--	12.1	1 Wk.	55 hrs.
2	13.0	11.8	11.8	11.7	11.5	11.5	2 Wks.	Can failure

Unit No.	Hourly Voltages 0	1	2	3	4	5	160°F Storage	Capacity to 10 Volts
3	14.0	13.0	12.6	12.5	12.4	12.3	2 Wk.	53 hrs.
4	14.1	13.7	13.2	12.6	12.5	12.4	1 Wk.	70 hrs.
5	13.8	13.3	12.4	11.8	11.9	12.0	1 Wk.	61 hrs.
6	14.0	13.5	12.9	12.4	12.3	12.2	1 Wk.	66 hrs.
7	14.2	13.2	12.2	12.3	12.3	12.4	1 Wk.	65 hrs.
8	14.3	13.2	12.8	12.1	12.2	12.3	1 Wk.	62 hrs.
9	13.8	12.5	11.6	12.4	12.1	12.2	1 Wk.	65 hrs.
10	12.3	12.3	12.2	12.2	12.1	12.0	1 Wk.	Can failure
11	13.3	12.7	12.5	12.3	12.2	12.0	2 Wks.	54 hrs.

Cathode Mix

It has been found that a cathode mix containing 67% chemical ore, 22% natural ore, 7% carbon, 3% barium chromate, and 1% magnesium hydroxide and combined with a wetter containing 21% magnesium bromide so that 32.8% of the mix is wetter has an extremely sharp drop in moisture retaining ability versus wet mixing time. On a scale of 0 to 100 where 100 wetness rating is extremely difficult to extrude and 30 rating is easy to extrude the wet mix time varies from 15 seconds for 100 rating, to 60 seconds for 30 rating. The extruded mix is altered by the act of extrusion so that the effective wetness rating of the formed cake is much less than the material before extrusion. This change is sufficient so that a wetness rating of 30 is too mobile to be used in the cell construction noted in Fig. 2, i.e. large opening in cell wrap for cathode collector. The pressure of assembly of the cells into battery stacks would cause electrolyte to extrude. It has also been found that the mix with any wetness rating will, on storage at 160°F under compression of battery assembly, release electrolyte. This last item enters into the cell wrap problem discussed later in this report.

The mix was changed to a 31.4% wetter content to extend the wet mix time to a controllable length and the wetness rating was set at 60-70 which is extrudable and has sufficient body to allow the Fig. 2 construction and does not extrude electrolyte on cell compression into battery stacks. It was found necessary to limit the extrusion of the material to a single pass with damaged cell mix material discarded rather than re-extruded as is the usual practice due to the reduced wetter containment on additional working of the mix.

Adhesive ring weld protector

Units stored two weeks at 160°F were dismantled and found to have a degree of moisture present between the vapor shield and the cell wrap on the anode side. The reason for the presence of this moisture was not clear until three and four week 160°F storage samples were examined. This is covered in the section on cell wrap later in this report. The moisture noted caused corrosion of the anode-vapor shield weld which was sufficient to cause a high ratio of failure of two week samples. A ring of adhesive was placed between Item 1 vapor shield and Item 3 cell wrap of Figs. 1 and 2. This excluded the moisture and increased the ratio of batteries to survive two weeks at 160°F.

Cell Wrap

Five Ba4386 units with cell construction of Fig. 2 and four Ba4386 units of cell construction of Fig. 1 with added adhesive ring weld protector were made. These units were stored one month at 160°F. None of the units survived the storage and examination showed complete degradation of the rubber hydrochloride cell wrap film between the rolled tin plated steel moisture barrier and mangesium anode. This degradation did not occur to the cell wrap film between the moisture barrier and the cathode mix cake. Apparently the necessary conditions to degrade rubber hydrochloride film include liquid on the anode side of the film, intimate contact with the tin coated steel and elevated temperature. This was confirmed by having distilled water, rubber hydrochloride film and tin plate steel reproduce the result outside of a battery.

One of the products of this degradation was hydrochloric acid which caused severe damage to the welds, moisture barrier, internal leads, and the anode plates. In retrospect, most of the extreme difficulty found in maintaining electrical contact between the vapor shield and anode can be traced to this degradation of the cell wrap.

There are four approaches to handling this problem.

1. Add some material to the mix to prevent liquid electrolyte from being extruded under conditions of elevated temperature and battery assembly compression.
2. Protect the rubber hydrochloride film from the moisture barrier by adding a sheet of polyester film.
3. Use a different cell wrap material that will not be subject to this degrading effect.

4. Use a moisture barrier material that does not have this effect.

All of these approaches are being investigated.

The most promising of early results are itesm 2 and 4. The least promising is item 1. Initial tests on the addition of gum materials indicate that the electrolyte is still released on storage at 160°F and the capacity of the batteries is reduced to a damaging degree.

The protective film (Item 2) construction is shown in Fig. 3. This tends to make the cell construction excessively complicated. The most probable alternate moisture barrier material (Item 4) is copper. This change does not increase the complexity of the cell.

At present, the most likely cell wrap film replacement material would be Dow Chemical Company's PZ-2000.21 or PZ-2000.03 Experimental Films. There are some difficulties attendant to the use of this film, particularly in hot melt adhesives.

Ba4386--Battery Assembly

The construction of a full Ba4386 battery consisting of two 9 cell sections in parallel (A_2) and a 2 cell A_1 connected in parallel with the 2 negative end terminal cells of each $\frac{1}{2}$ A_2 section, presented a few problems with interstack contact, terminal insulation and cell protection during can closing that have been handled, at present, with the design shown in Fig. 4.

Item	Description
1. Terminal board	0.093" black hard fibre board 3-5/16" X 1-15/16" with 1/4" R corners. Three contact rivets on center line with center rivet

Item	Description
	on center line intersection. Other with spaced one inch from center. Board microcrystalline wax impregnated
2. Conductive coating	Each contact rivet is coated with a proprietary conductive material.
3. Protective cover	0.010" Duplex paper 4-1/8" X 2-11/16" with three 19/32" holes for terminal board contact rivets. 3/8" X 3/8" corner cut-outs to allow sides to fold down and protect top cell during can closing procedure.
4. Terminal insulator	0.010" Duplex paper 3-1/4" X 1-3/4"
5. Anode Lead	1/2" X 0.002" rolled tin plated steel 11-5/8" long, welded to bottom anode plate of lower A_2 section and folded between top A_2 section, and A_1 section as shown. Insulated on both sides with electrical tape (3M-No. 3)
6. A_1 cathode lead	1/2" X 0.002" rolled tin plated steel 1-1/2" long spot welded to top cell vapor shield of A_1 section. Folded over terminal insulator. Strip insulated on both sides with electrical tape (3 M - No. 3)
A_1 (Top A_2 section)	
Parallel cathode lead	1/2" X 0.002" rolled tin plated steel 3.5 in. long welded to vapor shield of third cell from anode contact brought up middle of battery side. Folded over terminal insulator. Strip insulated on both sides with electrical tape (3M-No.3)
A_1 (Lower A_2 Section)	
Parallel cathode lead	1/2" X 0.002" rolled tin plated steel 9 inch long weld to vapor shield of third cell from anode contact brought up middle of battery side and folded over

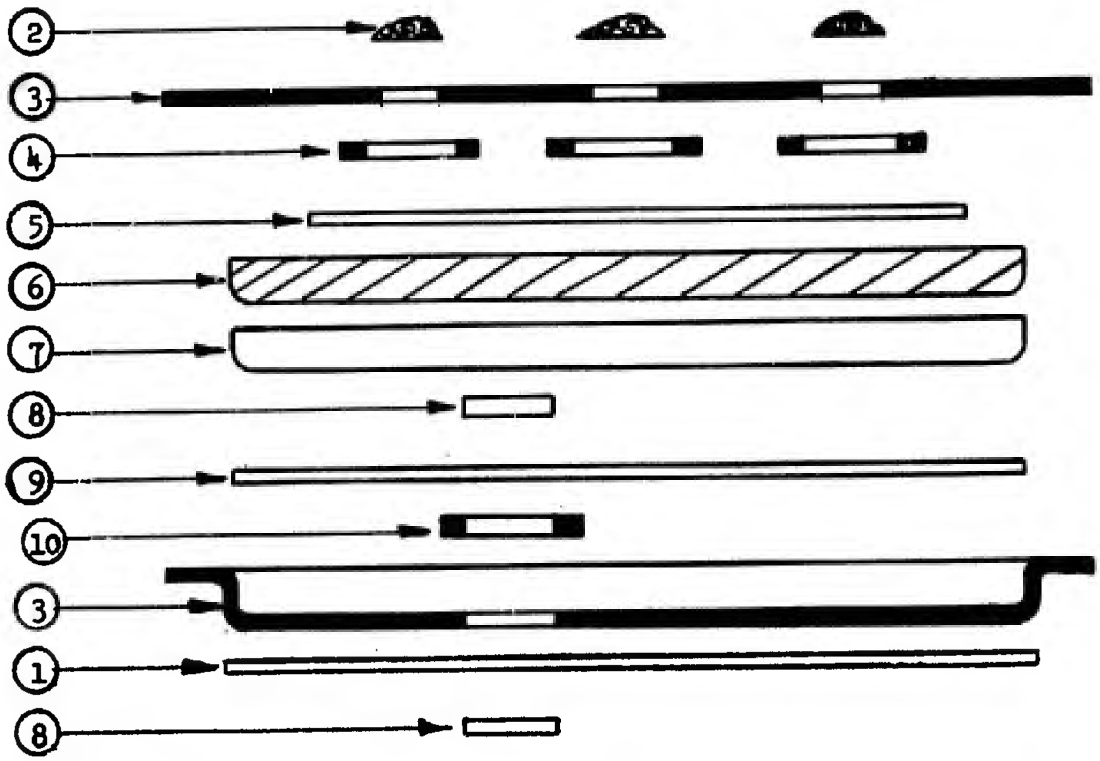
	terminal insulator. Strip insulated on both sides with electrical tape (3M-No. 3)
A_1 Terminal connection	A proprietary conductive material is used to make complete electrical contact between the three A_1 conductive strips.
7. Vapor shields --	Per cell description
8. Interstack Connectors	A proprietary conductive material is placed between metal-to-metal (vapor shields) to insure contact after extended storage.
9. A_2 cathode lead	1/2" X 0.002" rolled tin plated steel 5-3/4" long spot welded to last vapor shield of top A_2 section. Insulated on both sides with electrical tape (3M - No.3) and brought up small side of battery as shown and folded over terminal insulation.
10. End insulator	0.010" Duplex paper 3-1/4" X 1-3/4"
Screen wrap	The completed cell assembly is wrapped in fibre glass screen 8" X 14".
Sealing	The screen wrapped cell assembly is dipped in microcrystalline wax and placed in a polyethylene bag.
Can Assembly	The best can assembly, to date, consists of edge welding 0.020 inch thick steel cups to a 0.010 inch thick steel sleeve. The top cup has three 19/32" holes located to match terminal board contact rivets.

CONCLUSIONS AND PROPOSED WORK

A battery can be made to survive one week storage at 160°F with consistent results. Approximately 50% of the batteries with the additional ring seal for the anode-vapor barrier weld will survive two weeks storage at 160°F. One month storage at 160°F produced a complete breakdown of the cell wrap material.

Replacement of the rubber hydrochloride cell wrap with Dow Experimental films PZ-2000.21 or PZ-2000.03 or replacement of the tin plated steel vapor barrier with a copper foil vapor barrier are to be researched. A third alternative of protecting the rubber hydrochloride film wrap with a polyester film insert will also be investigated but is a third choice as a result of the increase in cell construction complexity.

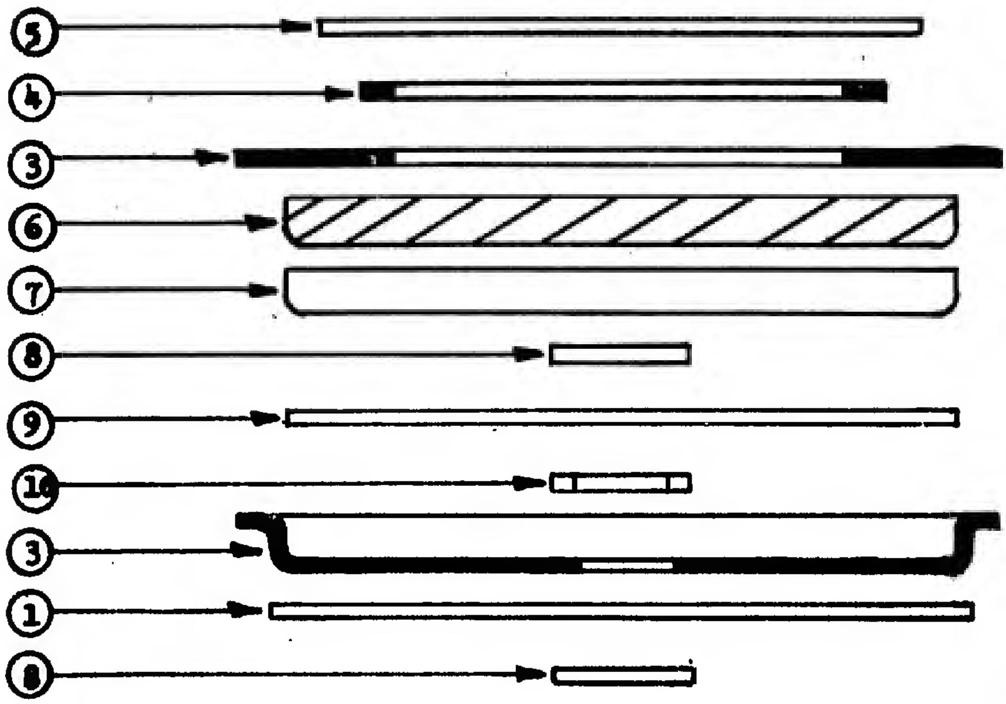
MAGNESIUM "F" WAFER CELL



1. Metallic Moisture Barrier
2. Inter-cell Connector
3. Cell Wrap
4. Adhesive Ring
5. Carbon Cloth
6. Cathode Mix
7. Separator
8. Nonpermeable Dot
9. Anode (Magnesium)
10. Adhesive Ring

FIGURE 1

MAGNESIUM "F" WAFER CELL



1. Metallic Moisture Barrier
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4. Adhesive Ring
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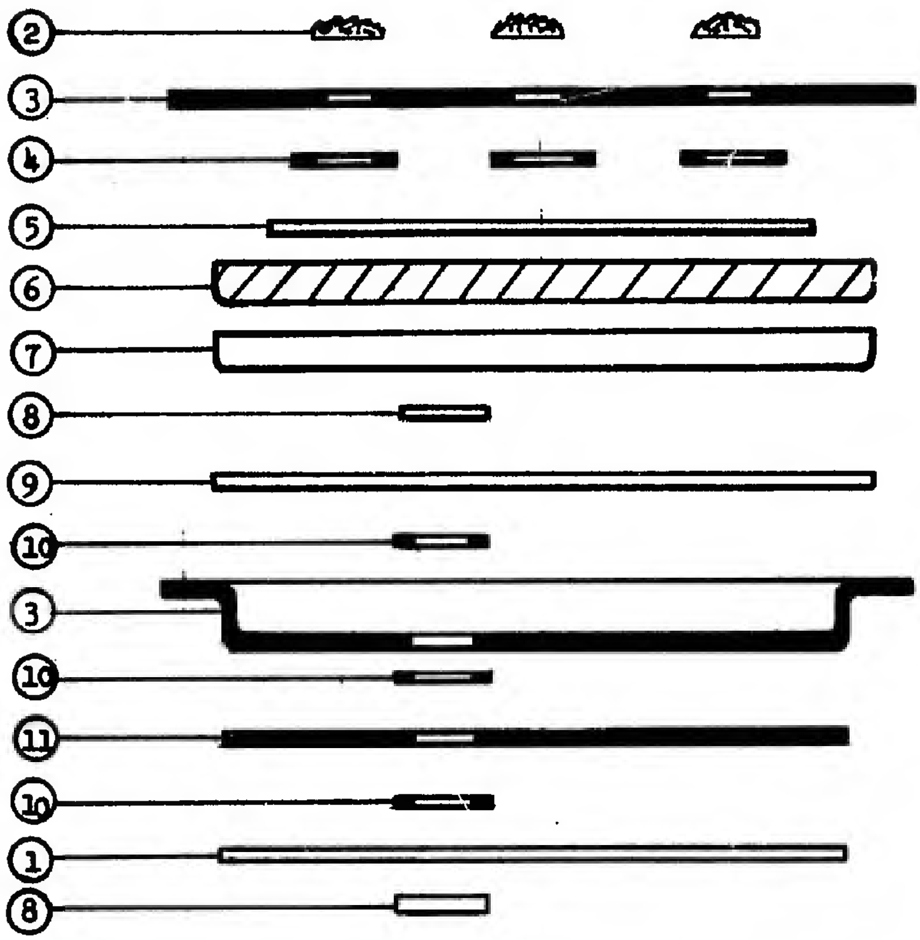
7. Separator
8. Nonpermeable Dot
9. Anode (Magnesium)
10. Adhesive Ring

FIGURE II

MAGNESIUM "F" WAFER CELL



1. Metallic Moisture Barrier
2. Inter-cell Connector
3. Cell Wrap
4. Adhesive Ring
5. Carbon Cloth
6. Cathode Mix
7. Separator
8. Nonpermeable Dot
9. Anode (Magnesium)
10. Adhesive Ring
11. Cell Wrap Protection

FIGURE III

A-4

BA 4386 ASSEMBLY

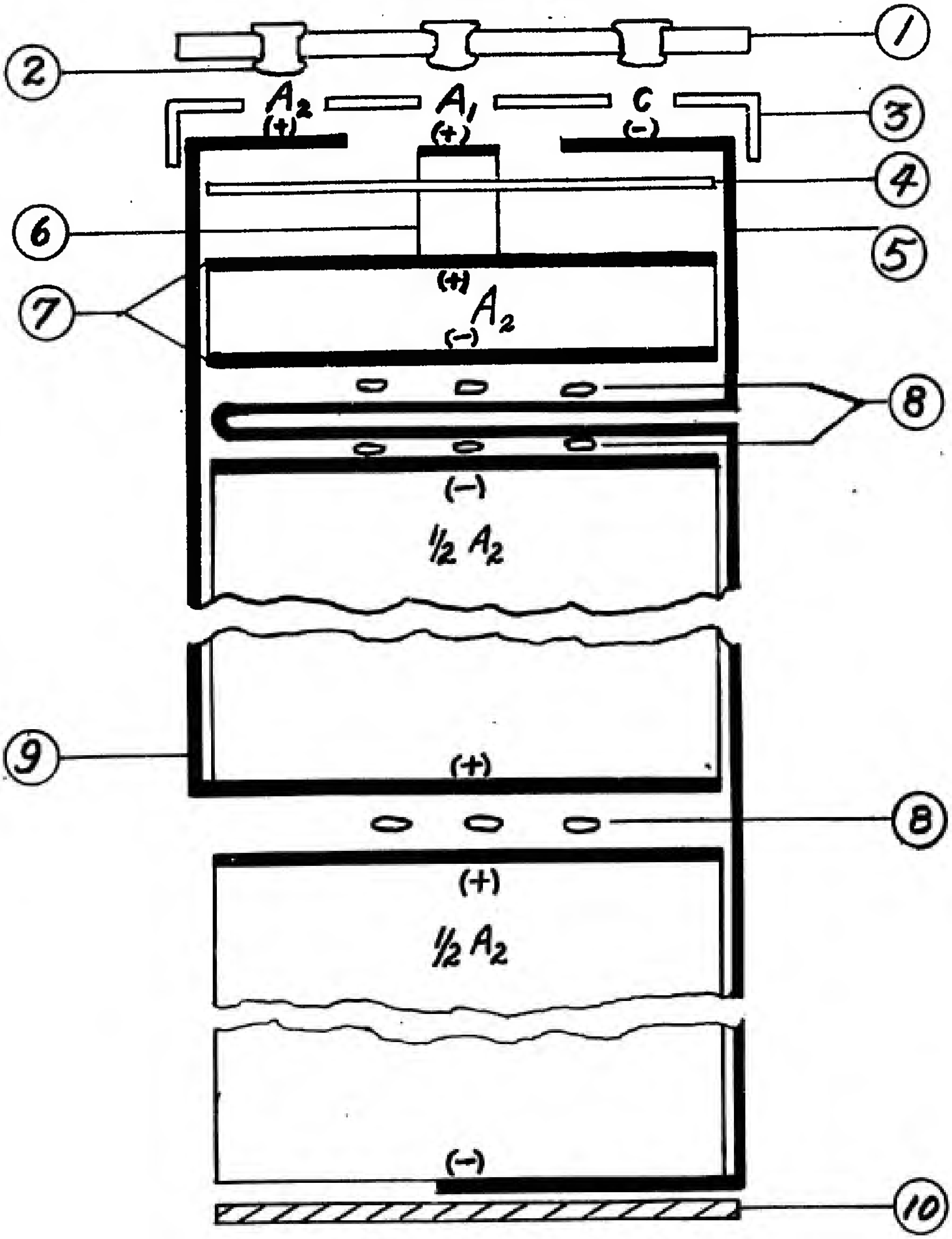


FIG. 4

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13. ABSTRACT

Battery units have been made that survive two weeks storage at 160°F. Battery units stored one month at 160°F suffered a complete degradation of the cell wrap necessitating a review of the construction with respect to materials and assembly to protect the cell wrap and anode moisture barrier contact.

The most likely material changes that will produce early results are use of Dow Chemical Company Experimental Plastic Film PZ-2000.03 or PZ2000.21 as cell wrap or the replacement of the rolled tin plated steel vapor barrier with a copper foil vapor barrier. The addition of a polyester film separator between the moisture barrier and cell wrap on the anode side is also to be considered even though the complexity of the cell is greatly increased. (Author)

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Primary Cells Magnesium Dry Cells Flat Cells						

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