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ECOM 02135-5

DEVELOPMENT OF MAGNESIUM WAFER CELLS

Semi-Annual Report

by

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February 1968

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

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DEVELOPMENT OF MAGNESIUM WAFER CELLS

Semi-Annual Report
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Abstract

Contract No. Da28 043 AMC 02135(E)

Ba4386/PRC-25 units, made with rubber hydrochloride cell wrap, rolled tin plated steel moisture barriers welded to anode and "Mylar" polyester film between the cell wrap and moisture barrier to protect the cell wrap from degradation by the tin, failed 100% after storage for one month at 160°F.

Ba4386/PRC-25 units and flat cell versions of the B_1 section of the BA-4270/U with Dow Chemical Company Experimental Plastic Film PZ2000.21 as cell wrap and rolled tin plated steel moisture barriers failed 100% after storage for one month at 160°F.

Ba4386/PRC-25 units made with rubber hydrochloride cell wrap and copper foil moisture barrier welded to anode had 14.6% run in excess of 40 hours after storage for one month at 160°F.

Twenty-four (24) cell B_1 units of the Ba4270/U, made with flat cells using rubber hydrochloride cell wrap and copper moisture barriers welded to anode, discharged with 6/7 of the normal B_1 load, had 71% run in excess of 40 hours after storage for one month at 160°F.

The principal failure of magnesium bromide batteries has been the degree of corrosion of the magnesium anode on the contact side that progresses under the cell wrap seal and increases the resistance of the contact or destroys the contact. It has been concluded that the presence of air is causing the anode to be attacked on the contact (non-reactive) side to an excessive degree and that the anode in a flat cell needs complete protection on the non-reactive side.

Magnesium perchlorate cathode material seems to intensify the action on the non-reactive side of the anode and there is a strong suggestion that the rubber hydrochloride cell wrap is being degraded by the oxidizing nature of the perchlorate at 160^{o}F. causing leakage and the destruction of the batteries stored at 160^{o}F.

Publications, Lectures, Reports and Conferences

Publications: None

Reports: None

Lectures: None

Conferences:

1. 1 August 1967, outlined progress to date and objectives. Held at Burgess Battery, Freeport, Illinois. Attended by Donald B. Wood, David Linden, John Hovendon, William Shorr, and Ed Chapman of the U. S. Army Electronics Command, Joseph J. Coleman, Milton Wilke, Terry Messing, and Lloyd W. Eaton of Burgess.

2. 9 November 1967, outlined progress to date and objectives. Held at ECOM, Fort Monmouth, New Jersey. Attended by John J. Murphy, Donald B. Wood of the U. S. Army Electronics Command and Howard J. Strauss and Lloyd W. Eaton of Burgess.

CELL AND BATTERY CONSTRUCTION

The three approaches to the breakdown of the rubber hydrochloride cell wrap material noted in the Technical Report ECOM 02135-4 were as follows:

1. Use a polyester film insert between the rolled tin plated steel foil moisture barrier to physically separate the cell wrap from the tin.

2. Replace the rubber hydrochloride cell wrap with Dow Experimental film PZ 2000.21 using rolled tin plated steel foil moisture barrier.

3. Replace the rolled tin plated steel foil with copper foil.

The construction of the cell in approach No. 1 is as shown in Fig. I, page A-8, of the appendix, and described in detail in Technical Reports ECOM 02135-3 and -4. The rolled tin plated steel moisture barrier was spot welded to the magnesium anode. The polyester insert is noted as Item 11 and is sealed to the cell wrap and moisture barrier by hot melt rings. Three one half A_2 sections of the Ba4386/PRC-25 and twenty-one full Ba4386/PRC-25 units were made, stored one month at $160^{\circ}F$ and discharged with the results noted in Table #1, page A-1 of the appendix. A 100% failure occurred with loss of contact to the magnesium the primary cause of failure, this loss being due to corrosion of the area of the weld.

The construction of the cell in approach No. 2 is as shown in Fig. 2, page A-9 of the appendix, and is also described in detail in Technical Reports ECOM 02135-3 and -4. Four one half A_2 sections of the Ba4386/PRC-25 and four flat cell versions of a B_1 (6/7) section of the Ba4270/U with the rolled tin plated steel foil moisture barrier spot welded to the magnesium anode. 100% of the Ba4386 units failed to survive one month storage at 160°F. One 24 cell B_1 section of the Ba4270/U survived with 51.9 hours discharge capacity to 29.1 volts with a variable contact within the unit.

The construction of the cell in approach No. 3 is also as shown in Fig. 2, page A-9 of the appendix. The copper moisture barrier is welded to the magnesium anode by a five point spot weld. The non-permeable dot (Item 8) weld protection was omitted as it is not necessary with copper. The results of Ba4386/PRC-25 batteries made in this manner is given in Table No. 3, page A-4 of the appendix. The first ten units employed an asphalt ring seal between the cell wrap and conductive carbon cloth (Item 4, Fig. 2). The units that survived one month storage at 160°F. exhibited a capacity of 28 to 32 hours to 10 volt on the A_2 section. Examination of these units showed that the asphalt ring had migrated into the conductive carbon cathode collector in the contact area increasing the resistance..

All other units had the asphalt ring replaced with a hot melt ring that did not affect the conductive carbon material. The capacity increased to in excess of 55 hours on the successful units. The principal failure remained a corrosion of the contact area that usually destroyed most of the weld points and caused increased resistance or open circuit.

Twenty-four (24) cell B_1 units of the Ba4270/U battery were made with the cell construction shown as Fig. 3, page A-10 of appendix. The construction of the "V" cell is as follows:

Item	Description
1. Intercell connector	Conductive compound that has a binder that does not affect the cathode collector (Item 4)
2. Cell wrap	Two sheets 0.001" X 3" X 3" rubber hydrochloride film. Single 15/32" hole for cathode collector and single 11/32" dia. hole for anode contact. The holes are centered.
3. Ring Seal	Hot melt adhesive
4. Cathode Collector	1" X 1" piece of conductive carbon plastic sheet with corners clipped.
5. Cathode Mix	Bromide electrolyte per Technical Reports ECOM 02135-3, and-4. 9 gms of material per cell.
6. Separator	00 Kraft paper. coated on one side with Methocel, 1-5/16" X 1-5/16". Methocell side placed against anode.
7. Non-permeable dot	Pliobond
8. Anode	Magnesium alloy AZ21, 1-1/8" X 1-1/8" X 0.025" with 1/4" R round corners
9. Moisture barrier	Copper foil 0.002" X 1-1/8" X 1-1/8" with 1/4 R rounded corners spot welded at five points to anode in center.
Battery assembly	24 cells compressed to 5-3/4", wrapped and heat sealed with mylar-pliofilm laminate. Battery placed in steel sleeve with steel end caps edge welded to sleeve. Battery sealed by vacuum waxing with cerese wax.

The results of these 24 cell B_1 sections of Ba4270/U batteries stored one month at 160°F. and discharged to 29.1 volts with a load 6/7 of the normal B_1 section load are given in Table No. 4, page A-6 of the appendix. The principal difficulty noted in these batteries was again a degree of corrosion of the anode in the weld area causing increased resistance and an occasional open circuit. A good percentage had capacities in excess of 40 hours. A fresh unit has a capacity of 50-55 hours.

Since the welding of the moisture barrier to the magnesium anode must be done blind with intervening parts in the assembly it is felt that a large production of these cells would pose considerable difficulty in manufacture. The "V" cell is, with the exception of the moisture barrier, remarkably similar in construction to a standard zinc "V" cell manufactured by Burgess Battery with existing machinery. As one of the objectives of this contract was to develop a cell that could be easily manufactured, the construction was modified so that the cell could be made by machine and the moisture barrier added to the finished cell as a separate operation. Fig. 4, page A-11 of the appendix shows this design change. The contact between the moisture barrier and magnesium anode is a conductive compound that is not limited in its properties as is the intercell material on the conductive cathode collector. It is essential, however, that the cell with the moisture barrier attached be flat as possible. This was accomplished by using a meltable medium and applying heat and pressure to the contact point after attachment of the barrier to make it flat. The conductive material completely covers the anode cell wrap opening essentially closing the area to moisture penetration from outside the cell.

The discharge results obtained with this construction after storage for one month at 160° F. are shown in Table #5, page A-7 of the appendix. Examination of these discharged units again showed a degree of corrosion in the contact area that caused an increase in resistance and an occasional open circuit. The capacities, compared to a fresh unit 50-55 hours are quite good, the variability being caused by the above noted corrosion.

Magnesium Perchlorate

The Ba4386/PRC-25 battery that has been the target of this work has a delay time requirement that cannot be met by a unit employing magnesium bromide electrolyte cathode mix. A series of twenty Ba4386/PRC-25 batteries were made using a cathode mix of the following composition:

Dry Material

Chemical Ore	86%
Carbon	10%
Barium Chromate	3%
Magnesium Hydroxide	1%

Wetter Composition

Magnesium perchlorate hydrate solution is prepared with a specific gravity of 1.330 - 1.378.

The wetter composition is:

99.4% Magnesium perchlorate solution

0.6% Lithium chromate solution (30%).

The mix contained 29.7% by weight of this wetter and the "wetness" adjusted to approximately 70, in accordance with Technical Reports ECOM 02135-3 and -4, for extrusion.

The construction of the cells was as shown in Fig. 2, page A-9 of appendix modified per Figure 4, page A-11 of the appendix, so that welding was not necessary. The extra seal ring between the moisture barrier and cell wrap was omitted.

A 100% failure occurred in these twenty batteries stored one month at 160°F. with a destruction greatly in excess of anything encountered in the project. Severe corrosion of the anode occurred on the non-reactive side, severe perforation of the anodes, corrosion of the internal leads and shorted cells were found. The cell wrap was found to be ruptured on a number of cells and cracks in the cell wrap on the cathode side near the seal area were found. The evidence strongly suggests the oxidizing character of the magnesium perchlorate wetter degrades the rubber hydrochloride film at 160°F. releasing electrolyte which caused the damage.

Battery Sealing

The battery sealing technique noted in Technical Report ECOM 02135-4 had been changed to a battery wrap of mylar-pliofilm laminate, heat sealed, and the canned battery vacuum waxed with cerese wax. The cerese wax does not melt at 160°F. and remains in the battery. The moisture seal, as evident in some of the modified flat cell versions of the B_1 section of Ba4270/U units described, appears to be quite good. However, in fresh batteries discharged at a rate that will evolve hydrogen gas at an appreciable rate, the wax seal does not pass the gas at a sufficient rate to prevent the gas, trapped between the cell stack and wax, from expanding the can. This expansion sometimes causes loss of contact in the battery until pressure is relieved. The can of the modified B_1 sections of the

Ba4270/U is distorted and the seam placed under considerable stress. This gas entrapment during discharge on batteries stored one month at 160°F. is very much reduced probably due to rearrangement of wax by "cold flow" under these conditions.

Vented batteries, as expected, do not exhibit this characteristic. However, a vent design able to remain open when the canned unit is vacuum waxed has not been devised yet.

Battery Cans

The cans for the Ba4386/PRC-25 batteries using seamed covers 0.010 inch thick, and edge welded covers 0.020 inches thick have not contained the discharge expansion of the cells satisfactorily. The expansion is normal to the anode surface of the cell and the 3-5/8 can side dimension is too long to provide sufficient strength to prevent this expansion from being transferred to the sides of the can causing the seam edge or welded edge to bend outward exceeding the specification limit. The cup of the cell stack cover is indeed reversed by this force transfer. The incorporation of compressible members such as 1/4" thick balsa wood or 1/4" thick sponge rubber proved to be futile.

The discharge expansion in the modified B_1 sections of a Ba4270/U with edge welded covers has not been a problem. The 1-1/8" X 1-1/8" cross section seems sufficient to withstand the pressure transfer to the can sides without distortion. Trouble with seamed covers is not anticipated.

CONCLUSIONS

The following conclusions have been drawn from the work:

1. The corrosion in the anode contact area is caused by moisture getting into the space. The moisture source had been assumed to be external to the cell and all effort had been directed to its exclusion. The persistence of this corrosion required a reappraisal. Careful examination of cells with magnesium bromide electrolyte stored one month at 160°F. showed that the unprotected non-reactive side of the anode (contact side) undergoes a surface corrosion and passivates. This surface corrosion however, proceeds under the sealing hot melt ring and eventually provides a porous path for moisture from within the cell to get to the contact area. Future cells will have the entire area of the non-reactive side of the anode around the contact area completely protected by either a hot melt coating or nonpermeable paint coating with a hot melt sealing ring between the paint and cell wrap.

2. The rolled tin plated steel moisture barrier provides a poor contact with the magnesium anode. This includes the spot welding technique and the use of a conductive compound. Copper foil will be the material of choice for the remainder of the contract.

3. Vacuum waxing of the batteries with cerese wax is an effective moisture barrier. A vent will be needed to release gas formed on discharge that does not plug with wax when sealing operation is performed.

4. The design of the Ba4386/PRC-25 battery can needs review with respect to the strength of the 3-5/8" side dimension to resist the discharge expansion force of the cells. Evidence indicates that the 3-5/8" dimension

is too long and is not rigid enough to resist bending outward and allowing the cup of the cover to be reversed. The possibility of sectionalizing the battery itself into two or even four sections to redistribute the force should be considered. The 1-1/8" X 1-1/8" "V" size cell batteries do not appear to cause expansion trouble.

5. Magnesium perchlorate mix apparently degrades rubber hydrochloride, allowing the release of electrolyte into the battery to cause shorting and corrosion. The cell wrap material of future perchlorate units will be Dow's PZ2000.21 film entirely or PZ2000.21 film bottom anode section and polyethylene coated paper top or cathode collector section.

6. The 1-1/8 X 1-1/8 "V" size cell produces a battery that shows considerable promise of surviving physically a month at 160°F and producing a capacity on discharge that probably will be close to fresh capacity without the disruptive expansion of the discharge products.

Proposed Work

The following objectives are proposed for the next six month period:

1. Verify the theory that the contact area protection from moisture requires complete protection of the non-active side of magnesium anode.

2. Determine the most effective material for providing the corrosion protection of the non-reactive side of the magnesium anode.

3. Verify the supposed destructive effect of perchlorate on rubber hydrochloride cell wrap.

4. Qualify PZ2000.21 (Dow) film as a cell wrap material for perchlorate mix cells.

5. Qualify polyethylene coated paper as a cell wrap material for perchlorate mix cells.

6. Test seamed cans for the 1-1/8" X 1-1/8" size batteries, as full B_1 sections of the Ba4270/U, for containment of the cell expansion.

7. Devise a wax proof gas leak device for 1-1/8" X 1-1/8" size battery to relieve the hydrogen gas, produced on discharge, that is contained by the sealing in a fresh battery .

8. Test methods of redistributing expansion forces in the Ba-4386 flat cell battery to allow containment of the battery within the design limits.

9. Assuming perchlorate battery cell wrap problems are overcome and a surviving battery can be made, determine the delay characteristics of voltage build-up.

10. Test batteries stored at 145°F.

APPENDIX

Table #1

Rubber hydrochloride cell wrap and rolled tin plated steel moisture barriers welded to magnesium anode. Cell wrap protected from tin of moisture barrier by sheet of "Mylar" polyester film between the cell wrap and moisture barrier.

Hours capacity A_2 to 10.0/9.0 volt; A_1 to 2.12 volt

Storage period at 160°F.

Unit Size	1 Wk.	2 Wks.	3 Wks.	1 Mo.	
	A_2	A_2	A_2	A_2	A_1
1/2 Ba4386 A_2	0/0	1.5/1.6	0.9/1.3	0/0	----
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/6.2	0
1/2 Ba4386 A_2	----	31.0/74.3	----	0/0	----
1/2 Ba4386 A_2	----	15.3/63.4	----	0/0	----
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0.5/1.8	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0

Table #1 Cont'd

Unit Size	1 Wk. A_2	2 Wks. A_2	3 Wks. A_2	1 Mo. A_2	A_1
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0
Ba4386	----	----	----	0/0	0

Table #2

Dow Chemical Company Experimental Plastic Film PL2000.21 as cell wrap with rolled tin plated steel foil welded to magnesium anode as moisture barrier.

Unit Size	Hours Capacity to end voltage after Storage at 160°F.			
	2 Wks.	3 Wks.	1 Mon.	
	A_2	A_2	A_2	A_1
1/2 Ba4386 A_2	----	0/0	0/0	----
1/2 Ba4386 A_2	----	----	0/0	----
1/2 Ba4386 A_2	----	----	0/0	----
1/2 Ba4386 A_2	----	----	0/0	----
6/7 B_1 of Ba4270/U	49.8	----	1.3	
6/7 B_1 of Ba4270/U	----	----	1.9	
6/7 B_1 of Ba4270/U	----	----	51.9	variable contact
6/7 B_1 of Ba4270/U	----	----	0	

Table #3

Rubber hydrochloride cell wrap with copper foil welded to magnesium anode as moisture barrier. Ba4386 and 1/2 Ba4386 units with 10.0/9.0 volt A_2 end points and 2.12 volt A_1 end point.

	Hours capacity to end voltage after Storage at 160°F.		
Unit	2 Wk.	1 Mo.	
Size	A_2	A_2	A_1
1/2 Ba4386A_2	55.7/81.2	39.5/67.2	----
Ba4386	----	0/0	0
Ba4386	----	16.5/33.9	0
Ba4386	----	0/0	44.8
Ba4386	----	32.2/58.6	62.7
Ba4386	----	0/0	23.7
Ba4386	----	32.0/55.7	34.9
Ba4386	----	0/0	0
Ba4386	----	28.0/55.7	4.0
Ba4386	----	0/0	0
Ba4386	----	19.0/24.0	25.0
Ba4386	----	0/0	168 +
Ba4386	----	0/0	168 +
Ba4386	----	44.1/65.3	17.6
Ba4386	----	59 1/82.8	92.4
Ba4386	----	5.7/13.7	0
Ba4386	----	1.0/7.3	0
Ba4386	----	55.0/75.0	93.0
Ba4386	----	58.0/78.8	58.3

Table #3 Cont.

Unit Size	2 Wk.	A_2	1 Mon. A_1
Ba4386	----	0/0	0
Ba4386	----	0/0	0
Ba4386	----	0/0	0
Ba4386	----	0/0	0
Ba4386	----	0/0	0
Ba4386	----	0/0	0
Ba4386	----	25.7/44.7	0
Ba4386	----	0/0	0
Ba4386	----	0/0	0
Ba4386	----	8.6/22.7	95.7
Ba4386	----	55.0/74.3	72.0
Ba4386	----	67.3/80.4	58.7
Ba4386	----	8.1/19.5	95.7
Ba4386	----	0/0	0
Ba4386	----	0/49	0
Ba4386	----	0/0	0
Ba4386	----	0/0	0

Table #4

Rubber hydrochloride cell wrap with copper foil welded to magnesium anode as moisture barrier. 6/7 of B_1 unit of Ba4270/U. End point 29.1 volts. Hours capacity after one month storage at 160°F

Unit No.	Capacity	Unit No.	Capacity
1	40.4	15	45.6
2	43.5	16	40.8
3	0	17*	36.5
4	0	18*	4.2
5	52.3	19*	0
6	49.5	20*	0
7	47.7	21	49.2
8	0	22	48.2
9	47.1	23	48.1
10	52.4	24	0.3
11	47.5	25	34.1
12	0	26	42.7
13	44.5	27	1.7
14	49.3	28	46.0

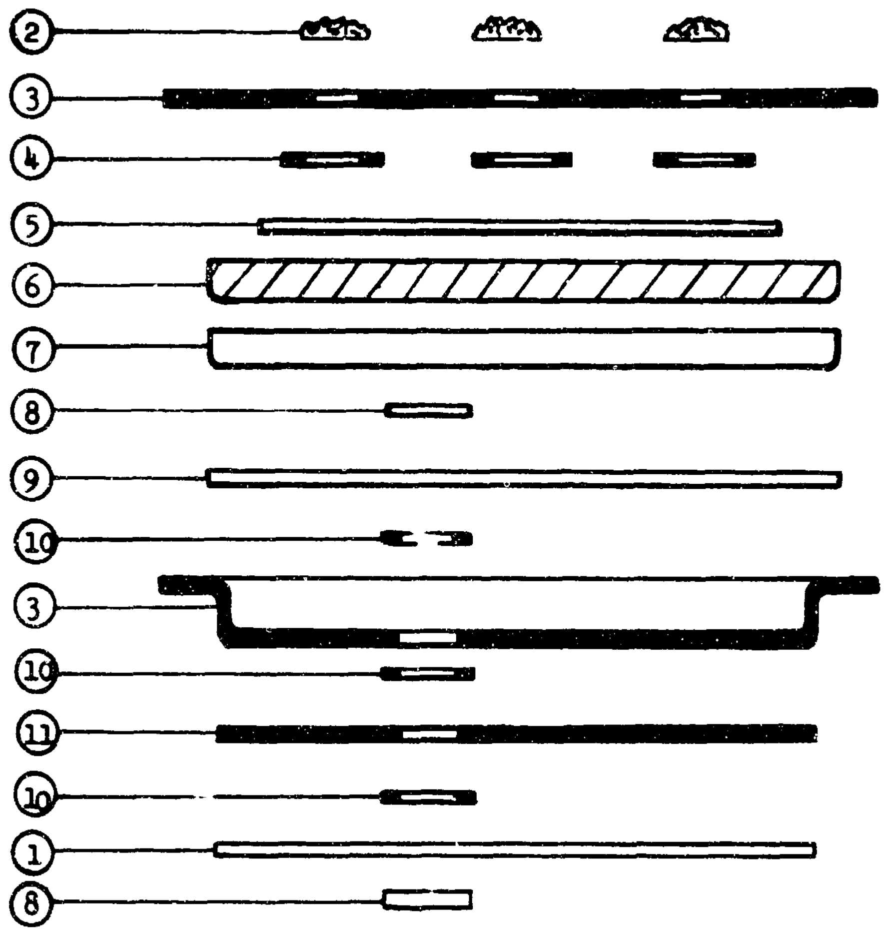
* These units constituted an experiment in weld protection that failed and are not included in the per centage noted in text.

Table #5

Rubber hydrochloride cell wrap with copper foil moisture barrier. Electrical contact between magnesium anode and copper barrier through a conductive compound. 6/7 of B_1 unit of Ba4270/U. End point 29.1 volts Hours capacity after one month storage at 160°F

Unit No.	Capacity	Unit No.	Capacity
1	42.1	7	48.6
2	39.9	8	0
3	50.3	9	2.3
4	46.3	10	46.0
5	46.9	11	51.0
6	36.5	12	0

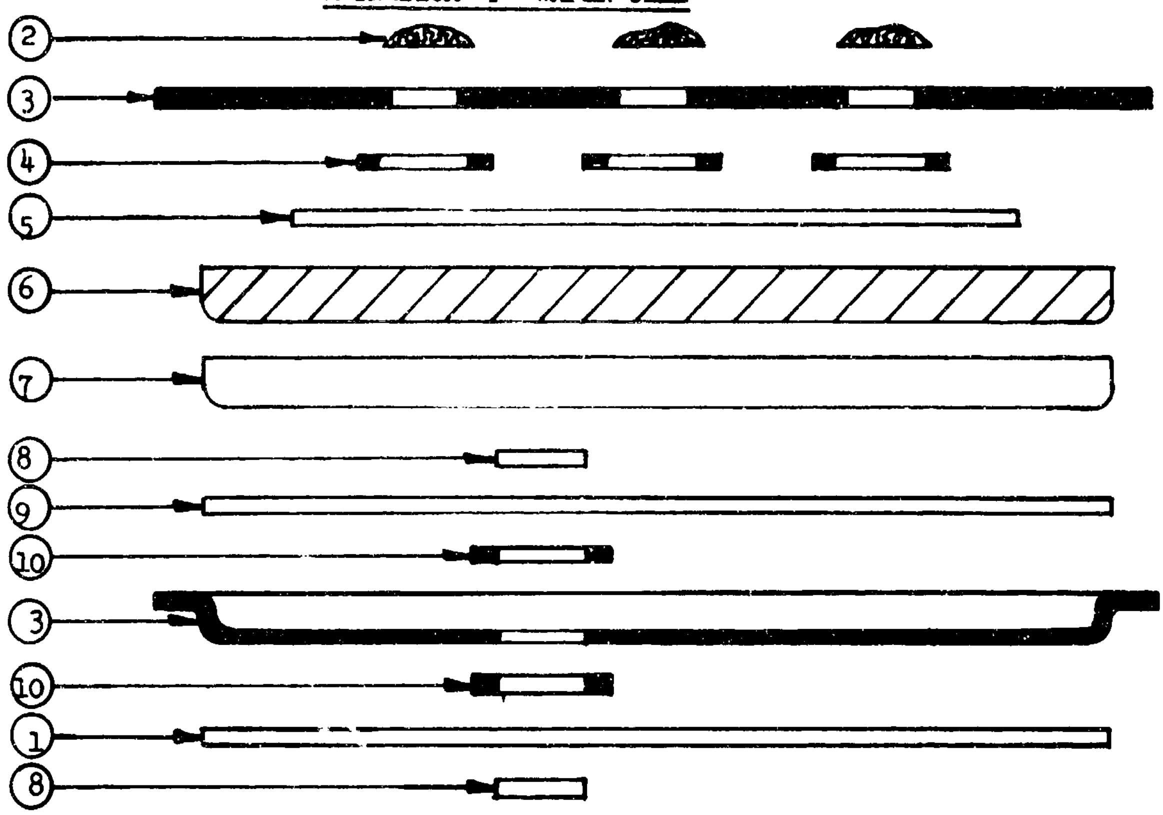
MAGNESIUM "F" WAFER CELL



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 I

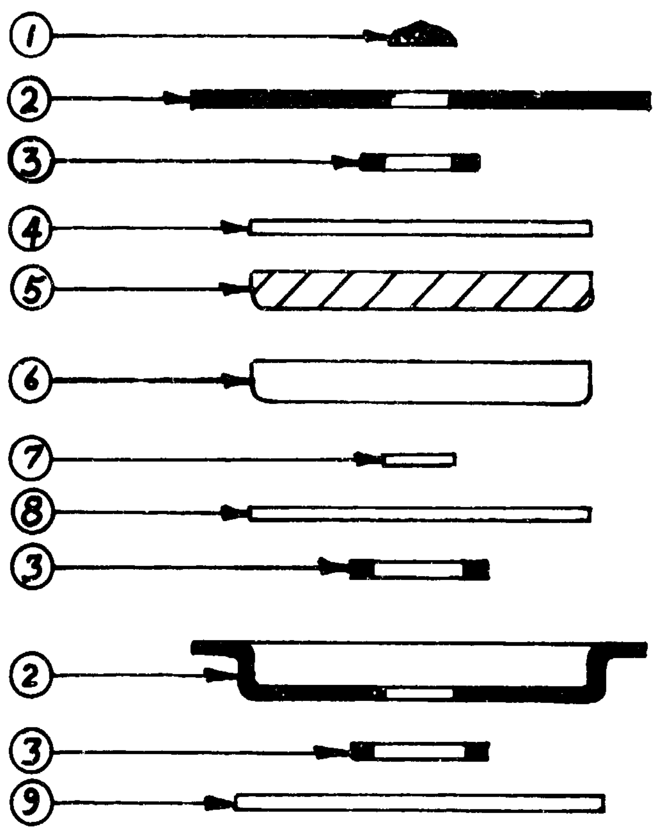
MAGNESIUM "F" WAFER CELL



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 2

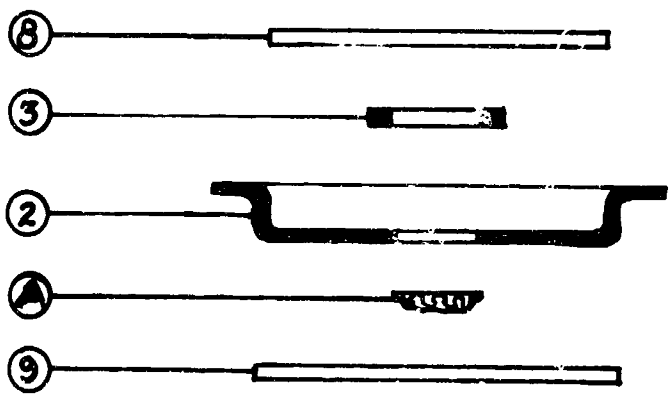
Magnesium "V" Wafer Cell



1. Conductive Intercell
2. Cell Wrap
3. Adhesive ring (seal)
4. Conductive Carbon Collector
5. Cathode Mix
6. Separator
7. Nonpermeable Dot
8. Anode (Magnesium)
9. Metallic Moisture Barrier

Figure 3

Magnesium "V" Wafer Cell



8. Anode (Magnesium)

3. Adhesive ring (seal)

2. Cell Wrap

A. Conductive Contact Material

9. Metallic Moisture Barrier

Figure 4

Security Classification

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
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13. ABSTRACT

The principal failure of magnesium bromide batteries has been the degree of corrosion of the magnesium anode on the contact side that progresses under the cell wrap seal and increases the resistance of the contact or destroys the contact. It has been concluded that the presence of air is causing the anode to be attacked on the contact (non-reactive) side to an excessive degree and that the anode in a flat cell needs complete protection on the non-reactive side.

Magnesium perchlorate cathode material seems to intensify the action on the non-reactive side of the anode and there is a strong suggestion that the rubber hydrochloride cell wrap is being degraded by the oxidizing nature of the perchlorate at 160°F. causing leakage and the destruction of the batteries stored at 160°F.

Security Classification

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

Security Classification