LEVEL II
DEFENCE RESEARCH ESTABLISHMENT OTTAWA

DREO TECHNICAL NOTE NO. 78-6
DREO-TN-78-6

NICKEL/Cadmium Aircraft Batteries: Experience with Celgard Barrier Layers at DREO

by Keiva Feldman G. Nerville

Mar 78
12 pp.

PROJECT NO. 54-63-87
78 07 17 078

78 07 17 078
CAUTION
This information is furnished with the express understanding that proprietary and patent rights will be protected.
RESEARCH AND DEVELOPMENT BRANCH

DEPARTMENT OF NATIONAL DEFENCE
CANADA

DEFENCE RESEARCH ESTABLISHMENT OTTAWA

TECHNICAL NOTE NO. 78-6

NICKEL/Cadmium Aircraft Batteries:
Experience with Celgard Barrier Layers at DREO

by

K. Feldman* and G. Verville
Energy Conversion Division

PROJECT NO. 54-03-07

APRIL 1978
OTTAWA

* On contract from Computing Devices Company
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT/RÉSUMÉ</td>
<td>(v)</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>BARRIER LAYER REQUIREMENTS</td>
<td>2</td>
</tr>
<tr>
<td>THE CELGARD FAMILY</td>
<td>2</td>
</tr>
<tr>
<td>EARLY WORK WITH CELGARD</td>
<td>3</td>
</tr>
<tr>
<td>LATER EXPERIENCE WITH CELGARD</td>
<td>5</td>
</tr>
<tr>
<td>THE FLOAT CHARGE TEST</td>
<td>5</td>
</tr>
<tr>
<td>BARRIER CIRCUMVENTION</td>
<td>6</td>
</tr>
<tr>
<td>(a) Double Celgard Construction</td>
<td>6</td>
</tr>
<tr>
<td>(b) Closed Bottom Construction</td>
<td>7</td>
</tr>
<tr>
<td>CYCLE LIFE AND FAILURE MODES</td>
<td>7</td>
</tr>
<tr>
<td>SEVERE USAGE</td>
<td>8</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>9</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>10</td>
</tr>
</tbody>
</table>
ABSTRACT

Problems arise with nickel/cadmium aircraft batteries as a result of deterioration of the conventional cellophane barrier layer in the separators. The cellophane deteriorates especially rapidly in the cells at elevated temperatures. Tests have shown that Celgard, a polypropylene microporous polymeric film manufactured by the Celanese Plastics Company, can be substituted for the cellophane and can readily withstand the oxidizing environment in the cell even at elevated temperatures.

Celgard is available with several variations in characteristics but most of them were not studied in detail. Problems may be experienced with deterioration of wetting characteristics but these do not appear to be serious. Examples of laboratory experience which illustrates the ability of the Celgard to withstand severe usage are given.

RÉSUMÉ

Les accumulateurs nickel/cadmium posent certains problèmes, car la membrane de cellophane couramment utilisée comme séparateur se détériore, et cette détérioration est particulièrement rapide lorsque la température est élevée. Des essais ont démontré que cette membrane peut être remplacée par une membrane Celgard (pellicule en polypropylène microporeux, fabriquée par la Celanese Plastics Company) qui résiste facilement aux conditions oxydantes, même à des températures élevées.

Diverses variantes de pellicules Celgard présentant chacune plusieurs caractéristiques sont actuellement disponibles sur le marché, mais la plupart n'ont pas été étudiées en détails. La diminution de la mouillabilité peut être à l'origine de certains problèmes, mais il ne semble pas s'agir là d'un inconvénient vraiment grave. On donne quelques exemples illustrant la capacité de la pellicule Celgard à résister à des conditions très oxydantes.

(v)

NON-CLASSIFIÉ
INTRODUCTION

At the request of the Directorate of Avionics and Armament Engineering (DAASE) the Defence Research Establishment Ottawa (DREO) undertook the investigation of various problems with nickel/cadmium aircraft batteries. Some of the more serious problems with these batteries, especially at elevated temperatures, are due to the degradation in the potassium hydroxide electrolyte of the cellophane barrier layer. After a preliminary survey of various materials, DREO, about four years ago, began investigating the possibility of replacing the cellophane with Celgard*. To avoid unnecessary duplication of work then in progress in the United States, Permion** was excluded from the investigation except for limited study for orientation purposes.

The initial experiments in the laboratory with cells containing Celgard were sufficiently encouraging to prompt a decision to parallel the continuing work at DREO with field tests. A number of cells were therefore commercially rebuilt† with Celgard instead of cellophane. Some of these were tested at the Quality Engineering Test Establishment (QETE) and some were subsequently given preliminary flight trials at the Aircraft Maintenance Development Unit (AMDU). These tests were followed by the procurement of a larger number of cells with Celgard and more extensive field tests were initiated under the surveillance of DAASE. These tests were still in progress at the time this paper was being written.

Results of the studies at DREO are reported periodically to the tasking authorities. This paper briefly reviews and updates the information previously submitted. It also gives a brief introduction to the varieties of Celgard available and draws attention to areas which have not been investigated to date at DREO.

---

* "Celgard" is a family of polypropylene microporous polymeric films developed by the Celanese Plastics Company, Summit, New Jersey, U.S.A.

** "Permion" is a family of grafted ion exchange membranes manufactured by the RAI Research Corporation, Hauppauge, L.I., New York, U.S.A.

† Used cells were rebuilt by Air Battery Industries Ltd., Montreal, Quebec.
BARRIER LAYER REQUIREMENTS

The barrier layer in nickel/cadmium aircraft batteries is required to perform a number of functions. It must permit adequate ionic current flow, it must stop cadmium migrating species from forming electron conducting paths between the positive and negative plates, and it must prevent oxygen gas generated at the positive plate during overcharge from reaching the negative plate. In addition it should be able to withstand the oxidizing environment in the cell over the temperature range of interest, and some consideration must be given to cost, availability, ease of handling, longevity, failure modes, etc.

Ionic conductivity may take place through the layer by means of electrical activity of the membrane structure (ion exchange membranes) or it may occur by ions moving (mass transport) through electrolyte in the pores which provide continuity through the film. Celgard permits flow by the latter process. Also bubbles of oxygen do not pass through the pores when they are filled with liquid.

THE CELGARD FAMILY

Celgard is a polypropylene microporous polymeric film available in several variations, some of which are of interest in the present context. As discussed in the previous section, ionic current must flow through the barrier layer in batteries. However, the polypropylene film with a critical surface tension of 35 dynes/cm, is inherently hydrophobic (1) and the pores would therefore not fill with the potassium hydroxide electrolyte which has a surface tension of about 90 dynes/cm. To circumvent this the film is rendered hydrophilic by coating it with a surfactant during the manufacturing process. Celgard is available with either of two surfactants. These are identified by a "0" or a "1" in last digit of the manufacturers four digit code.

Two pore sizes are available. The pores are claimed to be oblong and approximately 0.02 microns by 0.20 microns for the smaller pores. The larger pores are approximately 0.04 by 0.40 microns. However, the pore
volumes of the respective films are claimed to be about 38% and 45% respectively. The films with the different pore sizes are distinguished from each other by the second digit in the code with "4" designating the smaller and "5" the larger pores.

The Celgard film is relatively strong in the transverse direction, but, once split, tears easily in the lengthwise (machine) direction. The manufacturer has developed a web lamination process for heat sealing a light polypropylene web to the film to prevent this from happening. It was suggested that nylon or similar separator material normally used in cells to protect the barrier film may not be needed on the web side of such Celgard and that if suitable web laminations were provided on both sides, a single sheet of this material could possibly replace the present three-layer separator. Such double-laminated Celgard has been produced, at least on an experimental basis.

All of the possible combinations of surfactant, pore size and web laminations are, of course, available.

The scope of the work reviewed here did not permit extensive simultaneous work on all of the above variations. In the interest of early solution of the more serious problems in the field, work was concentrated on the Celgard films with the smaller pores and no web laminations. Some work was carried out with other variations, but this was insufficient to properly assess these products. In particular, the effects of the larger pores on cell resistance at low temperatures, and the overall effects of web laminations were not evaluated.

EARLY WORK WITH CELGARD

Initially the search for a replacement for cellophane barriers involved direct chemical and electrical tests. These narrowed the choice to Celgard and one other material. The latter was later eliminated when it was found to be superior to cellophane but still deteriorated fairly rapidly in cells at elevated temperatures. Previously used cells were then rebuilt in the laboratory with these materials as barriers. Control cells were made with new cellophane. The Celgard used was the precursor of Celgard 3400, then designated as 2400W.

Conventionally, the cell separator consists of the barrier layer sandwiched between two layers of nylon cloth or other such material. The three-layer combination is interleaved back and forth between the adjacent plates in the pack. Thus it separates the positive from the negative plates but does not completely enclose the bottom edges of the plates, nor the alternate side edges. However, the cells under discussion were rebuilt with a variety of different wrapping configurations in an effort to investigate a variety of factors. The experiments carried out, unfortunately, indicated
that the variability from cell to cell was too great to permit assessment of some of these factors with the low numbers of cells in each configuration. The primary objective of finding a superior substitute for cellophane was attained, however, and information to guide further investigation was obtained.

In general the cells with Celgard performed as well or better than cells with cellophane. For example, the carbonate concentration in a number of cells was reduced to below 1%. After identical cycling and other experiments it was found that the carbonate concentration in the cells with cellophane had risen to above 6% while in those with Celgard it remained below 2%. In another experiment discharged cells were stored at 70°C for two successive 72 hour periods. Subsequently, in overcharge tests the cells with Celgard behaved normally. Those with cellophane heated up rapidly and gas emission rate was about one-half of normal, showing severe cellophane damage (2). Thus from this early research it was concluded that (a) Celgard withstands without noticeable degradation cell operation at elevated temperatures which destroy cellophane, and (b) in cells with Celgard, carbonate contamination of the electrolyte does not increase with cycling as it does in cells with cellophane.

It was also found that the high temperature storage in the discharged state caused a permanent loss in cell capacity regardless of barrier material used. However, it was noted that the loss was smaller in cells using Celgard "pocket wrap" over the negative plates. In this construction the Celgard was sealed along three edges and pulled upward over each cadmium plate. It seems possible that the capacity loss was due to the loss of cadmium hydroxide from the plates by dissolution and diffusion, and that the pocket construction reduced this loss. However, no further investigation was done.

Some of the cells were built with the Celgard cut into lengths that were "U" wrapped over the negative plates to cover the bottom edges. Nylon was "fan" wrapped over the Celgard in the conventional manner. After about 10 months of use a short circuit started developing in one of the cells. It was found that an inadvertent fold in the Celgard had resulted in a wedge shaped portion along one edge of one plate being separated from the adjacent plate only by woven nylon. This area was saturated with migrating cadmium products which were presumably beginning to form electronic conducting paths. This method of construction is obviously undesirable because of the difficulty of ensuring proper placement of the barrier layer under the nylon covering.

In some cells, not wrapped in the conventional manner, strips of Celgard were used with the machine direction vertical. In these, when subjected to high temperature, a small amount of shrinkage was noted in that direction. This does not take place when the material is used in the conventional manner so that the machine direction in the Celgard is restrained by the plates.
LATER EXPERIENCE WITH CELGARD

The early work reviewed above was carried out with Celgard coded 2400W. Some months after this material was received, it was found that a quantity on the shelf would no longer wet. No problems were experienced with the cells which had been built previously since once electrolyte fills the pores it tends to remain there. Some of the Celgard still on the shelf was subsequently rewetted and used successfully in cells rebuilt in the laboratory.

Celgard 3401, which uses a different surfactant, was claimed to have better shelf life. It was therefore used during most of the laboratory investigations which followed and in most of the batteries under field test until recently. Its general performance seemed identical to that of Celgard 2400W (subsequently coded 3400), except that occasionally mild foaming problems were experienced during overcharge. In the laboratory this was readily controlled by the use of an antifoaming agent. Recently, it was claimed that the wetting characteristics of Celgard 3400 had been improved and also that it is free from foaming problems. Further work with this has been started.

Three areas of the more detailed work with Celgard 3401 are of interest and are discussed in the following sections.

THE FLOAT CHARGE TEST

Test Specification CF-B-70 includes a test referred to as the float charge test. In part, and in general terms, the test requires that a fully charged battery be put on charge at 1.5 volts per cell in a chamber maintained at 49°C. To pass the test the current after the first two hours must not exceed 4A and the battery temperature must not exceed 71°C, for a period of 50 hours.

Batteries can pass this test only if oxygen, generated at the nickel plate, does not reach the cadmium plate (3). Batteries with cellophane
barriers generally did not pass the test and the cellophane was severely damaged at the temperatures which resulted. Because of this, study of processes within the cell was handicapped. Celgard is not damaged at these temperatures and permits more extensive investigation. Significant experiments are briefly described below.

BARRIER CIRCUMVENTION

As mentioned earlier, the standard wrapping configuration does not enclose the bottoms or alternate edges of the plates. To establish whether or not gas exits from the plate pack via the bottom openings, a cell was constructed in the laboratory as follows. The conventional configuration was used but the Celgard layer was permitted to project about two inches below the plates. The projection was folded over and placed between the side of the pack and the cell case wall. When the cell was placed on overcharge, a steady stream of gas bubbles was seen to emerge from the opening in the folded over Celgard. This gave direct evidence that relatively large quantities of gas may be forced out of the bottom of the pack. It follows that with the normal configuration, some of this oxygen is free to contact the cadmium plates either at their bottom or side edges. The resulting recombination is sufficient to lower the back electromotive force, increase the charge current and raise the cell temperature in the float charge test.

It may be noted that the above process is independent of the material used in the barrier layer and has been observed at DREO with cellophane and with Permion as well as with Celgard. If it happens even in only one cell in a battery (with any of these barrier materials) the float charge test cannot be passed. To determine whether prevention of oxygen access to cadmium via the bottom of the pack would enable Celgard batteries to pass the float charge test, the following experiments were carried out:

(a) Double Celgard Construction

A battery was assembled with cells constructed in the laboratory with separators which contained only Celgard. Two layers were used. One consisted of "U" shaped strips folded upward over the positive plates, thus closing the bottom edges. The second layer was wrapped in the conventional manner, over the first layer. In this way, except for the two minor points at the bottom corners of each positive plate, oxygen could escape from the positive plate only via the top of the pack.

This battery readily and repeatedly passed the float charge test even when the tolerance extremes (charge voltage = 29V, chamber temperature = 51°C) were used and the time was extended beyond 50 hours. It is noteworthy that during these tests the current stabilized and remained essentially constant for the remainder of the test, and the battery temperature remained at approximately the chamber temperature throughout the test. (The internal cell resistance with a double Celgard layer is too high for high-rate applications).
(b) Closed Bottom Construction

A battery was assembled of cells constructed in the laboratory as described above under "Barrier Circumvention", i.e. with the normal wrapping configuration except for the Celgard projection being turned up between the pack and the cell wall. This would ensure that oxygen escaping from the bottom of the pack would be released harmlessly between the positive plate and the cell wall. Also the beginning and the end of the Celgard strip were folded over the pack to cover the side edges of the plates. In this way it was expected that the objectives achieved in (a) above could be repeated without increased cell resistance.

In the float charge test, this battery behaved in a manner similar to that in (a) for about 12 hours. Then indications of oxygen-cadmium recombination started to appear in one or two cells. Short term application of a vacuum to the vents in the affected cells returned them temporarily to the stable state.

It was assumed that large quantities of gas were trapped in the plate pack and, at the elevated temperature, caused some of the pores in the Celgard to dry out. This allowed small quantities of oxygen to penetrate the barrier. After the battery cooled to room temperature, tests showed a slightly reduced gas emission rate on overcharge. Thus it appears that the dried out pores did not rewet.

The above experiment was carried out with Celgard 3401. It is not known whether the same behaviour would occur with Celgard 3400 or whether this process is of significance except in connection with the float charge test. No operational problems have been encountered in the laboratory and no problems have been reported from the field. Woven nylon was used on each side of the Celgard barrier and it is not known whether other separator materials would permit freer gas flow and eliminate the gas trapping problem.

CYCLE LIFE AND FAILURE MODES

A limited amount of work was carried out to investigate cycle life and failure modes of Celgard. Cycle life was studied by exercising groups of cells on equipment which automatically and repeatedly carried out the following sequence: the charged cells were discharged into a fixed load for a period of 15 minutes at approximately 20A; this was followed by a 30-minute charge at a fixed potential, usually 1.5 volts per cell with a maximum current of 20A; a 15-minute period of open circuit completed the 1-hour cycle. In some tests a 15-second discharge at about 150A was carried out midway in the rest period. Cycling proceeded continuously but was interrupted every 200 cycles, approximately, for deep cycling and various diagnostic measurements.
Current and temperatures were monitored during the cycling.

All of the cells cycled had been rebuilt to include the desired barrier materials but most of the plate packs had been used extensively before this. In some cases it was obvious that subsequent short circuits were caused by sharp projections on plates, but normally damage in the vicinity of a short circuit obscured possible causes. The cycle life times observed should presumably be regarded as minimum figures. Two typical sets of cells are discussed here. One set was cycled 2400 times. This set contained two cells with cellophane, two with Permion 6001E, and ten with Celgard. Both cells with cellophane developed short circuits after about 1200 cycles. One cell with Celgard failed similarly after about 1400 cycles. One cell with Permion and one with Celgard failed at about 2000 cycles. The remainder were still performing satisfactorily at the end of the 2400 cycles.

Another set of 10 cells all with Celgard, was cycled 4000 times. This set had previously been subjected to extensive testing including numerous high-rate discharges and elevated temperatures. Three of these cells developed short circuits after 1400, 2800 and 3600 cycles respectively.

It was noted that when short circuits were located close to a cell wall, a hole in the wall frequently resulted. However, the damage was not as severe as is frequently observed when similar short circuits occur in cells with cellophane, and in the cases observed, never resulted in destruction of the adjacent cell. This is presumably due to the ability of Celgard to withstand considerably higher temperatures than cellophane.

The ultimate cell failure mode, as with other barrier materials, therefore is the formation of short circuit paths. These do not occur as rapidly as with cellophane and when they occur do not seem to cause as much damage to other cells in the battery. Any drying out of pores observed so far has been minor and would be classed as minor deterioration rather than failure. Also, it was possible to treat the cell so as to cause these pores to rewet.

SEVERE USAGE

The ability of Celgard to withstand conditions which severely damage cellophane has been frequently observed. Typical is a test in which a battery was heat soaked at 70°C and then was given two successive discharges simulating turbine engine starts. No discernable damage resulted. In another case a battery* was subjected to a modified float charge test at QETE. In this test the normal procedure of charging a fully charged battery

* This battery was rebuilt with Celgard by Air Battery Industries Ltd., Montreal, Quebec.

UNCLASSIFIED
in a chamber at 49°C was followed. However, the normal maximum current limitation was deleted and the normal battery temperature limitation of 71°C was relaxed to 85°C. The test continued until this temperature was reached after a period of 29 hours. About 1.5 hours previously a current peak of over 17A had been reached. The current then started to decrease, presumably due to low electrolyte levels in the cells. Subsequently, on examination at DREO, it was found the battery contained one cell with a manufacturing defect which had caused a short circuit, and two cells with cellophane instead of Celgard. No intact cellophane remained in these two cells after the test. However, after the addition of 75 ml of water to each of the cells (22 Ah), those with Celgard performed normally.

Thus it is seen that Celgard can withstand the severe treatment which may occasionally be expected to occur in the field. More recent experience has further confirmed this assessment.

**SUMMARY**

Celgard is a polypropylene polymeric microporous film available with either of two pore sizes, either of two wetting agents, and with or without polypropylene web laminations heat sealed to the film. All of these forms serve reasonably well as barrier layers in nickel/cadmium aircraft batteries. Extensive testing at DREO, however, has been concentrated on the film with the smaller pores and without web laminations, and possible advantages of the other variations have not been examined.

Laboratory work has shown Celgard to be far superior to the normally used cellophane as a barrier material in nickel/cadmium aircraft batteries. It is easy to handle during cell wrapping and easily withstands the oxidizing environment in the cell even at elevated temperatures. No problems have been detected in repeated use in turbine engine starting types of high-rate discharges.

It has been found that, at least under laboratory conditions, extensive overcharge at elevated temperatures may result in some drying out of pores in the material. It is not known whether this happens under field conditions and no adverse effects have so far been reported.
REFERENCES


Problems arise with nickel/cadmium aircraft batteries as a result of deterioration of the conventional cellophane barrier layer in the separators. The cellophane deteriorates especially rapidly in the cells at elevated temperatures. Tests have shown that Celgard, a polypropylene microporous polymeric film manufactured by the Celanese Plastics Company, can be substituted for the cellophane and can readily withstand the oxidizing environment in the cell even at elevated temperatures.

Celgard is available with several variations in characteristics but most of them were not studied in detail. Problems may be experienced with deterioration of wetting characteristics but these do not appear to be serious. Examples of laboratory experience which illustrates the ability of the Celgard to withstand severe usage are given.
### Key Words

- Nickel/Cadmium Batteries
- Aircraft Batteries
- Separators
- Barrier Layer
- Celgard
- Float Charge Test
- Life Cycling
- Failure Mode

### InSTRUCTIONS

1. **Originating Activity:** Enter the name and address of the organization issuing the document.

2a. **Document Security Classification:** Enter the overall security classification of the document including special warning terms whenever applicable.

2b. **Group:** Enter security reclassification group number. The three groups are defined in Appendix M of the DAE Security Regulations.

3. **Document Title:** Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.

4. **Descriptive Notes:** Enter the category of the document, e.g., technical report, technical note, or technical letter. If appropriate, enter the type of document, e.g., interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.

5. **Authors:** Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.

6. **Document Date:** Enter the date (month, year) of establishment approval for publication of the document.

7a. **Total Number of Pages:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **Number of References:** Enter the total number of references cited in the document.

8a. **Project or Grant Number:** If appropriate, enter the applicable research and development project or grant number under which the document was written.

8b. **Contract Number:** If appropriate, enter the applicable number under which the document was written.

9a. **Originator's Document Number(s):** Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.

9b. **Other Document Number(s):** If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).

10. **Distribution Statement:** Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:

   1. “Qualified requesters may obtain copies of this document from their defense documentation center.”

   2. “Announcement and dissemination of this document is not authorized without prior approval from originating activity.”

11. **Supplementary Notes:** Use for additional explanatory notes.

12. **Sponsoring Activity:** Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.

13. **Abstract:** Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (SI), (C), (R), or (U). The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7½ inches long.

14. **Key Words:** Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.