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DEVELOPMENT OF IMPROVED SEPARATORS FOR ALKALINE ZINC BATTERIES

BY W. A. PARKHURST

RESEARCH AND TECHNOLOGY DEPARTMENT

28 FEBRUARY 1982

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report is a summary of the development of separator materials for rechargeable alkaline zinc batteries over a seven year period. It summarizes studies performed during the earlier years of polyphenylquinoxaline (PPQ) polymer blends as separator materials. The expense of large scale production and the marginal improvement demonstrated for PPQ blends over existing cellulose based separator materials led to redirection of the work. The current limited effort in the development of nickel coated separator materials		

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is described. Because of a lack of funding, the characterization of nickel coated separator materials was not completed. Further characterization, testing and evaluation of the feasibility of such electrically conductive separator film materials is recommended.

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FOREWORD

This final report on the development of an improved separator material for alkaline zinc batteries summarizes the accomplishments of seven years of R and D and recommends further study in specific areas of separator development. This work was jointly funded by NAVSEASYSOM and DOE under Task Number 62543N/SF43431302/1R33JE701.

The assistance of Dr. I. Angres, Mr. B. F. Larrick and Mr. A. Himy (NAVSEA 5433), is gratefully acknowledged.

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BACKGROUND

This work has addressed the need for improved charge-discharge cycle life in secondary alkaline batteries employing zinc negative plates. The objective was to develop new separator materials to overcome a major cause of shortened cycle life, that is the short-circuiting of cells by zinc dendrite penetration through the separator.

In order to fully understand the need for a new separator material one must first be aware of the function of a separator and of the desirable characteristics of a good separator material. There are two basic functions of a separator: 1) to impose a gap between the positive and negative plates and 2) to provide an electrolyte reservoir. The gap between the positive and negative plate prevents a direct electronic path in the internal circuit. In a silver oxide-zinc cell the separator prevents diffusion of the silver species to the negative plate. In both silver oxide-zinc and nickel-zinc cells, the separator prevents the growth of zinc trails toward the positive plate (commonly referred to as zinc dendrite growth). There are two immediate problems connected with the extension of the useful life (both calendar and cycle) of alkaline zinc batteries: 1) a capacity loss due to shape change of the zinc electrode on cycling, and 2) internal shorting of the battery due to separator failure. The development of a separator to overcome the second problem is the focal point for research and development at NSWC. The objective of this project is to produce an improved battery separator with enhanced charge retention, cycle life, and resistance to deterioration with age.

The development of improved separators for alkaline zinc batteries has been underway for several years. Cellophane, a widely-used commercially available separator material, despite its low electrical resistance, suffers extensive deterioration in alkaline electrolyte and is only a moderate barrier to zinc penetration.¹ These drawbacks have led to the search for a replacement separator material.

PPQ POLYMER BLENDS

The initial approach toward developing an improved separator material was the development of a membrane based on polymer blends of polyphenylquinoxaline

¹Post, R. E., "The Nature of Cellulose as Related to Its Application as a Zinc-Silver Oxide Battery Separator," Zinc-Silver Oxide Batteries, Fleisher, A. and Lander, J. J., eds., (New York: John Wiley and Sons, Inc., 1971), pp. 263-269.

(PPQ), a product of polymer research at NSWC/WO (Reference 2). Extensive studies were carried out to determine the appropriate compositions of various polymer blends which could have desirable separator properties. The composition having the most promise was a blend of 60% PPQ with 40% cellulose acetate (CA) prepared by a phase inversion process. This blend had a resistivity close to that of cellophane but was more resistant to deterioration due to oxidation in 45% KOH electrolyte and to zinc penetration. Some properties of the PPQ blend are compared with those of cellophane in Table 1. Based on these properties, there was a slight improvement in the separator properties of the PPQ blend over those of cellophane.

A complete record of the development and characterization of the PPQ polymer blend as a separator material is presented in References 3 through 10. Reference 10 is the final report for the PPQ study. One conclusion of the report was that the improvement in zinc penetration resistance, and therefore cycle life, was not sufficient to justify the added expense of manufacturing. Also, the increased resistance to deterioration of the polymer was due largely to the fact that it was less easily wetted by the electrolyte than other

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- ²Augl, J. M. and Wrasidlo, W. J., "Synthesis and Evaluation of New Phenylated Polyphenylquinoxaline," NOL/TR 69-102, 1969.
 - ³Angres, I., "Compatibilization of Polyphenylquinoxaline with Other Polymers Using Chloroform as the Solvent in the Preparation of Polymeric Membranes," NSWC/WOL TR 77-118, Nov 1977.
 - ⁴Angres, I., Duffy, J. V. and Matesky, S., "Polymeric Membranes Which Contain Polyphenylquinoxalines and Which are Useful as Battery Separators," U.S. Patent No. 4,158,649, 19 Jun 1979.
 - ⁵Angres, I., "Battery Separators from Polyphenylquinoxaline Polymer Blends," NSWC/WOL/TR 78-56, Apr 1978.
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 - ⁸Angres, I., "Separators for Zinc Systems," at the Electrochemical Contractors Conference, DOE, Dec 1979.
 - ⁹Angres, I. and Parkhurst, W., "Pore Size, Zinc Penetration and Zinc Diffusion Studies on PPQ/CA Separators," NSWC TR 80-319, 2 Feb 1981.
 - ¹⁰Angres, I., Kowalchik, L., and Parkhurst, W., "Battery Separators Based on Polyphenylquinoxaline Polymer Blends," NSWC TR 81-17, 1 Apr 1981.

TABLE 1 60/40 PPQ/CA BLEND COMPARED WITH CELLOPHANE*

Property	PPQ/CA Blend	Cellophane
Resistivity	17m Ω - inch ²	13 m Ω - inch ²
OH Diffusion	1.06 X 10 ⁻³ mole/min - in ²	1.61 X 10 ⁻³ mole/min - in ²
Zinc Diffusion Flux	5.1 X 10 ⁻⁶ mole/sec - in ²	6.7 X 10 ⁻⁶ mole/sec - in ²
Zinc Penetration Resistance--Hours to short per mil	1.45	1.37
Pore Diameter	0.23 μ by Hg Porosimetry 0.34 μ by Bubble Pressure Method	0.002 μ
Cycle Life	Less than 25% improvement over Cellophane	---

*Data for the preparation of this table was obtained from
References 9 and 10.

commercially available separator materials. For these reasons, the development of an improved separator was redirected.

NICKEL COATED SEPARATORS

The new approach was to develop nickel coated polymer membranes for control of zinc dendrite penetration. Nickel coated separators were chosen based on the work of Wagner and Himy (Reference 11) which suggests that the nickel coating acts as an absolute dendrite barrier. In effect, the nickel coated surface serves to "short-circuit" the zinc dendrite before it can penetrate the separator system and reach the positive plate. The techniques that were available for applying a thin nickel coating to a membrane were vacuum deposition (thermal evaporation), ion beam sputtering, and coating with a nickel slurry. The vacuum deposition method was not feasible because of the high energy requirements which made the technique very expensive. Also, the heat involved would structurally damage most available separator materials.

ION BEAM SPUTTERING

In order to determine the feasibility of nickel coating membranes on a small scale, the ion beam sputtering technique was chosen. In this technique, the coating material was sputtered from one surface and was deposited on the membrane surface as a thin film. A plasma was generated in an ion gun and a collimated beam of energetic ions was accelerated at a high potential toward the target. The plasma was contained in the ion gun to isolate the sample from the plasma environment.

To calibrate this technique, a glass substrate was coated with metallic nickel powder, and the rate of deposition and coating thickness were determined. Battery grade Pellon (2502 K-4 from the Pellon Corporation, Chelmsford, MA) was then coated using the technique. Pellon was chosen because of its wide-spread use as a separator in both silver oxide-zinc and nickel-zinc batteries. The thickness of the nickel coating was varied from 200 to 600 Angstroms. The ion beam sputtering for all of the samples was carried out by Technics (Springfield, VA).

Testing of the separator was carried out by Otto C. Wagner of ERADCOM (Fort Monmouth, NJ). The major test was vibration of the samples in KOH electrolyte. Other tests included charge-discharge cycling. The preliminary results indicated shedding of the nickel during use. As a result, it was determined that a binder would be necessary to prevent the nickel shedding. In addition, because of the expense and inavailability of continuous coating equipment, the ion beam sputtering technique was discontinued in further studies.

NICKEL FLAKE SLURRY

Because of the drawbacks of the ion beam sputtering technique, coating with a nickel flake slurry was tested. This technique involves the use of a binder mixed with the nickel powder in a slurry form. The technique is also

¹¹Himy, A. and Wagner, O. C., "Mass Transport Separator for Alkaline Nickel-Zinc Cells," U.S. Patent No. 4,192,908, 11 Mar 1980.

commercially available for continuous coating of membrane material. The advantages of this technique over the ion beam sputtering technique are that it employs a binder, is less costly and is commercially available. The primary disadvantage is that there is a lower ability to control the thickness of the coating over the surface of the material.

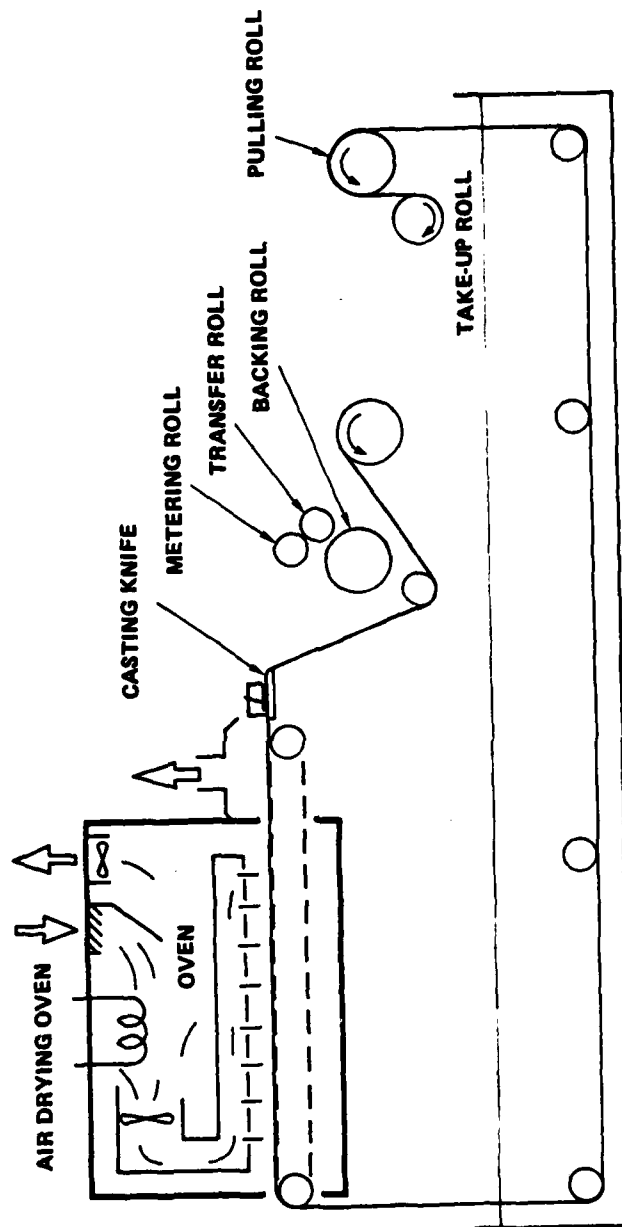
In February 1981, a contract was negotiated with Celanese Research Company (Summit, NJ) to coat battery grade Pellon (2502 K-4 from the Pellon Corporation, Chelmsford, MA) with a Celanese proprietary nickel slurry. The slurry basically contains nickel powder and cellulose acetate, as the binder, in a 2:1 ratio and is referred to as a K317 coating mixture. The pellon was coated using a conventional reverse roll coater set up in the knife casting mode (Figure 1). It was coated at 0.01 cm (4 mils, wet thickness, Roll 1) and 0.018 cm (7 mils, Roll 2) thickness at a rate of 6 m/min (20 ft/min). The dry coating thickness and the resistivity of the coated samples were measured by Celanese and are shown in Table 2. The resistivities were determined in 31% KOH in a cell fitted with Hg/HgO reference electrodes. The apparatus is shown in Figure 2.

Based on the data in Table 2, the nickel coated pellon is viewed as a feasible separator material. Currently, battery manufacturers are providing silver oxide-zinc and nickel-zinc batteries for testing at the Naval Weapons Support Center (NWSC, Crane Indiana) using the nickel coated pellon as part of the separator system. Additional purchases of the pellon have been made to fulfill the manufacturers' needs. Upon receipt of the additional pellon, tests to characterize the nickel coated pellon as a separator material were planned. The plans included zinc penetration testing as described in Reference 9 and 12 with a few cell design changes.

RECOMMENDATION

Funding limitations have forced the postponement of this separator development effort. As a result, no definitive data on separator performance in complete cells have been obtained for the nickel coated pellon separator material. Further studies of electrically conductive separator film materials are recommended to establish their potential usefulness.

¹²Wagner, O. C., "High Cycle Life, High Energy Density Nickel-Zinc Batteries-- Report No. 4," ERADCOM report no. PSD-4C, Jan 1981.



MODE

FIGURE 1 REVERSE ROLL COATER

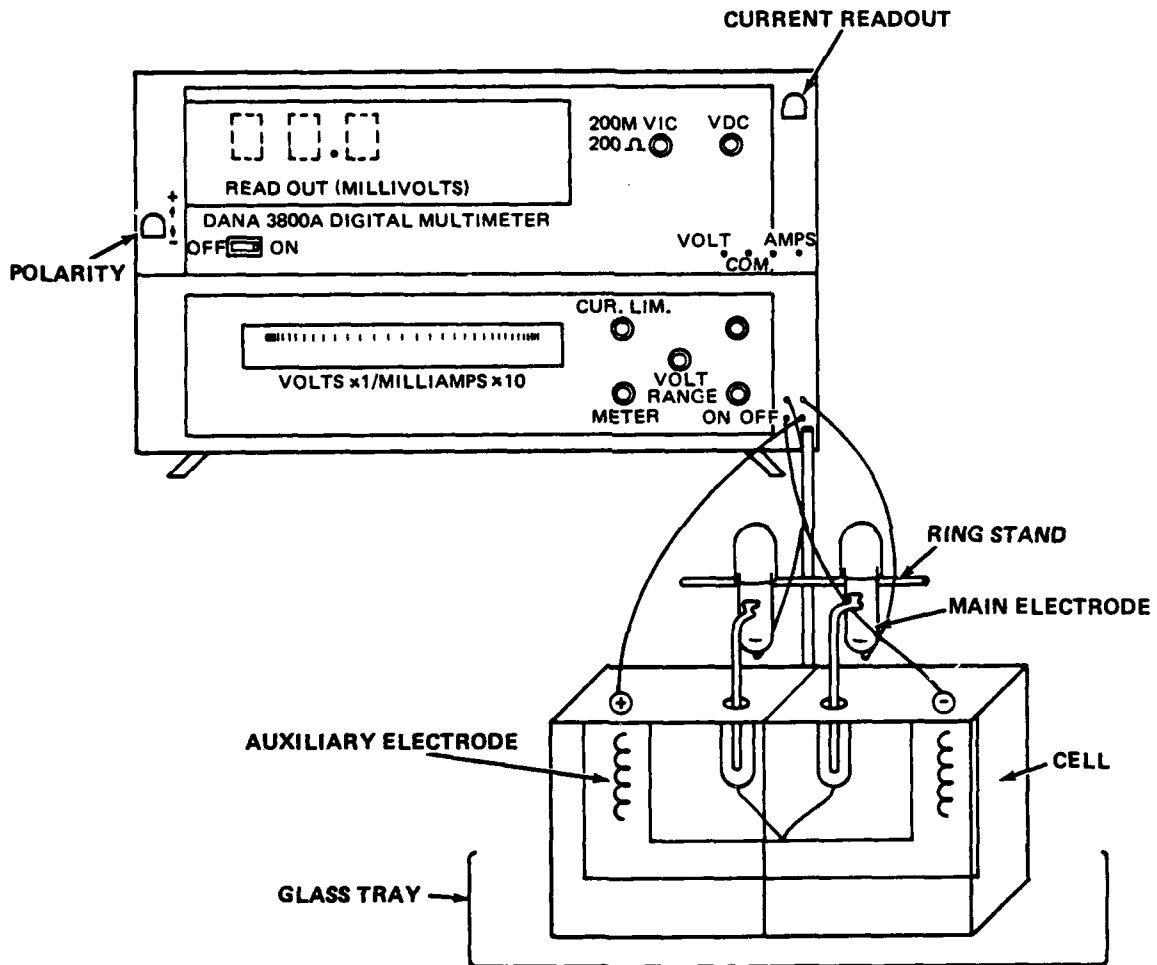


FIGURE 2. DIAGRAM OF ELECTRICAL RESISTANCE CELL

TABLE 2 COATING THICKNESS AND RESISTIVITY
FOR NICKEL COATED PELLON

Roll No.	Sample No.	Total Thickness* mils	Coating Thickness mils	Resistivity $\mu\Omega\text{-in}^2$
1	1	7.54 ± 0.42	0.54	---
	2	7.55 ± 0.48	0.55	---
	3	---	---	6
2	1	7.94 ± 0.42	0.94	---
	2	7.88 ± 0.38	0.88	---
	3	---	---	7
Non-coated Pellon	1	7.00	---	6

*Thickness of substrate with Ni coating. Average of 15 measurements on one square foot of Sample no. 1 and 20 measurements on Sample no. 2.

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11. Himy, A. and Wagner, O. C., "Mass Transport Separator for Alkaline Nickel-Zinc Cells," U.S. Patent No. 4,192,908, 11 Mar 1980.
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