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SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

L. C. Scala and G. D. Dixon

July 31, 1968

Contract No. 951525

"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, pursuant to a sub-contract issued under Prime Contract NAS 7-100 between the California Institute of Technology and the United States of America represented by the National Aeronautics and Space Administration."

Westinghouse Electric Corporation
Research Laboratories
Pittsburgh, Pennsylvania 15235

Eighth Quarterly Report

Period: April 1 to June 30, 1968

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SEPARATOR DEVELOPMENT FOR A HEAT
STERILIZABLE BATTERY

Eighth Quarterly Report

L. C. Scala and G. D. Dixon

ABSTRACT

It is now possible continuously to dip-coat Webril support tape which is 12 inches wide. Long runs have been made producing separator material having satisfactory resistivity values and hydroxyl ion diffusion rates. Several alternative supporting tapes have been evaluated. Flame absorption spectroscopic analysis indicated that zincate ion diffusion was very slow. The addition of free zirconia to the sterilizing mixture reduced the weight loss and decreased the resistivity of most separators.

I. INTRODUCTION

This quarterly report covers the work done during the period April 1 to June 30. The effort expended during this time and reported here includes:

1. Evaluation of the industrial size coating tower for continuous preparation of separator material.
2. Investigation of the varying parameters involved in a continuous coating process.
3. Evaluation of new candidate substrates by sterilization tests.
4. Investigation of the effects of adding zirconia to sterilizing medium.

5. Study of the effects upon separators of aging in a 40% KOH solution containing silver ions.
6. Measurements of zincate ion diffusion through the separators.

II. PROGRESS

1. Modification of coating tower

Coating supporting tapes using a dip tank and wiper rods has proven to be the best method tried. However, because the coating mixture is a slurry, an efficient means of agitation is necessary to prevent the inorganic filler from settling out. This problem has been solved by re-designing the dipping tank so that a circulating pump could be included.

In order to reduce the amount of tape shrinkage at the temperatures used to give a dry coated tape, the vertical drying oven was doubled in length. This resulted in higher coating speeds at lower temperatures giving dry coated tapes with little or no shrinkage.

Most of the work has been done using 3" wide supporting tape. Several runs have been made with 12" wide tape and these showed the need to modify the take-up system which is under way. With rollers only 12" wide, the tape continuously overlapped the rollers. Also better roller alignment is necessary because the web-guiding system did not work. This is controlled by a light beam and the coated tape was transparent to this beam. A pneumatic web-guide, or curved spreader rollers will probably obviate this problem.

2. Coating of candidate supporting tapes

A new Webril tape (E1403, 5 mil thick printed polypropylene, 3 inches wide, similar to H739 and H751 which were previously tested) was tower coated with a mixture consisting of 3:1 20-50 oxide: PS and 1% Alkaterage by weight of solids. The coating mixture covered the tape very well at speeds ranging from 3.5 to 6 feet per minute. The coated tape was thick, ranging from 6.8 to 7.3 mils. In all cases very

minute, regularly spaced pinholes were visible; they allowed the electrolyte through relatively rapidly (pH 13 reached in 5 minutes); however, the specific resistivity of these samples ranged from 10 to 20 ohms-inch. This material appears to be promising, even though it is rather thick, because of the regularity of its structure which presents no large voids.

Two long runs were made (C58-67-1 and C58-67-2) using Webril type 1403, mentioned above. This material, although possibly too thick, has already been shown to hold promise for our applications. Resin mix C58-67-1 consisted of 3:1 oxide (20:50 mesh): polysulfone, and 1% Alkaterge E; mix C58-67-2 was the same, except that the oxide used was of 100-200 mesh. Both runs gave good looking, regularly coated tapes at coating speeds of 4,5,6 and 7 feet per minute, except where the Webril tape presented ragged edges. The build varied from 1.2 to 1.8 mils, and curling of the coated tape edges was not very pronounced, probably due to the fact that the temperature of the oven did not exceed 60°C. Only at 7 ft/min was the coated tape slightly damp; in general, the coatings were smooth and uniform. Extremely small pinholes showed when a strong light was shined at the tapes; however, they may have been coated over with a very thin film of polysulfone:oxide. The resistance to electrolyte flow of samples from all coating speeds was low and decreased with increasing speed of coating. Although the resistivity values were low, they were not so low as to indicate excessively rapid KOH passage. Again, this material seems well suited to our application.

As requested by the contract, the ability to supply one-foot wide battery separators must be demonstrated. To this aim the coating tower used to coat 3 inch wide tape was modified to accept 12 inch wide tape; new, larger and improved dip and coagulating tanks were constructed, together with longer driving and take up rollers. The first run was made using formulation C58-70-4 (3:1 zirconia: PS, 1% Alkaterge, 10% extra DMAC) and 12 inch wide Webril 1403, which was about 2 mils thick and exhibited the nonuniform, weak characteristics discussed in the previous quarter. With this arrangement, the operation was performed

at about 6 feet per minute, at a temperature ranging from 40 to 60°C in the oven. About 100 feet of tape was run through. General observations on this run are as follows: a. the coating mixture was too thin; b. the heater temperature gave best results at around 40°C; c. some shrinking was noticed due to the open weave of the tape and to the high oven heat.

A second run employing the same 12 inch wide Webril fabric was made using a thicker mix (C58-70-5); adjustments were made on the tower to correct misalignments. This run was considerably better than the first one. At a coating speed of 5 feet per minute and at 35-40°C in the oven, the tape coated uniformly and showed no pinholes. Difficulties were encountered in the taking up of the coated tape, which was wrinkled but otherwise looked promising. After about 50 feet, pinholes appeared, due to severe stretching of the coated tape over the top sheaves. This problem was cured by over driving the pay-off rollers. In general, this run showed the feasibility of coating one foot wide tape. Stronger and more uniform tape would cure most of the problems mentioned above.

Work on modification of the coating tower to accept one foot wide tape is continuing. During this work, a material balance of the coating mixture was determined for two runs. These showed that, while the solids content decreased only slightly as a function of coating time, the oxide: polysulphone ratio decreased considerably, showing that the oxide was used up at a faster rate than the polysulphone.

3. Sterilization tests on new candidate substrates and coated tapes

Coating runs C58-67-1, C58-67-2 and C58-61-2 (see monthly Report No. 21) were distinguished by having been made with a Webril tape which is about 5 mils thick and which exhibits a much more uniform and stronger structure than the Webril tape used up to now. The electrical and mechanical properties obtained using this kind of tape were satisfactory and reproducible. As commonly found, the sterilization cycle lowered the resistivity of the samples, rather considerably in some cases. However, it was noticed that the weight losses were relatively high. It is

postulated that the increased thickness of tape and coating (to an average value of 7 mils) may have trapped some of the solvent, which then subverted the original weight measurements.

Some new materials were received and tested. From Union Carbide we received very small samples of their new and very expensive yttria-stabilized zirconia cloth, with nominal thicknesses of about 15 mil. These samples appeared to be relatively weak mechanically, and to be filled with some powder or dust. They were immersed in 40% KOH for 2 days; when they were taken out of the caustic for resistivity measurements, it was found that their mechanical strength had diminished further, to the point where they could hardly be handled. Only one sample could be tested for resistivity; all the others had practically disintegrated in the KOH. As it appears now, this material is too fragile for our purposes.

Two 9 x 11 inch sheets of DALKASEP film were received from Dewey and Almy; they intend to manufacture it in continuous lengths if it becomes commercial. This material consists of microporous polyethylene designed for use as separator in alkaline batteries, particularly silver-zinc batteries.

Samples of DALKASEP underwent standard sterilization cycle (60 hours in 40% KOH at 135°C). At the end of the test the samples had shrunk drastically, losing about 80% of their original area. Conversely, their thickness had increased two fold. Their resistivity before cycling was too low to measure on our meter; after cycling the samples were too small to fit our resistivity cell. In addition, the weight of the samples after sterilization had increased fifty percent, probably indicating a chemical reaction with the caustic. These results indicate that this material does not lend itself to use as battery separator material which must be able to withstand a temperature of 135°C in 40% KOH. Dewey and Almy later confirmed that 135°C "approaches what we consider to be the upper temperature limit for DALKASEP."

Two polypropylene substrates, Pellon styles 2530 and FT 2140, were tested for resistivity and electrolyte flow properties. The thickness of the former was 6 mils on the average, while the latter averaged 7 mils. They both looked uniform in their felt-like structure, but were soft and compressible. They were, however, recommended in a recent Texas Instrument Co. report for use as sterilizable battery separators.

Tape style 2530 offered negligible resistance to KOH passage (pH 14 in 1.5 minutes) and exhibited a specific resistivity of 10 ohm-inch. Style FT 2140 tape had higher electrolyte flow resistance (pH 14 in 25 minutes, 13.5 in 2.5 minutes) and a specific resistivity of 23 ohm-inch. Several rolls both 3 and 12 inches wide have been ordered from the Pellon Company.

4. Addition of free zirconia to sterilizing system

The possibility of reducing the weight loss, sustained by battery separator material as a result of sterilization, by introducing free zirconia in the Teflon cells used in the sterilization cycle, was investigated. Fresh samples of runs which had already been tested were sterilized in the presence of 0.01 g of 20-50 mesh zirconia (approximately 10% of the weight of zirconia in the sample). The results indicated that, except in one case, the presence of free zirconia lowered the weight loss induced by the sterilization step; in three cases the specific resistivity values also declined, and in all cases the resistivity was below the limit imposed by the contract.

This effect was further evaluated by increasing the amount of added zirconia to 0.03 g (approximately 30% of total zirconia present). It was shown that a larger amount of free zirconia in the cells further reduces the sterilization weight loss. Again, except in one case, the resistivity values also decrease as the amount of zirconia in the cell increases. On the basis of these results it seems advisable to add free zirconia, in the ratio of between 10 and 30% of the weight of the battery separator composite, to the battery cell in order to reduce both

dissolution of zirconia from the separator into the electrolyte and the resistivity of the separator.

5. Separator aging in 40% KOH containing silver ions

In order to find out whether long term aging in concentrated caustic in the presence of silver affected the electrical and physical properties of battery separators, the samples of Webril-polysulfone-zirconia separators used to determine silver ion transfer were tested for resistivity and for physical damage. They had been aged for about three months. The resistivity tests were carried out as follows: the first series was run on the samples as they came out of the original KOH solution, and the second series was run after the samples had been vigorously washed in water (in an attempt to remove the black silver or silver oxide precipitate) and then had been resoaked in KOH before testing.

In 75% of the cases the long term aging in KOH with silver present has no deleterious effect on the specific resistivity of the untreated samples. However, the simple act of washing the samples with water resulted in greatly increased specific resistivity values. It is conceivable that the washing action shook loose the solid particles of the silver or silver oxide precipitate, which then redistributed themselves and obstructed the pores of the separator composite. No obvious correlations could be made between the resistivity values and the different formulations and coating speeds of the samples. No physical changes were observed.

6. Measurement of zincate ion diffusion

The apparatus consisted of two Teflon cups (2" I.D., 100 cc.) each with a flat edge. A hole (1/2" diam.) was drilled in each flat face, a square of separator to be tested placed between the holes, and the cups clamped together. One cup was filled with 40% KOH and the other cup filled with 40% KOH containing 40 p.p.m. zinc ions. 1 cc samples were taken at regular intervals and the zinc concentration

measured by flame absorption spectroscopy. The samples tested had previously been tested for silver ion diffusion. The results showed that the rate of zincate ion diffusion was of the same order as silver ion diffusion, with a maximum of 4.2 ppm after 150 hours.

In the case of silver ion permeability, a comparison between values obtained by the Goddard Space Flight Center on Dewey and Almy E-5114 membrane and values obtained on our separator specimens indicates that the D. and A. membrane's permeability is three orders of magnitude greater than that of our membranes (83×10^{-10} vs 70×10^{-13} moles/sec/cm²).

III. FUTURE WORK

While new and promising polypropylene substrates will continue to be tested, the main effort will be directed toward establishing a coating procedure for the production of 12 inch wide coated tape exhibiting resproducible and satisfactory sterilizable battery separator properties.