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SEPARATOR DEVELOPMENT FOR A HEAT STERILIZABLE BATTERY

L. C. Scala and G. D. Dixon

March 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
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Pittsburgh, Pennsylvania 15235

Seventh Quarterly Report

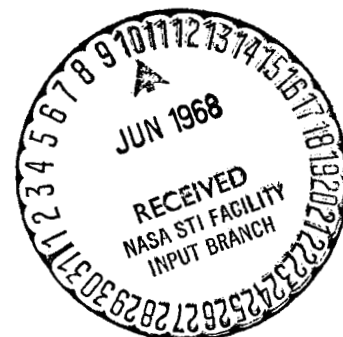
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SEPARATOR DEVELOPMENT FOR A HEAT
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ABSTRACT

Dip coating of Webril support tape was found to be feasible; when this procedure was used on a commercial foil coating tower, relatively long runs of satisfactorily coated tape were obtained. In the presence of a wetting agent, coated tapes were obtained which exhibited satisfactory resistivity and resistance to sterilization in hot caustic. Polarographic analysis indicated that diffusion of silver ions through separator membranes obtained as described above is generally negligible.

I. INTRODUCTION

This Quarterly Report covers the work done during the period January 1 to March 31, 1968. The effort expended during this time and reported here includes:

1. Investigation of the possibility of changing the coating procedure of the Webril tape from the use of a Gardner knife type applicator to a system involving dip-coating and wiper rods.
2. Scaling up of laboratory size coating technique to a method employing an industrial size coating tower, and determination of coating parameters.
3. Use and effect of wetting agents.
4. Variations in tape properties.
5. Sterilization tests.

6. Silver ion diffusion analysis by polarography.
7. Zinc ion diffusion analysis.

II. PROGRESS

1. Method of application of coating mixture to supporting tape

Drawbacks have been constantly encountered in the course of coating experiments carried out using a temporary laboratory coating tower which employs a Gardner knife applicator; they are due to the fact that the zirconia:polysulfone:DMAC mixture is difficult to apply evenly and uniformly onto the tape mainly because the blade alignment is hard to maintain and because the two knife blades act as collectors or filters for the solid oxide. Ultimately, the coat applied to the tape possesses a different composition from that of the original coating mixture.

Therefore it was decided to test a coating method which would eliminate knife applicators and would, instead, involve the use of a dip-coating method. The correct coat thickness would be insured by the use and the correct placement of wiper rods. If this method worked only moderately well in the experimental tower, then the whole procedure would be transferred to an industrial foil coating tower with the proper modifications.

The laboratory tower was modified by the installation of a dip-pan equipped with a freely moving roller, two wiper rods (which originally were grooved pins, and later were replaced by more efficient Teflon rods one half inch in diameter). A vertical six foot high furnace was installed: it was heated by strip heaters and heating lamps to a temperature that never exceeded about 50°C. Experimental runs were made with and without a coagulating water: dioxane bath (1:3 by volume): it was found that the absence of the bath prevented the coated tape from drying properly in the vertical oven.

Several continuous dip-coating runs were made in which the ingredient ratios in the coating mixture were varied to check the effects of viscosity and solids contents. The coating mixture needed to be

agitated thoroughly in order to prevent inhomogeneous coatings, but care had to be taken to eliminate sources of pinholes in the coated tape. Coating speeds ranged from 0.5 to 7 feet per minute; at the latter speed the coated tape emerged wet from the oven.

The best results were obtained at a speed of 3 ft/min.; the resistivity of the samples from this run (3:1 oxide:PS) was of the order of 70 ohm inch and the electrolyte diffusion rates were acceptable (12.5 pH units after 30 minutes' exposure). In general, the thickness of the coated tape remained constant, but there occurred some shrinking across the tape.

On the basis of the results obtained in this set of experiments, it was decided that dip-coating was a promising method for manufacturing sterilizable battery separators in a continuous manner.

2. Continuous dip-coating in industrial foil coating tower

Reasonably successful coatings of 3 inch wide Webril tape using a dip-coating method and an experimental, laboratory size coating tower led us to attempt the scaling up of this process. To this purpose a semi-commercial metal foil coating tower was modified to accept our coating conditions.

From the beginning there were several difficulties to surmount. It was found, for example, that the Webril tape by itself would quickly shrink and melt if left standing in the oven which was maintained at 75 - 85°C. If, however, the tape was coated and moving at a speed of at least 3 feet per minute, the heat from the tower oven would only curl and shrink the coated tape slightly. As the coating speed increased, the shrinkage diminished but the coated tape would emerge wet from the oven.

If the DMAC solvent from the coating mix was not simply evaporated in the heating tower but it was dissolved away by a water:dioxane bath (which also coagulated the resin and supposedly increased the porosity of the separator), then the wet tape problem was alleviated,

but a host of other difficulties arose; they were mainly due to mechanical stresses introduced by the very sharp turning angles over wiper rods incurred by the just-coated tape on its way to the coagulating bath.

A very severe problem was also encountered due to the jerkiness of the motion with which the tape was paid out and rolled up. This jerkiness was in great part due to the stretch of the tape itself, and was cured by installing driving rollers at the pay-off station, synchronized with the take-up rollers.

Several continuous runs were made on this tower to investigate some parameters, such as viscosity of mix, oxide:polysulfone ratios, and coarser versus finer zirconia. On the basis of coatability, the best combination appears to be, at present, that containing a 3:1 oxide:PS ratio. Best results were obtained at a speed of 3.0 - 3.5 ft/minute. The oxide used here was the 20-50 mesh zirconia. Even in this type of run, however, there was shrinkage across the coated tape which resulted in creases running longitudinally. We think that the open weave of the Webril tape is responsible for the creasing.

The mechanical arrangement in use now consists of a pay-off roller from which the tape proceeds to two driving rollers; then the tape is dipped in the pan containing the stirred coating mixture and runs between two 1-inch Teflon wiper rods. It subsequently proceeds over the top wiper rod at a very sharp angle, down into the water:dioxane bath, around a roller at the bottom of the bath, up through the oven and then on to the wind-up rollers.

This arrangement is reasonably satisfactory for screening purposes. However, the stirring of the mixture is inefficient and a new pump system should be installed. In addition, the various angles assumed by the tape in its course must be softened to reduce tape stretching. This temporary setup works only with 3 inch wide tape: provisions must be made to replace it with one able to accommodate foot-wide tape as required by the contract.

3. Use and effects of wetting agents

After rearranging the settings of the parts of the tower to deliver the best combination of coating properties, several coating runs were made to reduce the number of parameters influencing the properties of the resulting separator material. In all cases it was possible to coat several dozen feet of tape for each set of conditions, the common drawback being the sticking of incompletely dry tape to the top tower sheaves. The initial criteria for a satisfactory coating run were: (1) dry coated tape; (2) no pinholes; (3) no excessive shrinking, and (4) no excessive curling.

The coated tape sections which passed the above mentioned criteria were then tested to determine their resistivity, their resistance to electrolyte flow and, in some cases, their resistance to sterilization conditions.

While the formulation of the coating mix generally consisted of 3:1 20-50 mesh oxide: polysulfone in DMAC, in some cases wetting agents were added in varying proportions. For example, Alkaterge E was added in 0.5, 1.0 and 2.0 percent ratios, on the basis of solid weight, to mixes of different viscosities. The best results were obtained in the cases where the Alkaterge E was added in the proportion of 1%. Because of the low efficiency of the stirring of the coating mixture (due to the temporary character of the modifications to the tower), it was found that the rate of deposition of zirconia was faster than that of the polysulfone, especially at the beginning of the run.

4. Variation of properties of Webril tapes

The latest batches of Webril tape have been of a very inferior nature; the weave is very rough and the voids are large and more irregular, so that the coating mixture has more difficulty in covering over these substantial holes. Thus, pinholes result. In addition, this kind of tape represents less of a support for the organic-oxide film than did previous batches of the same tape, so that heat shrinking is very pronounced (about 1/8 inch over 3 inches of original width).

We have contacted the Kendall Company (makers of Webril) about the conditions of the new batches. They have answered that the company supplying the polypropylene yarn is now supplying coarser denier yarn; this results in thicker but coarser tape. They sent us several other types of polypropylene tape, samples of which have undergone sterilization tests, together with some promising coated tapes.

5. Sterilization tests

The sterilization tables included here show the results of exposing samples of six continuous runs (C58-43-1, -44-1, -53-2, -56-1(A), -57-1 and -58-1), and of five new Webril fabrics, to a sterilizing cycle consisting of 60 hours immersion in 40% KOH at 135°C. The table immediately below shows the compositions involved in the above mentioned runs.

TABLE I
Identification of Samples for Resistance to Sterilization Tests

<u>Sample No.</u>	<u>Oxide:PS Ratio</u>	<u>Solids Content</u>	<u>Additive</u>	<u>Oxide Mesh</u>
C58-43-1	2	10.7	-	20-50
C58-44-1	3.5	14.9	-	20-50
C58-53-2	3	14.9	1% Alkaterge E	20-50
C58-56-1	4	14.9	1% Alkaterge E	100-200
C58-57-1	3	14.9	0.5% Alkaterge E	20-50
C58-58-1	3	14.9	2% Alkaterge E	20-50

In the case of the coated tapes, in general, sterilization brought the resistivity values down, in many instances below the top permissible resistivity limit (about 60 ohms-inch). The weight losses averaged 10% and most of the coated samples were not physically affected by the sterilization step; thickness of samples before and after sterilization also seemed relatively unchanged.

In addition, the samples obtained from mixtures containing 1% Alkaterge E (an amine type wetting agent) exhibited relatively low

resistivities both before and after sterilization, although their weight losses were slightly higher than normal. This may have been due to yet another change in the quality of the Webril tape.

All the plain Webril samples exhibited low weight losses, comparable to those sustained by the original Webril samples under the same conditions. In a few cases the thicknesses increased after sterilization especially in the case of H739 and H751. It was thought that some swelling liquid had been retained by the samples after washing and drying; however, prolonged drying did not reduce the thickness values measured after sterilization nor did it increase the weight loss. This probably means that the Webril fibers were permanently rearranged by the KOH treatment. The yellow-green color present in the KOH solution after sterilization, and the curling of the samples may indicate the presence of bonding agents in the non-woven Webril. Four of these new tapes were so tightly made that they showed some resistivity even without being coated. The results of the sterilization cycle on the new plain Webril tapes, some of which are too thick, lead us to the conclusion that the tape used until now may be the best, even though it is now of a coarser grade. We may, however, be forced to reformulate the coating mixtures to take into account the more open structure of the Webril tape to be used.

6. Silver ion diffusion rates

Several samples of battery separator membranes, which were previously found to have a satisfactory resistivity and sterilization properties, underwent tests to measure polarographically the flow of silver ions through them as a function of time. Special cells were used to contain the concentrated KOH:Ag solution.

Measurements were carried out continuously over a period ranging from 44 to 140 hours for each membrane sample which was placed between two Teflon cells, one containing the known Ag solution in 40% KOH and the other straight 40% KOH. The runs were made under a blanket of N_2 to prevent formation of potassium carbonate.

The results of this series of experiments were: of six samples tested, five had negligible Ag ion flow after no less than 43 hours of exposure to a saturated KOH:Ag solution; in fact, one lasted 140 hours without perceptible ion flow. A sixth sample showed the passage of 35 ppm Ag after 118 hours, but it took about 48 hours to show the passage of only about 4 ppm of Ag.

7. Zinc ion diffusion rates

Preliminary experiments have shown that the measurement of the zincate ion cannot be carried out satisfactorily by polarography. The half-wave of the zincate ion occurs very close to that for the reduction of water. In practice, a characteristic zincate plateau was difficult to identify in 40% KOH. Further, in solutions containing very small amounts of zincate ion, of the order of 15 parts per million, no such step was observed.

Therefore, analyses for zinc ion diffusion will be carried out using flame absorption spectroscopy.

III. FUTURE WORK

The principal aim will be that of modifying the industrial foil coating tower, used until now, to accept one foot wide Webril tape. This will involve acquiring new rollers to replace the old short ones (including drive rollers and take up rollers), lengthening the drying tower to about 12 feet, designing and manufacturing wider and more efficient dip-tank and coagulation bath, and adding better stirring devices for both dip-tank and coagulating bath.

Testing of more wetting agents is contemplated.

The effect of the presence of free zirconia in the sterilizing cells on the coated tape weight loss will be investigated

STERILIZATION PROGRAM (135°C FOR 60 HOURS IN 40% KOH)

Sample No.	ft/min	Thickness Before Sterilization in Mils	Sample Appearance (Color, physical, mechanical properties and size)	Thickness After Sterilization in Mils	Percent Wt. Change	Specific Resistivity Before Sterilization Ω-in	Specific Resistivity After Sterilization Ω-in
C58-43-1 Beginning	2	1.9 2.1 2.18	Unchanged	2.0 2.1 2.1	1.9 2.1 -12	>200	42
C58-43-1 End	2	2.4 2.1 2.4	Unchanged	2.1 2.2 2.4	2.25 2.1 -9.5	>200	55
C58-43-1 Beginning	3	2.1 2.3 2.05	Unchanged	2.1 2.0 2.4	2.15 2.0 -10.3	>200	122
C58-43-1 End	3	2.1 2.1 1.9	Unchanged	1.95 2.1 2.15	1.9 1.7 -11.2	>200	135
C58-43-1 Beginning	4	2.1 2.18 2.2	Unchanged	2.25 2.3 2.0	2.0 2.2 -12.1	>200	60
C58-43-1 End	4	2.18 2.2 2.2	Unchanged	2.1 2.4 2.15	2.4 2.0 -10.4	>200	51
C58-43-1 Beginning	5	2.15 2.2 1.9	KOH clear, sample slightly yellow	2.6 2.55 2.0	2.4 2.2 -8.6	>200	40
C58-43-1 End	5	2.15 2.2 2.2	KOH clear, sample slightly yellow	2.15 2.15 2.1	2.3 2.1 -27.5	>200	30
C58-44-1 Beginning	4.5	2.85 2.6 2.6	Unchanged	3.15 2.8 2.4	2.4 2.5 -10%	>170	120

STERILIZATION PROGRAM (135°C FOR 60 HOURS IN 40% KOH)

Sample No.	ft/min	Thickness Before Sterilization in Mils	Sample Appearance (Color, physical, mechanical properties and size)	Thickness After Sterilization in Mils	Percent Wt. Change	Specific Resistivity Before Sterilization Ω-in	Specific Resistivity After Sterilization Ω-in
C58-44-1 End	4.5	3.0	Unchanged	2.9	-9.6	>170	130
		3.2		3.3	2.7		
C58-44-1 Beginning	5	2.9	Unchanged	2.5	-9.3	>170	85
		2.85		2.65	2.7		
C58-44-1 End	5	2.7	Unchanged	2.65	-10.4	>170	45
		2.9		2.55	3.0		
C58-44-1 End	5.5	2.85	Unchanged	2.9	-8.0	>170	>170
		2.75		2.5	3.0		
Plain Webril EM-476	--	3.0	KOH and sample both green/ yellow color (badly curled)	2.4	-0.49	0	0
		3.1		3.8	3.1		
Plain Webril H-751	--	4.4	KOH clear, sample slightly yellow color (badly curled)	6.9	-0.6		300
		4.9		7.4	7.4		
Plain Webril E1451	--	5.6	KOH clear, sample yellow/ green color	5.7	-0.71		7
		5.5		6.5	6.4		
Plain Webril E1452	--	5.9	KOH clear, sample yellow/ green color	6.2	-1.0		35
		5.9		6.3	5.8		
Plain Webril H739	--	5.1	KOH clear, sample curled - sample yellow/green color	9.4	-1.4		35
		5.3		8.3	9.0		

STERILIZATION PROGRAM

(135°C for 60 hrs. in 40% KOH)

Sample No.	ft./min. and Temp.	Thickness Before Sterilization in Mils	Sample Appearance (Color, Physical, Mechanical, Properties and Size After Sterilization)	Thickness After Sterilization in Mils	Percent Wt. Change	Specific Resistivity Before Sterilization Ω-inch	Specific Resistivity After Sterilization Ω-inch
C58-53-2	3 (71°C)	4.6	No change	4.4	-13.3%	50	41
		4.2		3.8			
C58-53-2	3.5 (71°C)	5.0	No change	3.6	-18.4%	50	39
		4.4		4.7			
C58-53-2	4 (70°C)	4.8	KOH Light Green No change in Sample	3.65	-12.0	73	85
		4.4		4.4			
C58-53-2	4 (71°C)	4.25	No change	3.75	-12.9	58	14
		4.25		4.55			
C58-56-1 "A"	3 (71°C)	3.4	No change	3.15	-14.4%	97	24
		3.25		3.0			
C58-57-1	3.5 (70°C)	5.3	No change	3.75	-11.8	254	92
		5.2		4.7			
C58-58-1	3.5 (78°C)	3.5	No change	3.2	-13.3	160	60
		3.4		3.1			