TO: NST-44/Scientific and Technical Information Division
   Attn: Shirley Peigare

FROM: GP-4/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP-4 and Code NST-44, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,442,674

Government or Contractor Employee: Borden, Inc.

NASA Case No. : XGS-05584

NOTE - If this patent covers an invention made by a contractor employee under a NASA contract, the following is applicable:

YES / / NO / /

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of Column No. 1 of the specification, following the words "...with respect to an invention of...."
AQUEOUS ALKALI METAL HYDROXIDE INSOLUBLE CELLULOSE ETHER MEMBRANE

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6 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a membrane that is insoluble in an aqueous alkali metal hydroxide medium, said membrane comprising a resin which is a water-soluble C₂-C₄ hydroxyalkyl cellulose ether polymer and an insolubilizing agent for controlled water sorption, a diatyclic and electrodialytic membrane and is particularly useful as a separator between electrodes or plates in an alkaline storage battery and will be described in connection therewith.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

Generally, in electric storage batteries of this type, one electrode is silver oxide, the other is zinc or cadmium, and the medium providing the bath between the electrodes is an aqueous solution of potassium hydroxide. There may be used for some purposes other alkali metal hydroxides, e.g., sodium or lithium hydroxide. The zinc or cadmium may be replaced by other metals that have a valence of at least 2 and are above cadmium in the electromotive series of the chemical elements, examples being aluminum, manganese and chromium. In such batteries, it is necessary to have low electrical resistance of the membrane. It is a problem in batteries of this type, particularly when used for space exploration, to obtain membranes of adequate strength and stability when in contact with the alkali and silver oxide without the membrane being excessive in weight.

In our co-pending application, Ser. No. 396,716, filed Sept. 15, 1964, now abandoned, we have therein disclosed a battery separator membrane comprising a film which is a combination or solid solution of a cellulose ether such as methyl cellulose together with a resin which is either a polymer with dependent carboxyl groups such as sodium carboxy methyl cellulose or a polymer or copolymer of an alpha-unsaturated aliphatic acid. We have found that, although the membrane of the co-pending application has excellent conductivity and its tensile strength is superior to that of cellophane membranes which have previously been used in alkaline batteries, a separator membrane is required having still further improved tensile strengths. This property of higher tensile strength is especially needed in the course of assembling battery cells. The dry membrane should be capable of being wrapped around the electrodes without suffering physical damage.

The present invention provides a membrane that absorbs sufficient alkali solution to make sufficiently low the electrical resistance but is of very high tensile strength, even after immersion in and long contact with 25%—45% potassium hydroxide solution, said solution having silver oxide dispersed and dissolved therein. This is the corrosive environment to which the membrane is exposed when the battery is in operation.

Briefly stated, the invention provides a membrane which may also be referred to as a film or sheet, wherein said membrane comprises a resin that is a cellulose ether polymer with dependent hydroxyalkyl groups. The resin may be further combined with insolubilizing agents in order to prevent solutions of membranes made with said resin and the alkali concentration of the cell lowered to and below the threshold concentration at which the resin used to make the membrane is soluble. An example of a resin and insolubilizing agent that in combination illustrates one embodiment of the present invention is hydroxyethyl cellulose and methyl cellulose.

Using this combination of insolubilizing agent and resin, for instance, we have obtained membrane strengths from about 120% to 780% of the strength given by the control membrane consisting of regenerated cellulose sheeting (cellophane). Strength tests were conducted on membranes after immersion for 72 hours in a 30% potassium hydroxide solution which had been saturated with silver oxide (Ag₂O). Our membranes also are satisfactorily low in electrical resistance, all provided that the critical proportions hereinafter described are used in the membrane.

As to the resin, the lower hydroxyalkyl cellulose polymers are best suited and C₂—C₄ hydroxyalkyl cellulose ethers are preferred. Examples that illustrate the class to be used are hydroxy-ethyl, iso- and n-propyl and butyl cellulose. The degree of replacement of hydrogen atoms of the hydroxyl groups by hydroxyalkyl groups is between about .8 and 1.5 per glucose unit in the cellulose molecule. As to the insolubilizing agent, lower alkyl cellulose ethers are preferred. Methyl and ethyl cellulose are satisfactory, particularly the methyl ether having a degree of substitution by CH₃ groups or if a higher alkyl ether is used, the corresponding alkyl radical, corresponding to replacement of 1.0—2.4 hydroxyalkyl cellulose ethers is about to 8.1.5 per glucose unit in the cellulose molecule.

The silver oxide used as one electrode is of grade and in form that is conventional in the commercial alkaline batteries, there being some uncertainty as to whether the compound that is active in the battery function is silver oxide (Ag₂O) or silver peroxide (AgO₂). AgO₂ is used throughout as representative of the oxide.

As to the proportions, when an insolubilizing agent is used, the ratio of the agent to the resin is dependent upon the concentration of alkali in the battery cell. Insolubilizing agents of the lower alkyl cellulose ether type and resins of the lower alkyl hydroxy cellulose type are separately soluble in water. Further, lower alkyl hydroxy cellulose resins are soluble in alkali solutions in concentrations up to about 40%. It has therefore been found necessary to add increasing proportions of insolubilizing agents to the resin composition as the alkali concentration of the cell is reduced below 40%. If insufficient quantities of said agent were to be used in the membrane composition for a specific alkali solution strength, the membrane would dissolve and therefore be useless for its intended purpose. Generally, up to 100% resin can be used at alkali concentrations of 40% and greater, and proportionately less resin as the concentration is reduced.

The following table shows proportions of ingredients at various alkali solution concentrations. The proportions are shown as illustrative of the proper range for best results. It is understood that the ranges given in the
The membranes of columns "0" and "Cellophane Control" are not a part of the present invention. The results show generally, the superiority of our membrane over the control membrane and methyl cellulose membrane, particularly in tensile strength and resistance measurements. Not tabulated is the fact that the silver oxide-KOH solution, having substantial oxidizing power, rendered the cellophane membrane opaque by a heavy coating of silver oxide, whereas the films of this invention, when disintegrated or dissolved in KOH solution at this concentration.

Example 1

700 grams of a 10% methyl cellulose solution (Methocel 15) and 300 grams of 10% hydroxyethyl cellulose (Cellulose QPO9) were completely mixed at 5°C. The ratio of methyl cellulose to hydroxyethyl cellulose was 7:3. Films were cast on levelled plate glass by the drawdown procedure using a 20 mil clearance on the doctor blade. Clear, homogeneous films of about 1.5 mil thickness were obtained. By similar process films were made in which the ratios of hydroxyethyl cellulose to methyl cellulose were respectively, 1.9, 2.8, 3.5:6.5 and 5:5. The 3:5 and greater ratios are considered unsatisfactory for use in 30% KOH as the film disintegrated or dissolved in KOH solution of this concentration.

Samples of films were tested for tensile strength after, (1) conditioning at 50% relative humidity (R.H.) and 73°F for one week; (2) immersion for 72 hours in 30% KOH solution and, (3) immersion for 72 hours in 30% KOH solution saturated with silver oxide (there was continuous stirring in the last mentioned solution). In each series, the conditioned membranes were blotted, to remove surface solution, and immediately tested on the tensile strength machine. Table 2 tabulates the results obtained with films of this invention, in comparison with each other, with a cellophane (control) membrane of the prior art and with membranes made separately from each constituent component.
of charging and discharging before termination whereas control cells using battery grade cellophane failed after 15 to 21 cycles.

Example 2

The procedure and composition of Example 1 are used but with replacement of the hydroxyethyl cellulose by hydroxyiso- and n-propyl, and hydroxybutyl cellulose used separately and in turn in the various proportions of hydroxyalkyl cellulose to the total membrane combination as shown in Table 1. The films cast and dried are likewise clear and homogeneous. The test results are similar to those tabulated in Table 2.

Example 3

The procedure and compositions of Example 1 are followed in making membranes except that ethyl cellulose replaces methyl cellulose as the insolubilizing agent. The properties of the resulting membranes, with proportions varying as in Table 1, are similar to those tabulated in Table 2. The ethyl cellulose is water soluble. The films of this invention may also be prepared from an organic solvent in place of the aqueous solvent. The organic solvent is a solvent for the resin and agent, such as butyl and higher alkyl alcohols.

It will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

We claim:

1. A membrane of high tensile strength being insoluble in aqueous alkali metal hydroxide medium, comprising a resin which is a water-soluble C2–4 hydroxyalkyl cellulose ether polymer having between about 0.8 and 1.5 hydroxyalkyl groups per glucose unit in said cellulose polymer, and a water-soluble lower alkyl cellulose ether having from about 1 to about 2 alkyl groups per glucose unit in said lower alkyl cellulose ether, said water-soluble lower alkyl cellulose ether being present in an amount sufficient to keep the membrane from dissolving into the aqueous alkali metal hydroxide medium.

2. The membrane of claim 1, wherein said alkyl groups of said resin are selected from the groups consisting of ethyl, iso- and n-propyl and butyl.

3. The membrane of claim 1 wherein said resin is hydroxyethyl cellulose.

4. A separator membrane of high tensile strength being insoluble in aqueous alkali metal hydroxide medium, wherein said medium comprises alkali metal hydroxide in proportion up to about 45% by weight, comprising up to 100% by weight of resin which is a water-soluble C2–4 hydroxyalkyl cellulose ether polymer having between about 0.8 and 1.5 hydroxyalkyl groups per glucose unit in said cellulose polymer, the difference from said 100% of said resin being an insolubilizing agent which is a water-soluble lower alkyl cellulose ether having from about 1 to about 2 alkyl groups per glucose unit in said lower alkyl cellulose ether, the proportion of said agent being increased as the concentration of said metal hydroxide is decreased in said medium.

5. The membrane of claim 4 wherein said alkyl group of said resin is selected from the group consisting of ethyl, iso- and n-propyl and butyl, and said agent is selected from the group consisting of methyl and ethyl cellulose.

6. A membrane of high tensile strength being insoluble in aqueous alkali metal hydroxide medium, said medium comprising between about 28% and 42% by weight of said alkali metal hydroxide, consisting essentially of hydroxyethyl cellulose having between about 0.8 and 1.5 hydroxyethyl groups per glucose unit in said hydroxyethyl cellulose and methyl cellulose having from about 1 to about 2 methyl groups per glucose unit in said methyl cellulose, in proportion between about 1 and 10 parts of hydroxyethyl cellulose for 10 parts of total membrane, the proportion of said hydroxyethyl cellulose being decreased as the concentration of said metal hydroxide is decreased in said medium.

References Cited

UNITED STATES PATENTS

2,763,030 9/1956 Erickson ___________ 106—197
2,810,659 10/1957 Greminger et al ______ 106—197
2,988,455 6/1961 Rosenberg et al. _____ 106—197
3,057,942 10/1962 Smith et al __________ 136—179
3,091,542 5/1963 Anderson _____________ 106—197

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