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COMPLETE SPECIFICATION

Anode Films for Dry Cells

We, UNION CARBIDE CORPORATION (formerly UNION CARBIDE AND CARBON CORPORATION), of 30, East 42nd Street, New York, State of New York, United States of America, a Corporation organised under the Laws of the State of New York, United States of America (Assignee of Margaret Peoples Korver jointly with Nelson Corey Cahoon), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to permeable bibulous coagulated methyl cellulose ether films adapted for use as anode films in primary galvanic dry cells and to dry cell assemblies containing such anode films. The invention also relates to methods for producing such films.

It is an object of this invention to provide coagulated water-soluble methyl cellulose ether film, containing a substantial amount of the coagulating agent residing therein from coagulation, which is adapted for employment as an anode film in zinc anode primary galvanic dry cells in that all components of such coagulated film, including the substantial amount of residual coagulating agent, are compatible with and non-deleterious to storage and operation of such dry cells in which such film is incorporated.

Another object of the invention is to provide methods for coagulating water-soluble methyl cellulose ether film wherein the coagulating agent is compatible with and non-deleterious to dry cell storage and operation, thus obviating necessity for removal of the substantial amount of coagulating agent residing in such film after coagulation.

A common form of dry cell comprises a zinc anode, a carbonaceous cathode and an intermediately disposed depolarizer mix which is moistened with an appropriate electrolyte. A permeable separating medium is interposed between the anode and the mix to prevent internal short-circuit of the electrodes while permitting passage of the electrolyte and soluble anode decomposition products. The separating medium must be disposed adjacent to the anode and at least the face of the separating medium thus adjacent to the anode must, when wetted with electrolyte, securely adhere to and maintain good electrical contact with the anode. Thus at least the face of the film adjacent to the anode must, when wetted with electrolyte, become adhesive, tacky and firmly adhere to the anode so that the desired electrical contact is maintained under all conditions of cell storage and operation. A film or film portion which exhibits these properties of adhesion to the metal anode is here termed an "anode film". A film or film portion which may be disposed between the anode film and the depolarizer mix to protect the anode film from undue attack by moisture in the electrolyte may be termed a "barrier film". Separator media comprising a separate anode film and barrier film are proposed in United Kingdom Patent No. 603,927 and there designated a "composite diaphragm". That patent also proposed a unitary film comprising water-soluble alkyl cellulose ether film insolubilised on one surface by treatment with citric acid or the like.

It has previously been known that water-soluble alkyl cellulose ether films produced by evaporation of water from a film layer of a water solution of water-soluble cellulose ether, often referred to as "cast films", could be used as anode film. Such films are, of course, free from impurities and foreign materials, such as metal salts, and are assembled in dry cells as dry film which becomes tacky on exposure to electrolyte.

Water-soluble alkyl cellulose ether films

produced by evaporation of water from a water solution of the cellulose ether, while affording satisfactory anode films, are undesirably expensive for the reason that it is necessary to evaporate from 6 to 9 pounds of water per pound of film produced. Thus neither that film nor the process for its production is commercially attractive.

We have now found that methyl cellulose ether film admirably adapted to serve as an anode film or film portion in dry cells may be produced by coagulation of the film by chemical treatment according to this invention.

Accordingly the present invention provides a method of making a coagulated methyl cellulose film which comprises forming a layer or film of an aqueous solution of a water-soluble methyl cellulose ether and thereafter coagulating the formed layer or film by contacting said layer or film with an aqueous solution of a coagulating agent comprising a sulphate or chloride of ammonia or a water-soluble sulphate or chloride of a metal more electropositive than zinc, or zinc sulphate, or mixtures of such sulphates and/or chlorides.

The coagulated undried films of this invention are non-tacky, strong, rubbery and tough and, despite their striking wet strength which permits their manipulation by hand or machine without damage, they may readily be cut. They are thus well adapted to economical large scale commercial production and to mechanical handling incident to their assembly in dry cell components.

In contrast to the prior water-soluble alkyl cellulose ether film produced by evaporation of water from an aqueous solution of the cellulose ether, the product of this invention contains the substantial residual amount of coagulating agent which is absorbed into the film during coagulation. By suitable selection of coagulating media, as disclosed herein, the function of the film as a dry cell anode film is in nowise impaired by the presence of this desidual coagulating agent. Moreover, the coagulated film of this invention is assembled, in its wet state, into the dry cell. Thus necessity for drying the film is eliminated and the liquid volume of electrolyte introduced into the cell in the depolarizer mix or otherwise is not substantially depleted by adsorption into the anode film.

The process of this invention comprises treating a film layer of an aqueous solution of water-soluble methyl cellulose ether of desired thickness with an aqueous solution of coagulant, selected as disclosed herein. The wet coagulated film thus produced may then be utilised in dry cell construction in its wet undried state. The wet coagulated film may also be applied to a barrier film and the laminated film disposed in a galvanic cell with the wet anode film portion against the anode. In any case, no removal of absorbed coagulant as by washing or by other means is attempted and drying is eliminated.

The coagulant solution may be applied to the layer of aqueous solution of methyl cellulose ether by immersing a supported layer in a coagulant bath, by flowing coagulant bath over a supported layer, by extruding a layer of methyl cellulose ether solution into a coagulating bath or by any other means which allows suitable contact of the coagulant solution with the methyl cellulose layer.

Coagulant solutions encompassed by this invention comprise aqueous solutions of ammonium chloride, ammonium sulphate and water-soluble chlorides and sulphates of metals more electropositive than zinc and zinc sulphate. Aqueous solutions containing 20%-35% of these sulphates or chlorides coagulate film layers of aqueous solutions of water-soluble methyl cellulose ethers to form tough rubbery films. While salts of other metals coagulate water-soluble methyl cellulose ether, the chloride or sulphate of a metal less electropositive than zinc should not be employed if the resulting film is to be used in dry cells having zinc anodes. A metal will replace from a metal salt another metal which is more electronegative. Employment of a coagulant comprising a chloride or a sulphate of a metal more electronegative than zinc results in displacement of the metal of the residual absorbed coagulant metal salt from that salt by the zinc anode metal. There would thus be wasteful corrosion and pitting of the anode and also objectionable deposit of such metal other than zinc at the anode—anode film interface, contributing to decreased storage and service life. Thus, water-soluble chloride or sulphate of any metal more electropositive than zinc may be employed without danger of corrosion or pitting of the anode or deleterious deposit of such. By water-soluble sulphates or chlorides, as herein referred to, is meant sulphates or chlorides which are soluble in water to the extent of ten parts by weight per hundred parts of solution. There is no tendency for zinc to displace the ammonium ion from ammonium chloride or ammonium sulphate.

As above stated, zinc sulphate may be employed as a coagulant according to this invention. However, it has been found that zinc chloride is unsatisfactory as coagulant, not exerting sufficient or satisfactory coagulating action. In this respect it differs from the metal chlorides of metals more electropositive than chromium.

Perhaps it is this curious lack of coagu-

lating action by zinc chloride which allows cellulose ethers coagulated according to this invention to be so satisfactorily employed as anode films. The zinc chloride present in electrolyte of zinc anode primary galvanic cells appears to exert a softening or surface solubilizing action which enables suitable adhesion of the anode film to the zinc anode.

The aqueous solution of methyl cellulose ether to be coagulated should contain the cellulose ether in relatively high concentration and should also be of relatively high viscosity. The maximum attainable concentration varies with viscosity type (viscosity of 2% solution at 20°C. in centipoises) of methyl cellulose ether, the lower the viscosity type the higher the maximum attainable concentration in weight per cent. We prefer to employ the higher viscosity types of methyl cellulose ether, for example those which have a viscosity in 2% solution at 20°C. of 1000 cps. or more. An aqueous solution containing 10% by weight of 4000 cps. viscosity type methyl cellulose is well adapted to formation of satisfactory film according to this invention. More generally, solutions containing 8%-14% methyl cellulose ether of 1000 cps. or higher viscosity type may be employed. The temperature at which the coagulation is carried out may vary between 0°C. and 45°C. We prefer to avoid a temperature at which the particular aqueous solution of methyl cellulose gels. The coagulating bath should comprise a relatively concentrated solution of the chloride or sulphate. Although concentrations as low as 10% may be used, aqueous solutions containing 15%-40% by weight of the coagulating agent are preferred. Mixtures of chlorides and sulphates of ammonia or the same or different metals more electropositive than chromium may be employed as coagulants. Suitable plasticizers, and softeners may also be added to the coagulating bath if desired, without departing from this invention.

Analysis of film coagulated according to this invention reveals that a substantial amount of the coagulant is absorbed into the cellulose ether film. Analysis of film coagulated in an aqueous solution of calcium chloride of different concentrations shows a content of $CaCl_2$ in the film calculated on a dry basis, as follows:

		Coagulant in Film	
Film No.	*% $CaCl_2$ in bath*	*% Ca.*	*Equivalent % $CaCl_2$*
1	20	6.14	17.0
2	20	5.61	15.5
3	35	9.12	25.2
4	31	8.32	23.0
5	25	7.41	20.5

The following are illustrative embodiments of aspects of our invention.

EXAMPLE I.

A 10% aqueous solution of 4000 cps. water-soluble methyl cellulose was spread in a thin layer on a glass plate and immersed in an aqueous 25% solution of NH_4Cl at 20°C. After five minutes contact with the solution the glass plate was removed from the solution and the tough, rubbery, elastic and non-tacky film was removed from the glass surface. It was cut to desired size and wrapped around a prefabricated dry cell cathode bobbin which was wet with a $ZnCl_2 - NH_4Cl - H_2O$ electrolyte and included depolarizer mix. The bobbin had previously been wrapped with a barrier film comprising alkyl cellulose ether insolubilized by treatment with citric acid as disclosed in United Kingdom Patent No. 603,927. The bobbin thus wrapped with both barrier and anode film was then charged into a zinc anode can, the charge was tamped and the top of the assembled cell was sealed. The resulting dry cell had excellent storage and service characteristics. The anode film being wet and bibulous when assembled in the cell did not draw any discernible amount of electrolyte solution from the cathode bobbin.

EXAMPLE II.

A 10% aqueous solution of 4000 cps. viscosity type water-soluble methyl cellulose was spread in a thin layer on a glass plate and the plate immersed in an aqueous 25% solution of $CaCl_2$. After four minutes contact with the solution a non-tacky, rubbery, tough, elastic layer was removed from the glass surface and from the solution and assembled into a dry cell as described in Example I with similarly good results.

EXAMPLE III.

A film-like layer of a 10% solution of 4000 cps, viscosity grade methyl cellulose was extruded on to a glass roller upon which the layer was subjected to the action of a coagulating bath comprising a 25% solution of $ZnSO_4$. After a contact time of three minutes with the coagulating solution the film was peeled from the roll, cut to size and utilized as an anode film in assembly of zinc anode dry cells, as set forth in Example I.

EXAMPLE IV.

A layer of 10% aqueous solution of water-soluble methyl cellulose was distributed over the inside surface of a zinc anode can. A coagulant solution containing 25% by weight of ammonium chloride was placed in the can. After a residence time of three minutes the coagulating solution was removed. A tough, rubbery film of coagulated methyl cellulose lined the inside of the anode can. A prefabricated cathode bobbin containing depolarizer mix, $ZnCl_2$

$-NH_4Cl$ $-H_2O$ electrolyte and wrapped with a barrier film as described in Example I was fitted and tamped into the can and the top of the cell was sealed.

That a methyl cellulose film coagulated by solutions of chlorides and sulphates will, upon wetting with electrolyte containing relatively high concentrations of one or more of the coagulating agents, adhere to the metal anode to the necessary degree is surprising. One would expect that coagulation would be irreversible, but it has been found that with the coagulating agents of the present invention, a reversible coagulation is obtained and that the resulting film is sufficiently de-coagulated when wetted by the electrolyte to give the sticky adherence to the metal anode which is the necessary function of a satisfactory anode film.

If desired, mercuric chloride or other suitable mercury compound may be added to the methyl cellulose, either before or after coagulation in known manner to further facilitate amalgamation of the zinc anode by the anode film.

WHAT WE CLAIM IS:—

1. A method of making a coagulated methyl cellulose ether film, which comprises forming a layer or film of an aqueous solution of a water-soluble methyl cellulose ether and thereafter coagulating the formed layer or film by contacting said layer or film with an aqueous solution of a coagulating agent comprising a chloride or sulphate of ammonia, or a water-soluble chloride or sulphate of a metal more electropositive than zinc, or zinc sulphate, or mixtures of such sulphates and/or chlorides.

2. A method as claimed in Claim 1, in which the water-soluble methyl cellulose ether layer is formed from an aqueous solution containing from 8 per cent to 14 per cent by weight of methyl cellulose ether having a viscosity of at least 1000 centipoises.

3. A method as claimed in Claim 2, in which the layer is formed from an aqueous solution containing 10 per cent by weight of methyl cellulose ether having a viscosity of 4000 centipoises.

4. A method as claimed in any one of Claims 1 to 3, in which the aqueous solution of the coagulating agent contains from 10 per cent to 40 per cent by weight of the coagulating agent.

5. A method as claimed in Claim 4, in which the aqueous solution contains at least 15 per cent by weight of the coagulating agent.

6. A method as claimed in any one of Claims 1 to 5, in which coagulation is carried out by immersing the water-soluble methyl cellulose ether layer in the aqueous solution of coagulating agent.

7. A method as claimed in any of Claims 1 to 5, in which coagulation is carried out by extruding the water-soluble methyl cellulose ether layer into the aqueous solution of coagulating agent.

8. A method as claimed in any one of Claims 1 to 5, in which the cellulose ether film is formed by causing a layer of a solution of the ether to flow on a support and contacting the thus formed layer with the coagulating agent.

9. A method as claimed in any one of Claims 1 to 8, in which coagulation is carried out at a temperature within the range of from 0°C. to 45°C.

10. A method as claimed in any one of Claims 1 to 9, in which the aqueous solution of coagulating agent also contains a plasticizer or softener.

11. A primary galvanic dry cell comprising a zinc anode, a carbonaceous cathode, an electrolyte, a depolarizer, an anode film and a barrier film, in which the anode film is produced by the method claimed in any of Claims 1 to 10.

12. A method of making a coagulated methyl cellulose ether film composition suitable for use in a primary galvanic dry cell substantially as hereinbefore described with reference to the Examples.

13. A primary galvanic dry cell containing an anode film produced by the method substantially as hereinbefore described with reference to the Examples.

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$-NH_4Cl-H_2O$ electrolyte and wrapped with a barrier film as described in Example I was fitted and tamped into the can and the top of the cell was sealed.

That a methyl film coagulated by solutions of chlorides and sulphates will, upon wetting with electrolyte containing relatively high concentrations of one or more of the coagulating agents, adhere to the metal anode to the necessary degree is surprising. One would expect that coagulation would be irreversible, but it has been found that with the coagulating agents of the present invention, a reversible coagulation is obtained and that the resulting film is sufficiently de-coagulated when wetted by the electrolyte to give the sticky adherence to the metal anode which is the necessary function of a satisfactory anode film.

If desired, mercuric chloride or other suitable mercury compound may be added to the methyl cellulose, either before or after coagulation in known manner to further facilitate amalgamation of the zinc anode by the anode film.

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1. A method of making a coagulated methyl cellulose ether film, which comprises forming a layer or film of an aqueous solution of a water-soluble methyl cellulose ether and thereafter coagulating the formed layer or film by contacting said layer or film with an aqueous solution of a coagulating agent comprising a chloride or sulphate of ammonia, or a water-soluble chloride or sulphate of a metal more electropositive than zinc, or zinc sulphate, or mixtures of such sulphates and/or chlorides.

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3. A method as claimed in Claim 2, in which the layer is formed from an aqueous solution containing 10 per cent by weight of methyl cellulose ether having a viscosity of 4000 centipoises.

4. A method as claimed in any one of Claims 1 to 3, in which the aqueous solution of the coagulating agent contains from 10 per cent to 40 per cent by weight of the coagulating agent.

5. A method as claimed in Claim 4, in which the aqueous solution contains at least 15 per cent by weight of the coagulating agent.

6. A method as claimed in any one of Claims 1 to 5, in which coagulation is carried out by immersing the water-soluble methyl cellulose ether layer in the aqueous solution of coagulating agent.

7. A method as claimed in any of Claims 1 to 5, in which coagulation is carried out by extruding the water-soluble methyl cellulose ether layer into the aqueous solution of coagulating agent.

8. A method as claimed in any one of Claims 1 to 5, in which the cellulose ether film is formed by causing a layer of a solution of the ether to flow on a support and contacting the thus formed layer with the coagulating agent.

9. A method as claimed in any one of Claims 1 to 8, in which coagulation is carried out at a temperature within the range of from 0°C. to 45°C.

10. A method as claimed in any one of Claims 1 to 9, in which the aqueous solution of coagulating agent also contains a plasticizer or softener.

11. A primary galvanic dry cell comprising a zinc anode, a carbonaceous cathode, an electrolyte, a depolarizer, an anode film and a barrier film, in which the anode film is produced by the method claimed in any of Claims 1 to 10.

12. A method of making a coagulated methyl cellulose ether film composition suitable for use in a primary galvanic dry cell substantially as hereinbefore described with reference to the Examples.

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