(54) Title: BATTERY SEPARATORS

(57) Abstract: Cellulose films wherein the cellulose thereof has been cross-linked with melamine formaldehyde show increased oxidation resistance compared with similar cellulose films which have not been cross-linked. The cross-linked films can be used with advantage as the insulating membrane of batteries in which highly oxidizing environments occur, for example silver-zinc, zinc-air, nickel-zinc, nickel-metal hydride and nickel-cadmium cells.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
BATTERY SEPARATORS

This invention relates to batteries and separators for use therein.

Batteries, such as alkaline batteries, are commonly used as energy sources. Generally, alkaline batteries have a cathode, an anode, a separator and an electrolytic solution. The cathode is typically formed of manganese dioxide, carbon particles and a binder. The anode can be formed of a gel including zinc particles. A separator is usually disposed between the cathode and the anode. The electrolytic solution, which is disposed throughout the battery, can be a hydroxide solution.

The separator is designed to allow good electrolyte ion flow between the anode and the cathode whilst reducing dendrite and soft shorting between the anode and the cathode. Dendrite shorting refers to the situation where soluble salts or ions containing alkaline, alkaline earth or transition metals, such as potassium zincate, migrate between the electrodes of the battery and is reduced to the metal, e.g. zinc, on charging of the battery. Soft shorting refers to the case where active material becomes solubilized in the electrolyte solution and migrates away from the electrode, resulting in loss of capacity or reaction with active material of the other electrode.

US 6159634 (Duracell) describes batteries having thin cellulose film as a separator. This reference teaches that thinness is the major requirement for improved separator performance. US 6159634 does not appreciate many of the other properties necessary to provide a good separator and thus teaches that in the limit infinitely thin films would be
acceptable. However, thinness in the separator is not the only requirement to optimize battery performance. Not all thinner separators will exhibit better properties for battery use if one fails to consider and balance other competing properties required for the separator.

5 Thinner separators occupy a smaller volume inside the battery cell which increases the volume available for cathode material, anode material and/or electrolytic solution (active materials) in a battery of a given standard size (e.g. AA, AAA, AAAA, C or D). The differences may be small as reducing the thickness of the cellulose film component of the separator from 25 microns to 21 microns reduces the separator volume in a typical battery by about 14%, which leads to an increase in volume of the active material of only 1%. A thinner film may also have a lower ionic resistance when wet. These effects together can result in a small improvement in battery performance if one compares thin separators with thicker ones identical apart from thickness. However, as one makes a thinner conventional separator there are some disadvantages which increase the thinner the separator. The separator has a lower durability and strength, the separator web is more prone to break during production, the time taken to slit the separator (and its thinner component layers) is increased; production efficiency and throughput are reduced; there is a reduced conversion efficiency of the component layers into separator (and separator into batteries); and/or reduced barrier to dendrite or soft shorting. All of these factors can increase the production cost of using thinner separators and outweigh the small advantage in battery performance so gained.

A suitable separator comprises a cellulose film, especially a regenerated or coagulated cellulose film. A typical separator construction comprises a laminate of a wicking layer adhered to a flat porous membrane which allows ion transport thereacross, for example the wicking layer may be a nonwoven layer comprising fibers and the membrane be cellulosic film.

The mechanical and physical properties of a separator and both its component nonwoven and cellulose film layers must be such that they are durable when dry (so they can be handled and laminated as a web on a production machine). They also require sufficient strength when wet (especially in the alkaline electrolyte of an alkaline battery), especially if the separator is to be used in a rechargeable battery where it must survive the rigors of repeated cycles of charging and discharging. So a thinner separator even if it achieves low wet ionic resistance or allows greater volume of active material in the battery, it must also exhibit acceptable mechanical and other properties to provide the same or better overall battery performance than that obtained by a thinner film.
Another problem which occurs when using cellulusic films in battery separators is that they are subject to oxidative degradation as a result of chemical processes which occur within batteries during use, resulting in decreased battery life. Thicker cellulusic films would be expected to delay breakdown of battery separators made from them, whilst thinner films would be expected to break down more readily. Furthermore, in addition to thicker films leading to reduced volume for other battery components within the container of a specified battery type, they also lead to greater resistance to electrolyte species within the battery, and so to lower output. However, whilst thinner films can result in lower resistance to electrolyte species within the battery, such films have relatively poor oxidative resistance and poor resistance to dendrite or soft shorting.

In theory it might be possible to increase the oxidative resistance of cellulose films used for battery separators using an antioxidant. However, such antioxidants would need to be compatible with the conditions within the battery, which severely limits the choice, but more of a problem is that it would be consumed during battery use and so limit the life of the battery.

So the above factors must be balanced when producing separator film. Thus it can be seen that the demands on separator properties are varied and complex and cannot be reduced to a simplistic "the thinner the better" without considering other factors.

It is desired to improve the properties of separators and the component layers thereof to overcome some or all of the problems with separators, for example with thin separators.

Therefore broadly in accordance with the present invention there is provided a cellulose film wherein the cellulose thereof has been cross-linked with melamine formaldehyde.

Film in accordance with the present invention preferably have melamine formaldehyde contents of at least 0.1% based on the weight of cellulose in the film. The melamine formaldehyde content of the films is preferably not more than 5.0% based on the weight of cellulose in the film. More preferably the melamine formaldehyde content of the films is from 0.2 to 3.0% based on the weight of cellulose in the films.

Films in accordance with the present invention preferably have a degree of polymerization as measured by TAPPI method T-230 after treatment with a mixture of 5 parts of a 40% w/w aqueous potassium hydroxide solution and 1 part by weight of 2.8 volume aqueous
hydrogen peroxide solution for 24 hours is not less than 50% of that of the film before such
treatment, and more preferably not less than 30% of that of the film before the treatment.

Film in accordance with the present invention preferably exhibit a pressure flux of water of
at least 1600g/m²/day, and more preferably at least 1700g/m²/day under an applied
pressure of 0.55MPa.

Cross-linking of the cellulose with melamine formaldehyde has the effect of increasing the
oxidative resistance of battery separators made from it and it can also increase the
porosity of the separators, thereby leading to increased battery performance.

Separators of and used in the present invention comprise material(s) that can form a
porous preferably semi-permeable sheet and are substantially inert to the electrolytic
solution and capable of reducing dendrite shorting but the separator allows ion transport
thereacross for good electrolyte ion flow between the cathode and anode. Usually, the
separator and any component layers thereof do not include wettable material coatings,
metal coatings or fillers such as, for example, inorganic particles.

A typical separator construction comprises a laminate of a wicking layer (for example a
nonwoven layer comprising fibers) adhered to a porous insulating cellulosic film. In a
preferred embodiment, the laminate is made according to the method disclosed in US
4,902,590, which is hereby incorporated by reference.

Although a wicking layer will be used for the separators of some types of battery in
accordance with the present invention, the separators of other batteries in accordance
with the present invention can consist of a melamine formaldehyde treated cellulose film in
accordance with the present invention without a wicking layer, that is on their own or in
combination with other materials for example such as are known in the art for producing
battery separators, for example asbestos matting or a porous polyolefin film.

Insulating membrane

Preferably the cellulose film used in the present invention is cellulose regenerated from a
cellulose derivative or coagulated from a cellulose dispersion in a non-solvating fluid (such
as but not limited to NMMO, LiCl/N,N-dimethylpyrrolidone, LiCl/N,N-dimethyl acetamide).
One specific example of a cellulose derivative is "viscose" which is sodium cellulose
xanthate in caustic soda. Cellulose can be cast into film from a derivative or a dispersion
by regenerating or coagulating the cellulose in situ by a suitable treatment (e.g. addition of a suitable reagent which for viscose can be dilute sulfuric acid). Such cellulose is known herein as regenerated or coagulated cellulose and preferred films of the present invention comprise regenerated cellulose.

More preferred films used as the separator membrane comprise cellulose which is substantially continuous, more preferably non-woven and/or entangled, in structure. Most preferably the film comprises non-microbial cellulose.

Conveniently films used in the present invention substantially comprise cellulose, for example from a wood source or cotton linters, most preferably at least 90% of the cellulosic material being from a wood source.

Cross-linking of the cellulose will usually be effected by treating the cellulosic dispersion in a non-solvating fluid with melamine formaldehyde prior to regeneration of the cellulose and/or by treating the regenerated cellulosic film with melamine formaldehyde. Generally it is preferred to add melamine formaldehyde both prior to and after regeneration of the cellulose. When the film is treated with melamine formaldehyde after regeneration of the cellulose, the treatment is preferably effected with the cellulose film in a swollen state prior to drying.

The amount of cross-linking can be varied, in particular by varying the concentration of the melamine formaldehyde in the cellulosic dispersion of the cellulose prior to regeneration and by varying the concentration of melamine formaldehyde in the treatment bath used to treat the film after regeneration.

In general the concentration of melamine formaldehyde in the cellulosic dispersion and that in the treatment bath used after regeneration, which can be the same or different, will be not more than 6.5% with respect to the weight of cellulose in the final film. The melamine formaldehyde concentration in the cellulosic dispersion is preferably not more than 0.7% but it is also preferably at least 0.03%. The melamine formaldehyde concentration in the treatment bath used after regeneration is preferably not more than 0.5% and more preferably not more than 0.2%, but it is also preferably at least 0.03%. It has been found that if the treatment bath contains about 0.04% by weight of melamine formaldehyde the films after treatment generally have a melamine formaldehyde content of about 0.2% by weight of the cellulose content of the film, and if the treatment bath contains about 0.7% by weight of melamine formaldehyde the films after treatment generally have a
melonialdehyde content of about 4% by weight of the cellulose content of the film.

The amount of melamine formaldehyde taken up by the film will in general depend on the both the temperature of the treatment bath and the residence time of the film in the bath. Preferred treatment bath temperatures are at least 25°C, and they are preferably not more than 45°C, a preferred temperature range being from 30 to 40°C. Preferred residence times in the treatment bath are at least 5 seconds. However, they will usually be not more than 30 seconds, and more preferably not more than 15 seconds. A preferred range of residence times is from 5 to 10 seconds.

The cellulose may include one or more plasticizers, but, typically, such plasticizers are not included. In order to increase the porosity of the cellulose of films of the present invention, and thereby increase transport of ions through the film, it is generally preferred to include a suitable filler in the cellulosic dispersion in a non-solating fluid prior to regeneration of the cellulose, and more preferably prior to the addition of the melamine formaldehyde.

Adhesive

When an adhesive is used to construct battery separators in accordance with the present invention it can in general be any material that is substantially inert to the electrolytic solution and that can form a physical and/or chemical bond between the wicking layer and insulating membrane sufficient that separator forms an integral unit without increasing the barrier to good ion flow. Suitable materials especially for use in alkaline batteries, comprise polyacrylic acids (such as that available commercially from B. F. Goodrich under the trade name Carbopol 940), grafted starch materials (such as that available from Grain Processing Corporation, Muscatine, Iowa, USA under the trade name Waterlock A221), carboxymethylcellulose and mixtures thereof. The amount of material in the adhesion layer is preferably less than about 6 gm⁻², more preferably from about 1 gm⁻² to about 5gm⁻², and most preferably about 3 gm⁻².

Wicking Layer

The wicking layer is designed to allow fast filling of the cell with electrolyte and wetting of the cellulose. Preferred wicking layers may be formed of one or more nonwoven materials (such as cellulose, PVA, polyamides, polysulfones and mixtures thereof) optionally having fibers thereon. More preferably the nonwoven layer comprises a matrix of PVA fibers; PVA binder; cellulose fibers (for example those fibers available from Acordis under the
trade marks Tencel and/or Lyocel) and/or rayon fibers. The cellulose fibers may be about 1.5 denier at 6 millimeters long, and the PVA fibers may be about 0.5 denier at 6 millimeters long. Optionally the nonwoven layer may comprise from about 20% to about 40% (for example about 30%) by weight of rayon and/or cellulose fibers; from about 55% to about 65% by weight (for example about 57%) of PVA fibers; and/or from about 5% to about 15% (for example 13%) by weight of PVA binder.

Films in accordance with the present invention can be used with advantage in separators for batteries in which highly oxidizing environments occur, and in particular in silver-zinc, zinc-air, nickel-zinc, nickel-metal hydride and nickel-cadmium cells. Particularly preferred batteries are alkaline batteries having a thin separator, for example with a general construction as disclosed in any of the embodiments or drawings of US 6,159,634 (Duracell). The contents of US 6,159,634 are hereby incorporated by reference for the other preferred features of the separators (and components thereof) and batteries of the present invention.

The invention will now be illustrated by the following non-limiting examples.

**Example 1**

Cellulose xanthate viscose was prepared in conventional manner and cast through a slot die into a bath of aqueous sulfuric acid to produce a regenerated cellulose film. The resulting film was then passed through one of three different aqueous treatment baths, the baths respectively containing 0%, 0.2% or 0.8% of melamine formaldehyde and 0.18% of formic acid, the percentages being based on the weight of water in the bath. The temperature of each of these various baths was 35°C, and the residence time of the respective films in the different baths was 17 seconds in each case. Each of these films after leaving the respective treatment baths was dried at 95°C by passing them over steam heated rollers for a period of 50 seconds. The individual films, which were 25μm thick, were then wound up.

The different amounts of melamine formaldehyde in the three different treatment baths resulted in the resulting regenerated cellulose films containing up to 5% by weight of melamine formaldehyde based on the dried weight of the final films.

The oxidation resistance of each of these three films was then evaluated as the percentage reduction in the degree of polymerization of the cellulose of these films as
measured by TAPPI method T-230 after leaving samples of the films in a bath consisting of 250cc of 40% w/w of potassium hydroxide and 50cc of 2.8 volume hydrogen peroxide. The results of these tests are shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Treatment Bath - Melamine Formaldehyde (%)</th>
<th>Degree of Polymerization (start)</th>
<th>Degree of Polymerization (after 24 hrs)</th>
<th>Percentage Reduction in Degree of Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>395</td>
<td>187</td>
<td>53</td>
</tr>
<tr>
<td>0.20</td>
<td>397</td>
<td>211</td>
<td>47</td>
</tr>
<tr>
<td>0.80</td>
<td>384</td>
<td>273</td>
<td>29</td>
</tr>
</tbody>
</table>

As can be seen from Table 1, increasing the amounts of melamine formaldehyde in the treatment baths resulted in a lessening of the reduction in the degree of polymerization of the cellulose following exposure of the regenerated cellulose films to oxidative conditions.

Example 2

Cellulose xanthate for producing regenerated cellulose films was produced in conventional manner and then blended with melamine formaldehyde to produce a blend containing 0.05% by weight of melamine formaldehyde based on the weight of the original cellulose.

The blend was then extruded through a slot die into a bath of aqueous sulfuric acid to form a regenerated cellulose film which was then passed through aqueous treatment baths containing from zero to 0.2% by weight of melamine formaldehyde.

The addition of melamine formaldehyde to the films in their swollen state following regeneration was found to increase the porosity of the films, provided the addition was above a minimum level. More particularly, the porosity of the films showed a maximum between 0.04 and 0.07% by weight of melamine formaldehyde in the treatment bath, this corresponding to a melamine formaldehyde content of approximately 0.22% by weight based on the cellulose content of the film.

The porosity of the various films was measured as pressure flux which was the amount of water passing through 1cm² of the film under a pressure of 0.55MPa.
The results obtained are shown graphically in Fig. 1.
CLAIMS

10. A cellulose film wherein the cellulose thereof has been cross-linked with melamine formaldehyde.

11. A film according to claim 1, wherein the melamine formaldehyde content thereof is at least 0.1% based on A regenerated cellulose film wherein the cellulose has been cross-linked with the weight of cellulose in the film.

12. A film according to claim 1 or claim 2, wherein the melamine formaldehyde content thereof is not more than 5.0% based on the weight of cellulose in the film.

13. A film according to any of the preceding claims, wherein the melamine formaldehyde content thereof is from 0.2 to 3.0% based on the weight of cellulose in the film.

14. A film according to any of the preceding claims, wherein the degree of polymerization as measured by TAPPI method T-230 after treatment with a mixture of 5 parts of a 40% w/w aqueous potassium hydroxide solution and 1 part by weight of 2.8 volume aqueous hydrogen peroxide solution is not less than 50% of that of the film before such treatment.

15. A film according to claim 5, wherein the degree of polymerization is not less than 30% of that of the film before the treatment.

16. A film according to any of the preceding claims, wherein the pressure flux thereof is at least 1600g/m²/day under an applied pressure of 0.55MPa.

17. A film according to any of the preceding claims, wherein the pressure flux thereof is at least 1700g/m²/day under an applied pressure of 0.55MPa.

9. A battery separator comprising an insulating membrane comprising a cross-linked regenerated cellulose film according to any of the preceding claims, and a non-woven material.

10. A battery separator according to claim 9, wherein the film is adhered to the non-woven material.
11. A battery separator according to claim 9 or claim 10, wherein the non-woven material comprises an asbestos mat or a porous polyolefin film.

12. A battery including a separator comprising a cellulose film according to any of claims 1 to 8.

13. A battery according to claim claim 12, wherein the separator is as defined in any of claims 9 to 11.