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SEPARATORS FOR ELECTROCHEMICAL CELLS

The present invention relates to separators for electrochemical cells which help to eliminate or reduce undesirable effects which can arise during storage and use of such cells.

The history of electrochemical cells goes back to 1866 when Leclanché first discovered the principle on which they are based. The manufacture and design of electrochemical cells has come a long way since that time, but problems still remain. Cells (also known as batteries, although the term technically relates to a series of cells) essentially consist of an anode, a cathode and an electrolyte. In the present day version of the Leclanché cell, the anode is zinc, the cathode is manganese dioxide and the electrolyte is an aqueous solution of varying proportions of zinc chloride and ammonium chloride. In other primary cells, the electrolyte is frequently an aqueous solution of potassium or sodium hydroxide. In any event, it is necessary to seal the various components into a can in order to prevent the possibly dangerous escape of the constituents, as well as to prevent the atmosphere from affecting the constituents.

The problem of leakage of the electrolyte and corrosion of the can (zinc in Leclanché cells) was very largely overcome by the addition of cadmium and mercury, but especially mercury, to the cell ingredients.

Thus, mercury was responsible for reducing perforation of the can during abuse conditions, reducing corrosion and preventing perforation during storage, and it also had the advantage that it assisted in discharge. However, now that mercury is viewed as a major environmental pollutant, there has been a very major push to develop cells with no added mercury and, to a lesser extent, cells with no added cadmium.

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The essential problem with cells which have no added mercury is that no one has yet found any additive which is capable of recreating the advantages of cells which contain mercury. In fact, even the optimum selection of all of the currently known additives is not as good as mercury.

One factor for assessing the performance of cells is performance retention. This is measured by initially storing cells at high temperatures for long periods (for example, 13 weeks at 45°C and 50% r.h. [relative humidity]) and then calculating performance retention as a measure of performance compared with similar batteries kept for two weeks at 20°C. The results are ideally in excess of 80%. Known additives generally have a performance retention in the region of only 75% by comparison with cells containing no additives, which typically have a performance retention in the region of 82%.

Apart from the necessary anode, cathode and electrolyte, practical considerations demand that a separator is provided between the anode and the cathode in order to avoid possible contact between the anode and cathode, which could lead to undesirable short circuiting.

In general, one of two types of separator is employed, and is either a gel/paste composition or coated paper. With the drive to greater efficiency and performance, the coated paper separators are particularly preferred, as they take up less space in the cell.

The coated paper separators are coated with starch which, in the presence of the electrolyte, is ionically conductive, but not electronically conductive.

We have now, surprisingly, discovered that the nature of the starch used to coat the separator can have a very significant effect on the problems encountered using cells which have no added mercury.

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Thus, in a first aspect, the present invention provides a coated paper separator for electrochemical cells, characterised in that the coating comprises a highly crosslinked starch and an etherified cellulose derivative as a gelling agent. The invention also provides coating preparations suitable for the preparation of such separators.

An advantage of the invention is that the separators generally remain substantially stable with time.

It is well known in the starch industry that different starches have different properties, and that different starches react differently in the presence of water. Essentially, without being bound by theory, it is believed that water hydrates the starch molecule, causing the molecule to unwind from its normal tertiary configuration, so that the viscosity of the solution increases. The greater the crosslinking in a starch molecule, the less the molecule is able to hydrate and gel.

Crosslinked starch molecules are a necessary part of the coating, as is a gum (or gelling agent). It is not certain precisely what functions these components perform, but we believe that the crosslinked starch molecules provide a lattice in which the gelled electrolyte is located, the gum or gelling agent also being required to provide the necessary consistency of the coating, as well as to provide adhesion to the zinc can.

Accordingly, many crosslinked, but not necessarily highly crosslinked, starches are used as the primary material of the coating, and many gums and other gelling agents are used as the secondary material (primary and secondary are used herein only for purposes of convenience, and have no other significance).

All of the combinations of materials used in the art are approximately as good as any other when subject to the tests

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employed by the art. That is to say, the prior art combinations of materials all provide the necessary ionic conductance and electronic barriers, without any overt impairment of fresh performance of the cell when assembled.

However, what has not previously been recognised in the art is that some of the materials are unstable in the presence of an aqueous zinc chloride solution which is, for example, a major drawback in the field of carbon-zinc cell technology.

For the first time in the industry, we have performed sedimentation tests, and the results have been striking. In these tests, the starch is added to an aqueous solution of zinc chloride, typically 25 or 46%, and the sample is stored at 45°C with monitoring over time. Although the time is not crucial, the test is often performed over a period of weeks, a period of around 13 weeks generally providing indicative results. The results are surprising. We find that some starches discolour or blacken with time, indicating a breakdown of the starch, whilst other starches gel initially, for example, but have a continuous increase in sediment volume with time, indicative of an undesirable lack of stability. The best starches neither discolour nor produce any change in sediment volume.

In addition, we have developed a further two new tests which we have termed the High Drain Continuous Test (HDCT) and the Low Drain Continuous Test (LDCT). The High Drain Continuous Test is intended to simulate abuse conditions, such as might be found in leaving a flashlight in the "on" condition over a period of time, even after the battery had, to the user, gone "flat". The Low Drain Continuous Test simulates the conditions experienced by a battery in, for example, a clock. HDCT results are measured in terms of the amount of leakage, whilst LDCT results are measured in terms of failure of the battery due to perforation or splitting of the can. Again, these tests are novel, and produce highly

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informative results in considerably less time than would otherwise be experienced in the conditions being simulated. Results are generally available in around 4 and 10 weeks respectively, although it will be appreciated that the amount of time required will depend on such factors as the cell which is to be tested and the extent to which it is desired to test the cell, for example.

These new tests (details of which are provided below) have enabled us to quickly and easily assay the effects of various constituents used in cell construction. In particular, we have assayed the various starches used in the industry and, in conjunction with the sedimentation test described above, we have established that a combination of highly crosslinked starches and etherified cellulose derivatives together provide an extremely superior form of separator coating which is generally more stable and helps to prevent splitting and leakage, compared with the separators of the art.

The term "highly crosslinked" is well known in the starch industry and, with respect to batteries, the preferred starches are corn, wheat and potato starches, and we have established that cells constructed with separators comprising highly crosslinked corn starch are surprisingly better in both the low drain and the high drain continuous tests. In the sedimentation tests, there is very little to choose between corn, wheat and potato starches.

Suitable examples of highly crosslinked corn starch include: Vulca 90 and Vulca 84 (Trademarks of National), Celex (Trademark of Nippon Starch Refining Company Limited) and the starches produced by Roquette, such as Lab 2211. Suitable examples of highly crosslinked potato starch include Vector R140 and Vector R120 (Trademarks of Roquette). A suitable example of a wheat starch is Lab 2214 (Roquette).

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While we prefer that the starch used in the coating is only a highly crosslinked starch, such as described above, it is also possible that other starches may be used in the coating. In such an instance, it is preferable to keep the proportion of highly crosslinked starch as high as possible, preferably substantially over 50% of the dry weight of the coating mix, more preferably over 80% and ideally over 90%.

The various soluble starch gellants and natural gums used to manufacture separators all appear to decompose during storage. However, the etherified cellulose derivatives appear to be stable in the sedimentation test, and suitable examples for use in the present invention include: Tylose MH200K (Trademark of Hoechst), Tylose MH50, Culminal MHPC100 (Trademark of Aqualon) and Courtaulds DP 1209.

Etherified cellulose derivatives may be any that are suitable, by which is meant that the compound should swell and gel substantially immediately and remain stable in the presence of water, at least during the duration of the sedimentation tests described above.

Suitable examples of etherified celluloses include methyl cellulose, ethyl cellulose, hydroxymethyl cellulose, carboxymethyl cellulose (including salts, such as the sodium salt), hydroxyethyl cellulose, ethylhydroxyethyl cellulose, methylhydroxyethyl cellulose, 2-hydroxypropyl cellulose, methylhydroxypropyl cellulose and 2-hydroxypropylmethyl cellulose.

We have also established that viscosity is an important factor. If the separator mix is outside certain viscosity limits, typically in the region of 3000 to 70000 cP (3 to 7.0 Pa.s), undesirable results and poor cells are usually obtained. Below 3000 cP (3 Pa.s), the mix is often so liquid that it soaks straight into the paper, which can lead to the tearing of the paper, for example. Above 70000 cP (70 Pa.s),

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the mix is generally too thick to spread on the paper satisfactorily.

Accordingly, it is desirable to provide a mix which falls within the limits defined above, and this is generally possible by using an etherified cellulose derivative having a viscosity of between about 20 cP (0.02 Pa.s) and about 300 cP (0.3 Pa.s). As used herein (unless otherwise specified) the viscosity of a substance is defined in terms of a 2% w/v aqueous solution of that substance at 20°C at a neutral pH. Ideally the viscosity is between 50 and 100 cP (0.05 and 0.1 Pa.s).

The following etherified cellulose derivatives are useful in the present invention and fall into the above category. The number following the name of each gellant is indicative of the viscosity in centipoise of that gellant, as expected by the manufacturer. For example, Hoechst Tylose H 20 has an expected viscosity of 20 cP. The gellants are as follows:

Hydroxyethylcellulose

Hoechst Tylose H 20

Hoechst Tylose H 300

Methylhydroxyethylcellulose

Hoechst Tylose MH 50

Hoechst Tylose MH 200

Hoechst Tylose MH 200K

Hoechst Tylose MH 300

Berol Modocoll E 20

Berol Modocoll E 100

Na Carboxymethylcellulose

Hoechst Tylose C 30

Hoechst Tylose C 300

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Methylhydroxypropylcellulose

Aqualon Culminal MHPC50
Aqualon Culminal MHPC100
Dow Methocel K4M (200)
Courtaulds HPM 100 DS
Courtaulds DP 1208 (100)
Courtaulds DP 1209 (50)

Methylcellulose

Aqualon Culminal MC25 S
Aqualon Culminal MC40
Aqualon Culminal MC60 S
Dow Methocel A4M (200)
Courtaulds MM20P

Particularly preferred combinations for use in preparing the coatings of the present invention comprise or consist of Vulca 90 with Tylose MH200K, Tylose MH50 or Courtaulds DP 1209.

The proportion of highly crosslinked starch to gelling agent (the terms gelling agent and etherified cellulose derivative are used interchangeably herein) may be any that is suitable and recognised in the industry, and the generally preferred range is from 1 : 1 to 100 : 1 by weight, more preferably from about 20 : 1 to 5 : 1, with a ratio of about 10.5 : 1 of starch to gellant being particularly preferred. The coating of the separator comprises the mix of starch and gellant together with water, generally in excess of 50% in order to provide an easily applied coating. The amount of water is not critical, as the coating is applied to the paper separator and then dried before insertion into the can. However, it will be appreciated that the liquid coating generally should not be too thin or too thick to prevent convenient application to the paper (see the above discussion of viscosity).

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A suitable method of application of the coating is to have the paper run between 2 rollers and to allow a thin layer of the separator mix to be attached to the paper. The amount of separator mix on the paper can be controlled by the gap between the rollers.

Drying may be by any suitable means, such as infrared, passage over a steam drum, hot air or oven drying.

The nature of the paper to be used is not critical to the present invention, and may be any that is known in the art for use as a separator. Suitable simplex papers include Enso 80 (Trademark of Enso), Amatfors 57 and Sibille Dalle 64, while suitable duplex papers include PBDE 100 and PBDE 70 (NKK).

We have also found that it is advantageous to employ a polyoxyalkylene nitrogen containing compound as an additive when the cell has an acidic electrolyte, as this can further help to reduce gassing and leakage.

We have found that polyoxyalkylene nitrogen containing compounds generally perform as well as, or better than, any single other additive intended to prevent gassing, leakage or corrosion. In addition, we have also found that performance is often enhanced.

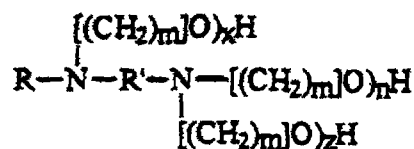
The most useful such additives seem to be polyoxyethylene nitrogen containing compounds, especially the polyoxyethylene amines. A particularly preferred additive is Crodamet C20, which is a monoamine having two polyoxyethylene side chains, the number of oxyethylene units being 20 moles per mole of Crodamet C20.

Suitable formulae for the additives are as shown below:

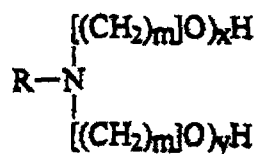
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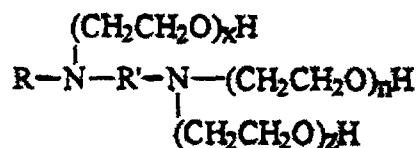
10



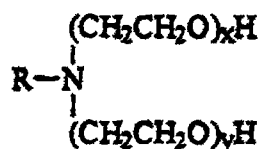
and



[wherein R represents an optionally substituted alkyl group having from 1 to 30 carbon atoms, R' represents an alkyl group having from 2 to 10 carbon atoms, each m is the same or different and represents an integer from 1 to 4 inclusive, and n, x, y, and z are the same or different, and each represents an integer between 1 and 30]. More preferred are compounds having the following formulae:



and



Particularly preferred compounds are those wherein R has an average of around 10 carbon atoms, R' has 3 or 4 carbon atoms, each m is 2 and n, x, y and z each averages about 10. The optional substituents are as noted above, but there are preferably no substituents.

The additives may be added at any stage during the preparation of the electrochemical cell. There is no particularly preferred method of addition to the cells of the invention, provided that the additives are able to dissolve in the electrolyte.

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The additives can be added to the cell by coating a dilute aqueous solution of the additive on the inside of the can. The solvent is then allowed to dry out leaving a coated can. However, this method is not generally industrially practicable.

The cells with which the additives can be used typically have a cathode made of manganese dioxide and acetylene black, the manganese dioxide being in finely divided form and mixed with acetylene black before mixing with the electrolyte, as is well known in the art. Thus, it is convenient to incorporate the additive with the dry components of the cathode, or to introduce it together with the electrolyte. Preferred quantities of additive are typically in a proportion of about 0.01 to 2% w/w (additive/mix), preferably about 0.04 to 1%, and most preferably 0.1%.

We prefer to introduce the additive into the separator coating. To do this, it is generally necessary to add the additive and the gellant to the water before adding starch in order to provide the least complications with regard to uneven distribution. The coating can then be applied to the paper as described above, and the resulting separator is then ready for use in an electrochemical cell. A suitable amount of the additive of the present invention to incorporate into an electrochemical cell will be readily apparent to a man skilled in the art. However, a suitable amount to add to the separator, for example, is, with respect to the dry coating weight of the coating, from 0.1 to 10%, more preferably from 0.5 to 5% and especially about 1.5%. It will be appreciated that this method is preferable to incorporation of the additive into the cathode mix, as it uses less additive.

Typical cells in which the separators of the present invention can be used include primary and secondary zinc carbon cells, including those cells known as Leclanché and zinc chloride cells. The electrolyte in such cells is typically as follows: Leclanché electrolyte - 5-20% zinc

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chloride, 30-40% ammonium chloride, remainder water; zinc chloride electrolyte - 15-35% zinc chloride, 0-10% ammonium chloride, the remainder water. Some other suitable cells for use in the present invention are described in Chapter 5 of the Handbook of Batteries and Fuel Cells (edited by David Linden, published by McGraw Hill).

The cells in which the separators of the present invention can be used may also be of any suitable configuration, such as round, square or flat. Thus, in addition to the aspects described above, the present invention also provides a cell comprising a separator of the invention, optionally together with a compound as described above when the cell contains an acidic electrolyte.

The present invention further provides a sedimentation test as described above, but it will be understood that the concentration of zinc chloride may be adjusted as appropriate, and that any constituent of the separator coating may be tested, as desired.

The present invention further provides a Low Drain Continuous Test for an electrochemical cell characterised in that the can is sealed but left uncovered, a high resistance is secured between the poles of the cell so as to complete a circuit, and the cell is monitored as to its condition.

It will be understood that, in this test, monitoring the cell is intended to ascertain whether the cell fails during testing. The typical lifetime of a D-size zinc carbon cell is up to about 10 weeks when the resistance is about 300 Ω . Other resistances may be used as appropriate, although 300 Ω provides useful results. An appropriate resistance for a C-size cell is about 500 Ω while, for an AA-size cell it is about 810 Ω . The omission of the bottom cover and the over tube is to expose the can to a surrounding atmosphere, thereby enhancing any failure that might occur, which is one

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reason why this test can be performed in 10 weeks, when it might take 2 years in a clock, for example.

The present invention further provides a High Drain Continuous Test for an electrochemical cell, the cell being preferably fitted with a bottom cover, a low resistance being secured between the top cover and a point on the can wall proximal to the top cover and, thereafter, sliding an overtube onto the can so as to cover substantially as much of the can as possible without dislodging the resistance, weighing the resulting assembly, storing the cell at ambient temperature, preferably 20°C, weighing the cell at intervals during storage if desired, and determining the amount of electrolyte lost during storage by weighing to establish leakage. This last weighing may be effected by removing and weighing the over tube after storage or weighing the cell without the over tube but with the resistance, or both. Addition of the bottom cover during this test is particularly advantageous in preventing corrosion at the bottom of the can during the test.

A suitable resistance for this test for a D-size cell is 3.9 Ω and about 5 Ω for an AA-size cell, and the test is typically carried out for 4 weeks, testing at weekly intervals. The normal discharge life for a D cell is about 6 hours in this test until the cell becomes useless. Testing for 4 weeks, for example, establishes how the cell stands up to abuse conditions.

The present invention will now be illustrated with respect to the accompanying Examples wherein percentages are by weight, unless otherwise specified. The Test Examples are followed by certain Test Protocols appropriate to the Test Examples or which are not known in the art. Unless otherwise stated, the zinc cans used in the present examples typically comprise 0.4% lead and 0.03% manganese and have a wall thickness of 0.46 ± 0.03 mm. The mix for the cathode typically comprises 52% manganese dioxide, 0.4% zinc oxide,

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6% acetylene black and 41.6% zinc chloride solution (26.5% zinc chloride w/v). Otherwise, cells are generally manufactured in accordance with EP-A-303737.

EXAMPLE 1**SEDIMENTATION TEST**

The test was performed by mixing 1 g of test material with 100 ml of 26% or 46.5% zinc chloride solution and allowing the mixture to stand in a closed measuring cylinder at 45°C. The mixture was observed over 13 weeks, and the results are shown in Table 1 below. The results show the % swelling of the test material at 2, 6 and 13 weeks (2w, 6w and 13w).

Table 1

	26% ZnCl ₂				46.5% ZnCl ₂			
	Initial	2w	6w	13w	Initial	2w	6w	13w
Stable Class 1 Highly Cross Linked Corn Starch								
National Vulca 90	5%	5%	6%	6%	5%	5%	7%	7%
Nippon Starch Refining Celex	4%	6%	7%	7%	5%	19%	20%	24%
Roquette	2%	2%	2%	2%	5%	7%	7%	7%
Stable Class 1 Highly Cross Linked Potato Starch								
Roquette Vector R140	5%	5%	7%	7%	5%	5%	7%	7%
Roquette Vector R120	5%	6%	14%	14%	6%	7%	14%	14%
Unstable Class 2 Highly Cross Linked Corn Starch								
Nippon Starch Refining Rongum CE3	15%	25%	28%	29%	22%	38%	42%	46%
National Cleargel	10%	15%	18%	18%	24%	40%	80%	26%
Stable Class 3 PVP Adhesive								
ISP PVP K120	100%	10%	100%	100%	100%	100%	100%	100%
Stable Class 3 Methyl Cellulose Ether Gellant								
Hoechst Tylose MH200K	100%	100%	100%	100%	100%	100%	100%	100%
Hoechst Tylose MH50	100%	100%	100%	100%	100%	100%	100%	100%
Aqualon Culminal MHPC100	100%	100%	100%	100%	100%	100%	100%	100%
Courtaulds 1209	100%	100%	100%	100%	100%	100%	100%	100%
Unstable Class 3 Natural Gum (decomposes during storage)								
Nippon Starch Refining Kiprogon	100%	100%	100%	100%	100%	100%	100%	100%
Unstable Class 3 Soluble Starch Gellant (decomposes during storage)								
National Instant Pureflo	40%	86%	100%	100%	100%	100%	100%	100%

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Key

Class 1: Little or no swelling and small changes with time

Class 2: Some initial gelling and increasing sediment with time

Class 3: Rapid and complete gelling.

Stable: no colour change

Unstable: colour changed with time

ResultsStable Class 1 Highly Cross Linked Corn Starch

Vulca 90

Celex

Roquette 2211

Stable Class 1 Highly Cross Linked Potato Starch

Roquette (Vector R120 or R140)

Unstable Class 2 Corn Starch

Rongum CE3

Cleargel

Stable Class 3 Gellants

Methyl Cellulose Ethers :-

Tylose MH200K

Tylose MH50

Culminal MHPC100

Courtaulds 1209

Polyvinylpyrrolidone

Unstable Class 3 Gellants

Instant Pureflo

Kiproglum

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EXAMPLE 2**Testing Combinations of Starch and Gellant in Low Density and High Density Continuous Tests**

Separators were made up as described in the Test Protocols and were tested on both the LDCT and HDCT tests for 4 weeks (4w) and 7 weeks (7w) respectively. In Table 2, an X indicates the absence of a substance, while the figure associated with each individual ingredient is the % by weight of that ingredient in the dry coating preparation.

Table 2

Separator coating contains components as indicated below.

<u>Stable</u> Class 1 Highly Cross Linked Corn	<u>Stable</u> Class 3 Methyl Cellulose Ether	<u>Stable</u> Class 1 Highly Cross Linked Potato	<u>Unstable</u> Class 2 Moderate Cross Linked Corn	<u>Unstable</u> Class 3 Gum	<u>Unstable</u> Class 3 Soluble Starch	4w HDCT	7w LDCT
Vulca 90 91.3%	Tylose MH200K 8.7%	X	X	X	X	1.6g	21%
Vulca 90 95.0%	X	X	X	Kiprogum 5.0%	X	1.5g	40%
X	Tylose MH200K 8.7%	Vector R120 91.3%	X	X	X	1.9g	80%
Vulca 90 45.7%	Tylose MH200K 8.7%	X	Rongum CE3 45.6%	X	X	1.6g	100%
X	Tylose MH200K 8.7%	X	Rongum CE3 91.3%	X	X	1.5g	100%
Vulca 90 75.1%	X	X	Cleargel 18.8%	X	Instant Pureflo 6.1%	2.0g	90%
X	X	Vector R120 75.1%	Cleargel 18.8%	X	Instant Pureflo 6.1%	2.2g	100%

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From the above Table, it can be seen that it is necessary to provide a highly crosslinked starch as a major component in the dry coating preparation. If starches are used in the coating preparation which are not highly crosslinked, then these should comprise substantially less than 50% of the dry coating preparation.

EXAMPLE 3

Comparison of Different Separators

Separators were made as described, and the results of various tests are shown below in Table 3. The separators (designated as Sep. 1 - 5) were made from:-

Sep. 1.	Stable Class 1 Highly cross-linked corn starch Unstable Class 2 corn starch Unstable Class 3 soluble starch Arysulphonate	Vulca 90 Cleargel Instant Pureflo Na Toluenesulphonate
Sep. 2.	Stable Class 1 Highly cross-linked potato starch Stable Class 3 Methyl Cellulose Ether gellant Tylose Fluoropolyoxyethylene Ether	Vector R120 MH200K Forafac 1110D
Sep. 3	Stable Class 1 Highly cross-linked corn starch Unstable Class 2 corn starch Unstable Class 3 gum gellant Additive free	Celex Rongum CE3 Kiprofum
Sep. 4.	Stable Class 1 Highly cross-linked corn starch Stable Class 3 Methyl Cellulose Ether gellant Tylose Trimethyl Alkyl Ammonium	Vulca 90 MH200K Cetrimide
Sep. 5.	Stable Class 1 Highly cross-linked corn starch Stable Class 3 Methyl Cellulose Ether gellant Tylose Coconut Polyoxyethylene Amine	Vulca 90 MH200K Crodamet C20

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TABLE 3

	HDCT	LDCT	Gassing	Fresh Perf.	Fresh SCA	Performance after 13w/45°C/50% r.h.
Sep. 1	1.9g	60%	231%	100%	6.2A	100%
Sep. 2	2.6g	78%	100%	103%	6.6A	99%
Sep. 3	4.2g	100%	217%	99%	7.0A	106%
Sep. 4	1.4g	30%	140%	99%	5.7A	93%
Sep. 5	1.2g	10%	50%	102%	6.3A	105%

In the above Table, Separator 2 was taken as the standard (100%) in the gassing test, and Separator 1 was taken as the standard (100%) in the performance tests.

It can be seen that, especially in the gassing test, separators of the invention perform better and that the best separator incorporated a polyoxyethylene amine.

EXAMPLE 4Comparison Testing of Combinations of Additives and Coating Compositions

Various additives were tested in combination with various separators coated with various starches and gellants in both the LDCT and the HDCT tests. The results are shown in Table 4.

It can clearly be seen from the results that highly cross-linked starches and methylcellulose ether are preferable as coatings in these tests, while polyoxyethylene amines are preferable to the compounds of the art. The tallow compounds preferably have polyoxyethylene side chains which are at least 10 units long, and preferably at least 40 units long, on average.

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Table 4

Stable Class 1 Highly Cross Linked Corn Starch Stable Class 3 Methyl Cellulose Ether Stable Class 1 Highly Cross Linked Potato Starch Unstable Class 3 Moderate Cross Linked Corn Starch Unstable Class 3 Soluble Starch	Vulca 90 Tylose M1200K	Vulca 90 Cleargel Instant Pureflo	Tylose M1200K Vector R120	Vector R120 Cleargel Instant Pureflo	Tylose M1200K Rengum CE3	
Additive Coated on Can 3w & 5w LBCT						
Fluoroalkyl Polyoxymethylene Ether NONE	3w 5w 100% 40%	3w 5w 58% 100%	3w 5w 92% 100%	3w 5w 100% 100%	3w 5w 100% 100%	AVERAGE 3w 5w 67% 85%
Trimethyl Alkyl Ammonium Aryl Sulphur	0% 7% 0% 47%	60% 70% 30% 70%	0% 30% 100% 100%	100% 100% 80% 100%	100% 100% 100% 100%	68% 88% 53% 69%
Tallow-polyoxymethylene mono-amine x+y=5 Ethylan TT05	0% 40%	60% 100%	0% 100%	90% 100%	100% 100%	63% 79%
Tallow-polyoxymethylene mono-amine x+y=40 Ethylan TT40	0% 10%	80% 100%	0% 100%	100% 100%	100% 100%	75% 83%
Coconut-polyoxymethylene mono-amine x+y=5 Crodamet C5	0% 10%	10% 60%	0% 20%	80% 100%	90% 100%	70% 78%
Coconut-polyoxymethylene mono-amine x+y=20 Crodamet C20	0% 0%	0% 20%	0% 20%	70% 100%	42% 80%	43% 65%
AVERAGE	4% 25%	49% 78%	48% 63%	90% 108%	91% 98%	28% 50%
Additive Coated on Can 4w HBCT						
Fluoroalkyl Polyoxymethylene Ether NONE	4w 2.4	4w 2.4	4w 2.6	4w 2.4	4w 2.8	AVERAGE 4w 2.5
Trimethyl Alkyl Ammonium Aryl Sulphur	2.4 1.8	2.2 2.3	1.8 2.4	2.3 1.8	2.7 3.1	2.4 2.2
Tallow-polyoxymethylene mono-amine x+y=5 Ethylan TT05	2.0 1.8	1.8 1.9	2.4	2.0 2.1	2.2 2.3	2.1 2.3
Tallow-polyoxymethylene mono-amine x+y=40 Ethylan TT40	2.0 1.6	2.2 1.8	1.7	2.0 1.9	2.2 2.4	2.0 1.9
Coconut-polyoxymethylene mono-amine x+y=5 Crodamet C5	1.5 1.9	1.5 2.1	1.7	1.6 2.0	2.2 2.6	1.9 1.8
Coconut-polyoxymethylene mono-amine x+y=20 Crodamet C20						
AVERAGE	1.9	2.1	2.1	2.0	2.6	

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Test Protocols

Preparation of Separators

The first step in the preparation of a separator is to prepare the paste to be used for the coating of the paper. The formulations used in the present Examples were as follows:

Water		64.3%
Organic Additive	(e.g. Crodamet C20)	0.5%
Gellant	(e.g. Tylose MH200K)	3.1%
Starch	(e.g. Vulca 90)	32.1%

Three methods were commonly employed for making up the paste. These were as follows:

Paste Method 1 (Used for the separators of the Examples).

1. Add the organic additive and gellant to water and mix, using a high shear mixer, such as a Silversen type mixer (Silversen Machine Mixer Emulsifier Model L2R, UK).
2. Place the resulting mixture in a paddle mixer, such as a Hobart mixer, add the starch, and mix until a smooth paste is obtained.

Paste Method 2

1. Add the gellant to the water and mix in a paddle mixer, such as a VMI mixer (Rayneri Model R5001, France).
2. Add the starch and continue mixing.
3. Add the organic additive and continue mixing until a smooth paste is obtained.

Paste Method 3

1. Mix the powders together.
2. Add the mixed, dry powders to the water and stir in a paddle mixer.
3. Add organic additive and continue mixing until a smooth paste is formed.

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The end products of these methods are virtually identical, and any method is suitable.

The separator paste is then coated onto the paper. The technique used in the above Examples is to run the coated paper between two rollers set apart by a predetermined distance in order to provide the desired coating weight when dry. The rollers are suitably set so that they run in opposite directions, with the forward roller running fastest. A suitable coating machine is made by Dixons (Dixons Pilot Coating Machine Model 160, UK).

The dry coating weight is measured in gm^{-2} (gsm). Suitable gsm are 40 (for D cells), 30 (for C cells) and 20 (for AA cells).

The coated paper in the above Examples is then dried either by oven-drying at $100-140^{\circ}\text{C}$ and/or by steam drum-drying at $100-150^{\circ}\text{C}$.

HDCT (High Drain Continuous Test)

1. Cell is manufactured as above. The bottom cover is added but no overtube.
2. 3.9Ω resistors are soldered between the cover and the top of the can adjacent the cover. Cells are weighed (w_1)
3. Overtubes are weighed (w_2)
4. The overtube is pushed on cell but NOT spun in. The cell is weighed (w_3).
5. The HDCT cells are stored at 20°C for 4w. The normal discharge life for D on a 3.9Ω test is -6h. 4w represents an abuse test to simulate a consumer leaving equipment switched on.
6. At weekly intervals (1w, 2w, 3w & 4w) 1/4 of the original cells are removed and measurements are taken. The complete discharged cell is weighed (w_4).
7. The overtube is removed and weighed (w_5).

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8. The resulting cell with soldered resistor still intact is weighed (w_6).
9. The HDCT leakage is $w_6 - w_1$.

LDCT (Low Drain Continuous Test)

1. Cell is manufactured as above. For LDCT NO bottom cover is added and NO overtube.
2. 300 Ω resistors are soldered between the cover and the top of the can adjacent the cover.
3. Cells are monitored at weekly intervals up to 10w. This would be the normal lifetime for a D cell on a 300 Ω test. This test is a simulation of a cell being used on a long duration test such as a clock.
4. A failure is when perforation or splitting of the can is observed. This would allow O₂ into the cell causing premature failure when on a long duration test.

SCA Test

The cell is shorted and the current passed is measured on zero (very low) impedance meter. The resulting measurement is the SCA (Short Circuit Current) of the cell.

IEC Discharge Performance Tests

These are Industrial Standard tests which are measured on Fresh cells (1 - 2 weeks at 20°C) and Aged cells (13weeks @ 45°C and 50% r.h.).

Gassing Test

Cells are not fitted with a sealant or closure, allowing gas generated in the cell to escape. Cells are sealed in a glass container fitted with a stopper and a glass tube. The containers are immersed in a water bath at the required temperature. The open end of the glass tube is placed in a water bath and a water-filled graduated gas tube is

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positioned to collect any gas from the tube. The volume of gas generated is measured over 30 days.

Corrosion Test

A container is filled with 25% zinc chloride solution containing 0.01% of a potential inhibitor. Strips of battery zinc alloy are immersed in the solution and the container closed to exclude air. The test specimen is stored at 45°C.

Visual examination of the strip is made at 3-weekly intervals and strips are assessed by 4 criteria:

1. General attack;
2. Small pits (<0.1mm);
3. Large pits (>0.1mm);
4. Uniformity of corrosion.

Each criterion is measured on a scale of 1 (low) to 5 (high). The scores are totalled, and the overall score is the corrosion index (CI). Controls are performed using no potential inhibitors.

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Claims

1. A coated paper separator for electrochemical cells, characterised in that the coating comprises a highly crosslinked starch and an etherified cellulose derivative as a gelling agent.
2. A coated paper separator according to claim 1, wherein both of the starch and the gelling agent are substantially stable over time in the presence of an aqueous zinc chloride solution.
3. A coated paper separator according to claim 1 or 2, wherein the highly crosslinked starch is selected from the group consisting of corn, wheat and potato starches.
4. A coated paper separator according to claim 3, wherein the highly crosslinked starch is corn starch.
5. A coated paper separator according to claim 1 or 2, wherein the highly crosslinked starch is corn starch selected from Vulca 90, Vulca 84, Celex and Lab 2211.
6. A coated paper separator according to claim 1 or 2, wherein the highly crosslinked starch is potato starch selected from Vector R140 and Vector R120.
7. A coated paper separator according to claim 1 or 2, wherein the highly crosslinked starch is Lab 2214 wheat starch.
8. A coated paper separator of any preceding claim, wherein the etherified cellulose derivatives are selected from Tylose MH200K, Tylose MH50, Culminal MHPC100 and Courtaulds DP 1209.
9. A coated paper separator of any preceding claim, wherein a 2% w/v aqueous solution of the coating at 20°C has a viscosity of less than 3000 cP.

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10. A coated paper separator of any preceding claim, wherein a 2% w/v aqueous solution of the etherified cellulose derivative at 20°C has a viscosity of between about 20 and about 300 cP.

11. A coated paper separator of any preceding claim, wherein a 2% w/v aqueous solution of the etherified cellulose derivative at 20°C has a viscosity of between about 50 and 100 cP.

12. A coated paper separator of any preceding claim, wherein the etherified cellulose derivative is selected from:

Hydroxyethylcellulose

Hoechst Tylose H 20

Hoechst Tylose H 300

Methylhydroxyethylcellulose

Hoechst Tylose MH 50

Hoechst Tylose MH 200

Hoechst Tylose MH 200K

Hoechst Tylose MH 300

Berol Modocoll E 20

Berol Modocoll E 100

Na Carboxymethylcellulose

Hoechst Tylose C 30

Hoechst Tylose C 300

Methylhydroxypropylcellulose

Aqualon Culминаl MHPC50

Aqualon Culминаl MHPC100

Dow Methocel K4M (200)

Courtaulds HPM 100 DS

Courtaulds DP 1208 (100)

Courtaulds DP 1209 (50)



* C L M S *

Methylcellulose

Aqualon Culминаl MC25 S

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Aqualon Culminal MC40
Aqualon Culminal MC60 S
Dow Methocel A4M (200) and
Courtaulds MM20P.

13. A coated paper separator of any preceding claim, wherein the coating comprises a combination selected from: Vulca 90 with Tylose MH200K, Vulca 90 with Tylose MH50 and Vulca 90 with Courtaulds DP 1209.

14. A coated paper separator of any preceding claim, wherein the proportion of highly crosslinked starch to gelling agent is from 35 : 35 to 100 : 35 by weight.

15. A coated paper separator according to claim 14, wherein the proportion of highly crosslinked starch to gelling agent is from about 20 : 35 to 5 : 1.

16. A coated paper separator according to claim 14, wherein the proportion of highly crosslinked starch to gelling agent is about 10.5 : 1.

17. A coated paper separator of any preceding claim, wherein the paper is selected from Enso 80, Amatfors 57, Sibille Dalle 64, PDE 100 and PDE 70.

18. A test for a starch or a gelling agent used in the manufacture of separators for electrochemical cells, comprising addition of the starch or gelling agent to an aqueous solution of zinc chloride and observing the condition of the starch or gelling agent over time.

19. A test according to claim 18, wherein the aqueous solution of zinc chloride is at a concentration of 25%.

20. A test according to claim 18, wherein the aqueous solution of zinc chloride is at a concentration of 46%.

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21. A test according to claim 18, 19 or 20, wherein the aqueous solution of zinc chloride is kept at a temperature of 45°C during the test.
22. A test according to any of claims 18 to 21, wherein the duration of the test is 13 weeks.
23. A low drain continuous test for an electrochemical cell characterised in that the can is sealed but left uncovered, a high resistance is secured between the poles of the cell so as to complete a circuit, and the cell is monitored as to its condition.
24. A test according to claim 23, wherein the high resistance is selected from the group consisting of 300 Ω for a D size cell, 500 Ω for a C-size cell and 810 Ω for an AA size cell.
25. A test according to claim 23 or 24, carried out at 20°C.
26. A high drain continuous test for an electrochemical cell, a low resistance being secured between the top cover and a point on the can wall proximal to the top cover and, thereafter, sliding an overtube onto the can so as to cover substantially as much of the can as possible without dislodging the resistance, weighing the resulting assembly, storing the cell at ambient temperature, weighing the cell at intervals during storage if desired, and determining the amount of electrolyte lost during storage by weighing to establish leakage.
27. A test according to claim 26, wherein the cell is fitted with a bottom cover.
28. A test according to claim 26 or 27, wherein the test is performed at 20°C.



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29. A test according to any of claims 26, 27 or 28, wherein the amount of electrolyte lost during storage is determined by a comparison between the weight of the overtube before and after storage.

30. A test according to any of claims 26 to 29, wherein the amount of electrolyte lost during storage is determined by a comparison between the weight of the cell without the overtube before and after storage.

31. A test according to any of claims 26 to 30, wherein the amount of electrolyte lost during storage is determined by a comparison between the weight of the overtube before and after storage and by a comparison between the weight of the cell without the overtube before and after storage.

32. A test according to any of claims 26 to 31, wherein the resistance is selected from the group consisting of 3.9 Ω for a D size cell 5 Ω for an AA size cell.

33. A coating composition for a coated paper separator as defined in any of claims 1 to 17, comprising a mixture of the highly crosslinked starch and the etherified cellulose derivative.

34. An electrochemical cell comprising a separator according to any of claims 1 to 17.

35. An electrochemical cell comprising a separator according to any of claims 1 to 17 and a polyoxyalkylene additive.



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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: H01M 6/06, 6/50	A2	(11) International Publication Number: WO 96/38869 (43) International Publication Date: 5 December 1996 (05.12.96)
(21) International Application Number: PCT/GB96/01318 (22) International Filing Date: 3 June 1996 (03.06.96) (30) Priority Data: 9511205.8 2 June 1995 (02.06.95) GB (71) Applicant (for all designated States except US): EVER READY LIMITED [GB/GB]; Ever Ready House, 93 Burleigh Gardens, Southgate, London N14 5AQ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): RANDELL, Christopher, Fred [GB/GB]; 20 Wolsingham Drive, Newton Hall, Durham DH1 5SP (GB). WHITE, Neal, Charles [GB/GB]; Hilllands, Leazes Lane, Hexham, Northumberland NE46 3AT (GB). (74) Agent: LORD, Hilton, David; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARING patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: SEPARATORS FOR ELECTROCHEMICAL CELLS (57) Abstract The invention provides a coated paper separator for use in an electrochemical cell, wherein A coating comprises a highly crosslinked starch and an etherified cellulose derivative as a gelling agent, such separators being useful to reduce gassing, for example.		