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A METHOD FOR A SEPARATOR FOR CELLS

Tokuniro Takakaki and Yoshiko Tsujino

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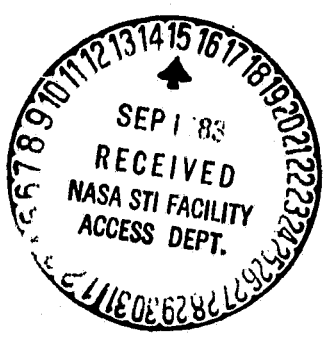

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16. Abstract

The invention presents a method for manufacturing a separator for cells which is characterized by the fact that the spaces or small holes in the porous body are made even smaller, and therefore the porous body is made physically stronger.

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54. A METHOD FOR MANUFACTURING A SEPARATOR FOR CELLS /143*

72. Inventors: Tokuniro (illegible)
Japan Storage Battery Co., Ltd.,
1 Kissho-in Nishinosho
Inoki Baba, Minami-ku, Tokyo

Yoshiko Tsujino
Japan Storage Battery Co., Ltd.,
1 Kissho-in Nishinosho
Inoki Baba, Minamu-ku, Tokyo

71. Applicant: Japan Storage Battery Co., Ltd.
1 Kissho-in Nishinosho
Inoki Baba, Minami-ku, Tokyo

74. Agent: Patent Attorney Akira Suzuki

57. Scope of the Patent Claim

A method for manufacturing a separator for cells which is characterized by the fact that a porous body serving as the separator substrate is impregnated with an emulsion or suspension, which has been prepared by mixing mixture M, which is a mixture of a monomer having one ethylene bond and a monomer having at least 2 polymerizable double bonds, and solvent S at a volume ratio of M/S=1 or less, and then the aforementioned solvent is separated from the porous body after monomer mixture M has been polymerized by irradiation with ultraviolet rays or radiation when crystals (M + S) begin to form inside the aforementioned porous body upon cooling.

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Detailed Explanation of the Invention

The purpose of this invention is to improve conventional separators. The invention presents a method for manufacturing a separator for cells which is characterized by the fact that the spaces or small holes in the porous body having a relatively large hole diameter are made even smaller and therefore, the porous body is made physically stronger.

Heretofore, porous bodies such as (a) cellulose systems impregnated with phenol and formaldehyde resin (b) those made by sintering thermoplastic resin powders, (c) nonwoven cloth made from organic or inorganic fibers, etc. have been used as separators for cells.

Nevertheless, it cannot be said that these separators are suitable from the aspect of properties (particulary, cell life span) because damaging impurities can easily move through the cell when it is being used due to the fact that the hole diameter is relatively large (about 60-30μ or more). Moreover, some of these porous bodies are not really satisfactory from the aspect of physical strength. Consequently, at the present time the desired cell life span is being maintained by increasing the thickness of porous bodies used as separators in the cells.

This invention cancels the aforementioned disadvantages of conventional separators by producing a porous body with suitable spaces or small holes using a liquid (M + S) prepared from monomer M and solvent S. The details of this invention will be explained below with the manufacturing process.

In basic terms, the separator in this invention is made by

1. impregnation of a suitable porous body with a preparation (M + S) made from monomer M and solvent S,
2. configuration of monomer M with crystallization of solvent S inside the spaces or small holes by cooling the porous body,
3. polymerization of monomer M, and
4. removal of solvent S.

Each of the processes will be explained in detail below. /144

1. When the suitable porous body is impregnated with the preparation (M + S) made from monomer M and solvent S, the preparation exists inside the spaces or holes of this porous body.

2. Then, when the porous body is cooled, the preparation within the holes or spaces crystallizes, with solvent S solidifying first. Thereupon, monomer M comes to exist between the capillary-like spaces that are formed between the solvent S crystals. That is, monomer M fills the inside of the spaces or small holes of the porous body with a continuous mesh structure in this crystalline substrate.

3. Monomer M is polymerized with outside ultraviolet ray or radiation irradition of the crystal produced in 2.

4. After polymerization of monomer M, a porous body, or that is, a porous separator, is formed with even finer holes than were formed in the original porous body by washing away the solvent crystals by heating the crystal to a temperature higher than the melting point of solvent S.

The porosity of the substance formed from the spaces and holes of the suitable porous body is equivalent to the amount of solvent S used to form the crystal substrate. However, a change in the hole diameter is not seen even when porosity is increased.

On the other hand, there is a tendency for the hole diameter to be controlled by the hole diameter of the original porous body. In general, when the hole diameter of the original porous body is small, the hole diameter of the porous body formed from the spaces and holes in this original porous body is even smaller. In any case, this porous body is characterized by the fact that its pore diameter is about 30μ or less.

It is essential that the volume ratio of monomer M and solvent S used in this invention be M/S=1 or less in order to obtain a separator for cells with a uniform porosity. It is difficult to improve uniform porosity when the M/S ratio is greater than 1 and therefore, the porous body that is obtained is not suitable as a separator for cells.

A monomer mixture of monomer M having 1 ethylene bond and monomer M_2 having at least 2 polymerizable double bonds can be used as the crude monomer M that forms the porous body in this invention ($M=M_1+M_2$). However, the mixture ratio of M_1 and M_2 (molar ratio) will determine the properties of the copolymer that is produced. In general, a copolymer with good thermoplasticity can be obtained if M_2 has cross linking ability and the M_2 ratio

is high. However, when the M_2 ratio is not very high (M_2/M_1=1 or more), the copolymer that is obtained will be glass-like and easily destroyed.

In order to obtain the desired properties of the separator used for cells, the M_2 ratio should be at least 50% or less, and preferably, 20 molar % or less. The M_2 component provides the copolymer that is obtained with heat resistance. However, only a very small amount of M_2 is necessary. For instance, when 2 molar % or more of M_2 is used, (illegible) never form at high temperatures of 300 °C or more, good (illegible) is displayed, and high stability is obtained.

Acrylic acid or methacrylic acid methyl esters, ethyl esters, n-propyl ester, n-butyl esters, isobutyl esters, n-hexyl esters, and lauryl esters or acrylamide, methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, etc. may be used as monomer M having 1 ethylene bond in this invention. These monomer M_1 may also be used in mixtures. Vinyl chloride, styrol, etc. may also be used in a mixture with the monomers previously mentioned.

Di- esters made from acrylic acid and methacrylic acid, such as ethylene diacrylate, ethylene dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, 1,3-butylene dimethacrylate, etc. may be used as the monomer M_2 having at least 2 polymerizable double bonds used in this invention. Divinyl esters of dicarboxylic acid having olefinic double bonds, such as divinyl maleate, divinyl fumate, etc. may also be used. Moreover, polyvalent olefinic unsaturated carboxylic acid amides, such as di-amines of acrylic acid or methacyrlic acid, may also be used.

It goes without saying that the type of monomer used in this invention and the mixture ratio that is employed in manufacturing the separator should be the most suitable for the purpose for which the separator will be used.

Of course, in this invention it is necessary to select a solvent S that will form a (illegible) and uniform crystal substrate since it is one of the most important factors in determining the micro structure of the separator in this invention. Moreover, it is also preferred that the removal of the solvent after monomer polymerization be a simple process.

As a result of carrying out various tests on (i) separated crystals obtained during cooling, (ii) properties of the copolymer that is obtained, (iii) reaction speed of the monomer, (iv) economics, etc., it was determined that water, glacial acetic acid, tert-butyl alcohol, anhydrous maleic acid, trioxane, etc. are the most suitable for the solvent used to manufacture the separator in this invention.

When water is used as solvent A in this invention, the monomer mixture is actually an emulsion or suspension and a conventional emulsifier is employed to prepare the emulsion or suspension. Anionic, cationic, and nonionic emulsifiers are all suitable. 01-10 wt% emulsifier per total weight of monomer is generally used. However, in special circumstances, the operation may be carried out without an emulsifier. /145

Nonwoven or woven cloth made from polyolefin, polyacrylic, polyester, or polyamide fiber or cellulose and glass fiber, or mixtures of these, may be used as the suitable porous body used to manufacture the separator in this invention. Moreover, the conventional separator used for cells that were mentioned in the first paragraphs may also be used. However, it goes without saying that these porous materials should be selected based on the type of cell in which they will be used.

This invention will now be explained with examples.

The ultraviolet ray polymerization recorded in the examples is intensified light polymerization using a high pressure mercury lamp as the light source. A small amount of light sensitizer is used to start polymerization. Benzoin, butyloin*, benzoin**, methyl ether, bezoin ethyl ether, α-alkyl benzoin, and other polynuclear quinones can be used as the light sensitizer.

A closed polymerization reaction chamber was used in the production of the separator for cells in this invention. The chamber was set up so that after the porous body was placed inside the reaction chamber, the preparation (M + S) could be introduced and cooling and heating could be carried out from the outside of the chamber. Ultraviolet ray irradiation could be carried out through the glass surface. The mixture ratio of the monomer mixture M and solvent S in these examples is expressed with volume ratio (parts).

The hole diameter of the porous body and product of this invention was measured with the mercury pressure method and the tensile strength was measured with the method recorded in JIS C-231.

Example 1

The suitable porous body was (illegible) using polyolefin nonwoven cloth (thickness of 0.3 m/m). A preparation consisting of 20 parts of a monomer mixture (M, M_1:M_2=80:20 molar %) of methyl methacrylate M_1 and ethylene dimethacrylate M_2 and 80 parts glacial acetic acid S containing a small amount of sensitizer (benzoin) was used.

The porous body production preparations (operations) are as recorded below.

The preparation (M + S) was made to impregnate the porous body with an introduction device while the porous body was inside the polymerization reaction chamber. After the polymerization chamber was closed, a crystal was produced by immersing the porous body in a freezing mixture (dry ice and methanol at -78° C). Then the monomer was polymerized by placing the reaction chamber in an atmosphere of - 20±3° C and irradiating ultraviolet rays (high pressure mercury lamp, 400 W) for 30 minutes at a distance of 17 cm.

A comparison of the properties of the porous body that was obtained and the nonwoven cloth before processing is shown in the following table. /146

	hole diameter (μ)	tensile strength $(kg/mm)^2$
polyolefin nonwoven cloth before processing	34	0.25
finished good from Example 1	13	0.45

Example 2

The same operation as in Example 1 was carried out, with the exception that polyester nonwoven cloth (thickness of 0.2 m/m) was used as the suitable porous body and a mixture of 10 parts of a monomer made by adding ethylene dimethacrylate M_2 to a monomer mixture of ethyl acrylate and methyl methacrylate (M_1 molar ratio of 1:1) and 90 parts of glacial acetic acid S containing a small amount of light sensitizer was used as the preparation. A separator for cells was obtained.

A comparison between the properties of the porous body that was obtained and the nonwoven cloth before processing is shown in the following table.

	hole diameter (μ)	tensile strength (kg/mm^2)
polyester nonwoven cloth before processing	more than 60	0.18
finished good from Example 2	21	0.32

Example 3

A finished good was obtained by carrying out the same operation and using the same preparation as in Example 1. The only exception was that a mixed paper (0.1 m/m thick) of cotton linter pulp and polyolefin fibers was used as the suitable porous body.

A comparison of the properties of the porous body that was produced and the mixed paper before processing is shown in the following table.

	hole diameter (μ)	tensile strength (kg/mm^2)
mixed paper beforeprocessing	25	0.35
finished good from Example 3	8	1.60

Example 4

Glass nonwoven cloth (thickness of 0.2 m/m) was used as the suitable porous body. A preparation (M + S) made from 10 parts of a monomer mixture of ethyl methacrylate M_1 and ethylene dimethacrylate M_2 ($M, M_1:M_2$=9.8:2 molar %) and 90 parts glacial acetic acid was made to impregnate the nonwoven cloth, which was placed in the reaction chamber, using an introduction device. A crystal was then produced by immersing the cloth in a freezing mixture (dry ice and methanol, -78° C) after the polymerization reaction chamber had been closed. Then the monomer was polymerized with Co60 irradiation from the outside of the chamber. After the polymerization reaction was finished, the cloth was heated to remove the internal components. Then it was dried after rinsing to obtain the finished good. A comparison between the properties of the porous body that was obtained and the nonwoven cloth before processing is shown in the following table.

	hole diameter (μ)	tensile strength (kg/mm^2)
nonwoven glass cloth before processing	62	0.88
finished good from Example 4	17	210

Example 5

The same operation as in Example 1 was carried out with the exception that sintered polyolefin powder was used as the suitable porous body (thickness of 0.3 m/m) and a mixture of 5 parts of a monomer mixture ($M, M_1:M_2$=90:0 molar %) made by adding ethylene dimethacrylate M_2 to a monomer mixture of ethyl acrylate and methyl methacrylate (M_1, molar ratio of 1:1) and 95 parts of glacial acetic acid S containing a small amount of

light sensitizer was used as the preparation. A comparison of the properties of the porous body that was obtained and the nonwoven cloth before processing is shown in the following table.

	hole diameter (μ)	tensile strength (kg/mm^2)
polyolefin porous body before processing	34	0.25
finished good in Example 5	15	0.35

Example 6

The same operation was carried out using the porous body obtained in Example 5 and the same preparation as used in Example 5.

A comparison of the properties of the porous body that was obtained and the porous body obtained in Example 5 is shown in the following table.

	hole diameter (μ)	tensile strength (kg/mm^2)
finished good from Example 5	15	0.35
finished good from Example 6	5	0.68

As was explained in the previous examples, it is easy to make the spaces or holes of the porous body from this invention even smaller than those of the suitable porous body and to easily improve physical strength with the method for manufacturing the separator in this invention. Moreover, the invention is characterized by the fact that the smaller the holes or spaces in the original porous body, the smaller the holes or spaces in the separator. In addition to forming uniform holes in the direction of the thickness of the porous body that is used, it is also easy to make tiny holes on one side of the separator. However, this would depend on the purpose for which the porous body is finally used. Moreover, a separator with even smaller spaces or fine holes may be produced by repeating the operation recorded in the examples.

This invention is very advantageous from an industrial viewpoint in that both the manufacturing process and properties of the separator are superior in comparison to those of conventional separators and the methods being used to manufacture these separators.