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(54) SULPHUR CROSS-LINKED GRAFT COPOLYMERIC MATERIAL FOR USE AS A SEPARATOR FOR ALKALINE CELLS

(71) We, ESB INTERNATIONAL CORPORATION, a corporation organised under the laws of the State of Delaware, of 2625 Concord Pike, Wilmington, Delaware 19803, U.S.A., 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:—

The present invention relates to a graft copolymerised material suitable for use as a separator in alkaline cells, and process for its production.

Alkaline battery systems such as silver-zinc, mercury-zinc, nickel-cadmium, silver-cadmium, manganese-zinc and mercury-cadmium normally require a separator between the anode and cathode to effect a physical barrier to prevent internal shorting. The separator must be permeable so that ions can travel from one plate to another, have sufficient physical strength to prevent internal shorting, and should not impede the progress of ions migrating through the electrolyte so as to markedly raise the impedance of the cell. The separator material must also be capable of withstanding the chemically hostile environment produced by the combination of the electrolyte (typically a strong caustic such as potassium hydroxide or sodium hydroxide) and oxidation due to strong oxidizers such as divalent silver which is often used as a positive electrode.

Modified polyethylene films have been widely used as separators, usually in the form of a graft copolymerised film, or laminated with Cellophane (Registered Trade Mark). The grafted separator is conventionally a thin film of polyethylene which is exposed to radiation in contact with an ethylenically unsaturated monomer such as methacrylic acid whereby carboxyl groups are grafted to the polyethylene and act as carriers for ionic charge through the separator. The extent of grafting is however limited by the degree of swelling which the film may undergo because of the cross-linking of the polyethylene, and consequently the bulk of the separator tends to be free of grafts. The laminated separators are produced by treating porous polyethylene sheet with methacrylic acid and laminating it between sheets of Cellophane. This is an effective separator, but is brittle and fractures easily, making it difficult to handle and form. In general most polyethylene separators (both with and without Cellophane laminates) are undesirably brittle and resistances of other types of separator is not satisfactory due to oxidation and leads to unduly short shelf-life of the alkaline cell incorporating them.

The present invention is based on the discovery of a material which can be used as a separator for alkaline cells and which is physically tougher than those used hitherto, and which at the same time has good resistance to oxidation in the cell.

According to the present invention a material suitable for use as a separator for alkaline cells comprises a polyolefin having grafted side chains derived from ethylenically unsaturated ionogenic monomers and which is cross-linked by sulphur. The material is prepared by fusing together a substantially uniform mixture of sulphur and a quantity of a finely divided polyolefin having grafted side chains derived from ethylenically unsaturated ionogenic monomers, and exposing the fused blend to ultraviolet light to enhance cross-linking. The cross-linked grafted polyolefin can be shaped by conventional processes.

Suitable polyolefins include polyethylene, polypropylene and polybutene, of which polyethylene and polypropylene are preferred. Although both high density and low density polyethylene can be used, it has been found that low density polyethylene reacts more completely and hence is the more preferred. By "low density" is meant, polyethylene exhibiting a density of less than 0.92 g/cm^3.

The polyolefin should be finely divided. By "finely divided" is meant a polyolefin having particles which have an average diameter of from 5 to 50 microns. Preferably, the diameter of these particles will range from 15 to 25 microns.

The side chains grafted to the polyolefin are derived from ethylenically ionogenic monomers. Suitable monomers include sodium styrene sulphonate, sodium vinyl sulphonate, crotonic acid, methacrylic acid, acrylic acid, vinyl pyridine, vinyl benzylchloride and vinyl pyrrolidine. The preferred monomers are acrylic acid and methacrylic acid, most preferably methacrylic acid which produces a graft polymer containing carboxyl groups.

The sulphur used to cross-link the grafted polyolefin during exposure to ultraviolet light while fusing is a purified sulphur such as flowers of sulphur, recovered sulphur or sublimed sulphur normally in an amount ranging from 2 to 20% by weight of the grafted polyolefin. The preferred range is 10 to 20% sulphur by weight of the grafted polyolefin, preferably about 15%.

In order to produce the grafted polyolefin, the polyolefin must be treated to prepare sites suitable for grafting. Conventional treatments include the use of gamma radiation, Van de Graaf radiation, ultraviolet radiation and ozonizing of the polyolefin film.

In a preferred embodiment and as more fully set forth in our U.S. Patent 4131637 the finely divided polyolefin is ozonized by maintaining it in a fluidised bed.

In that process, a small amount (at least 0.1% by weight) of powdered silica is added to achieve fluidity and to prevent agglomeration of the polyolefin particles. The use of 0.5 to 5% silica, especially fumed silica, is preferred, preferably about 0.5%. At this level the silica provides the necessary fluidity without substantially entering into the reactions during ozonization or in subsequent processing.

The fluidising bed is maintained in a state of constant agitation to assist in the process. Ozone is introduced into the inflowing gas so as to pass through the fluidised material and come into intimate contact with the finely divided polyolefin. The silica polyolefin is activated by the ozone. By "activated" is meant, the preparation of the polyolefin for subsequent grafting wherein incipient labile sites are produced at various points along the chain-like molecules of the polyolefin.

When low density polyethylene is utilised, the ozonization is continued until the amount of ozone absorbed is approximately 500 to 600 (preferably 540) milligrams of ozone per 100 grams of polyethylene. The degree of ozonization is commonly measured by the Iodometric determination of the peroxide value of the polyethylene. In this process, the peroxide values may range from 20 to 60 mole peroxide per kilogram of polyethylene. The preferred values for use in this invention are from 30 to 40 mole per kilogram, preferably about 38 mole per kilogram.

One way to achieve ozonization while maintaining the polyolefin in a fluidised bed comprises placing the finely divided polyolefin in a vessel having a diffuser at its bottom and forcing a carrier gas such as air upwardly through the diffuser and through the body of the finely divided polyolefin so as to maintain the polyolefin in a fluidised state and to ensure the even distribution of activated sites through the polyolefin. The activated polyolefin may then react with the ethylenically unsaturated ionogenic monomer. This polymerisation may be carried out by loading the activated polyolefin material into an appropriate container with an aqueous solution of the monomer and then refluxing. The activated polyolefin reacts with the ethylenically unsaturated inogenic monomer to produce a graft polymer in which groups from the monomer are attached to the previously prepared labile sites.

By using activated low density polyethylene having a peroxide value from 20 to 60 and by varying the ratio of methacrylic acid to activated polyolefin, the resulting level of graft polymerisation is from 30 to 440% by weight.

The grafted polyolefin may be converted into its salt form by reacting it with alkaline compounds such as alkaline metal oxides and hydroxides, alkaline earth oxides and hydroxides, amines and amine hydroxides. The preferred are alkali metal and ammonium hydroxides, preferably potassium hydroxide. After conversion to the salt form, the grafted polyolefin may be washed and dried to form a finely divided powder. This may be formed into films and used as a separator for alkaline cells without further treatment, but we have found that the properties of such a separator can be vastly enhanced through the addition of sulphur and exposure to ultraviolet light during fusing.

According to one aspect of the present invention the dried grafted polyolefin is applied to the rolls of a two-roll rubber mill, the rolls being heated to a temperature in excess of the melting point of the polyolefin. As the polyolefin is added to the mill, a fused mass begins to build up on and between the rolls to which powdered sulphur is added slowly. While the portions of sulphur may be varied as described above, a preferred ratio is approximately 10 parts polyolefin to 1 part sulphur.

A small amount of powder polytetrafluoroethylene (PTFE) can be added to the mix in approximate proportion of 10 parts sulphur to 1 part PTFE by weight, but this is not essential. Further operation of the mill thoroughly distributes the powdered sulphur throughout the volume of the polyolefin and further sinters and fibulates the PTFE. This causes proliferation of long intertwined strands of PTFE oriented randomly throughout the mixture. While the PTFE is not believed to affect the chemical or electrochemical properties of the resulting material, it does provide a fibrous matrix which lends additional strength and resiliency to the material.

After the complete mixing of the sulphur and the grafted polyolefin, the mix is exposed to ultraviolet light normally for from 1 minute to 30 minutes. The preferred exposure time is within the range from 3 to 10 minutes, preferably 4 to 6 minutes. It has been found that beyond the 30 minutes time of exposure to ultraviolet light, the polyolefin becomes degraded.

In one embodiment of the invention the exposure to ultraviolet light is accomplished by mounting a 1200 watt ultraviolet lamp approximately 76.2 mm from the surface of one of the moving mill rolls with the mill adjusted to produce a band having a thickness of approximately 0.152 mm. The bulk of the fused material is repeatedly fed around the rolls. As the material passes through the roll nip a new band is created such that the bulk of the mix continually present a new surface to the ultraviolet light. Ultimately the eitre volume of the material is exposed to ultraviolet light.

When the bulk of the mix has been exposed to the desired degree of ultraviolet light, the lamp is turned off, removed from the mill roll area and the mill readjusted to produce a film of the desired thickness.

Other processes for mixing and exposing the material to ultraviolet light include the use of a Banbury mixer and having the ultraviolet light exposure on the holding mill, or using a mixer extruder in which the extruder film is exposed to ultraviolet light during calendaring. Preferably, the films of the grafted polyolefin will range from 50.8 to 381 μm thickness. However, thicker films can also be produced. The preferred thickness for use as a separator in a battery is 101.6 to 254 μm. After cooling the film may be soaked in an alkaline wash, preferably a potassium hydroxide wash, for several hours and subsequently dried.

The material of this invention when formed into a film exhibits markedly improved physical properties. In particular, it is an extremely tough resilient material and the electrical and chemical characteristics of the film make it particularly suitable for use as a cell separator. The resistivity of the material is low, being in the range of approximately 20 ohms per centimeter.

Using the process of this invention, a wide variation of sulphur cross-linked grafted polyolefin, ultraviolet treated films have been formed. Grafted polyolefins having ozonization peroxide values of from 20 to 60 were subsequently treated with methacrylic acid to produce grafts ranging from 30 to 440%. They were blended and cross-linked with sulphur in amounts ranging from 2 to 20% by weight. Films have been formed of these materials. Based on the test results which are shown in the Examples, the material which is most preferred as a separator has the following characteristics.

Ozonization Peroxide value — 38
Methacrylic Acid Graft — 175%
Sulphur — 15%
Ultraviolet exposure time — 5 minutes
Film thickness — 101.6 to 177.8 μm
Potassium hydroxide 40% solution

The shelf life of alkaline cells having separators made from the above preferred material improves two fold, particularly when stored at elevated temperatures. The shelf life of cells employing this new material was substantially greater than commercially available material used in controlled cells designated RAI in Table 2. Moreover separators made by a similar process but without sulphur or ultraviolet light exposure exhibit a substantially shorter shelf life than those in which sulphur and ultraviolet light exposure was used. This material is particularly useful as a separator in alkaline cells in which the positive electrode is monovalent or divalent silver oxide, and the negative electrode is zinc. The electrolyte is an alkali metal hydroxide, preferably NaOH or KOH. Some examples will now be given.

Example 1.

Material for a cell separator was prepared by placing low density polyethylene powder (Microthene FN-500 sold by U.S.I. Corp.) having a particle size of approximately 20 μ in a container having an air-diffuser lower surface. $\frac{1}{2}$% by weight of fumed silica powder [Cab—O—Sil (Trade Mark) sold by Cabot Corp.] was added. Ozone was passed through the fluidised polyethylene-silica until the amount of ozone absorbed was about 540 mg. ozone per 100 g of low density polyethylene. This amount of absorption has a peroxide value of 38, measured by the Iodometric method. From the above blend 280 g. of ozonized polyethylene was mixed with 4.31 of deionised water and 480 g of methacrylic acid. The mixture was heated to reflux temperature, and maintained at reflux, with stirring, for four hours. The reaction mixture was cooled and the precipitate was washed and then converted to the salt form in a mixture of 720 g of 45% KOH and 4 litres of methanol. Based on the neutralisation equivalent the product was 175% graft in the potassium salt form. The product was filtered and dried preparatory to being processed into film.

A pre-heated two-roll mill was prepared to receive 80 g of the powder product, heated on the mill to the molten state, and then 8 g sublimed sulphur (10% based on weight of powder) slowly added to the kneeling nip of the mill. To the mixing mass 0.88 PTFE [DuPont 6A powdered Teflon (Trade Mark)] was added. A 1200 W (Ge Mercury Arc lamp, model 9TO4—40170), was disposed approximately 3 inches from the turning roll, and parallel to the roll axis. The molten mix on the roll was allowed to repeatedly pass beneath the ultraviolet lamp for 5 minutes. The lamp was then turned off, the nip of the mill rolls closed and a 0.51 mm thick film fed from the mill. The film was laid on a flat surface, and allowed to cool. Subsequently, the films were soaked in 40% aqueous solution of KOH for six hours, then dried. The important values are summarised below:

Ozone — Peroxide Value 38
Methacrylic Acid Grafted 175%
Sulphur Added 10%
U.V. Light Exposure: 5 min.

Example 2.

16 separators were prepared as in Example 1 but varying either in the peroxide value, methacrylic acid graft, amount of sulphur added or duration of ultraviolet light exposure.

Table 1 summarises these variations.

TABLE 1

Separator No.	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ozone-peroxide value	20	20	20	20	20	20	20	20	50	50	50	50	50	50	50	50
Methacrylic Acid Graft %	150	150	150	150	200	200	200	200	150	150	150	150	200	200	200	200
Sulphur Added %	10	10	15	15	10	10	15	15	10	10	15	15	10	10	15	15
UV Light Exposure min	5	10	5	10	5	10	5	10	5	10	5	10	5	10	5	10

The 16 separators were evaluated in tests in Ray-O-Vac type RW 44 silver-zinc button cells and cells using RAI-2192 separators were used as controls. Prior to incorporation into the RW-44 cells, specific resistivity in ohms-cm was measured for each example and control.

Specific resistivity was measured by the method, "Electrical Resistance Alternating Current Method," as detailed in "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries," edited by J. E. Cooper Air Force, Aero Propulsion Laboratory, Wright-Patterson AFB Ohio and Arthur Fleischer, Consultant Electrochemistry and Chemical Technology, AD-447301, 1970.

Initial capacity is the capacity of a freshly built cell given in milliampere hours. Cells were allowed to stand at least overnight before testing.

The data reports results at 300 ohm and 625 ohm constant load for 16 hours per day.

The delayed data was obtained at either 300 ohm or 625 ohm load discharge for 16 hours per day after storage at 54.4°C, 50% relatively humidity for four, eight and twelve weeks respectively. High temperatures were used to accelerate life testing, and shorten test programmes. The capacity retention was derived by dividing the capacity after stated periods of time by the original capacity of the fresh cell and multiplying by 100.

Shelf life data is reported as a ratio of number of cells failing, to number of cells tested at 54.4°C and 71.1°C. A cell was considered to have failed when the voltage indicated less than 0.9 volts. The results obtained are shown in Table 2.

The data in Table 2 demonstrates that the cells using the separator of this invention show superior rate capability at both the 300 ohms and 625 ohm discharge tests. For example, use of separator gives cells with a capacity of 137 mAh after 12 weeks storage at 54.4°C 50% relative humidity as compared to 61 mAh for the commercially available material. This represents a capacity retention, in terms of the original capacity of 100% as compared to 56% for the commercial material. In terms of shelf life data, cells with separators 2, 3, 4, 5 and 13 show no failures after 4 weeks at 71.1°C whereas one sample of commercial material shows 4 out of 6 cells failed at this temperature. This data then reflects the overall superior performance of cells using the separator made from the composition of this invention compared to commercially available separators.

TABLE 2

	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	RAI	
Specific Resistivity (Ω/cm)	73	61	52	86	23	27	24	26	22	22	26	23	20	22	21	25	20	20
Initial Capacity																		
300ΩmAh	117	127	110	114	135	147	140	136	128	147	155	136	129	121	112	110	79	108
625Ω	158	152	151	146	166	169	168	166	158	168	162	163	148	162	151	147	143	143
Delayed mAh																		
300Ω																		
4 weeks					151	150	144	145	137	140	139	149	116	146	136	134		99
8 weeks					147	147	146	130	131	126	132	134	132	90	108	106		78
12 weeks					137	143	134	113	103	118	122	116	—	—	—	—		61
625Ω																		
4 weeks	147	149	135	125	—	—	—	—	—	—	—	—	—	—	—	—	105	
8 weeks	112	138	125	107	—	—	—	—	—	—	—	—	—	—	—	—	60	
12 weeks	121	116	98	92	—	—	—	—	—	—	—	—	—	—	—	—	54	
% Capacity Retention																		
4 weeks	93	98	89	86	100	100	100	100	100	95	90	100	78	90	90	91.1	73	92
8 weeks	90	91	83	73	100	100	100	96	100	86	85	98	89	56	71	72	42	72
12 weeks	77	76	65	63	100	97	96	83	805	80	79	85	—	—	—	—	38	56
Shelf life																		
54.4°C 50% Rel. Hum.																		
4 weeks	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12	0/12
8 weeks	1/9	0/9	0/9	0/9	0/9	0/9	0/9	0/9	0/9	0/9	0/9	0/9	4/9	6/9	4/9	4/9	0/9	0/9
12 weeks	2/6	0/6	0/6	0/6	0/6	0/6	0/6	1/6	0/6	1/6	0/6	0/6	6/6	5/6	5/6	6/6	0/6	0/6
71.1°C																		
1 week	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6	0/6
2 weeks	0/6	0/6	0/6	0/6	0/6	1/6	1/6	0/6	0/6	1/6	0/6	0/6	0/6	1/6	0/6	0/6	0/6	0/6
3 weeks	0/6	0/6	0/6	0/6	0/6	1/6	2/6	0/6	0/6	1/6	0/6	0/6	4/6	6/6	5/6	0/6	0/6	0/6
4 weeks	0/6	0/6	0/6	0/6	5/6	4/6	3/6	2/6	3/6	4/6	4/6	0/6	6/6	6/6	3/6	5/6	0/6	4/6
Room Temperature 3 months	0/6	0/6	0/6	0/6	0/7	0/7	0/7	0/7	0/7	0/7	0/7	0/7	0/6	0/6	0/6	0/6	0/6	0/6

WHAT WE CLAIM IS:—

1. A material suitable for use as a separator for alkaline cells comprising a polyolefin having grafted side chains derived from ethylenically unsaturated ionogenic monomers and cross-linked by sulphur.

2. A material as claimed in claim 1 in which the polyolefin is polyethylene, polypropylene or polybutene.

3. A material as claimed in claim 1 or 2 in which the ethylenically unsaturated ionogenic monomer is sodium styrene sulphonate, sodium vinyl sulphonate, crotonic acid, methacrylic acid, acrylic acid, vinyl pyridine, vinyl benzchloride or vinyl pyrrolidine.

4. A material as claimed in any preceding claim in which the ethylenically unsaturated ionogenic monomer is methacrylic acid and the olefin is polyethylene.

5. A process for making a material as claimed in claim 1 comprising fusing together a substantially uniform mixture of sulphur and a quantity of finely divided polyolefin having grafted side chains derived from ethylenically unsaturated ionogenic monomers and exposing the fused blend to ultraviolet light to enhance the cross linking.

6. A process as claimed in claim 5 in which the polyolefin is polyethylene, polypropylene or polybutene.

7. A process as claimed in claim 6 in which the ethylenically unsaturated ionogenic monomer is sodium styrene sulphonate, sodium vinyl sulphonate, crotonic acid, methacrylic acid, acrylic acid, vinyl pyridine, vinyl benzylchloride or vinyl pyrrolidine.

8. A process as claimed in any one of claims 5 to 7 in which the sulphur added is in the range from 2 to 20% by weight of the grafted polyolefin.

9. A process as claimed in claim 8 in which the range is 10 to 20%.

10. A process as claimed in any one of claims 5 to 9 in which the fused blend is exposed to ultraviolet light for 1 minute to 30 minutes.

11. A process as claimed in claim 10 in which the exposure to ultraviolet light is for 3 to 10 minutes.

12. A process as claimed in any one of claims 5 to 11 in which the grafted polyolefin is prepared by suspending and agitating a quantity of polyethylene of particle size 5 to 50 μm with 0.5 to 5% by weight of fumed silica in a fluidised bed and introducing ozone into the bed until 500 to 600 mg of ozone per 100 gm of polyethylene has been absorbed, and reacting the ozonated polyethylene with methacrylic acid until the graft polymerisation is from 30 to 440% by weight of polyethylene.

13. A separator for an alkaline cell when prepared by a process as claimed in any one of claims 5 to 12.

14. A separator for an alkaline cell when prepared from a material as claimed in any one of claims 1to 4.

15. A separator for an alkaline cell as claimed in claim 13 substantially as hereinbefore described having reference to any one of the Examples.

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