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Imamoto et al.

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(54) **ELECTRICITY STORAGE DEVICE**
CLADDING

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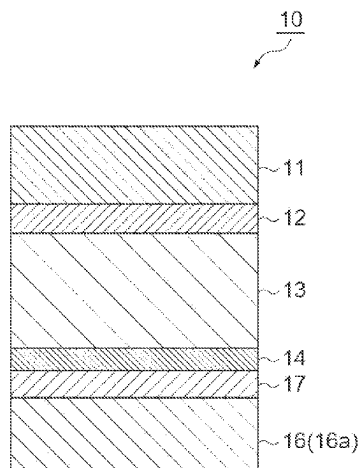
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(57) **ABSTRACT**

A packaging material for a power storage device, comprising
at least: a substrate layer; a metallic foil layer with an
anti-corrosion treatment layer being disposed on one face or
both faces thereof; and a sealant layer in this order, wherein
a sealant layer includes a resin layer containing a polypro-
pylene-based resin (A) and an incompatible component (B)
incompatible with a polypropylene-based resin (A), and as
for loss tangent $\tan \delta$ obtained by dynamic viscoelasticity
measurement at a frequency of 1.0 Hz, the sealant layer has
a maximal value of $\tan \delta$ at -30 to 30° C., and in addition,
a ratio (II/I) of the maximal value (II) of $\tan \delta$ at -30 to 30°
C. to a value (I) of $\tan \delta$ at -50° C. is 2.50 or more.

9 Claims, 8 Drawing Sheets



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H01M 50/145 (2021.01)
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B23B 15/085; H01G 11/78; C23C 22/07
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Fig. 1

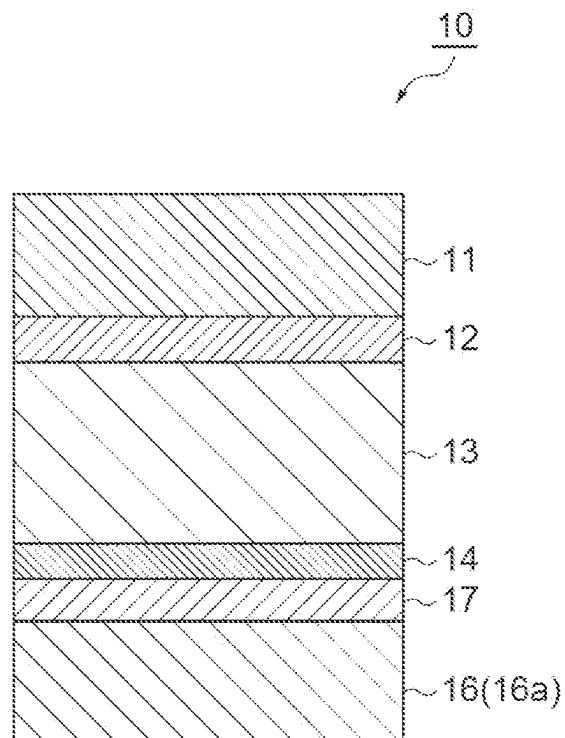


Fig. 2

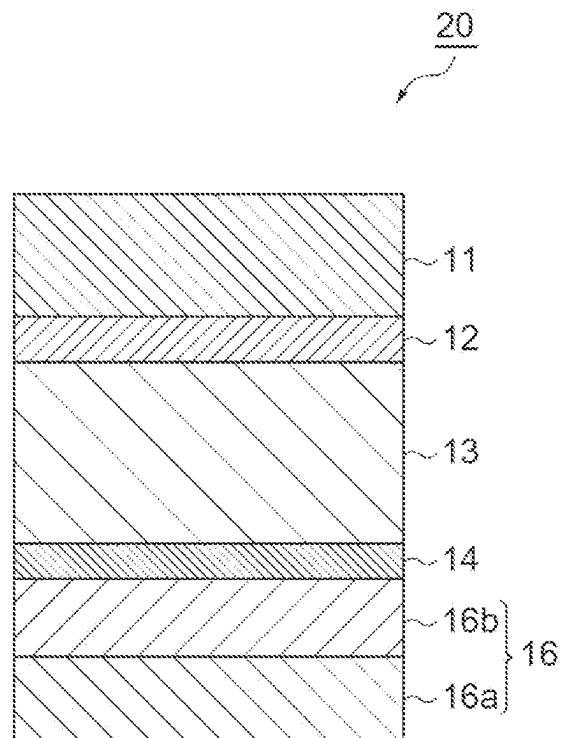


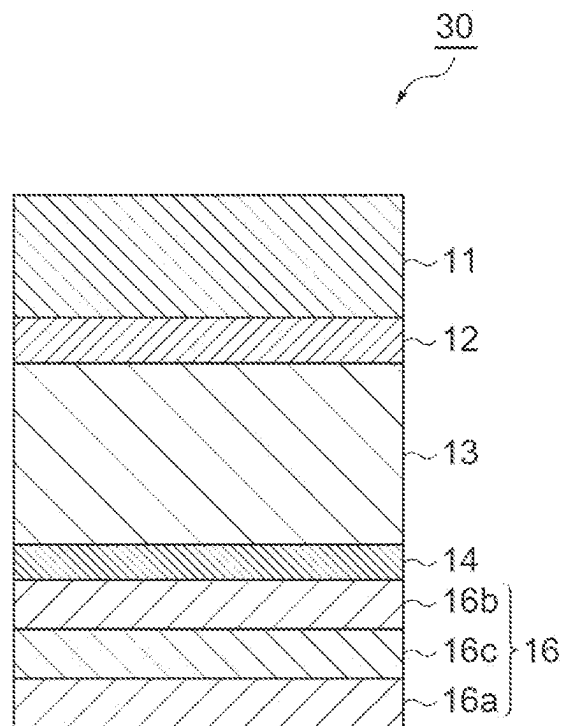
Fig. 3

Fig. 4

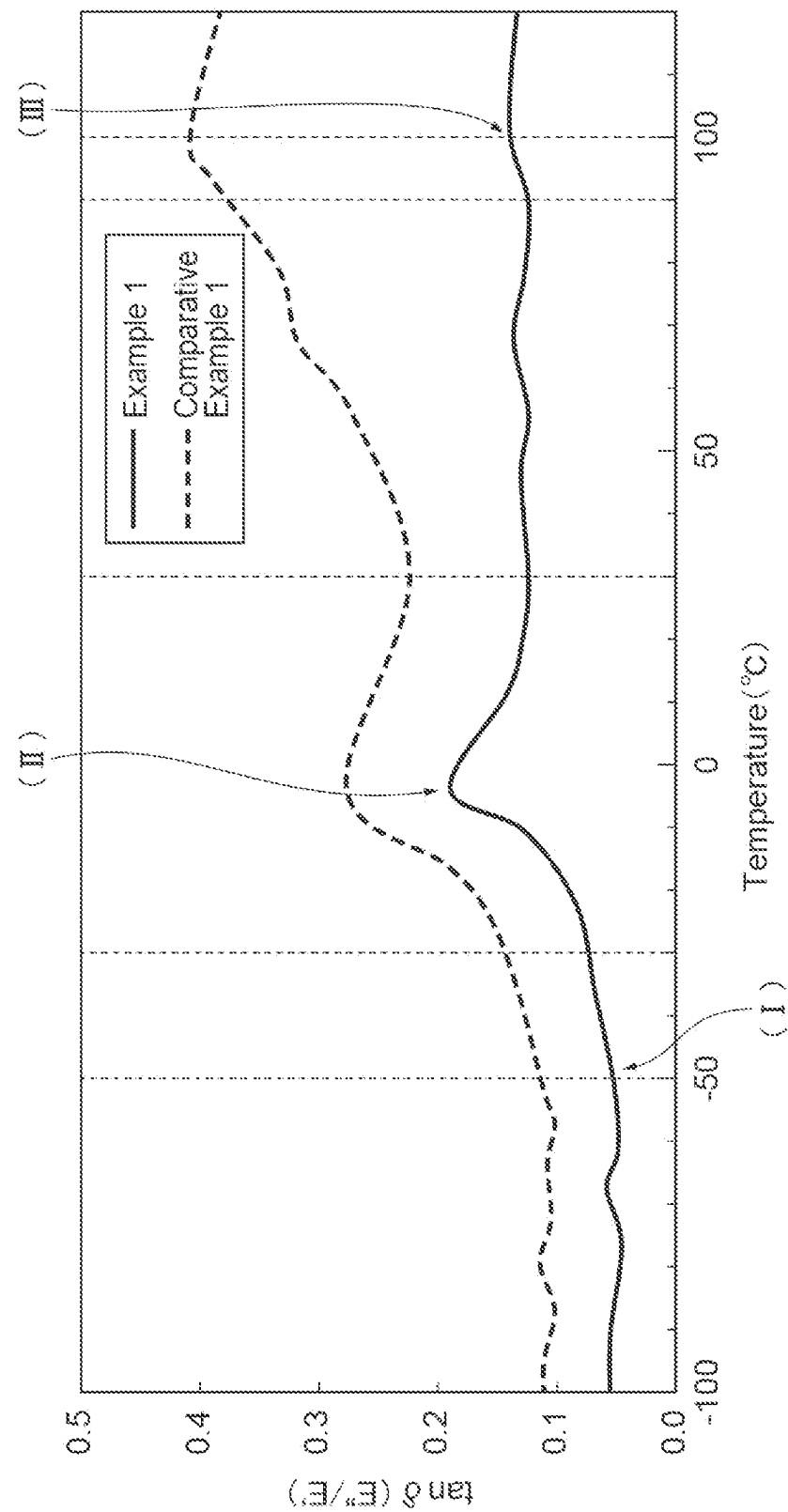


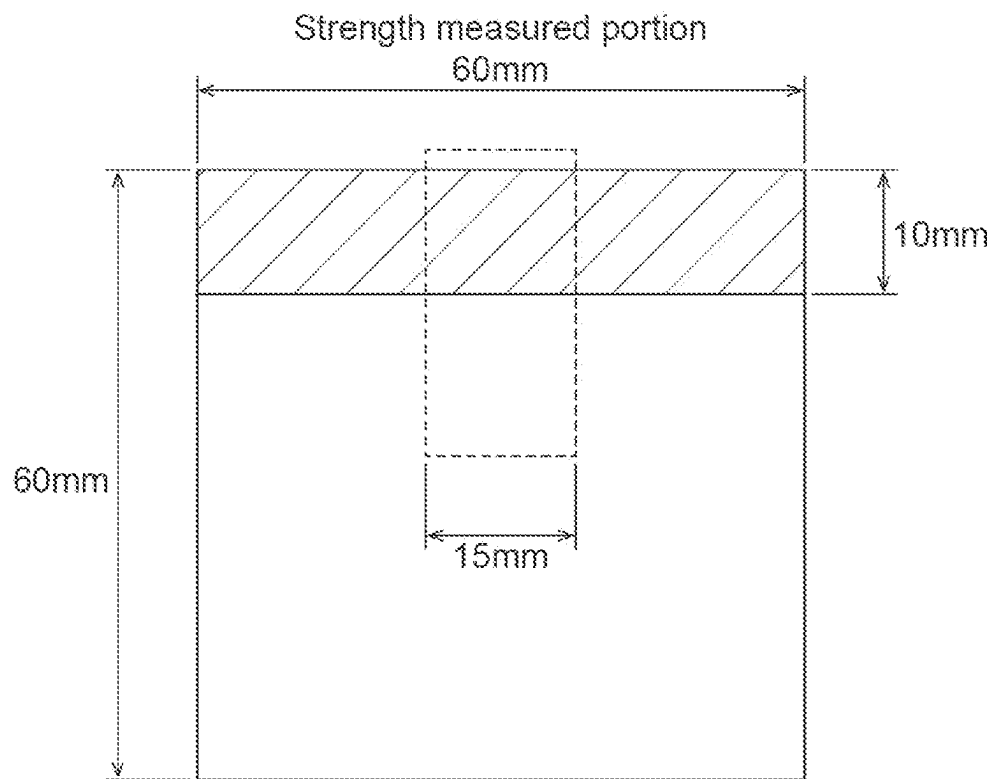
Fig.5

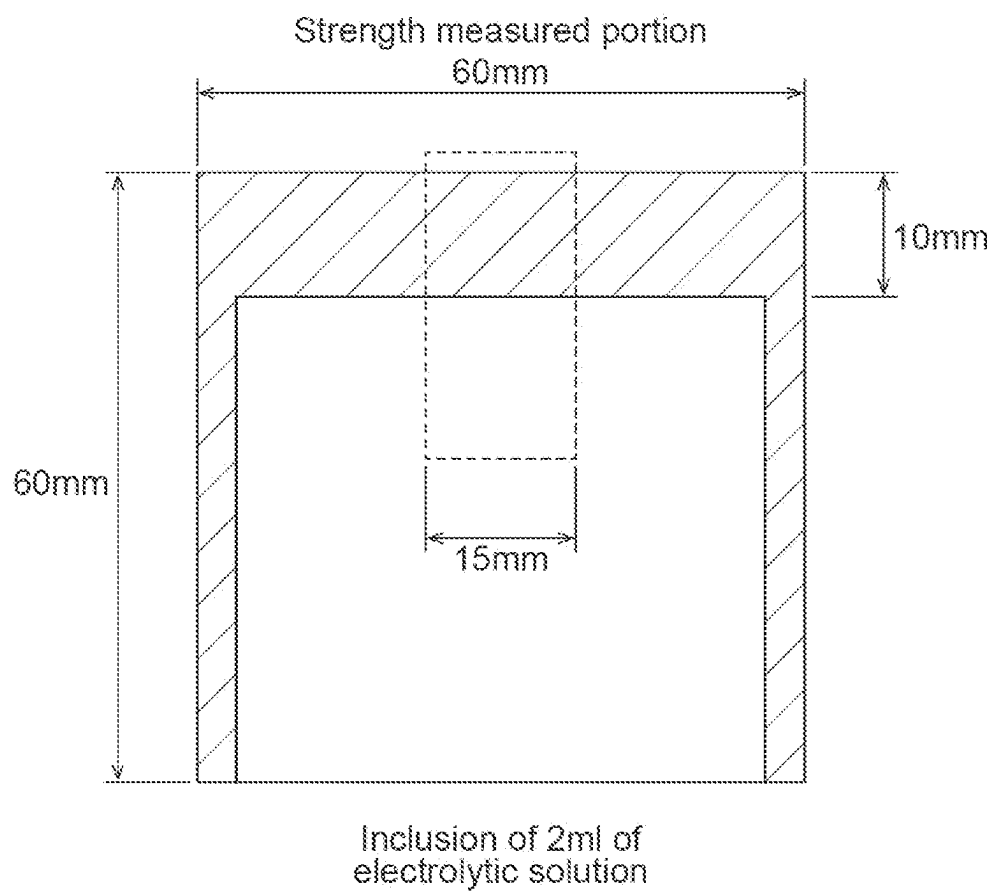
Fig.6

Fig. 7C

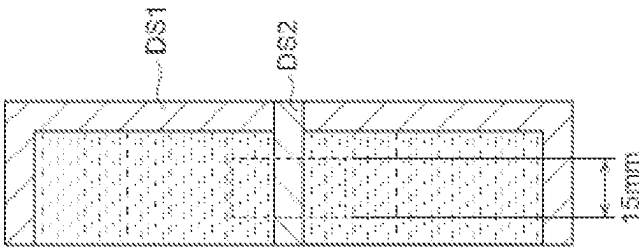


Fig. 7B

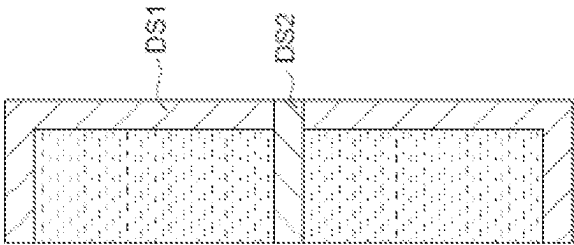


Fig. 7A

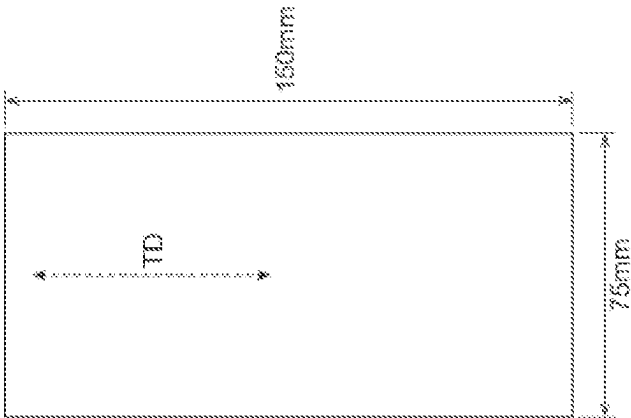


Fig. 8A

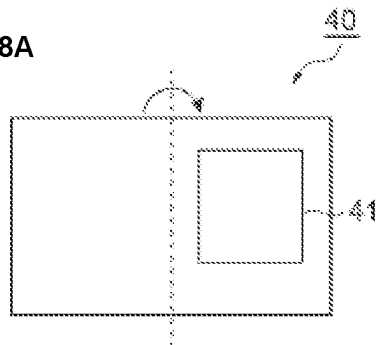


Fig. 8E

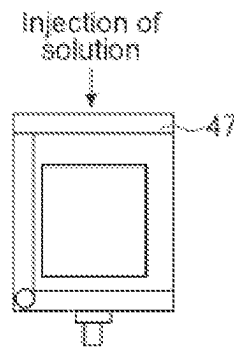


Fig. 8B

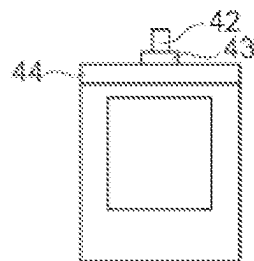


Fig. 8F

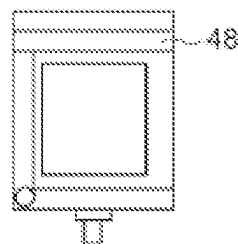


Fig. 8C

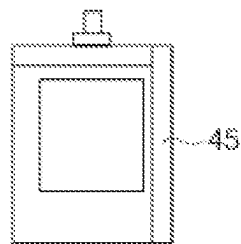


Fig. 8G

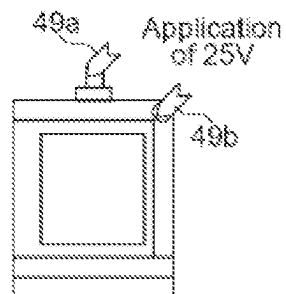
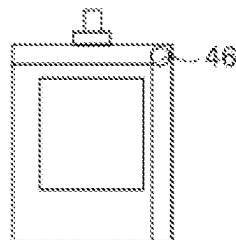


Fig. 8D



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**ELECTRICITY STORAGE DEVICE
CLADDING****CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a U.S. National Stage Application which claims the benefit under 35 U.S.C. § 371 of International Patent Application No. PCT/JP2019/004089 filed on Feb. 5, 2019, which claims foreign priority benefit under 35 U.S.C. § 119 of Japanese Patent Application No. 2018-097705 filed on May 22, 2018 in the Japanese Patent Office, the contents of both of which are incorporated herein by reference.

TECHNICAL FIELD

The present disclosure relates to a packaging material for a power storage device.

BACKGROUND ART

As power storage devices, secondary batteries such as lithium ion batteries, nickel-hydrogen batteries and lead storage batteries, as well as electrochemical capacitors such as electric double layer capacitors are known, for example. In view of downsizing of mobile devices, limitation in space for installation, or the like, further downsizing of power storage devices has been required, and lithium ion batteries with high energy density have been watched with interest. As packaging materials for use in lithium ion batteries, metallic cans had conventionally been used; however, multi-layered films with light weight, high heat releasing ability, and being able to be produced with a low cost (for example, films having a configuration like substrate layer/metallic foil layer/sealant layer) have started to be used.

In a lithium ion battery using the above multi-layered film as a packaging material, a configuration for covering the battery contents with a packaging material including an aluminum foil layer as a metallic foil layer has been employed in order to prevent infiltration of moisture into the interior of the lithium ion battery. Lithium ion batteries in which such a configuration is employed are referred to as lithium ion batteries of an aluminum laminated type. In battery contents within lithium ion batteries, a positive electrode, a negative electrode and a separator, as well as an electrolytic solution in which a lithium salt as an electrolyte has been dissolved into an aprotic solvent having osmotic force, such as propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate or the like, or an electrolyte layer consisting of a polymeric gel impregnated with the electrolytic solution are included.

As a lithium ion battery of an aluminum laminated type, an lithium ion battery of an embossed type in which a depressed part is formed on a portion of a packaging material by cold molding, and battery contents are held in the depressed part, and the remaining portion of the packaging material is folded back to seal the edge of the packaging material by heat seal is known, for example. Packaging materials constituting such a lithium ion battery have been required to exhibit steady sealability resulting from heat seal, and also required to tend not to occur decrease in laminating strength between an aluminum foil layer and a sealant layer due to an electrolytic solution of the battery contents.

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Also, in view of thickness reducing of smartphones, tablet PCs, and the like, also with regard to power storage devices to be installed in these, thin devices are required. Thinning of a substrate layer, a metallic foil layer and a sealant layer in a packaging material for a power storage device is advancing with thickness reducing of power storage devices, and as a result of this, decrease in the insulation properties or laminating strength due to the sealant layer being thinned is problematic.

Therefore, for example, in Patent Literature 1, a packaging material is proposed, the packaging material comprising a heat seal layer (sealant layer) including an adhesive polymethyl pentene layer, and as a result of this, the packaging material being able to be steadily sealed by heat and pressure in heat seal without short circuit between a barrier layer and tabs of the packaging body.

CITATION LIST**Patent Literature**

Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2002-245983

SUMMARY OF INVENTION**Technical Problem**

In a conventional packaging material as described in the above Patent Literature 1, a solution to decrease in insulation properties due to contact between tab leads and a metallic foil layer has been accomplished. However, it is considered that another factor regarding decrease in insulating properties is present. In order to allow a lithium ion battery to store energy, it is necessary to perform charge and discharge of the lithium ion battery under predetermined conditions of an electrical current value, a voltage value, an ambient temperature and the like to occur chemical change (chemical conversion). This chemical conversion step is performed with the lithium ion battery being a temporal battery to which an electrolytic solution is injected. Then, once the battery is opened for removal of a gas generated by chemical conversion or for reloading of the electrolytic solution, final seal is subsequently performed to manufacture a battery. This final seal seals a portion of the battery that have been dipped into the electrolytic solution once, this final seal is therefore a degassing seal (degassing heat seal) in which heat seal is performed while sandwiching the electrolytic solution between portions to be heat-sealed.

According to investigations by the present inventors up to now, it has been found that decrease in insulation properties are often caused by destruction of a sealant layer due to degassing heat sealing, and solution to this decrease in insulation properties is of highly importance. In Patent Literature 1, studies with regard to the destruction of a sealant layer due to degassing heat sealing have not been accomplished.

A degassing heat seal heat-seals portions while sandwiching the electrolytic solution between the portions to be heat-sealed when a packaging material accommodating battery contents is sealed by heat seal, and therefore, in some cases, the electrolytic solution bubbles and the sealant layer is destructed. Then, it is considered that the electrolytic solution enters from a portion of the sealant layer being destructed, and contacts a metallic layer, and as a result of this, insulation properties decrease.

In addition, the decrease in insulation properties resulting from the destruction of the sealant layer due to the degassing heat seal tends to be influenced by thinning of the sealant layer, and therefore, among improvements in insulation properties, a solution to this decrease in insulation properties is particularly demanded toward the future.

The present disclosure has been accomplished in view of the problems that the above conventional technology has, and it is an object of the present disclosure to provide a packaging material for a power storage device, the packaging material being able to maintain insulating properties after degassing heat sealing in a sufficient manner.

Solution to Problem

The present disclosure provides a packaging material for a power storage device, comprising at least:

- a substrate layer;
- a metallic foil layer with an anti-corrosion treatment layer being disposed on one face or both faces thereof; and
- a sealant layer in this order.

In the above packaging material, the sealant layer includes a resin layer containing a polypropylene-based resin (A) and an incompatible component (B) incompatible with the polypropylene-based resin (A). As for loss tangent $\tan \delta$ obtained by dynamic viscoelasticity measurement at a frequency of 1.0 Hz, this sealant layer has a maximal value of $\tan \delta$ at -30 to 30°C. , and in addition, a ratio (II/I) of the maximal value (II) of $\tan \delta$ at -30 to 30°C. to the value (I) of $\tan \delta$ at -50°C. is 2.50 or more.

On the basis of the above packaging material for a power storage device, even when the sealant layer is thinned, it is possible to maintain insulating properties after degassing heat sealing in a sufficient manner. The present inventors presume that the reason why the above packaging material for a power storage device achieves such an effect is as follows.

First of all, in degassing heat sealing, the sealant layer is swelled due to electrolytic solution, and heat seal is performed while sandwiching the electrolytic solution, and therefore, deformation of the sealant layer considered to be due to volatilization (bubbling) of the electrolytic solution occurs. Bubbling of the electrolytic solution tends to form voids the interface of sea-island structure formed by the polypropylene-based resin (A) and the incompatible component (B) possessed by the sealant layer, and the like, and it is considered that the metallic foil layer tends to be exposed to voids in the interior of the sealant layer, and the electrolytic solution enters the voids to cause the electrolytic solution to come into contact with the exposed portion of the metallic foil layer, and as a result of this, the insulating properties decreases. In particular, when the sealant layer is thinned, deformation of the sealant layer due to bubbling becomes large based on the thickness, and possibilities of decrease in insulating properties further increase.

By contrast to this, in the packaging material for a power storage device according to the present disclosure, adhesiveness between the polypropylene-based resin (A) and the incompatible component (B) in the interface of the above sea-island structure is high, and even when the electrolytic solution bubbles, voids using the above interface as a source tend not to occur. Therefore, it is considered that in a packaging material for a power storage device according to the present disclosure, insulating properties after degassing heat sealing can be sufficiently maintained even when the sealant layer is thinned.

It is preferable that with regard to the sealant layer, as for loss tangent $\tan \delta$ obtained by dynamic viscoelasticity measurement at a frequency of 1.0 Hz, a ratio (III/II) of the maximum value (III) of $\tan \delta$ at 90 to 100°C. to the maximal value (II) be 1.00 or less. As a result of this, while sufficiently maintaining insulating properties after degassing heat sealing, it is possible to improve the seal strength at high temperatures.

The resin layer may further contain a compatible component (C) compatible with a polypropylene-based resin (A). Also, in this case, the compatible component (C) may include a propylene- α -olefin copolymer.

The sealant layer may further include a second resin layer containing a polypropylene-based resin (D) and an incompatible component (E) incompatible with the polypropylene-based resin (D) on the side of the metallic foil layer. In this case, it is preferable that the second resin layer further contain a compatible component (F) compatible with the polypropylene-based resin (D), and the polypropylene-based resin (D) include acid-modified polypropylene, and the compatible component (F) include polypropylene with an atactic structure or a propylene- α -olefin copolymer with an atactic structure. As a result of this, it tends to facilitate to retain adhesiveness between the sealant layer and the metallic foil layer, and it is possible to prevent the generation of unsatisfactorily adhered components resulting in a source of bubbling of the electrolytic solution, and further effectively suppress decrease in insulating properties after degassing heat sealing.

The anti-corrosion treatment layer may include cerium oxide, 1 to 100 parts by mass of phosphoric acid or phosphoric acid salt per 100 parts by mass of the cerium oxide, and a cationic polymer. Also, the anti-corrosion treatment layer may be a layer formed by subjecting the metallic foil layer to the chemical conversion treatment, or a layer formed by subjecting the metallic foil layer to the chemical conversion treatment and including a cationic polymer. As a result of this, it tends to facilitate to retain adhesiveness between the sealant layer and the metallic foil layer, and it is possible to prevent the generation of sources of bubbling of the electrolytic solution, and further effectively suppress decrease in insulating properties after degassing heat sealing.

Note that the packaging material for a power storage device can further comprise an adhesive layer between the metallic foil layer and the sealant layer. The adhesive layer in this case may contain an acid-modified polyolefin, and at least one curing agent selected from the group consisting of a multifunctional isocyanate compound, a glycidyl compound, a compound having a carboxy group, a compound having an oxazoline group, and carbodiimide compound.

Advantageous Effects of Invention

According to the present disclosure, it is possible to provide a packaging material for a power storage device that can sufficiently maintain insulating properties after degassing heat sealing.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic cross-sectional view of a packaging material for a power storage device according to one embodiment of the present disclosure.

FIG. 2 is a schematic cross-sectional view of a packaging material for a power storage device according to one embodiment of the present disclosure.

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FIG. 3 is a schematic cross-sectional view of a packaging material for a power storage device according to one embodiment of the present disclosure.

FIG. 4 is a diagram showing the measurement results of $\tan \delta$ of the sealant layers in the packaging materials obtained in Example 1 and Comparative Example 1.

FIG. 5 is a schematic view illustrating a method for producing a sample to be evaluated in Examples.

FIG. 6 is a schematic view illustrating a method for producing a sample to be evaluated in Examples.

FIGS. 7A to 7C is a schematic view illustrating a method for producing a sample to be evaluated in Examples.

FIGS. 8A to 8G is a schematic view illustrating a method for producing a sample to be evaluated in Examples.

DESCRIPTION OF EMBODIMENTS

Suitable embodiments of the present disclosure will be illustrated in detail below with reference to the drawings as appropriate. Note that, in the drawings, the same or the corresponding parts are provided with the same reference signs, and the overlapping descriptions are omitted. Also, the dimensional ratios in the drawings are not limited to the ratios shown in the drawings.

[Packaging Material for Power Storage Device]

FIG. 1 is a cross-sectional view schematically illustrating one embodiment of a packaging material for a power storage device of the present disclosure. As shown in FIG. 1, a packaging material 10 (packaging material for a power storage device) of the present embodiment is a laminate in which a substrate layer 11, an adhesive layer 12 (sometimes referred to as first adhesive layer 12) formed on one face of the substrate layer 11, a metallic foil layer 13 formed on a face of the first adhesive layer 12 opposite to the substrate layer 11, an anti-corrosion treatment layer 14 formed on a face of the metallic foil layer 13 opposite to the first adhesive layer 12, an adhesive layer 17 (sometimes referred to as second adhesive layer 17) formed on a face opposite of the anti-corrosion treatment layer 14 to the metallic foil layer 13, and a sealant layer 16 formed on a face of the second adhesive layer 17 opposite to the anti-corrosion treatment layer 14 are successively laminated. In the packaging material 10, the substrate layer 11 is the outermost layer, and the sealant layer 16 is the innermost layer. In other words, the packaging material 10 is used such that the substrate layer 11 is directed toward the side of the exterior of the power storage device, and the sealant layer 16 is directed toward on the side of the interior of the power storage device. Each of the layers constituting the packaging material 10 will be specifically illustrated below.

<Substrate Layer 11>

The substrate layer 11 is provided for the purpose of imparting heat resistance in a sealing step in the production of a power storage device, and achieving the solution to pinholes that can be occurred during the processing or the distribution, and it is preferable to use a resin layer having insulation properties. As such a resin layer, for example, it is possible to use a stretched or unstretched film such as a polyester film, a polyamide film, a polypropylene film, as a single layer, or as a multi-layered film in which two or more thereof are laminated. It is also possible to use a co-extruded multilayered stretched film prepared by the coextrusion of a polyethylene terephthalate film (PET) and a nylon film (Ny) by using an adhesive resin followed by subjecting to stretching treatment.

The substrate layer 11 may be disposed by directly applying the substrate layer 11 on a metallic foil layer 13

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described below. In this case, a first adhesive layer 12 described below is not required. As a method for forming the substrate layer by application, it is possible to employ a method for conducting the application of a coating solution of a resin such as an urethane resin, an acrylic resin and a polyester resin, and conducting the curing by ultraviolet irradiation, heating at elevated temperatures, aging (curing) treatment and the like. The application method is not limited in particular, and it is possible to employ a variety of processes such as gravure coating, reverse coating, roll coating and bar coating.

It is preferable that the thickness of the substrate layer 11 be 3 to 40 μm , and it is more preferable that this thickness be 5 to 25 μm . As a result of the fact that the thickness of the substrate layer 11 is 3 μm or more, it tends to enable improvement in pinhole resistance and insulation properties of the packaging material for a power storage device 10.

<First Adhesive Layer 12>

The first adhesive layer 12 is a layer for adhering the substrate layer 11 to the metallic foil layer 13. Specific examples of materials constituting the first adhesive layer 12 include polyurethane resins prepared by reacting a base material such as polyester polyol, polyether polyol, acrylic polyol and carbonate polyol with a bifunctional or higher isocyanate compound.

Depending on functions and performance required for the packaging material, a variety of the polyols described above can be used alone, or used as a combination of two or more thereof.

Also, depending on performance required for the adhesive, it is also possible to formulate a variety of other additives and stabilizers into the above-described polyurethane resin.

Although the thickness of the first adhesive layer 12 is not limited in particular, it is preferable that the thickness of the first adhesive layer 12 be, for example, 1 to 10 μm , and it is more preferable that this thickness be 3 to 7 μm in view of achieving desired adhesive strength, conformability, processability and the like.

<Metallic Foil Layer 13>

The metallic foil layer 13 has steam barrier properties that prevent infiltration of moisture into the interior of the power storage device. Also, the metallic foil layer 13 has ductility for conducting deep drawing molding. As the metallic foil layer 13, it is possible to use a variety of metallic foils such as aluminum, stainless steel and copper, and in view of mass (specific gravity), moisture proofing, processability and cost, an aluminum foil is preferable.

As the aluminum foil, in view of the impartment of ductility in desired molding, it is possible to preferably use, in particular, a soft aluminum foil subjected to annealing treatment; however, for the purpose of the impartment of further pinhole resistance, and ductility in molding, it is more preferable to use an aluminum foil including iron. It is preferable that the content of iron in the aluminum foil be 0.1 to 9.0% by mass per 100% by mass of the aluminum foil, and it is more preferable that this content be 0.5 to 2.0% by mass. As a result of the fact that the content of iron is 0.1% by mass or more, it is possible to obtain a packaging material 10 having better pinhole resistance and ductility. As a result of the fact that the content of iron is 9.0% by mass or less, it is possible to obtain a packaging material 10 having better flexibility.

Although the thickness of the metallic foil layer 13 is not limited in particular, it is preferable that the thickness of the metallic foil layer 13 be 9 to 200 μm in view of barrier

properties, pinhole resistance and processability, and it is more preferable that this thickness be 15 to 100 μm .

When an aluminum foil is used as the metallic foil layer 13, as an aluminum foil, it is possible to use an untreated aluminum foil; however, it is preferable to use an aluminum foil subjected to degreasing treatment in view of the impartment of electrolytic solution resistance.

Note that, when the aluminum foil is subjected to the degreasing treatment, the degreasing treatment may be conducted on only one face of the aluminum foil, or both faces of the aluminum foil.

<Anti-Corrosion Treatment Layer 14>

The anti-corrosion treatment layer 14 is a layer that is disposed in order to prevent the corrosion of the metallic foil layer 13 by hydrofluoric acid generated from the reaction of the electrolytic solution or electrolytic solution with moisture. The anti-corrosion treatment layer 14 is formed, for example, by degreasing treatment, hydrothermal metamorphism treatment, positive electrode oxidizing treatment, chemical conversion treatment, or combination thereof.

Examples of the degreasing treatment include acid degreasing or alkali degreasing. Examples of the acid degreasing include methods in which an inorganic acid such as sulphuric acid, nitric acid, hydrochloric acid and hydrofluoric acid alone, or a solution of mixture thereof are used. Also, by using, as acid degreasing, an acid degreasing agent prepared by dissolving a fluorine-containing compound such as ammonium monosodium bifluoride with the above inorganic acid, and particularly in the case where an aluminum foil is used as the metallic foil layer 13, not only degreasing effect from aluminum is obtained, but also a fluoride of aluminum in the passivated form can be formed, and therefore, this is effective in view of hydrofluoric acid resistance. Examples of the alkali degreasing include methods using sodium hydroxide and the like.

Examples of the hydrothermal metamorphism treatment include boehmite treatment in which an aluminum foil is subjected to immersion treatment in boiled water with addition of triethanolamine.

Examples of the positive electrode oxidizing treatment include alumite treatment.

Examples of the chemical conversion treatment include chemical conversion treatment of a dipping type and chemical conversion treatment of an application type. Examples of the chemical conversion treatment of the dipping type include chromate treatment, zirconium treatment, titanium treatment, vanadium treatment, molybdenum treatment, calcium phosphate treatment, strontium hydroxide treatment, cerium treatment, ruthenium treatment, or a variety of chemical conversion treatment consisting of mixed phase thereof. On the other hand, examples of the chemical conversion treatment of the application type include a method for applying a coating agent having anti-corrosion performance on the metallic foil layer 13.

Among the anti-corrosion treatment, in the case where at least a portion of the anti-corrosion treatment layer is formed by any of the hydrothermal metamorphism treatment, the positive electrode oxidizing treatment, the chemical conversion treatment, it is preferable to conduct the above-described degreasing treatment in advance. Note that when a metallic foil that has been subjected to the degreasing treatment such as a metallic foil underwent the annealing step is used as the metallic foil layer 13, there is no need to conduct the degreasing treatment again in the formation of the anti-corrosion treatment layer 14.

The coating agent for use in the chemical conversion treatment of the application type preferably contains triva-

lent chrome. Also, at least one polymer selected from the group consisting of a cationic polymer and an anionic polymer that are described below may be included in the coating agent.

Also, among the above treatment, particularly with regard to the hydrothermal metamorphism treatment and the positive electrode oxidizing treatment, a surface of an aluminum foil is dissolved with a treating agent to form an aluminum compound (boehmite, alumite) excellent in corrosion resistance. As a result of this, a co-continuous structure from the metallic foil layer 13 using the aluminum foil up to the anti-corrosion treatment layer 14 forms, and therefore, the above treatment is encompassed in the definition of the chemical conversion treatment. On the other hand, it is also possible to form the anti-corrosion treatment layer 14 only by a simple coating approach that is not encompassed in the definition of the chemical conversion treatment as described below. Examples of this method include a method in which a sol of a rare earth element oxide such as cerium oxide with an average particle size of 100 nm or less is used as a material having anti-corrosion effect (inhibitor effect) due to aluminum, and being suitable with regard to an environmental aspect. By means of this method, it is possible to impart the anti-corrosion effect to a metallic foil such as an aluminum foil, even by a typical coating.

Examples of the above sol of the rare earth element oxide include sols obtained by using a variety of solvents such as water-based solvents, alcohol-based solvents, hydrocarbon-based solvents, ketone-based solvents, ester-based solvents and ether-based solvents. Among these, a water-based sol is preferable.

In the above sol of the rare earth element oxide, usually in order to stabilize the dispersion of the sol, inorganic acids such as nitric acid, hydrochloric acid and phosphoric acid, or salts thereof, and organic acids such as acetic acid, malic acid, ascorbic acid and lactic acid are used as dispersion stabilizing agents. Among these dispersion stabilizing agents, in particular, phosphoric acid is expected to, in the packaging material 10, (1) provide the stabilization of sol dispersion, (2) improve the adhesiveness to the metallic foil layer 13 by means of aluminum chelating ability of phosphoric acid, (3) impart the electrolytic solution resistance by trapping aluminum ions eluted under the influence of hydrofluoric acid (formation of passivated form), (4) improve the aggregation force of anti-corrosion treatment layer 14 (oxide layer) due to the fact that it tends to occur dehydration condensation of phosphoric acid at low temperatures, and the like.

Examples of the above phosphoric acid or a salt thereof include orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid, or alkali metal salts and ammonium salts thereof. Among these, in order to express functions in the packaging material 10, condensed phosphoric acids such as trimetaphosphoric acid, tetrametaphosphoric acid, hexametaphosphoric acid and ultrametaphosphoric acid, or alkali metal salts and ammonium salts thereof are preferable. Also, in view of dry film formability (drying ability, heat quantity) when the anti-corrosion treatment layer 14 consisting of the rare earth element oxide is formed by a variety of coating processes using the above sol of the rare earth element oxide, sodium salts are more preferable due to the dehydration condensation ability of sodium salts at low temperatures. As phosphates, water soluble salts are preferable.

It is preferable that the mixing ratio of phosphoric acid (or a salt thereof) to the rare earth element oxide be 1 to 100 parts by mass per 100 parts by mass of the rare earth element oxide. When the above mixing ratio is 1 part by mass or

more per 100 parts by mass of the rare earth element oxide, the sol of the rare earth element oxide become more stable, and the function of the packaging material **10** become better. It is more preferable that the above mixing ratio be 5 parts by mass or more per 100 parts by mass of the rare earth element oxide. Also, when the above mixing ratio is 100 parts by mass or less per 100 parts by mass of the rare earth element oxide, the function of the sol of the rare earth element oxide enhances, and the sol of the rare earth element oxide has good performance with regard to prevention of corrosion of the electrolytic solution. It is more preferable that the above mixing ratio be 50 parts by mass or less per 100 parts by mass of the rare earth element oxide, and it is further preferable that the above mixing ratio be 20 parts by mass or less.

The anti-corrosion treatment layer **14** formed by the above sol of the rare earth element oxide is an aggregate of inorganic particles, and therefore, even after undergoing a dry curing step, the aggregation force of this layer itself may be small. Therefore, it is preferable that the anti-corrosion treatment layer **14** in this case have been set to form a composite with the following anionic polymer or cationic polymer in order to supplement the aggregation force.

Examples of the anionic polymer include polymers having a carboxy group, such as poly(meth)acrylic acid (or a salt thereof), or a copolymer obtained by copolymerization of poly(meth)acrylic acids as a main component. Examples of the copolymerized components in this copolymer include alkyl (meth)acrylate-based monomer (as the alkyl group, methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, t-butyl group, 2-ethylhexyl group, cyclohexyl group, and the like.); amide group-containing monomers such as (meth)acrylamide, N-alkyl (meth)acrylamide, N,N-dialkyl (meth)acrylamide (as the alkyl group, methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, i-butyl group, t-butyl group, 2-ethylhexyl group, cyclohexyl group and the like.), N-alkoxy (meth)acrylamide, N,N-dialkoxy(meth)acrylamide (as the alkoxy group, methoxy group, ethoxy group, butoxy group, isobutoxy group, and the like.), N-methylol (meth)acrylamide, and N-phenyl(meth)acrylamide; hydroxy group-containing monomers such as 2-hydroxyethyl(meth)acrylate and 2-hydroxypropyl(meth)acrylate; glycidyl group-containing monomers such as glycidyl(meth)acrylate and allyl glycidylether; silane-containing monomers such as (meth)acryloxypropyltrimethoxysilane, (meth)acryloxypropyltriethoxysilane; and isocyanate group-containing monomers such as (meth)acryloxypropylisocyanate.

These anionic polymers play a role in improving the stability of the anti-corrosion treatment layer **14** (oxide layer) obtained by using the sol of the rare earth element oxide. This role is accomplished by the effect of protecting a hard but brittle oxide layer with an acrylic-based resin component, and the effect of trapping (cation trapping) an ion contaminant (in particular, a sodium ion) derived from a phosphate included in the sol of the rare earth element oxide. In short, when alkali metal ions and alkali earth metal ions such as sodium ions in particular are included in the anti-corrosion treatment layer **14** obtained by using the sol of the rare earth element oxide, the anti-corrosion treatment layer **14** tends to degrade with a site including these ions as an origin of the degradation. As a result of this, the resistance of the anti-corrosion treatment layer **14** enhances by immobilizing sodium ions and the like included in the sol of the rare earth element oxide due to the anionic polymer.

The anti-corrosion treatment layer **14** in which the anionic polymer and the sol of the rare earth element oxide are

combined has anti-corrosion performance equivalent to that of an anti-corrosion treatment layer **14** formed by subjecting an aluminum foil to chromate treatment. It is preferable that the anionic polymer have a structure in which polyanionic polymers, which are essentially water-soluble, are cross-linked. Examples of the crosslinking agent for forming this structure include compounds having an isocyanate group, a glycidyl group, a carboxy group, and an oxazoline group.

Examples of the compound having an isocyanate include diisocyanates such as tolylenediisocyanate, xylylene diisocyanate or hydrogenation products thereof, hexamethylenediisocyanate, 4,4' diphenylmethanediisocyanate or hydrogenation products thereof, and isophoronediiisocyanate; or polyisocyanates such as adducts prepared by reacting these isocyanates with polyhydric alcohols such as trimethylolpropane, biurets obtained by reacting these isocyanates with water, or trimeric isocyanurates; or blocked polyisocyanates prepared by blocking these polyisocyanates with alcohols, lactams, oximes and the like.

Examples of the compound having a glycidyl group include epoxy compounds obtained by reacting glycols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, 1,4-butanediol, 1,6-hexanediol and neopentylglycol with epichlorohydrin; epoxy compounds obtained by reacting polyhydric alcohols such as glycerin, polyglycerin, trimethylolpropane, pentaerythritol and sorbitol with epichlorohydrin; and epoxy compounds obtained by reacting dicarboxylic acids such as phthalic acid, terephthalic acid, oxalic acid and adipic acid with epichlorohydrin.

Examples of the compound having a carboxy group include a variety of aliphatic or aromatic dicarboxylic acids. Also, it is possible to use poly(meth)acrylic acids and alkali (earth) metal salts of poly(meth)acrylic acids.

Examples of the compound having an oxazoline group include low molecular compounds having two or more oxazoline units, or when using polymerizable monomers such as isopropenyl oxazoline, compounds copolymerized with acrylic-based monomers such as (meth)acrylic acid, alkyl (meth)acrylate esters and hydroxyalkyl (meth)acrylate.

Also, it is possible to react an anionic polymer and a silane coupling agent, more specifically, selectively react a carboxy group of the anionic polymer and a functional group of the silane coupling agent to achieve a crosslinking point as a siloxane bond. In this case, it is possible to use γ -glycidoxypolytrimethoxysilane, γ -glycidoxypolytriethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -chloropropylmethoxysilane, vinyltrichlorosilane, γ -mercaptopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, N- β (aminoethyl)- γ -aminopropyltrimethoxysilane, γ -isocyanatopropyltriethoxysilane, and the like. Among these, in view of reactivity with an anionic polymer or a copolymer thereof in particular, epoxy silane, aminosilane and isocyanate silane are preferable.

It is preferable that the ratio of these crosslinking agents to the anionic polymer be 1 to 50 parts by mass per 100 parts by mass of the anionic polymer, and it is more preferable that this ratio be 10 to 20 parts by mass. When this ratio of the crosslinking agent is 1 part by mass or more per 100 parts by mass of the anionic polymer, the crosslinked structure tends to be formed satisfactorily. When the ratio of the crosslinking agent is 50 parts by mass or less per 100 parts by mass of the anionic polymer, pot life of the coating solution increases.

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The process for crosslinking the anionic polymers is not limited to the above crosslinking agent, and may be a process for forming crosslinking of ions by using titanium or a zirconium compound.

Examples of the cationic polymer include polymers having an amine, and examples of the polymers having an amine include polyethyleneimine, ionic macromolecular complex consisting of polyethyleneimine and polymers having a carboxylic acid, primary amine grafted acrylic resins obtained by grafting a primary amine onto an acrylic main backbone, polyallylamine, or derivatives thereof, and cationic polymers such as aminophenol. Examples of the polyallylamine include homopolymers or copolymers of allylamines, allylamine amidosulfates, diallylamines, and dimethylallylamines. These amines can be free amines, or can be those stabilized by acetic acid or hydrochloric acid. Also, as the copolymerized components, it is possible to use maleic acid, sulfur dioxide, and the like. In addition, it is possible to use amines imparted with heat crosslinking ability by subjecting primary amine to partial methoxylation, and it is also possible to use aminophenol. In particular, allylamine or derivatives thereof is preferable.

It is preferable to use the cationic polymer in combination with a crosslinking agent having a functional group reactive with amine/imine such as a carboxy group and a glycidyl group. As the crosslinking agent used in combination with the cationic polymer, it is possible to use polymers having a carboxylic acid that forms ionic macromolecular complex with polyethyleneimine, and examples of these polymers include polycarboxylic acids (salts) such as polyacrylic acids or ionic salts thereof, or copolymers prepared by introducing comonomers in these polycarboxylic acids (salts), and polysaccharides having a carboxy group such as carboxymethyl cellulose or ionic salts thereof.

In the present embodiment, the cationic polymer is described as one constituent constituting the anti-corrosion treatment layer 14. The reason is that, as a result of diligent studies that have been made by means of various compounds in order to impart electrolytic solution resistance and hydrofluoric acid resistance required for a packaging material for a power storage device, it has been found that the cationic polymer itself is a compound that can impart electrolytic solution resistance and hydrofluoric acid resistance. The factor contributing to this is speculated to be the fact that damage of the aluminum foil is suppressed by trapping fluoride ions with cationic groups (anion trap).

The cationic polymer is more preferable material in view of improvement in adhesiveness. Also, the cationic polymer is water soluble in a manner analogous to the above anionic polymer, and it is therefore more preferable to form a crosslinked structure in the cationic polymer to impart water resistance to the cationic polymer. As a crosslinking agent for forming a crosslinked structure in the cationic polymer, it is possible to use the crosslinking agents illustrated in the section with regard to the anionic polymer. When the sol of the rare earth element oxide is used as the anti-corrosion treatment layer 14, the cationic polymer can be used as a protective layer of the anti-corrosion treatment layer 14, instead of using the above anionic polymer.

The anti-corrosion treatment layer resulting from the chemical conversion treatment represented by the chromate treatment is obtained by, in order to form an inclined structure in relation to the aluminum foil, treating an aluminum foil with a chemical conversion treating agent to which phosphoric acid, hydrofluoric acid, hydrochloric acid, nitric acid, sulphuric acid or salts thereof is mixed in particular, followed by reacting the aluminum foil with

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chromium-based or non-chromium-based compound to form a chemical conversion-treated layer on the aluminum foil. However, the above chemical conversion treatment uses acids as chemical conversion treating agents, and as a result of this, involves degradation of working conditions or corrosion in the coating device. On the other hand, in contrast to chemical conversion treatment represented by the chromate treatment, the above-described anti-corrosion treatment layer 14 of a coating type is not required to form an inclined structure in relation to the metallic foil layer 13 using the aluminum foil. Therefore, the nature of the coating agent is not limited with regard to acidic properties, alkaline properties, neutral properties and the like, and it is possible to accomplish good working conditions. In addition, due to the fact that alternative solution to the chromate treatment using a chromium compound is demanded in view of environmental sanitation, the anti-corrosion treatment layer 14 of the coating type is preferable.

In view of the content of the above description, combination examples of the above-described anti-corrosion treatment of the coating type include (1) the sol of the rare earth element oxide alone, (2) the anionic polymer alone, (3) the cationic polymer alone, (4) the sol of the rare earth element oxide+the anionic polymer (the formation of a composite by laminating), (5) the sol of the rare earth element oxide+the cationic polymer (the formation of a composite by laminating), (6) (the sol of the rare earth element oxide+the anionic polymer: the formation of a composite by laminating)/the cationic polymer (multilayering), (7) (the sol of the rare earth element oxide+the cationic polymer: the formation of a composite by laminating)/the anionic polymer (multilayering). Among these, (1) and (4) to (7) are preferable, (4) to (7) are particularly preferable. In this regard, the present embodiment is not limited to the above combinations. For example, as examples of the selection of anti-corrosion treatment, the cationic polymer is a very preferable material in view of the fact that the cationic polymer has good adhesiveness to a modified polyolefin resin illustrated in the description of the second adhesive layer or the sealant layer described below, and therefore, in a case where the second adhesive layer or sealant layer is configured with the modified polyolefin resin, it is possible to accomplish a design such that the cationic polymer is disposed on a face in contact with the second adhesive layer or the sealant layer (for example, a configuration such as configurations (5) and (6)).

Also, the anti-corrosion treatment layer 14 is not limited to the above-described layers. For example, in a manner analogous to as in chromate of an application type of known technology, it is possible to form the anti-corrosion treatment layer 14 by using a treating agent prepared by mixing phosphoric acid and a chromium compound into a resin binder (such as aminophenol). By means of this treating agent, it is possible to provide a layer with both anti-corrosion function and adhesiveness. Also, although stability of the coating solution has to be taken into consideration, by means of a coating agent in which a sol of a rare earth element oxide and an polycationic polymer or polyanionic polymer have been set to be a one-component in advance, it is possible to provide a layer with both the anti-corrosion function and the adhesiveness.

In either a multilayered structure or a single-layered structure, it is preferable that the mass of the anti-corrosion treatment layer 14 per unit area be 0.005 to 0.200 g/m², and it is more preferable that this mass be 0.010 to 0.100 g/m². When the above-described mass per unit area is 0.005 g/m² or more, it is easy to impart the anti-corrosion function to the

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metallic foil layer 13. Also, even when the above-described mass per unit area is greater than 0.200 g/m², the anti-corrosion function does not vary to a significant extent. On the other hand, in a case where the sol of the rare earth element oxide is used, curing by heat in drying is insufficient when the coating is thick, and decrease in aggregation force may occur. Note that the thickness of the anti-corrosion treatment layer 14 can be calculated from the specific gravity thereof.

In view of facilitating the adhesiveness between the sealant layer and the metallic foil layer to be retained, preventing the generation of a source of bubbling of the electrolytic solution, and further suppressing the decrease in insulating properties after degassing heat sealing, the anti-corrosion treatment layer 14 can be, for example, such that it includes cerium oxide, 1 to 100 parts by mass of phosphoric acid or a phosphate per 100 parts by mass of the cerium oxide, and a cationic polymer, can be such that it is formed by subjecting the metallic foil layer 13 to the chemical conversion treatment, or can be such that it is formed by subjecting the metallic foil layer 13 to the chemical conversion treatment, and includes a cationic polymer.

<Second Adhesive Layer 17>

The second adhesive layer 17 is a layer adhering the metallic foil layer 13 on which the anti-corrosion treatment layer 14 is formed, to the sealant layer 16. It is possible to use typical adhesive for adhering the metallic foil layer to the sealant layer in the second adhesive layer 17.

When the anti-corrosion treatment layer 14 has a layer including at least one polymer selected from the group consisting of the cationic polymers and the anionic polymers described above, it is preferable that the second adhesive layer 17 be a layer including a compound having reactivity with the above polymers included in the anti-corrosion treatment layer 14 (hereinafter, also referred to as "reactive compound").

For example, when the anti-corrosion treatment layer 14 includes a cationic polymer, the second adhesive layer 17 includes a compound having reactivity with the cationic polymer. When the anti-corrosion treatment layer 14 includes an anionic polymer, the second adhesive layer 17 includes a compound having reactivity with the anionic polymer.

Also, when the anti-corrosion treatment layer 14 includes a cationic polymer and an anionic polymer, the second adhesive layer 17 includes a compound having reactivity with the cationic polymer, and a compound having reactivity with the anionic polymer. Here, the second adhesive layer 17 does not necessarily have to include the above two compounds, and may include a compound having reactivity with both the cationic polymer and the anionic polymer. Here, "having reactivity" means to form a covalent bond with a cationic polymer or an anionic polymer. Also, the second adhesive layer 17 can further include an acid-modified polyolefin resin.

Examples of the compound having reactivity with a cationic polymer include at least one compound selected from the group consisting of a multifunctional isocyanate compound, a glycidyl compound, a compound having a carboxy group and a compound having an oxazoline group.

Examples of the multifunctional isocyanate compound, the glycidyl compound, the compound having a carboxy group and the compound having an oxazoline group include the multifunctional isocyanate compound, the glycidyl compound, the compound having a carboxy group and the compound having an oxazoline group illustrated above as a

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crosslinking agent for imparting a crosslinked structure to a cationic polymer. Among these, the multifunctional isocyanate compound is preferable due to the fact that the multifunctional isocyanate compound has high reactivity with the cationic polymer, and can easily form a crosslinked structure.

Examples of the compound having reactivity with an anionic polymer include at least one compound selected from the group consisting of the glycidyl compound and the compound having an oxazoline group. Examples of the glycidyl compound and the compound having an oxazoline group include the glycidyl compound and the compound having an oxazoline group illustrated above as a crosslinking agent for providing a cationic polymer with a crosslinked structure. Among these, the glycidyl compound is preferable due to the fact that glycidyl compound has high reactivity with the anionic polymers.

When the second adhesive layer 17 includes an acid-modified polyolefin resin, it is preferable that the reactive compound also have reactivity with an acidic group in the acid-modified polyolefin resin (in other words, forms a covalent bond with the acidic group). As a result of this, the adhesiveness to the anti-corrosion treatment layer 14 further increases. In addition, the acid-modified polyolefin resin is set to have a crosslinked structure, and the solvent resistance of the packaging material 10 further enhances.

It is preferable that the content of the reactive compound be from the same equivalents to ten times equivalents with respect to the acidic group in the acid-modified polyolefin resin. At equivalents or higher, the reactive compound satisfactorily reacts with the acidic group in the acid-modified polyolefin resin. On the other hand, when greater than the ten times equivalents, the crosslinking reaction with the acid-modified polyolefin resin fully reaches to saturation, and therefore, unreacted materials are present, and decrease in various kinds of performance is concerned. Therefore, by way of example, it is preferable that the content of the reactive compound be 5 to 20 parts by mass (the ratio by solids content) per 100 parts by mass of the acid-modified polyolefin resin.

The acid-modified polyolefin resin is prepared by introducing an acidic group to a polyolefin resin. Examples of the acidic group include a carboxy group, a sulfonic acid group, and an acid anhydride group, and a maleic acid anhydride group and a (meth)acrylic acid group are particularly preferable. As the acid-modified polyolefin resin, for example, it is possible to use those analogous to that described below as a modified polyolefin resin (a) for use in the first resin layer 16a.

It is also possible to formulate a variety of additives such as flame retardants, slip agents, anti-blocking agents, antioxidants, light stabilizers and tackifiers into the second adhesive layer 17.

In view of suppressing the decrease in laminating strength in the case of involvement of the electrolytic solution, and in view of further suppressing the decrease in insulation properties, the second adhesive layer 17 can include, for example, the acid-modified polyolefin, and at least one curing agent selected from the group consisting of the multifunctional isocyanate compound, the glycidyl compound, the compound having a carboxy group, the compound having an oxazoline group and a carbodiimide compound. Note that examples of the carbodiimide compound include N,N'-di-o-toluidyl carbodiimide, N,N'-diphenyl carbodiimide, N,N'-di-2,6-dimethylphenyl carbodiimide, N,N'-bis(2,6-diisopropylphenyl)carbodiimide, N,N'-dioctyldecyl carbodiimide, N-triyl-N'-cyclohexyl carbodiimide, N,N'-di-

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2,2-di-*t*-butylphenyl carbodiimide, N-triyl-N'-phenyl carbodiimide, N,N'-di-*p*-nitrophenyl carbodiimide, N,N'-di-*p*-aminophenyl carbodiimide, N,N'-di-*p*-hydroxyphenyl carbodiimide, N,N'-di-cyclohexyl carbodiimide, and N,N'-di-*p*-toluyl carbodiimide.

Also, as the adhesive forming the second adhesive layer 17, it is also possible to use, for example, a polyurethane-based adhesive prepared by formulating a polyester polyol consisting of a hydrogenated dimeric fatty acid and a diol, and a polyisocyanate.

In view of achieving a desired adhesive strength, processability and the like, it is preferable for the thickness of the second adhesive layer 17 to be, but not limited in particular, 1 to 10 μm , and it is more preferable for the thickness of the second adhesive layer 17 to be 3 to 7 μm .

<Sealant layer 16>

The sealant layer 16 is a layer imparting sealability resulting from heat seal to the packaging material 10. The sealant layer 16 includes a resin layer 16a (sometimes referred to as first resin layer 16a) containing a polypropylene-based resin (A) and an incompatible component (B) incompatible with the above polypropylene-based resin (A). In FIG. 1, the sealant layer 16 is configured by the first resin layer 16a.

As for loss tangent $\tan \delta$ obtained by dynamic viscoelasticity measurement at a frequency of 1.0 Hz, the sealant layer 16 has a maximal value of $\tan \delta$ at -30 to 30°C . Also, with regard to the sealant layer 16, a ratio (II/I) of the maximal value (II) of $\tan \delta$ at -30 to 30°C . to the value (I) of $\tan \delta$ at -50°C . is 2.50 or more.

As a result of the fact that the above ratio (II/I) in the sealant layer 16 is 2.50 or more, it is possible to maintain insulating properties after degassing heat sealing in a sufficient manner. The present inventors believe that the reason why such an effect is achieved is due to improvement in adhesion strength of the interface of sea-island structure present in the sealant layer 16, and the present inventors presume that the reason why the above effect is achieved due to the fact that the proportion of the above (II) to the above (I) is high, in other words, the fact that difference between the above (II) and the above (I) is large as follows. In other words, when the ratio (II/I) is 2.50 or more, it is possible to suppress action of the interface as a shock absorber, and as a result of this, adhesion strength of the interface enhances, and by contrast to this, when the ratio (II/I) is less than 2.50, the interface has action as a shock absorber to an excessive extent, and as a result of this, adhesion strength of the interface decreases. In a standpoint as described above, the ratio (II/I) in the sealant layer 16 is preferably 3.00 or more, and more preferably 3.50 or more. On the other hand, the upper limit value of (II/I) is not limited in particular; however, the upper limit value of (II/I) is 6.00 or less, for example.

It is preferable that, with regard to the sealant layer 16, as for loss tangent $\tan \delta$ obtained by dynamic viscoelasticity measurement at a frequency of 1.0 Hz, the ratio (III/II) of maximum value (III) of $\tan \delta$ at 90 to 100°C . to the above maximal value (II) be 1.00 or less. When the above ratio (III/II) in the sealant layer 16 is 1.00 or less, it is possible to further improve high-temperature heat seal strength of the sealant layer.

The fact that the ratio (III/II) is low, in other words, the value of III to II is low indicates that it is possible to suppress excessive increase in the viscosity of the resin, and as a result of this, it is considered that it is possible to further improve high-temperature heat seal strength of the sealant layer. In such a standpoint, the above ratio (III/II) in the

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sealant layer 16 is preferably 0.90 or less, and more preferably 0.85 or less. On the other hand, the lower limit value of (III/II) is not limited in particular; however, the lower limit value of (III/II) is, for example, 0.20 or more. As a result of enhancing high-temperature heat seal strength of the sealant layer, it is possible to improve the strength of the packaging material in thermal runaway of a lithium ion battery, and it is possible to provide a safer packaging material.

It is possible to adjust each of the values of $\tan \delta$ described above by the type, the content, and the like of each of the components shown below. Also, the above $\tan \delta$ can be, for example, calculated as loss tangent $\tan \delta$ from loss elastic modulus E'' and storage elastic modulus E' , by dipping the packaging material into an aqueous solution of sodium hydroxide to dissolve the metallic foil layer so as to obtain a film consisting solely of the sealant layer, and subjecting the obtained film to measurement in accordance with a method according to JIS K7244-4, using a dynamic viscoelasticity apparatus (manufactured by SII, trade name: DMS6100) and under following conditions.

Peeling Mode: Pulling

Rate of Temperature Rise: $2^\circ\text{C}/\text{min}$

Temperature Range: -100 to 120°C .

Frequency: 1.0 Hz

Note that, in the present description, "maximal value" of $\tan \delta$ means a value of $\tan \delta$ at a point at which, when a graph is created by plotting the values of $\tan \delta$ at the temperatures calculated by the above method, slope in the graph changes from positive to negative. When a plurality of maximal values is present in a specified temperature range, "maximal value" of $\tan \delta$ means a maximum value among the plurality of maximal values.

It is preferable that the above maximal value (II) be a maximum value of $\tan \delta$ in a measurement temperature range of -100 to 120°C .

The first resin layer 16a may further include a compatible component (C) compatible with a polypropylene-based resin (A). In the present description, optionally, the above polypropylene-based resin (A) may be referred to as "(A) component", the incompatible component (B) incompatible with the above (A) component may be referred to as "(B) component", and the compatible component (C) compatible with the above (A) component may be referred to as "(C) component", and the like. Here, "not having compatibility with the (A) component", and "incompatible with the (A) component" (incompatible) means to provide dispersion in the polypropylene-based resin constituting the (A) component with a disperse phase size of 200 nm or more and less than 50 μm . Also, "compatible with the (A) component", and "having compatibility with the (A) component" (compatible) means to provide dispersion in the polypropylene-based resin constituting the (A) component with a disperse phase size of 1 nm or more and less than 200 nm.

In the first resin layer 16a, it is preferable that the incompatible component (B) contain a compound (B1) having a portion compatible with the polypropylene-based resin (A). Hereinafter, optionally, a compound (B1) having a portion compatible with the above (A) component may be referred to as "compound (B1)" or "(B1) component", and the like. The incompatible component (B) may consist only of the compound (B1).

Due to the fact that the sealant layer 16 includes the first resin layer 16a containing the above (A) component and the above (B) component, a sea-island structure is formed in the resin layer. In other words, the first resin layer 16a has an existing region of the polypropylene-based resin (A), and a

plurality of existing regions of the incompatible component (B) surrounded by the above polypropylene-based resin (A). As a result of this, it is possible to improve the seal strength after heat seal. Due to the fact that the first resin layer 16a further includes the above (C) component, it is possible to impart flexibility to the sealant layer 16 further. Due to the fact that the sealant layer 16 has flexibility, it is possible to impart functions such as suppression of molding whitening, and it is possible to provide a packaging material having further improved functionalities.

Each of the components which can be contained in the first resin layer 16a will be illustrated below.

(Polypropylene-Based Resin (A))

The polypropylene-based resin (A) is a resin obtained from polymerized monomers including propylene. Examples of the polypropylene-based resin (A) include homopolypropylene and random polypropylene. In view of the fundamental performance of the packaging material such as heat seal strength, it is preferable that the polypropylene-based resin (A) be random polypropylene, and it is more preferable that the polypropylene-based resin (A) be a propylene-ethylene random copolymer. The propylene-ethylene random copolymer has excellent heat sealability at low temperatures, and can improve the sealing properties in the case of involvement of the electrolytic solution.

In the propylene-ethylene random copolymer, it is preferable that the content of ethylene be 0.1 to 10% by mass, it is more preferable that the content of ethylene be 1 to 7% by mass, and it is further preferable that the content of ethylene be 2 to 5% by mass. When the content of ethylene is 0.1% by mass or more, the effect of reducing the melting point by copolymerization of ethylene is satisfactorily achieved to enable further improvement in sealing properties in the case of involvement of the electrolytic solution, and in addition, to obtain the impact resistance, and it tends to enable improvement in sealing strength and molding whitening resistance. When the content of ethylene is 10% by mass or less, it tends to enable excessive decrease in melting point to be suppressed, and to enable generation of excessively sealed portions to be suppressed more satisfactorily. Note that the content of ethylene can be calculated from the mixing ratio of the monomers in polymerization.

It is preferable that the melting point of the propylene-ethylene random copolymer be 120 to 145° C., and it is more preferable that the melting point of the random polypropylene be 125 to 140° C. When this melting point is 120° C. or more, it tends to enable generation of excessively sealed portions to be suppressed more satisfactorily. When the melting point is 145° C. or less, it tends to enable further improvement in sealing properties in the case of involvement of the electrolytic solution.

The propylene-ethylene random copolymer may be acid-modified, and for example, can be an acid-modified propylene-ethylene random copolymer obtained by graft modification with maleic anhydride. By using the acid-modified propylene-ethylene random copolymer, it is possible to retain the adhesiveness to tab leads without a tab sealant.

With regard to the propylene-ethylene random copolymer, it is possible to use one alone, or to use a combination of two or more thereof.

In the first resin layer 16a, the content of the (A) component may be 50 to 99% by mass based on the total amount of solid contents of the first resin layer 16a, may be 50 to 95% by mass, and may be 50 to 85% by mass. As a result of the fact that the content of the (A) component is 50% by mass or more, it is possible to improve the sealing properties by an effect of using the (A) component by nature. Also, it

is possible to prevent excessive presence of the (B) component by setting the content of the (A) component to be 50% by mass or more, and therefore, a good sea-island structure tends to be formed, and in addition, it is possible to suppress the decrease in the heat resistance and the aggregation force of sealant layer 16. On the other hand, due to the fact that inclusion of 1% by mass or more of the (B) component can be achieved by setting the content of the (A) component to be 99% by mass or less, it is possible to improve the seal strength and the insulating properties due to the (B) component.

(Incompatible Component (B))

Examples of the incompatible component (B) include graft copolymers, block copolymers, and random copolymers. These copolymers have a portion incompatible with the (A) component in at least a portion thereof.

It is preferable that the incompatible component (B) contain a compound (B1) having a portion compatible with the polypropylene-based resin (A). It is possible to suppress the value of $\tan \delta$ (I) due to the fact that the incompatible component (B) contains the compound (B1), and therefore, it is possible to improve the ratio (II/I) in the sealant layer 16, and improve adhesion strength of the interface of sea-island structure, formation of voids associated with bubbling of the electrolytic solution is suppressed, and therefore, it is possible to improve the insulating properties further. Also, as a result of the improvement in the adhesion strength sea-island interface resulting from the compound (B1), the seal strength can also be improved. Such a compound (B1) can be obtained, for example, in the case where the incompatible component (B) is a graft copolymer or a block copolymer. Examples of the graft copolymer suitable for the compound (B1) include a graft copolymer consisting of a main chain of polyolefin and a side chain of polystyrene, and a graft copolymer consisting of a main chain of polyolefin and a side chain of styrene-acrylonitrile copolymer. As the above graft copolymer, for example, "MODIPER" manufactured by NOF Corporation, and the like are suitable.

Examples of the block copolymer suitable for the compound (B1) include a block copolymer having a block configured by styrene units and a block configured by ethylene-butylene units; a block copolymer having a block configured by styrene units, a block configured by ethylene-butylene units and a block configured by crystalline olefin units; a block copolymer having a block configured by crystalline ethylene units and a block configured by ethylene-butylene units; a block copolymer having a block configured by ethylene and a block configured by ethylene-octene-1; and a block copolymer having a block configured by propylene units and a block configured by ethylene units. For example, the block configured by propylene units is a portion compatible with the above (A) component, and the block configured by ethylene units is a portion incompatible with the above (A) component. As the above block copolymer, for example, "DYNARON" manufactured by JSR, "INTUNE" and "INFUSE" manufactured by DOW, and the like are suitable.

The incompatible component (B) may contain an incompatible elastomer. Examples of the incompatible elastomer include a polyolefin-based elastomers containing α -olefin as comonomers. In particular, by using ethylene- α -olefin copolymers, it tends to enable the impartment of functionalities to the sealant layer 16 without reducing the electrolytic solution laminating strength, or a variety of seal strengths in the case of involvement of the electrolytic solution. As the ethylene- α -olefin copolymer, it is possible to use a compound obtained by copolymerizing at least one α -olefin

selected from the group consisting of 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-pentene to ethylene, and it is preferably to use an ethylene-butene-1 random copolymer obtained by copolymerizing 1-butene to ethylene. As the ethylene- α -olefin copolymer, "TAFMER" manufactured by Mitsui Chemicals Inc., "EXCELLEN" manufactured by Sumitomo Chemical Company, Limited., and the like are suitable.

By providing a dispersion obtained by dispersing the incompatible component (B) in the polypropylene-based resin (A), and as a result of the use of the dispersion, the first resin layer 16a may contain a polypropylene-based resin (A), and incompatible component (B). Examples of such a dispersion include a dispersion obtained by microdispersing an elastomer in a polypropylene-based resin. As a result of the fact that the first resin layer 16a includes a dispersion obtained by dispersing the incompatible component (B) in the polypropylene-based resin (A) in advance, it tends to enable further improvement in the insulating properties and the seal strength. It is preferable that the incompatible component (B) in the above dispersion contain a graft copolymer or a block copolymer. As a result of the fact that the incompatible component (B) in the dispersion contains a graft copolymer or a block copolymer, it tends to enable further improvement in the adhesiveness of the sea-island interface.

As the incompatible component (B), the olefin-based and the styrene-based materials are described above; however, in view of the electrolytic solution resistance, it is preferable that the incompatible component (B) be an olefin-based material.

(Compatible Component (C))

The compatible component (C) may contain a compatible elastomer. Examples of the compatible elastomer include propylene- α -olefin copolymers. By using the propylene- α -olefin copolymer, it is possible to impart functionalities to the sealant layer 16 without reducing the electrolytic solution laminating strength, or a variety of seal strengths in the case of involvement of the electrolytic solution. As the propylene- α -olefin copolymer, it is possible to use a compound obtained by copolymerizing α -olefin selected from 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-pentene to propylene, and it is preferably possible to use a propylene-butene-1 random copolymer obtained by copolymerizing 1-butene to propylene.

It is preferable that the melting point of the polyolefin-based elastomer be 150° C. or less; however, in view of suppressing the excessively sealed portion, suppressing molding whitening, and improving the sealing properties in the case of involvement of the electrolytic solution, it is preferable that the melting point of the polyolefin-based elastomer be 60 to 120° C., and it is more preferable that the melting point of the polyolefin-based elastomer be 65 to 90° C. As a result of the fact that this melting point is 150° C. or less, it is possible to improve the sealing properties in the case of involvement of the electrolytic solution, in particular, the degassing heat sealing strength. Also, when this melting point is 60° C. or more, it is advantageous in view of suppressing the generation of the excessively sealed portions.

With regard to the polyolefin-based elastomer, it is possible to use one alone, or to use a combination of two or more thereof.

In the first resin layer 16a, the content of the (B) component is preferably 1 to 40% by mass based on the total amount of solid contents of the first resin layer 16a, and more preferably 2 to 25% by mass. As a result of the fact that

the content of the (B) component is 1% by mass or more, it is possible to impart impact resistance to the sealant layer 16, and it is possible to improve the seal strength and the insulating properties. On the other hand, it is possible to suppress the value of $\tan \delta$ (1) by setting the content of the (B) component to be 40% by mass or less, and therefore, it tends to form a good sea-island structure, and in addition, it is possible to improve the aggregation force of the entirety of the sealant layer 16, and improve the seal strength and the insulating properties. Note that, for the sake of convenience, the dispersion obtained by microdispersing an elastomer in a polypropylene-based resin is described as an incompatible component (B); however, in the above dispersion, the elastomer portion is classified as the (B) component, and the polypropylene-based resin is classified as the above (A) component.

When the first resin layer 16a includes the (C) component, the content of the (C) component in the first resin layer 16a is preferably 5 to 30% by mass, more preferably 10 to 25% by mass based on the total amount of solid contents of the first resin layer 16a. As a result of the fact that the content of the (C) component is 5% by mass or more, the flexibility of the sealant layer 16 tends to be achieved, and it is possible to impart functions such as suppression of molding whitening, and it is possible to provide a packaging material having further improved functionalities. On the other hand, by setting the content of the (C) component to be 30% by mass or less, it is possible to improve the aggregation force of the entirety of the sealant layer 16, and it is possible to improve the seal strength and the insulating properties.

Also, it is preferable that the ratio of the content of the compatible component (C) to the content of the incompatible component (B) (Mc/MB) be 0.2 to 3.0 based on the mass ratio, and it is more preferable that this ratio be 0.3 to 2.0. As a result of the fact that the ratio of these contents (Mc/MB) is in the above range, the seal strength tends to be improved.

When the incompatible component (B) contains the compound (B1), it is preferable that the content of the compound (B1) in the first resin layer 16a be 1 to 40% by mass based on the total amount of the first resin layer 16a, and it is more preferable that this content be 2 to 25% by mass. As a result of the fact that the content of the compound (B1) is 1% by mass or more, the adhesion strength of the sea-island interface tends to enhance, and an effect of improving the seal strength and the insulating properties tend to be achieved. On the other hand, by setting the content of the compound (B1) to be 40% by mass or less, it tends to suppress the aggregation force of the entirety of the sealant layer 16 as well as the seal strength and the decrease in insulating properties.

(Components to be Added)

The first resin layer 16a can further include other components other than the (A) to (C) component described above. As other components other than the (A) to (C) components, it is possible to add, for example, other resins such as LDPE (low density polyethylene) in order to improve take-up easiness and processability. It is preferable that the content of the other resin components to be added be 10 parts by mass or less when the total mass of the first resin layer 16a is regarded as 100 parts by mass. Also, examples of components other than resins include slip agents, anti-blocking agents, antioxidants, light stabilizers, and flame retardants. It is preferable that the content of the other component other than resins be 5 parts by mass or less when the total mass of the first resin layer 16a is regarded as 100 parts by mass.

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In the first resin layer **16a**, it is possible to identify the presence of α -olefin by attribution using FT-IR (Fourier transform infrared spectrophotometer). Also, it is possible to identify the content of α -olefin by producing a calibration curve with regard to transmittance or absorbance in characteristic absorption bands of the (A) to (C) components by using a first resin layer **16a** in which a known amount of elastomers including a known amount of α -olefin are mixed. In addition, it is possible to identify the content of α -olefin in each of the incompatible component (B) and the compatible component (C) by conducting imaging also in characteristic absorption band of FT-IR, and conducting the mapping of absorption band resulting from α -olefin by using microscopic FT-IR (transmission method). Note that in addition to FT-IR, it is possible to identify the presence and the content of α -olefin by measuring the first resin layer **16a** by NMR.

The thickness of the first resin layer **16a** is, for example, 5 to 100 μm . Due to a demand for downsizing power storage devices, the thickness of the first resin layer **16a** may be 10 to 80 μm , may be 10 to 60 μm , may be 10 to 45 μm , and may be 30 μm or less. Even in such a thin film configuration, the packaging material for a power storage device of the present embodiment can suppress decrease in insulating properties after heat seal, molding and degassing heat sealing.

Although preferable embodiments of the packaging material for a power storage device of the present embodiment have been described above in detail, the present disclosure is not limited to such certain embodiments, and a variety of variations and modifications can be made within the scope of the present disclosure defined in the claims.

For example, FIG. 1 shows the case where the anti-corrosion treatment layer **14** is formed on a face on the side of a second adhesive layer **17** of a metallic foil layer **13**; however, the anti-corrosion treatment layer **14** may be formed on a face on the side of a first adhesive layer **12** of a metallic foil layer **13**, or may be formed on both faces of the metallic foil layer **13**. In a case where the anti-corrosion treatment layer **14** is formed on both faces of the metallic foil layer **13**, a configuration for the anti-corrosion treatment layer **14** to be formed on the side of the first adhesive layer **12** of the metallic foil layer **13**, and a configuration for the anti-corrosion treatment layer **14** to be formed on the side of the second adhesive layer **17** of the metallic foil layer **13** may be the same as or different than each other.

Although FIG. 1 shows a case where the metallic foil layer **13** and the sealant layer **16** are laminated by use of the second adhesive layer **17**, as in the packaging material for a power storage device **20** shown in FIG. 2 and the packaging material for a power storage device **30** shown in FIG. 3, the sealant layer **16** may be directly formed on the metallic foil layer **13** without the interposition of the second adhesive layer **17**. On the other hand, the packaging material for a power storage device **20** shown in FIG. 2 and the packaging material for a power storage device **30** shown in FIG. 3 may comprise the second adhesive layer **17** between the metallic foil layer **13** and the sealant layer **16**.

FIG. 1 shows the case where the sealant layer **16** is formed by a single layer, in other words, in the case where the sealant layer **16** consists of a first resin layer **16a**; however, the sealant layer **16** may be formed by two or more of multiple layers, as in a packaging material for a power storage device **20** shown in FIG. 2, and a packaging material for a power storage device **30** shown in FIG. 3. Note that when the sealant layer **16** is formed by multiple layers, as for loss tangent $\tan \delta$ obtained by dynamic viscoelasticity measurement at a frequency of 1.0 Hz, sealant layers **16**

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constituting the multiple layers have, in their entirety, a maximal value of $\tan \delta$ at -30 to 30°C. , and a ratio (II/I) of the maximal value (II) of $\tan \delta$ at -30 to 30°C. to the value (I) of $\tan \delta$ at -50°C. is 2.50 or more. In a standpoint analogous to as described above, with regard to the sealant layers **16** constituting the multiple layers, in their entirety, a ratio (III/II) of a maximum value (III) of $\tan \delta$ at 90 to 100°C. to the above (II) may be 1.00 or less.

In a packaging material for a power storage device **20** shown in FIG. 2, the sealant layer **16** is configured by a first resin layer **16a** and a second resin layer **16b**. Here, the first resin layer **16a** is the innermost layer in the sealant layer **16**, and the second resin layer **16b** is the outermost layer disposed on the side of the metallic foil layer **13** in the sealant layer **16**.

In the packaging material for a power storage device **20**, the first resin layer **16a** is analogous to as those in the first resin layer **16a** in the above packaging material for a power storage device **10**, and the overlapping descriptions are omitted here.

The second resin layer **16b** may include a polypropylene-based resin (D) and an incompatible component (E) incompatible with the polypropylene-based resin (D). Also, it is preferable that the second resin layer **16b** further contain a compatible component (F) compatible with the polypropylene-based resin (D). The second resin layer **16b** may be formed by using constituents analogous to those in, for example, the first resin layer **16a**; however, in the second resin layer **16b**, for example, instead of constituents analogous to those in the first resin layer **16a**, it is preferable to use an adhesive constituent including, where appropriate, an additive component in view of the adhesiveness to the metallic foil layer. By using the above adhesive constituent as the second resin layer **16b**, it is possible to form a sealant layer on the metallic foil layer without the interposition of an adhesive layer. Hereby, it is possible to improve the adhesiveness of the sea-island interface, and in addition, it tends to facilitate the adhesiveness between the sealant layer and the metallic foil layer to be retained, to prevent the generation of voids associated with bubbling of the electrolytic solution, and to facilitate the decrease in insulating properties after degassing heat sealing to be further suppressed.

Each of the components which can be included in the second resin layer **16b** will be illustrated below.

(Polypropylene-Based Resin (D))

The polypropylene-based resin (D) may be analogous to the above polypropylene-based resin (A), and can be, for example, a modified polypropylene-based resin such as an acid-modified polypropylene-based resin. It is preferable that the modified polypropylene-based resin be a resin in which an unsaturated carboxylic acid derivative component derived from any of an unsaturated carboxylic acid, an acid anhydride of an unsaturated carboxylic acid, and an ester of an unsaturated carboxylic acid is graft-modified to a polypropylene-based resin. Examples of the polypropylene-based resin in this case include homopolypropylene and random polypropylene.

Examples of a compound for use in graft modification of these polypropylene-based resins include an unsaturated carboxylic acid derivative component derived from any of an unsaturated carboxylic acid, an acid anhydride of an unsaturated carboxylic acid, and an ester of an unsaturated carboxylic acid.

Specific examples of the unsaturated carboxylic acid include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, tetrahydrophthalic acid, and bicyclo[2,2,1]hept-2-en-5,6-dicarboxylic acid.

Examples of the acid anhydride of the unsaturated carboxylic acid include acid anhydride of an unsaturated carboxylic acid such as maleic anhydride, itaconic anhydride, citraconic anhydride, tetrahydrophthalic anhydride, and bicyclo[2,2,1]hept-2-en-5,6-dicarboxylic anhydride.

Examples of the ester of the unsaturated carboxylic acid include esters of an unsaturated carboxylic acid such as methyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, dimethyl maleate, monomethyl maleate, diethyl fumarate, dimethyl itaconate, diethyl citraconate, dimethyl tetrahydrophthalate anhydride, and dimethyl bicyclo[2,2,1]hept-2-en-5,6-dicarboxylate.

The modified polypropylene-based resin can be produced by graft polymerization (graft modification) of 0.2 to 100 parts by mass of the unsaturated carboxylic acid derivative component described above per 100 parts by mass of the polypropylene-based resin as a base component under the presence of a radical initiator. It is preferable that the reaction temperature of the graft modification be 50 to 250° C., and it is more preferable that it be 60 to 200° C. Also, the reaction time is appropriately set depending on the production method, and for example, in a case of melt graft polymerization by a twin-screw extruder, it is preferable that the reaction time be within the residence time in the extruder, and specifically 2 to 30 minutes, and it is more preferable that the reaction time be 5 to 10 minutes. Note that the graft modification can be conducted under conditions of either normal pressure or with pressurization.

Examples of the radical initiator for use in the graft modification include organic peroxide such as alkyl peroxide, aryl peroxide, acyl peroxide, ketone peroxide, peroxyketal, peroxy carbonate, peroxyester, and hydroperoxide.

It is possible to appropriately select and use the organic peroxide depending on conditions with regard to the reaction temperature and the reaction time described above. For example, in a case of melt graft polymerization with a twin-screw extruder, alkyl peroxide, peroxyketal, and peroxyester are preferable, and specifically, di-*t*-butyl peroxide, 2,5-dimethyl-2,5-di-*t*-butylperoxy-hexin-3, dicumyl peroxide and the like are preferable.

As the modified polypropylene-based resin, it is preferable that the polypropylene-based resin be modified with maleic anhydride, and for example, "ADMER" manufactured by Mitsui Chemicals Inc., and "MODIC" manufactured by Mitsubishi Chemical Corporation and the like are suitable. Such a modified polyolefin resin has good reactivity with polymers having a variety of metals and a variety of functional groups, and it is therefore possible to impart the adhesiveness to the second resin layer 16*b* using this reactivity, and to improve the electrolytic solution resistance. (Incompatible Component (E))

The incompatible component (E) is a component incompatible with the above polypropylene-based resin (D), and, for example, forms a macro-phase separated structure in which the disperse phase size is in a range of 200 nm or more and less than 50 μm in relation to the polypropylene-based resin (D). Due to the fact that the second resin layer 16*b* contains the incompatible component (E), it is possible to release residual stress generated when laminating the polypropylene-based resin (D) that can be a main component constituting the second resin layer 16*b*, and it is possible to impart the viscoelastic adhesiveness to the second resin layer 16*b*. As a result of this, the adhesiveness of the second resin layer 16*b* further enhances to obtain a packaging material 20 having better electrolytic solution resistance. Due to the fact that the second resin layer 16*b* contains the incompatible component (E), it is possible to impart the

impact resistance to the sealant layer 16, and it is possible to improve the seal strength and the insulating properties.

Such an incompatible component (E) is analogous to the above incompatible component (B), and it is possible to use a component (compound (E1)) corresponding to the above-described compound (B1); however, such an incompatible component (E) may be, for example, macro-phase separated thermoplastic elastomer, and the like. The macro-phase separated thermoplastic elastomer is present in the form of a sea-island structure in the modified polypropylene-based resin; however, when the disperse phase size is less than 200 nm, it is difficult to impart the improvement in viscoelastic adhesiveness. On the other hand, when the disperse phase size is 50 μm or more, since the modified polypropylene-based resin and the macro-phase separated thermoplastic elastomer are essentially incompatible with each other, the laminating suitability (processability) significantly decreases, and in addition, the physical strength of the second resin layer 16*b* tends to decrease. In view of the above-mentioned facts, it is preferable that the disperse phase size be 500 nm to 10 μm.

Examples of such a macro-phase separated thermoplastic elastomer include a polyethylene-based thermoplastic elastomer in which ethylene is copolymerized with an α -olefin selected from 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-pentene.

Also, as the macro-phase separated thermoplastic elastomer, it is possible to use commercially available products, and for example, "TAFMER" manufactured by Mitsui Chemicals Inc., "ZELAS" manufactured by Mitsubishi Chemical Corporation, "Catalloy" manufactured by Montell and the like are suitable.

In the second resin layer 16*b*, the content of the incompatible component (E) with respect to the polypropylene-based resin (D) is preferably 1 to 40 parts by mass per 100 parts by mass of the polypropylene-based resin (D), and more preferably 5 to 30 parts by mass. Here, when the content of the incompatible component (E) is less than 1 parts by mass, the adhesiveness of the second resin layer 16*b* is not expected to enhance. On the other hand, when the content of the incompatible component (E) is greater than 40 parts by mass, the polypropylene-based resin (D) and the incompatible component (E) have low compatibility with each other by nature, and therefore, the processability tends to decrease significantly. Also, the adhesiveness of the second resin layer 16*b* to other layers such as the first resin layer 16*a* and the anti-corrosion treatment layer 14 tends to decrease.

(Compatible Component (F))

It is preferable that the second resin layer 16*b* further contain a compatible component (F) compatible with the polypropylene-based resin (D). The compatible component (F) can be a compatible elastomer, and preferably includes polypropylene with an atactic structure or a propylene- α -olefin copolymer with an atactic structure. Here, the compatible component (F) is, for example, a fully amorphous resin component. Due to the fact that the second resin layer 16*b* includes the compatible component (F), it is possible to impart flexibility to the sealant layer 16. Due to the fact that the sealant layer 16 has flexibility, it is possible to impart functions such as suppression of molding whitening to the packaging material 20, and it is possible to provide a packaging material having further improved functionalities.

Note that the second resin layer 16*b* may further include a propylene- α -olefin copolymer with an isotactic structure corresponding to the (F) component as an additive component for the impartment of flexibility, in addition to poly-

propylene with the above atactic structure or a propylene- α -olefin copolymer with an atactic structure.

In the second resin layer **16b**, the total mass of the polypropylene-based resin (D) and the incompatible component (E) may be, for example, 60% by mass or more and 95% by mass or less based on the total mass of the second resin layer **16b**, and may be 70% by mass or more and 90% by mass or less.

In the second resin layer **16b**, it is preferable that the content of the compatible component (F) be, for example, 5% by mass or more and 40% by mass or less based on the total mass of the second resin layer **16b**. When the above content of the compatible component (F) is 5% by mass or more, it tends to facilitate for an effect resulting from the addition of as an additive described above to be achieved. On the other hand, this content is 40% by mass or less, the adhesiveness of the second resin layer **16b** to other layers such as the first resin layer **16a** and the anti-corrosion treatment layer **14** tends to be achieved.

Note that, as a method for analyzing the compatible component (F) in the second resin layer **16b**, for example, it is possible to conduct quantification by evaluation of tacticity by nuclear magnetic resonance spectroscopy (NMR).

In addition to the above components, the second resin layer **16b** can contain a variety of additives such as flame retardant, slip agent, anti-blocking agents, antioxidants, light stabilizers and tackifiers, where appropriate.

The thickness of the second resin layer **16b** is not limited in particular; however, in view of relaxation of stress and in view of permeation of moisture and electrolytic solution, it is preferable that the thickness of the second resin layer **16b** be equal to or less than that of the first resin layer **16a**.

In addition, also in a packaging material for a power storage device **20**, the thickness of the sealant layer **16** (the total thickness of the first resin layer **16a** and the second resin layer **16b**) may be 10 to 80 μm , may be 10 to 60 μm , may be 10 to 45 μm , and may be 30 μm or less in view of thinning. Even in such a thin film configuration, the packaging material for a power storage device of the present embodiment can suppress decrease in insulating properties after heat seal, molding and degassing heat sealing.

FIG. 2 shows a case where the sealant layer **16** is formed by two layers; however, sealant layer **16** may be formed by three layers, as in a packaging material for a power storage device **30** shown in FIG. 3. In a packaging material for a power storage device **30** shown in FIG. 3, the sealant layer **16** is configured by a first resin layer **16a**, a second resin layer **16b**, and a third resin layer **16c**. Here, the first resin layer **16a** is the innermost layer in the sealant layer **16**, and the third resin layer **16c** is an intermediate layer in the sealant layer **16**, and the second resin layer **16b** is the outermost layer (on the side of metallic foil layer **13**) in the sealant layer **16**.

Examples and preferable embodiments regarding the materials constituting the first resin layer **16a** and the second resin layer **16b** of the packaging material for a power storage device **30** are analogous to those in the first resin layer **16a** and the second resin layer **16b** of the packaging material for a power storage device **10** and **20**, and the overlapping descriptions are omitted here. Note that Examples and preferable embodiments regarding the materials constituting the third resin layer **16c** are not limited in particular, and can be analogous to those in the above first resin layer **16a** or the above second resin layer **16b**, for example.

In the packaging material for a power storage device **30**, the thickness of the second resin layer **16b** may be, for example, 2 to 30 μm , may be 5 to 20 μm , and may be 8 to

10 μm . The thickness of the first resin layer **16a** may be, for example, 5 to 80 μm , may be 13 to 40 μm , and may be 15 to 20 μm . The thickness of the third resin layer **16c** may be, for example, 2 to 30 μm , may be 5 to 20 μm , and may be 8 to 10 μm .

Also in the packaging material for a power storage device **30**, the thickness of the sealant layer **16** (the total thickness of the first resin layer **16a**, the second resin layer **16b**, and the third resin layer **16c**) may be 30 μm or less in view of thinning. Even in such a thin film configuration, the packaging material for a power storage device of the present embodiment can suppress decrease in insulating properties after heat seal, molding and degassing heat sealing.

[Method for Producing Packaging Material]

Next, one example of a method for producing the packaging material **10** shown in FIG. 1 will be illustrated. Note that the method for producing the packaging material **10** is not limited to the following method.

A method for producing the packaging material **10** of the present embodiment is generally configured by comprising a step of laminating the anti-corrosion treatment layer **14** on the metallic foil layer **13**, a step of bonding the substrate layer **11** and the metallic foil layer **13**, a step of further laminating the sealant layer **16** with the interposition of a second adhesive layer **17** to produce a laminate, and where appropriate, a step of subjecting the obtained laminate to aging treatment.

(Step of Laminating Anti-Corrosion Treatment Layer **14** on Metallic Foil Layer **13**)

The present step is a step of forming the anti-corrosion treatment layer **14** on the metallic foil layer **13**. Examples of the method for this step include methods of, subjecting the metallic foil layer **13** to degreasing treatment, hydrothermal metamorphism treatment, positive electrode oxidation treatment or chemical conversion treatment, or methods of applying a coating agent having anti-corrosion performance to the metallic foil layer **13**, as described above.

Also, when the anti-corrosion treatment layer **14** is multilayered, for example, it is possible to apply a coating solution (coating agent) constituting an anti-corrosion treatment layer on the side of the lower layer (on the side of the metallic foil layer **13**) to the metallic foil layer **13**, followed by burning to form a first layer, and subsequently, applying a coating solution (coating agent) constituting an anti-corrosion treatment layer on the side of the upper layer to the first layer, followed by burning to form a second layer.

It is possible to conduct the degreasing treatment by a spraying process or a dipping process. It is possible to conduct the hydrothermal metamorphism treatment and the positive electrode oxidizing treatment by a dipping process. It is possible to conduct the chemical conversion treatment, depending on the type of the chemical conversion treatment, by appropriately selecting a dipping process, a spraying process, coating process, or the like.

With regard to the coating process of the coating agent having anti-corrosion performance, it is possible to use a variety of methods such as gravure coating, reverse coating, roll coating, and bar coating.

As described above, a variety of treatment can be conducted on both faces or one face of the metallic foil; however, in the case where the treatment is conducted on one face of the metallic foil, with regard to the face to be treated, it is preferable to conduct the treatment on the side to which the second adhesive layer **17** is to be laminated. Note that, where appropriate, it is also possible to conduct the above treatment on a surface of the substrate layer **11**.

Also, it is preferable for each of the amounts of the coating agent for forming the first and second layers to be 0.005 to 0.200 g/m², and it is more preferable for each of the amounts to be 0.010 to 0.100 g/m².

Also, when dry curing is needed, depending on the drying conditions with regard to the anti-corrosion treatment layer 14 to be used, it is possible to conduct dry curing with the temperature of the base material in a range of 60 to 300° C. (Step of Bonding Substrate Layer 11 with Metallic Foil Layer 13)

The present step is a step of bonding the metallic foil layer 13 on which the anti-corrosion treatment layer 14 is disposed, and the substrate layer 11 with the interposition of the first adhesive layer 12. With regard to the bonding method, the metallic foil layer 13 and the substrate layer 11 are bonded by means of the materials constituting the above-described first adhesive layer 12 using approaches such as dry lamination, non-solvent lamination and wet lamination. The first adhesive layer 12 is provided to be in a range of 1 to 10 g/m², more preferably in a range of 3 to 7 g/m² on the basis of the amount for dry application.

(Step of Laminating Second Adhesive Layer 17 and Sealant Layer 16)

The present step is a step of bonding the sealant layer 16 to the side of the anti-corrosion treatment layer 14 of the metallic foil layer 13 with the interposition of the second adhesive layer 17. Examples of the method for this bonding include a wet process, and dry lamination, and the like.

In the case of the wet process, a solution or dispersion of the adhesive constituting the second adhesive layer 17 is coated on the anti-corrosion treatment layer 14, and the solvent is evaporated at a predetermined temperature (in a case where the adhesive includes an acid-modified polyolefin resin, at a temperature equal to or higher than the melting point of the acid-modified polyolefin resin), and drying and film forming are conducted, or where appropriate, burning treatments is conducted after drying and film forming. Next, the sealant layers 16 are laminated to produce the packaging material 10. Examples of the coating method include a variety of coating methods illustrated above.

In this case, the sealant layer 16 can be produced by, for example, a melt extruder. It is possible in a melt extruder to set the processing speed to be 80 m/min or more, in view of productivity.

(Step of Aging Treatment)

The present step is a step of subjecting the laminate to aging (curing) treatment. By subjecting the laminate to aging treatment, it is possible to promote adhesion between the metallic foil layer 13/the anti-corrosion treatment layer 14/the second adhesive layer 17/the sealant layer 16. The aging treatment can be conducted in a range of room temperature to 100° C. The aging time is, for example, 1 to 10 days.

In this way, it is possible to produce the packaging material 10 of the present embodiment as shown in FIG. 1.

Next, one example of a method for producing the packaging material 20 shown in FIG. 2 will be illustrated. Note that a method for producing the packaging material 20 is not limited to the following method.

A method for producing the packaging material 20 of the present embodiment is generally configured by comprising a step of laminating the anti-corrosion treatment layer 14 on the metallic foil layer 13, a step of bonding the substrate layer 11 and the metallic foil layer 13, a step of further laminating the second resin layer 16b and the first resin layer 16a to produce a laminate, and where appropriate, a step of

subjecting the obtained laminate to heat treatment. Note that it is possible to conduct the steps up to the step of bonding the substrate layer 11 and the metallic foil layer 13, in a manner analogous to as in the method for producing the above-described packaging material 10.

(Step of Laminating Second Resin Layer 16b and First Resin Layer 16a)

The present step is a step of forming the second resin layer 16b and the first resin layer 16a on the anti-corrosion treatment layer 14 formed by the previous step. Examples of the method for this step include a method for subjecting the second resin layer 16b together with the first resin layer 16a to sandwich lamination by use of an extrusion laminating machine. In addition, this laminating can be conducted by a tandem laminating process for extruding the first resin layer 16a and the second resin layer 16b, or by a coextrusion process. In the formation of the first resin layer 16a and the second resin layer 16b, for example, the components are mixed with each other so as to meet the configuration of the first resin layer 16a and the second resin layer 16b described above.

By means of the present step, a laminate in which each of the layers are laminated in order of the substrate layer 11/the first adhesive layer 12/the metallic foil layer 13/the anti-corrosion treatment layer 14/the second resin layer 16b/the first resin layer 16a as shown in FIG. 2 is obtained.

Note that the first resin layer 16a can be obtained by directly laminating materials that have been dry-blended by means of extrusion using an extrusion laminating machine so as to achieve the mixing composition of the materials described above. Alternatively, the first resin layer 16a can be obtained by laminating, by means of extrusion using an extrusion laminating machine, the granulated granulation products that have been subjected to melt blending with a melt kneading machine such as a single-screw extruder, a twin-screw extruder, and a Brabender mixer in advance.

The second resin layer 16b can be obtained by directly laminating, as constituents for forming the sealant layer, materials that have been dry-blended by means of extrusion using an extrusion laminating machine so as to achieve the mixing composition of the materials described above. Alternatively, the first resin layer 16a and the second resin layer 16b can be obtained by laminating, with an extrusion laminating machine, the granulation products that have been subjected to melt blending with a melt kneading machine such as a single-screw extruder, a twin-screw extruder, and a Brabender mixer in advance, according to a tandem laminating process for extruding the first resin layer 16a and the second resin layer 16b, or according to a coextrusion process. Also, by using the constituents for forming the sealant layer, it is possible to form a single film of the sealant as a casted film in advance, and it is possible to laminate the single film of the sealant by a method in which this film is subjected to sandwich lamination together with an adhesive resin, or it is possible to laminate the single film of the sealant by a dry lamination process using an adhesive. The formation speed (processing speed) of the resin layers 16a, 16b can be, for example, 80 m/min or more, in view of productivity.

(Step of Heat Treatment)

The present step is a step of subjecting the laminate to heat treatment. By subjecting the laminate to heat treatment, it is possible to improve the adhesion between the metallic foil layer 13/the anti-corrosion treatment layer 14/the second resin layer 16b/the first resin layer 16a to impart better electrolytic solution resistance and hydrofluoric acid resistance to the laminate. With regard to the method for heat

treatment, it is preferable to conduct the heat treatment at a temperature, at least higher than or equal to the melting points of the first resin layer 16a. Examples of the heat treatment include, but are not limited to, approaches such as heating by an oven, sandwiching by a heated roll (heat lamination), wrapping around a heated roll. Depending on an approach to conducting heat treatment, temperature conditions, and the like, it is possible to adjust the heat treatment time appropriately, in view of the performance (the adhesion strength (laminating strength) between the metallic foil layer 13/the anti-corrosion treatment layer 14/the second resin layer 16b/the first resin layer 16a) and in view of productivity. For example, when heat treatment is conducted by means of an approach to sandwiching by a heated roll or by means of an approach to wrapping around a heated roll, it is possible for the heat treatment time to be 0.5 seconds or more in view of the above performance, and it is possible for the heat treatment time to be 1.0 seconds or less in view of productivity.

In this way, it is possible to produce the packaging material 20 of the present embodiment as shown in FIG. 2.

Next, one example of a method for producing the packaging material 30 shown in FIG. 3 will be illustrated. Note that the method for producing the packaging material 30 is not limited to the following method.

A method for producing the packaging material 30 of the present embodiment is generally configured by comprising a step of laminating the anti-corrosion treatment layer 14 on the metallic foil layer 13, a step of bonding the substrate layer 11 and the metallic foil layer 13, a step of further laminating the second resin layer 16b, the third resin layer 16c and the first resin layer 16a to produce a laminate, and where appropriate, a step of subjecting the obtained laminate to heat treatment.

(Step of Laminating Second Resin Layer 16b, Third Resin Layer 16c, and First Resin Layer 16a)

The present step is a step of forming a second resin layer 16b, a third resin layer 16c and a first resin layer 16a on an anti-corrosion treatment layer 14. Examples of the method for this step include a tandem laminating process for extruding the second resin layer 16b, the third resin layer 16c, and the first resin layer 16a by use of an extrusion laminating machine, and a coextrusion process. In this case, as constituents for forming the resin layer, the second resin layer 16b, the third resin layer 16c, and the first resin layer 16a can be directly laminated by extruding, with an extrusion laminating machine, materials that have been dry-blended so as to achieve the mixing composition of the materials described above. Alternatively, the second resin layer 16b, the third resin layer 16c, and the first resin layer 16a can be laminated by a tandem laminating process for extruding the second resin layer 16b and the third resin layer 16c, and a first resin layer 16a by use of an extrusion laminating machine, or a coextrusion process, using the granulation products that have been subjected to melt blending with a melt kneading machine such as a single-screw extruder, a twin-screw extruder, and a Brabender mixer in advance.

The third resin layer 16c and the second resin layer 16b are formed as films by coextrusion, and these films may be laminated by a method for subjecting these films together with constituents for forming the first resin layer 16a to sandwich lamination. The formation speed (processing speed) of the resin layers 16a, 16b, 16c can be, for example, 80 m/min or more, in view of productivity. The method for producing the packaging material 30 of the present embodiment may comprise the step of heat treatment described above with reference to a method for producing the pack-

aging material 20. The approach to conducting heat treatment and the conditions of heat treatment can be analogous to those described above with reference to a method for producing the packaging material 20.

In this way, it is possible to produce the packaging material 30 of the present embodiment as shown in FIG. 3.

Although preferable embodiments of the packaging material for a power storage device according to the present disclosure have been described above in detail, the present disclosure is not limited to such certain embodiments, and a variety of variations and modifications can be made within the scope of the present disclosure defined in the claims. For example, in the case where a packaging material for a power storage device having no first adhesive layer 12 is produced, it is possible to apply or coat a resin material that can form the substrate layer 11 on the metallic foil layer 13 to form a substrate layer 11, as described above.

The packaging material for a power storage device of the present disclosure can be suitably used as a packaging material for a power storage device such as, for example, secondary batteries such as lithium ion batteries, nickel-hydrogen batteries and lead storage batteries, as well as electrochemical capacitors such as electric double layer capacitors.

Among these, the packaging material for a power storage device of the present disclosure is suitable as a packaging material for a lithium ion battery.

EXAMPLES

The present disclosure will be specifically illustrated below with reference to Examples; however, the present disclosure is not limited to the following Examples.

[Materials Used]

The material used in Examples and Comparison Examples are shown as follows.

<Substrate Layer (Thickness of 15 μm)>

A nylon film (Ny) (manufactured by Toyobo Co., Ltd.) was used.

<First Adhesive Layer (thickness of 4 μm)>

A polyurethane-based adhesive (manufactured by TOYO INK Co., Ltd.) in which a curing agent based on an adduct of tolylenediisocyanate is mixed into a polyester polyol-based base material was used.

<First Anti-Corrosion Treatment Layer (on the side of Substrate Layer) and Second Anti-Corrosion Treatment Layer (on the side of Sealant Layer)>

(CL-1): A "sol of sodium polyphosphate stabilized cerium oxide" in which the concentration of solids has been adjusted to 10% by mass using distilled water as a solvent was used. Note that the sol of sodium polyphosphate stabilized cerium oxide was obtained by the incorporation of 10 parts by mass of Na salt of phosphoric acid per 100 parts by mass of cerium oxide.

(CL-2): A composition consisting of 90% by mass of "polyallylamine (manufactured by Nitto Boseki Co., Ltd.)" in which the concentration of solids has been adjusted to 5% by mass using distilled water as a solvent, and 10% by mass of "polyglycerol polyglycidyl ether (manufactured by Nagase ChemteX Corporation)" was used.

(CL-3): On the basis of a water soluble phenol resin (manufactured by Sumitomo Bakelite Co., Ltd.) in which the concentration of solids has been adjusted to 1% by mass using an aqueous solution of phosphoric acid at the concentration of 1% by mass as a solvent, a chemical conversion treating agent in which the con-

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centration of chromium fluoride (CrF_3) has been adjusted to be 10 mg/m^2 in terms of the amount of Cr present in the final dried coat was used.

<Metallic Foil Layer (Thickness of $35 \text{ }\mu\text{m}$)>

A soft aluminum foil (manufactured by Toyo Aluminum K.K., "8079 material") subjected to annealing degreasing treatment was used.

<Second Adhesive Layer (Thickness of $3 \text{ }\mu\text{m}$)>

The following adhesives a, b were provided as adhesives for forming a second adhesive layer.

Adhesive a: an adhesive in which 10 parts by mass (the ratio by solids) of a polyisocyanate compound with an isocyanurate structure was mixed per 100 parts by mass of an acid-modified polyolefin resin dissolved in toluene.

Adhesive b: a polyurethane-based adhesive prepared by formulating a polyester polyol consisting of a hydrogenated dimeric fatty acid and a diol, and a polyisocyanate in a molar ratio (NCO/OH) of 2.

<Sealant Layer>

As components constituting a base resin composition for forming the sealant layer, the following materials were provided.

(Polypropylene (PP)-Based Resin)

PP-based resin 1 (acid-modified PP): an acid-modified polypropylene.

PP-based resin 2 (random PP): propylene-ethylene random copolymer.

(Incompatible Component)

Incompatible component 1 (block copolymer 1): a block copolymer configured by propylene units and ethylene units, and not having compatibility with acid-modified PP and random PP.

Incompatible component 2 (block copolymer 2): a block copolymer configured by crystalline ethylene units and ethylene-butylene units, and not having compatibility with acid-modified PP and random PP.

Incompatible component 3 (graft copolymer): a graft copolymer consisting of a main chain of polyolefin and a side chain of styrene-acrylonitrile copolymer.

Incompatible component 4 (reactor type TPO): a reactor TPO obtained by microdispersing an ethylene-based rubber to propylene-based resin.

Incompatible component 5 (ethylene- α -olefin copolymer): an ethylene-propylene copolymer elastomer not having compatibility with acid-modified PP and random PP.

Incompatible component 6 (ethylene-butene-1 random copolymer): an ethylene-butene-1 random copolymer elastomer not having compatibility with acid-modified PP and random PP.

(Compatible Component)

Compatible component 1 (a copolymer with an atactic structure): a propylene- α -olefin copolymer with an atactic structure having compatibility with acid-modified PP.

Compatible component 2 (propylene-butene-1 random copolymer): a propylene-butene-1 random copolymer elastomer having compatibility with random PP.

Production of Packaging Material

Example 1

First of all, the first and second anti-corrosion treatment layers were disposed on the metallic foil layer by the following procedure. In other words, (CL-1) was applied

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onto both faces of the metallic foil layer so as to achieve a dry amount to be applied of 70 mg/m^2 by microgravure coating, and was subjected to burning treatment at 200°C . in a drying unit. Then, (CL-2) was applied onto the obtained layer so as to achieve a dry amount to be applied of 20 mg/m^2 by microgravure coating to form a composite layer consisting of (CL-1) and (CL-2) as the first and second anti-corrosion treatment layers. This composite layer undergoes the expression of anti-corrosion performance by combination of two materials of (CL-1) and (CL-2).

Next, the side of the first anti-corrosion treatment layer of the metallic foil layer on which the first and second anti-corrosion treatment layers were disposed was bonded onto the substrate layer by a dry laminating approach using a polyurethane-based adhesive (first adhesive layer). This was placed at an unwinding unit of the extrusion laminating machine, and was coextruded together with the materials of the sealant layer on the second anti-corrosion treatment layer under processing conditions of 270°C . and 100 m/min to laminate, as sealant layers, a layer on the side of the metal-foil (the second resin layer, thickness of $8.3 \text{ }\mu\text{m}$), and the innermost layer (the first resin layer, thickness of $16.7 \text{ }\mu\text{m}$) in this order. Note that, with regard to the second resin layer and the first resin layer, a variety of compounds of their materials have been produced by a twin-screw extruder in advance, and after steps of water cooling and pelletization, were used in the above extrusion laminating. For the formation of the second resin layer, a mixture of a polypropylene-based resin 1 ((D) component, 50.0% by mass), an incompatible component 5 ((E) component, 18.2% by mass), an incompatible component 1 ((E1) component, 9.1% by mass), and a compatible component 1 ((F) component, 22.7% by mass) was used. For the formation of the first resin layer, a mixture of a polypropylene-based resin 2 ((A) component, 70.0% by mass), an incompatible component 1 ((B1) component, 10.0% by mass), and a compatible component 2 ((C) component, 20.0% by mass) was used. Note that the configuration of each of the layers is shown in the following Table 1. The numerical values within columns of Sealant Layer in Table 1 represent the contents or the thicknesses with regard to each layer in the sealant layer, or with regard to each component in the entirety of the sealant layer.

The laminate obtained in this way was subjected to heat treatment at 190°C . for 0.5 seconds by transferring the laminate wrapped around a roll heated at 190°C . to produce the packaging material of Example 1 (a laminate of the substrate layer/the first adhesive layer/the first anti-corrosion treatment layer/the metallic foil layer/the second anti-corrosion treatment layer/the sealant layer (second resin layer **16b**+first resin layer **16a**)).

Example 2

The packaging material of Example 2 was produced in a manner analogous to as in Example 1, except for the fact that a mixture of a PP-based resin 1 ((D) component, 50.0% by mass), an incompatible component 5 ((E) component, 18.2% by mass), an incompatible component 2 ((E1) component, 9.1% by mass), and a compatible component 1 ((F) component, 22.7% by mass) was used in the formation of the second resin layer, and a mixture of a PP-based resin 2 ((A) component, 70.0% by mass), an incompatible component 2 ((B1) component, 10.0% by mass), and a compatible component 2 ((C) component, 20.0% by mass) was used in the

60 The packaging material of Example 10 was produced in a manner analogous to as in Example 1, except for the fact that a mixture of a polypropylene-based resin 1 ((D) component, 50.0% by mass), an incompatible component 5 ((E) component, 2.3% by mass), an incompatible component 2 65 ((E1) component, 25.0% by mass), and a compatible component 1 ((F) component, 22.7% by mass) was used in the formation of the second resin layer, and a mixture of a

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polypropylene-based resin 2 ((A) component, 58.3% by mass), an incompatible component 2 ((B1) component, 25.0% by mass), and a compatible component 2 ((C) component, 16.7% by mass) was used in the formation of the first resin layer. Note that the configuration of each of the layers is shown in the following Table 1.

Example 11

The first and second anti-corrosion treatment layers were disposed on the metallic foil layer in a manner analogous to as in Example 1. The side of the first anti-corrosion treatment layer of the metallic foil layer on which the first and second anti-corrosion treatment layers were disposed was bonded onto the substrate layer by a dry laminating approach using a polyurethane-based adhesive (first adhesive layer). Then, the side of the second anti-corrosion treatment layer of the metallic foil layer on which the first and second anti-corrosion treatment layers were disposed was bonded to the sealant layer 16 (the first resin layer, thickness 25 μ m) by a dry laminating approach using the adhesive a (the second adhesive layer) to produce the packaging material of Example 11. For the formation of the first resin layer, a mixture of a polypropylene-based resin 2 ((A) component, 70.0% by mass), an incompatible component 1 ((B1) component, 10.0% by mass), and a compatible component 2 ((C) component, 20.0% by mass) was used. Note that the configuration of each of the layers is shown in the following Table 1.

Example 12

The first and second anti-corrosion treatment layers were disposed on the metallic foil layer in a manner analogous to as in Example 1. The side of the first anti-corrosion treatment layer of the metallic foil layer on which the first and second anti-corrosion treatment layers were disposed was bonded onto the substrate layer by a dry laminating approach using a polyurethane-based adhesive (first adhesive layer). Then, the side of the second anti-corrosion treatment layer of the metallic foil layer on which the first and second anti-corrosion treatment layers were disposed was bonded to the sealant layer 16 (the first resin layer, thickness of 25 μ m) by a dry laminating approach using the adhesive b (the second adhesive layer) to produce the packaging material of Example 11. For the formation of the first resin layer, a mixture of a polypropylene-based resin 2 ((A) component, 70.0% by mass), an incompatible component 1 ((B1) component, 10.0% by mass), and a compatible

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component 2 ((C) component, 20.0% by mass) was used. Note that the configuration of each of the layers is shown in the following Table 1.

Example 13

First of all, the first and second anti-corrosion treatment layers were disposed on the metallic foil layer by the following procedure. In other words, (CL-3) was applied onto both faces of the metallic foil layer so as to achieve a dry amount to be applied of 30 mg/m² by microgravure coating, and was subjected to burning treatment at 200° C. in a drying unit. Then, (CL-2) was applied onto the obtained layer so as to achieve a dry amount to be applied of 20 mg/m² by microgravure coating to form a composite layer consisting of (CL-3) and (CL-2) as the first and second anti-corrosion treatment layers. This composite layer undergoes the expression of anti-corrosion performance by combination of two materials of (CL-3) and (CL-2). In this way, the packaging material of Example 13 was produced in a manner analogous to as in Example 1, except for the fact that the metallic foil layer on which the first and second anti-corrosion treatment layers were disposed was used. Note that the configuration of each of the layers is shown in the following Table 1.

Example 14

The packaging material of Example 14 was produced in a manner analogous to as in Example 1, except for the fact that a mixture of a polypropylene-based resin 1 ((D) component, 72.7% by mass), an incompatible component 5 ((E) component, 18.2% by mass), and an incompatible component 1 ((E1) component, 9.1%) was used in the formation of the second resin layer. Note that the configuration of each of the layers is shown in the following Table 1.

Comparative Example 1

The packaging material of Comparative Example 1 was produced in a manner analogous to as in Example 1, except for the fact that a mixture of a polypropylene-based resin 1 ((D) component, 52.0% by mass), an incompatible component 5 ((E) component, 45.0% by mass), and a compatible component 1 ((F) component, 3.0% by mass) was used in the formation of the second resin layer, and a mixture of a polypropylene-based resin 2 ((A) component, 52.0% by mass), an incompatible component 6 ((B) component, 45.0% by mass), and a compatible component 2 ((C) component, 3.0% by mass) was used in the formation of the first resin layer. Note that the configuration of each of the layers is shown in the following Table 1.

TABLE 1

Sealant layer												
Anti-		Second resin layer					First resin layer				Content	Content
corro- sion treat- ment layer	Second adhe- sive layer	(D)	(E) Component			(F)	(A)	(B) Component		(C)	of (B)	of (C)
		Com- ponent	(% by mass)			Compo- nent	Compo- nent	(% by mass)		Component	compo- nent	compo- nent
		(% by mass)	(E1) Component			(% by mass)	(% by mass)	(B1) Component		(% by mass)	(% by mass)	(% by mass)
Example 1	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 1	Compatible component 1	PP- based resin 2	—	Incompatible component 1	Compatible component 2	15.8	20.9
		50.0	18.2	9.1	22.7	70.0		10.0	20.0			

TABLE 1-continued

	Anti-corrosion treatment layer	Second adhesive layer	Sealant layer								Content of (B) component (% by mass)	Content of (C) component (% by mass)
			Second resin layer				First resin layer					
			(D) Component (% by mass)	(E) Component (% by mass)		(F) Component (% by mass)	(A) Component (% by mass)	(B) Component (% by mass)		(C) Component (% by mass)		
			(E1) Component			(B1) Component						
Example 2	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 2	Compatible component 1	PP-based resin 2	—	Incompatible component 2	Compatible component 2	15.8	20.9
Example 3	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 3	Compatible component 1	PP-based resin 2	—	Incompatible component 3	Compatible component 2	15.8	20.9
Example 4	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 4	Compatible component 1	PP-based resin 2	—	Incompatible component 4	Compatible component 2	15.8	20.9
Example 5	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 1	Compatible component 1	PP-based resin 2	Incompatible component 6	Incompatible component 1	Compatible component 2	15.8	20.9
Example 6	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 1	Compatible component 1	PP-based resin 2	Incompatible component 6	Incompatible component 1	Compatible component 2	15.8	20.9
Example 7	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 1	Compatible component 1	PP-based resin 2	Incompatible component 6	Incompatible component 1	Compatible component 2	15.8	20.9
Example 8	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	—	Compatible component 1	PP-based resin 2	Incompatible component 6	—	Compatible component 2	15.8	20.9
Example 9	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 2	Compatible component 1	PP-based resin 2	—	Incompatible component 2	Compatible component 2	20.8	19.8
Example 10	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 2	Compatible component 1	PP-based resin 2	—	Incompatible component 2	Compatible component 2	25.8	18.7
Example 11	(CL-1) + (CL-2)	Adhesive a	—	—	—	—	PP-based resin 2	—	Incompatible component 1	Compatible component 2	10.0	20.0
Example 12	(CL-1) + (CL-2)	Adhesive b	—	—	—	—	PP-based resin 2	—	Incompatible component 1	Compatible component 2	10.0	20.0
Example 13	(CL-3) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 1	Compatible component 1	PP-based resin 2	—	Incompatible component 1	Compatible component 2	15.8	20.9
Example 14	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	Incompatible component 1	—	PP-based resin 2	—	Incompatible component 1	Compatible component 2	15.8	13.3
Comparative Example 1	(CL-1) + (CL-2)	—	PP-based resin 1	Incompatible component 5	—	Compatible component 1	PP-based resin 2	Incompatible component 6	—	Compatible component 2	45.0	3.0

<Evaluation>

The following evaluation tests were conducted on the packaging materials obtained in Examples and Comparative Examples.

(Loss Tangent Tan δ of Sealant Layer)

A film consisting solely of the sealant layer was obtained by dipping the obtained packaging material into an aqueous solution of sodium hydroxide to dissolve the metallic foil layer. Subsequently, the obtained film was cut with a width of 10 mm and a length of 30 mm to provide a measurement sample, and the distance between chucks was maintained to be 20 mm. As per a method according to JIS K7244-4, the measurement was conducted under the following conditions using a dynamic viscoelasticity apparatus (manufactured by SII, trade name: DMS6100) to calculate loss tangent $\tan \delta$ from loss elastic modulus E'' and storage elastic modulus E' . The measurement results of $\tan \delta$ of the sealant layers in the packaging materials obtained in Example 1 and Comparative Example 1 are shown in FIG. 4. Also, from the calculation results of the obtained $\tan \delta$, the value (I) of $\tan \delta$ at -50°C ., the maximal value (II) of $\tan \delta$ at -30 to 30°C ., and the maximum value (III) of $\tan \delta$ at 90 to 100°C ., were determined to calculate the respective values of II/I and III/II. Note that, in a temperature range of -100 to 120°C ., the maximum values of $\tan \delta$ were (II) for Examples 1 to 9 and Examples 11 to 14, and were (III) for Example 10 and Comparative Example 1.

Peeling Mode: Pulling

Rate of Temperature Rise: $2^\circ\text{C}/\text{min}$

Temperature Range: -100 to 120°C .

Frequency: 1.0 Hz

(Seal Strength)

A sample obtained by cutting the packaging material into $60\text{ mm}\times 120\text{ mm}$ was folded into two, and one side of the folded sample was heat-sealed with a sealing bar with a width of 10 mm at 190°C . and 0.5 MPa for 3 seconds. After storing the heat-sealed sample at room temperature for 24 hours, the firstly heat-sealed one side was cut to have a width of 15 mm (see FIG. 5), seal strength (T-PEEL STRENGTH) was continuously measured by a testing machine (manufactured by INSTRON). The test was conducted according to JIS K6854 at 23°C . under an atmosphere of 50% RH with a peeling rate of 50 mm/min. On the basis of the measurement results regarding the maximal value (burst strength) of the initial seal strength after the start of peeling, evaluation of the seal strength was conducted according to the following criteria.

S: burst strength is 60 N/15 mm or more

A: burst strength is 50 N/15 mm or more and less than 60 N/15 mm

B: burst strength is 40 N/15 mm or more and less than 50 N/15 mm

C: burst strength is 35 N/15 mm or more and less than 40 N/15 mm

D: burst strength is less than 35 N/15 mm

(Electrolytic Solution Laminating Strength)

An electrolytic solution in which LiPF_6 was added to a mixed solution of ethylene carbonate/diethyl carbonate/dimethyl carbonate=1/1/1 (mass ratio) to achieve an amount of 1 M was loaded in a Teflon® vessel, and a sample obtained by cutting the packaging material into $15\text{ mm}\times 100\text{ mm}$ was placed in this vessel, and after well-stoppered, this vessel was stored at 85°C . for 24 hours. Next, washing together was conducted, and laminating strength (T-peel strength) between the metallic foil layer/the sealant layer was measured by a testing machine (manufactured by INSTRON). The test was conducted according to JIS K6854

at 23°C . under an atmosphere of 50% RH with a peeling rate of 50 mm/min. On the basis of the results, evaluation was conducted according to the following criteria.

A: Laminating strength is greater than 7 N/15 mm

B: Laminating strength is 6 N/15 mm or more, and 7 N/15 mm or less

C: Laminating strength is 5 N/15 mm or more and less than 6 N/15 mm

D: Laminating strength is less than 5 N/15 mm

(Electrolytic Solution Heat Seal Strength (Electrolytic Solution Seal Strength))

A sample obtained by cutting the packaging material into $60\text{ mm}\times 120\text{ mm}$ was folded into two so as to locate the sealant layer at the inner side, and one side of the folded sample was heat-sealed with a sealing bar with a width of 10 mm at 190°C . and 0.5 MPa for 3 seconds to form a heat-sealed portion. Next, the remaining two sides of the folded sample were also heat-sealed to achieve a bag-shaped packaging material, and within this bag-shaped packaging material, the pouch in which 2 ml of electrolytic solution in which LiPF_6 was added to a mixed solution of ethylene carbonate/diethyl carbonate/dimethyl carbonate=1/1/1 (mass ratio) to achieve an amount of 1 M has been injected was stored at 60°C . for 24 hours, and subsequently, the firstly heat-sealed one side was cut to have a width of 15 mm (see FIG. 6), and from one end of the heat-sealed portion (the end on the side exposed to the electrolytic solution), the seal strength (T-peel strength) was continuously measured by a testing machine (manufactured by INSTRON). The test was conducted according to JIS K6854 at 23°C . under an atmosphere of 50% RH with a peeling rate of 50 mm/min. On the basis of the burst strength determined in a manner analogous to as in the section of "Seal Strength", evaluation was conducted according to the following criteria.

S: Burst strength is 50 N/15 mm or more

A: Burst strength is 45 N/15 mm or more and less than 50 N/15 mm

B: Burst strength is 35 N/15 mm or more and less than 45 N/15 mm

C: Burst strength is 25 N/15 mm or more and less than 35 N/15 mm

D: Burst strength is less than 25 N/15 mm

(High-temperature Heat Seal Strength (High-Temperature Seal Strength))

A sample obtained by cutting the packaging material into $60\text{ mm}\times 120\text{ mm}$ was folded into two, and one side of the folded sample was heat-sealed with a sealing bar with a width of 10 mm at 190°C ., 0.5 MPa for 3 seconds. Then, the firstly heat-sealed one side was cut into 15 mm (see FIG. 5), and was allowed to stand under the environment of 80°C . for 5 minutes, and subsequently, the seal strength (T-peel strength) was continuously measured by a testing machine (manufactured by INSTRON). The test was conducted according to JIS K6854 at 80°C . with a peeling rate of 50 mm/min. On the basis of the measurement results regarding the maximal value (burst strength) of the initial seal strength after the start of peeling, evaluation of the high-temperature heat seal strength was conducted according to the following criteria.

A: Burst strength is 30 N/15 mm or more

B: Burst strength is 20 N/15 mm or more and less than 30 N/15 mm

C: Burst strength is 15 N/15 mm or more and less than 20 N/15 mm

D: Burst strength is less than 15 N/15 mm

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(Degassing Heat Sealing Strength (Degas Seal Strength))

A sample obtained by cutting the packaging material into 75 mm×150 mm was folded into two to be 37.5 mm×150 mm so as to locate the sealant layer at the inner side (see FIG. 7A), and subsequently, the side of 150 mm length and one of the sides of 37.5 mm length were heat-sealed to produce a pouch. Next, into this pouch, 5 ml of electrolytic solution in which LiPF₆ was added to a mixed solution of ethylene carbonate/diethyl carbonate/dimethyl carbonate=1/1/1 (mass ratio) to achieve an amount of 1 M was injected, and the other side of 37.5 mm length was heat-sealed to obtain a pouch sealed by a sealed portion DS1. Then, after storing this pouch at 60°C. for 24 hours, the central portion of the pouch including the electrolytic solution was heat-sealed with a sealing bar with a width of 10 mm at 190° C. and 0.3 MPa for 2 seconds (degassing heat sealed portion DS2, see FIG. 7B). In order to stabilize the sealed portion, after stored at normal temperatures for 24 hours, the region including the degassing heat sealed portion DS2 was cut to have a width of 15 mm (see FIG. 7C), and from one end of the degassing heat sealed portion (the end on the side exposed to the electrolytic solution), the seal strength (T-peel strength) was measured by a testing machine (manufactured by INSTRON). The test was conducted according to JIS K6854 at 23° C. under an atmosphere of 50% RH with a peeling rate of 50 mm/min. On the basis of the burst strength determined in a manner analogous to as in the section of "Seal Strength", evaluation was conducted according to the following criteria.

S: Burst strength is 45 N/15 mm or more

A: Burst strength is 40 N/15 mm or more and less than 45 N/15 mm

B: Burst strength is 30 N/15 mm or more and less than 40 N/15 mm

C: Burst strength is 20 N/15 mm or more and less than 30 N/15 mm

D: Burst strength is less than 20 N/15 mm

(Insulation Properties after Degassing Heat Sealing (Degassing Insulation))

A sample 40 obtained by cutting the packaging material into 120 mm×200 mm was placed into a mold for cold molding so that the sealant layer comes into contact with a projected part of the molding machine, and deep drawing of 2.0 mm was conducted with a molding rate of 15 mm/sec to form a deep drawing portion 41, and subsequently, the sample 40 was folded into two to be 120 mm×100 mm (see FIG. 8A). Then, an upper side portion 44 of 100 mm was

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heat-sealed with interposing a tab 42 and a tab sealant 43 (see FIG. 8B), and subsequently, a lateral side portion 45 of 120 mm was heat-sealed to produce a pouch (see FIG. 8C). Next, in order to enable contact with the electrode, a portion of the outer layer of the sample 40 was cut away to form an exposed portion 46 of the metallic foil layer (see FIG. 8D). Then, 5 ml of electrolytic solution in which LiPF₆ was added to a mixed solution of ethylene carbonate/diethyl carbonate/dimethyl carbonate=1/1/1 (mass ratio) to achieve an amount of 1 M was injected in the pouch, and a lower side portion 47 of 100 mm was sealed by heat seal (see FIG. 8E). Next, this pouch was allowed to stand at 60° C. for 24 hours in a flatly placed state, and a portion 48 located at the inner side with respect to the heat-sealed lower side portion 47 was subjected to degassing heat seal while sandwiching the electrolytic solution between portions to be heat-sealed at 190° C. and 0.3 MPa (surface pressure) for 2 seconds (see FIG. 8F). Then, the tab 42 and the exposed portion 46 of the metallic foil layer were respectively connected with electrodes 49a, 49b, and by applying 25 V using a withstanding voltage/insulation resistance tester (manufactured by KIKUSUI ELECTRONICS CORPORATION, "TOS9201"), the resistance value at the moment was measured (see FIG. 8G). With regard to the sample of which the resistance value was less than 15 MΩ, 25 V was successively applied for 2 hours to identify the insulation diminished site. By applying voltage for a prolonged time, a reaction product of the metallic foil and the electrolytic solution precipitates from the insulation diminished site, and as a result of this, it is possible to identify the insulation diminished site. As the mold, a mold having molding area of 80 mm×70 mm (rectangular cylindrical shape) and punching corner radius (RCP) of 1.0 mm was used. On the basis of the results, evaluation was conducted according to the following criteria.

A: Resistance value is 200 MΩ or more

B: Resistance value is 100 MΩ or more, and less than 200 MΩ

C: Resistance value is 15 MΩ or more, and less than 100 MΩ

D: Resistance value is less than 15 MΩ

The results of the tan δ ratio, seal strength, electrolytic solution laminating strength, electrolytic solution seal strength, degas heat seal strength, and degassing insulation regarding the sealant layer evaluated as described above are shown in Table 2. In the following Table 2, the items having no evaluation of D with regard to the results of each evaluation are considered to have good overall quality.

TABLE 2

	Electrolytic		Electrolytic		High-	Degassing		Degassing
	tan δ ratio		solution		temperature	seal		insulating
	(I/I)	(II/II)	laminating	seal	seal	strength		Insulation
			strength	strength	strength			diminished
			strength	strength	strength			site
Example 1	3.68	0.73	S	A	S	A	S	A
Example 2	3.60	0.85	S	A	S	A	S	A
Example 3	3.55	0.75	S	A	S	A	S	A
Example 4	3.50	0.81	S	A	S	A	S	A
Example 5	3.50	0.80	S	A	S	A	S	A
Example 6	3.11	0.83	A	A	A	A	A	B
Example 7	2.86	0.85	B	A	B	A	A	B
Example 8	2.51	0.88	C	A	C	B	C	C
Example 9	3.61	0.91	S	A	S	B	S	A
Example 10	3.64	1.25	S	A	S	C	S	A
Example 11	3.70	0.79	S	A	S	A	S	A
Example 12	3.70	0.79	A	C	A	A	A	B

TABLE 2-continued

				Electrolytic	Electrolytic	High-		Degassing insulating
	tan δ ratio (II/I)	tan δ ratio (II/II)	Seal strength	solution laminating strength	solution seal strength	temperature seal strength	Degas seal strength	Insulation diminished site
Example 13	3.68	0.73	A	B	A	A	A	B
Example 14	3.50	0.69	A	B	A	A	A	B
Comparative Example 1	2.01	1.48	D	0	D	D	D	D
								Degas sealed portion

As is obvious from the results shown in Table 2, it has been confirmed that, with regard the packaging materials for a power storage device obtained in Examples 1 to 14, due to the fact that these packaging materials have a sealant layer with tan δ ratio (II/I) being 2.50 or more, any of these packaging material has excellent insulating properties after degassing heat sealing. In addition, it has been confirmed that the packaging materials of Examples 1 to 14 have sufficient performance, also with regard to the electrolytic solution laminating strength, electrolytic solution heat seal strength, high-temperature heat seal strength, degassing heat sealing strength. By contrast to this, it has been confirmed that, with regard to the packaging material of Comparative Example 1, the seal strength and the insulating properties are inferior.

REFERENCE SIGNS LIST

10, 20, 30 . . . packaging material for power storage device, 11 . . . substrate layer, 12 . . . first adhesive layer, 13 . . . metallic foil layer, 14 . . . anti-corrosion treatment layer, 16 . . . sealant layer, 16a . . . first resin layer, 16b . . . second resin layer, 16c . . . third resin layer, 17 . . . second adhesive layer, DS1 . . . Sealed portion, DS2 . . . Degassing heat sealed portion.

The invention claimed is:

1. A packaging material for a power storage device, comprising:

a substrate layer;
a metallic foil layer with an anti-corrosion treatment layer on one face or both faces thereof; and

a sealant layer,
in this order, wherein

the sealant layer includes a resin layer containing a polypropylene-based resin (A) and an incompatible component (B) incompatible with the polypropylene-based resin (A),

the sealant layer has a value (I) of loss tangent tan δ at -50° C. and a maximal value (II) of loss tangent tan δ at -30° C. to 30° C. determined by dynamic viscoelasticity measurement at a frequency of 1.0 Hz, and a ratio (II/I) of the maximal value (II) to the value (I) is 2.50 or more.

2. The packaging material for a power storage device according to claim 1, wherein the sealant layer further has a maximum value (III) of loss tangent tan δ at 90° C. to 100°

C., and a ratio (III/II) of the maximum value (III) to the maximal value (II) is 1.00 or less.

3. The packaging material for a power storage device according to claim 1, wherein the resin layer further includes a compatible component (C) compatible with the polypropylene-based resin (A).

4. The packaging material for a power storage device according to claim 3, wherein the compatible component (C) includes a propylene- α -olefin copolymer.

5. The packaging material for a power storage device according to claim 1, wherein

the resin layer is a first resin layer, and

the sealant layer further includes a second resin layer containing a polypropylene-based resin (D) and an incompatible component (E) incompatible with the polypropylene-based resin (D) between the first resin layer and the metallic foil layer.

6. The packaging material for a power storage device according to claim 5, wherein

the second resin layer further contains a compatible component (F) compatible with the polypropylene-based resin (D),

the polypropylene-based resin (D) includes acid-modified polypropylene, and

the compatible component (F) includes polypropylene with an atactic structure or a propylene- α -olefin copolymer with an atactic structure.

7. The packaging material for a power storage device according to claim 1, wherein the anti-corrosion treatment layer includes cerium oxide, 1 to 100 parts by mass of phosphoric acid or phosphoric acid salt per 100 parts by mass of the cerium oxide, and a cationic polymer.

8. The packaging material for a power storage device according to claim 1, wherein the anti-corrosion treatment layer includes a chemical conversion treatment layer, and/or a cationic polymer.

9. The packaging material for a power storage device according to claim 1, further comprising:

an adhesive layer between the metallic foil layer and the sealant layer, wherein

the adhesive layer contains an acid-modified polyolefin, and at least one curing agent selected from the group consisting of a multifunctional isocyanate compound, a glycidyl compound, a compound having a carboxy group, a compound having an oxazoline group and a carbodiimide compound.

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