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Description

This invention relates to packaging materials for photosensitive materials.

Packaging bags capable of shielding completely from light are used for packaging the articles or the materials which lose commercial values by exposing to light, such as photosensitive materials. The packaging bags are necessary to have sufficient physical strength, such as tensile strength, tear strength and impact puncture strength, according to the size and weight of the materials to be packaged, as well as the above light-shielding ability. Moreover, since the opening portion of the packaging bags are usually heat-sealed, suitable heat sealing properties are necessary, and in order to prevent static electrification due to the friction between the photosensitive materials and the packaging bag, antistatic property is also necessary.

Heretofore, as the packaging materials used for such a packaging bag, there is a laminated film composed of a high pressure branched low density polyethylene (LDPE) resin film layer containing a light-shielding material, an aluminum foil layer and a breached kraft paper layer laminated successively each through an LDPE resin extrusion adhesive layer. In general, single layer films are difficult to satisfy the various properties required as the packaging material for photographic photosensitive materials, and only a thick light-shielding LDPE resin single layer film containing carbon black was used for packaging light low photosensitivity photographic photosensitive materials placed in protective pad papers and for packaging light photographic printing papers.

As the packaging material, particularly the light-shielding heat seal bag, for packaging a roll of a photographic photosensitive material and sheets of a photosensitive material having a weight of heavier than 1 kg, the inventor has already disclosed the laminated film composed of a cross laminated film using uniaxially stretched high density polyethylene (HDPE) resin films having a great physical strength and a LDPE resin film containing at least either a light-shielding material or an antistatic agent (US-A-4,147,291). The inventor has also disclosed an inexpensive cross laminated film where heat sealing properties and light-shielding ability are improved (US-A-4,258,848).

Furthermore, the inventor has disclosed other packaging materials, composed of a laminated film containing a light-shielding film layer composed of linear low density polyethylene (L-LDPE) resin blended with carbon black, having a great physical strength, being excellent in heat sealing properties, and being inexpensive (US-A-4,701,359, Japanese Patent KOKAI No. 18547/1987). As a packaging material using a metallized film, the inventor has also disclosed a packaging material for photosensitive materials composed of a metallized film layer and two L-LDPE resin polymer layers containing more than 50 wt. % of L-LDPE resin laminated on both sides of the metallized film layer. One or both of the L-LDPE resin polymer layers contains 0.3 to 30 wt. % of a light-shielding material (US-A-4,663,218).

However, the aforementioned conventional laminated film composed of the LDPE resin film layer, the aluminum foil layer and the bleached kraft paper layer is thick and stiff, and therefore, packaging workability is inferior. Physical strength, such as tear strength, is small, and curling is great. Moreover, heat sealing properties are inferior, and it is expensive. As a result, the packaging material was difficult to secure light-shielding, moistureproofness and gas barrier because of the generation of dust, puncture, tear or separation of heat sealed portion during packaging work or transportation. In the case of the thick light-shielding LDPE resin single layer film, physical strength is small, and heat sealing properties are inferior. Therefore, it is difficult to secure the quality of the photosensitive materials completely.

The packaging materials having a cross laminated film disclosed in US-A-4,147,291 and US-A-4,258,848 have a strong physical strength such as tear strength and tensile strength, and they were put to practical use for packaging weight materials up to recently. However, since an uniaxially stretched HDPE resin film is used as the heat seal layer, they are stiff, and inferior in packaging workability and heat sealing properties. Moreover, the physical strength and heat seal strength varies and curling occurs due to the uneven thickness of an adhesive layer, the uneven draw ratio of the uniaxially stretched HDPE resin films, or the like. Therefore, troubles occurred in processing or packaging process, and occasionally, they were punctured, or the heat sealed portion was separated during transportation. Moreover, the cross laminated film where a longitudinally uniaxially stretched film was laminated to a laterally uniaxially stretched film so that their orientation axes were crossed each other was expensive, because two kinds of film molding machines were necessary.

Since the packaging materials having a light-shielding L-LDPE resin single layer film disclosed in US-A-4,701,359 or Japanese Patent KOKAI No. 18547/1987 are inexpensive and excellent in heat sealing properties and physical strength such as tear strength and impact puncture strength, they are excellent as the packaging material for photosensitive materials. However, in the case of packaging a weight photosensitive material or a photosensitive material having sharp edges, the light-shielding L-LDPE resin films were occasionally elongated and made thin due to their low Young's modulus, though they were not punctured nor torn. In this case, light-shielding and moistureproofness cannot be secured sufficiently. In addition, in the case of using a L-LDPE

resin having a density of less than 0.925 g/cm³, slipping character was insufficient, and blocking was liable to occur. In the packaging material disclosed in US-A-4,663,218, physical strength such as tear strength was improved. However, when a light-shielding material was incorporated into one side of the L-LDPE resin polymer layer alone, curling was great, and processibility was inferior. While, when the melting point of both L-LDPE resin polymer layers were almost identical with each other, the outside layer was melted and broken, unless the heat sealer was modified. As a result, pinhole occurred, and strength was decreased. Appearance was also inferior. Therefore, this packaging material was put to practical use as a laminated film laminated with an aluminum vacuum deposited nylon film or polyester film having a large Young's modulus and heat resistance. However, the curling of the laminated film was great, and the aluminum vacuum deposited nylon film and polyester film were expensive.

The inventor has also developed a coextruded multilayer inflation film comprising an L-LDPE resin film layer and a polyolefin resin film layer, as a film improved in physical strength such as impact puncture strength (Japanese Patent KOKAI No. 62-18548). Such a coextruded multilayer inflation film is formed by using an inflation film molding machine, such as shown in Figure 7. The inflation film molding machine is composed of extruders 8 heating and kneading the resin, ring die 9 extruding the molten resin from the slit (not indicated) into tube-shaped, blast tube 10 blowing compressed air, air ring 11 cooling the molten resin extruded in tube-shaped, guide rollers 12 guiding the tube-shaped resin film 13, guide plates 14 guiding the tube-shaped resin film 13 into flat, a pair of squeeze roll 15 (nip roll) nipping to attract the tube-shaped resin film 13, and winder 16 winding the film. When the aforementioned coextruded multilayer inflation film composed of an L-LDPE resin film layer and a polyolefin resin film layer is molded by using the inflation film molding machine, L-LDPE resin and HDPE resin having prescribed compositions respectively are melted and kneaded by the extruders 8 and extruded from the circular slit of the ring die 9 so that the L-LDPE resin film layer is disposed on the inside, i.e. the HDPE resin film layer is disposed on the outside. At that time, compressed air is blown from the blast tube 10, and cooling air is blown from the air ring 11. The tube-shaped resin film 13 having a prescribed diameter thus formed ascends with the guide of the guide rollers 12, ..., 12, and is led into flat by the guide plates 14. The film is made sheet shape by passing the squeeze roll 15, and wound with the winder 16.

However, in the above inflation film molding process wherein the L-LDPE resin film layer was disposed on the inside and the HDPE resin film layer was disposed on the outside, there was a problem that the L-LDPE resin film layer was contacted with each other to generate blocking at the time of winding it with the winder 16. Moreover, fatty acid or fatty acid compound such as fatty acid amide, paraffin wax or metal salt of fatty acid was added to the HDPE resin film layer in order to improve film moldability or to render halogen compounds harmless, the additive was exposed out of the HDPE resin film layer, and adhered to the guide rollers 12 resulting pressure mark and abrasion of the film 13. The adhered additive was detached from the guide rollers 12, adhered to the film in white lumps. When the film was wound, the white lumps rendered film rupture as well as pressure mark to the film. On the other hand, when the L-LDPE resin film layer was disposed on the outside and the HDPE resin film was disposed on the inside, wrinkling and furrows occurred, and the yield of the film decreased.

On the other hand, as the packaging bag for relatively heavy large photographic photosensitive materials, double-sheet bags were used. Such a double-sheet bag was, for example, composed of an outer sheet consisting of a Clupak paper, Duostress paper or unbleached kraft paper coated with polyethylene resin by extrusion laminating and an inner sheet consisting of an aluminum foil and two uniform polyethylene resin films containing carbon black laminated on both sides of the aluminum foil. The kind of the packaged product, instructions and the like were printed on the outer surface of the outer sheet during the packaging process or another process. The double-sheet bag is excellent in physical strength, and when the paper of the outer sheet contains a substance harmful for photographic photosensitive materials, its affect can be shielded by the inner sheet being in contact with the photographic photosensitive materials. However, the double-sheet bags have problems in inferior workability and in expensive packaging material cost. Therefore, various laminated films were developed for solving the inconvenience in bag-making process to make the bag double. An example of the laminated film shown in Figure 6 is composed of an aluminum foil layer 27, a bleached kraft paper layer 26 mainly composed of bleached kraft pulp and an LDPE resin film layer 28a blended with a light-shielding material laminated on both sides of the aluminum foil layer 27 each through an adhesive layer 3. When a bag is made, the bleached kraft paper layer 26 is disposed on the outside, i.e. the LDPE resin film layer 28a is disposed on the inside. The physical strength of the laminated film is sufficient in the case of light photographic photosensitive materials, but it is insufficient for packaging heavy photographic photosensitive materials. Moreover, fibers occasionally adhered to the packaged photographic photosensitive materials, and caused developing troubles. Photographic photosensitive materials are liable to deteriorate because of utilizing oxidation-reduction reaction and containing a dye liable to degrade by pH, moisture, heat or the like. Therefore, even in the case that it was necessary to use an oxidizing or reducing substance for the surface of the packaging ma-

terial to touch photographic photosensitive materials, the oxidizing or reducing substance was restricted in the kind and the blending amount. Moreover, unless the quality of the light-shielding material was limited in the particle size, pH, the content of impurities and the like, photographic troubles, such as fogging, spotting trouble and photosensitivity variation, occurred.

5 An object of the invention is to provide a packaging material for photographic photosensitive materials having sufficient physical strength for packaging heavy photographic photosensitive materials and little problem in developing trouble.

Another object of the invention is to provide a packaging material for photographic photosensitive materials not affecting adversely the photographic photosensitive materials packaged therein and being inexpensive.

10 Such objects have been achieved by a packaging material for photographic photosensitive materials which comprises an aluminum vacuum metallized biaxially stretched thermoplastic resin film layer, a long fiber paper layer, of which more than 50 % of the fibers have a fiber length of longer than 3 mm, containing a paper reinforcing agent and having a pH of 4 to 9 measured by cool water extracting method (JIS P-8133) laminated on one side of the above thermoplastic resin film layer, and a polyolefin resin film layer containing 0.1 to 15 wt. 15 % of carbon black having a pH of 4 to 9 and a mean particle size of 15 to 80 μm and more than 5 wt. % of an ethylene copolymer resin laminated on the other side.

Figures 1 to 4 are partially sectional views of preferred embodiment of the invention.

Figure 5 is a partially sectional view of a comparative packaging material.

Figure 6 is a partially sectional view of a conventional packaging material.

20 Figure 7 is a schematic front view of an inflation molding machine.

The aluminum vacuum metallized biaxially stretched thermoplastic resin film is a biaxially stretched thermoplastic resin film processed with the vacuum deposition method to form an aluminum vacuum deposition layer. The film improves tensile strength and bursting strength of the packaging material, and it prevents the generation of pinhole, bag rupture and thinning by the elongation of the packaging material, even when a heavy 25 product is placed. It also improves moistureproofness, gas barrier, antistatic property and light-shielding. By stretching the thermoplastic resin film biaxially, the stretched film has a high Young's modulus, and is excellent in moistureproofness and gas barrier, in spite that it is thin. Since the stretched film has heat stability, crazing hardly occurs at the time of forming the aluminum vacuum deposition layer. The crazing of the aluminum vacuum deposition layer is also prevented by the increased Young's modulus and the resistance to elongation. 30 The resin suitable for the film includes polyester resin, polyamide (nylon) resin, polyethylene resin, polystyrene resin, polypropylene resin, polyvinyl chloride resin, polyvinylidene chloride resin, vinylon resin, copolymer resins of the above resins and other resins, including binary, ternary or more copolymers polymerized by random copolymerization or block copolymerization, modified or crosslinked resins, and blend resins of the above resins and other resins. Stretching may be carried out by a known biaxial drawing method such as simultaneously 35 biaxial drawing or successively biaxial stretching, and both of the draw ratios in longitudinal direction (MD) and in lateral direction (CD) are 1.5 to 20 times, preferably 3 to 15 times, respectively. The drawing machine may be a known machine such as T die film molding machine or inflation film molding machine. A preferable thickness of the biaxially stretched thermoplastic resin film is 7 to 60 μm . When the thickness is less than 7 μm , wrinkling and cut occur in the laminating process. While, when the thickness is beyond 60 μm , the rigidity is too great. As a result, bag-making ability and handling are inferior, and the film is expensive. The biaxially 40 stretched thermoplastic resin film may be a single layer film or a coextruded multilayer film. Moreover, another resin, such as polyvinylidene chloride resin, silicone resin or teflon resin, is coated or printed, or a metal membrane is provided on the stretched film. The metal membrane may be provided by vacuum deposition, sputtering, ion plating, electron beam deposition, or the like.

45 A preferable thickness of the aluminum vacuum deposition layer is 55 to 1,200 Å, particularly 100 to 600 Å, in view of securing physical strength, light-shielding, antistatic property, moistureproofness and gas barrier, cost and quality. When the thickness is less than 55 Å, the static electrification generated around the aluminum vacuum deposition layer cannot be decreased. It is difficult to secure moistureproofness, gas barrier and light-shielding. While, when the thickness is beyond 1,200 Å, problems occur in the degradation of the stretched 50 film, the wrinkling due to shrinkage the crazing of the vacuum deposition layer, caused by the heat of vacuum deposition, and the decrease of physical strength of the packaging bag, though antistatic property, moistureproofness, gas barrier and light-shielding are still secured.

A protection layer may be provided on the aluminum vacuum deposition layer, if necessary. The usable resin for the protection layer includes acrylic resin, cellulose resins such as cellulose acetate resin, urethane resin, epoxy resin, polyester resin, ionomer resin, polyethylene resin, ethylene copolymer resin and polypropylene resin. Besides, wax, gelatin, polyvinyl alcohol or the like is also usable. The thickness of the protection layer is made extremely thin such as thinner than 50 μm , preferably thinner than 5 μm , in order to eliminate static electricity effectively. Such a protection layer may be formed by a known extrusion coating, solution coat-

ing or spray coating.

More than 50 %, preferably more than 70 % of the fibers composing the long fiber paper have a fiber length of longer than 3 mm, usually 3 mm to 7 mm. When the fiber length is shorter than 3 mm, the generation of paper powder and picking cannot be prevented effectively. When the fibers having a fiber length of longer than 3 mm are less than 50 % of total fibers, the generation of paper powder and picking cannot be prevented effectively. The paper reinforcing agent is incorporated into the long fiber paper in order to prevent the generation of paper powder and picking effectively. The paper reinforcing agent usable for the invention includes cation-induced styrene-acrylic copolymer, aminoamidepiclorohydrin condensate, carboxymethylcellulose, various polyacrylamides and copolymers thereof, carboxyl-modified polyacrylamide, polyethyleneimine, gum oleoresin, sodium silicate, synthetic rubber latex, unacetylated PVA fiber, various starches including modified starches, sulfomethylated resin, urea resin, alkylstyrene resin, alkylketene dimer, gelatin, PVA, casein, methacrylamide, polyamidaminepiclorohydrin, sodium polyacrylate, carboxyl-modified polyvinyl alcohol, hydroxylethylcellulose and the like. A suitable content of the paper reinforcing agent is 0.05 to 8 wt. %, preferably 0.3 to 5 wt. %. A cool water-extracting pH (JIS P-8133) of the long fiber paper is in the range of 4 to 9, preferably 5 to 9. When the cool water-extracting pH is less than 4 or beyond 9, harmful substances for photographic photosensitive material are produced. Long fiber neutral papers are particularly preferable. The contents of all of harmful substances for photographic photosensitive materials should be less 1,000 ppm. The harmful substances are radioactive substances and the materials obtained using a radioactive substance, such as the paper made using the river water, the pulp, chip or waste paper exposed to the rain, after a nuclear test, mercury, alloys thereof, mercury compounds and agents containing mercury, such as mercury, organic mercury agents, broken fluorescent lamp and slime control agent used for paper-making, secondary processed products of silicone, such as silicone oil and silicone grease, sulfur compounds, such as Na_2S , H_2S and $\text{Na}_2\text{S}_2\text{O}_3$, lead compounds, such as PbS and PbSO_4 , iron and iron compound, such as iron powder, Fe_2O_3 , FeO and FeCl_3 , copper and copper compounds, such as copper compounds, such as copper powder, CuO , CuSO_4 and CuCl_2 , and aldehydes, such as formaldehyde and acetaldehyde. When the content of one of the above substances is beyond 1,000 ppm, it adversely affect photographic photosensitive materials seriously. The adverse affect of the substance can be decreased by neutralization, adsorption or the like. In this case, the content of the above harmful substance may be beyond 1,000 ppm. For example, the adverse affect of iron, iron compounds and other metal compounds can be removed by adding a chelating agent, and the adverse affect of formaldehyde can be removed by adding urea, thiourea, a hydrazine compound, dicyandiamide or an acid salt thereof, hydroxylamine or an acid salt thereof, such as hydroxylamine hydrochloride or hydroxylamine sulfate, or formamide. The adverse affect of the harmful substances can also be removed by selecting the equipments and materials so that the contamination amounts are minimized, using clean water such as spring water, and forbidding the use of the pulp, chip and waste paper exposed to rain. In order to reduce the generation of paper powder, the surface of the long fiber paper is preferably processed by Yankee calender or supercalender, and the surface strength is preferably more than 6. In order to increase the surface strength of the paper, beating is necessary. The beating is necessary to be carried out so that more than 50 % of the fibers have a fiber length of longer than 3 mm. The long fiber paper may be a combination paper, and white or colored.

The polyolefin resin film layer contains 0.1 to 15 wt. % of carbon black having a pH of 4 to 9 and a mean particle size of 15 to 80 μm . The carbon black adsorbs harmful substances for photographic photosensitive materials, when the long fiber paper is contaminated, and it prevents the degradation of photographic properties, such as fogging, the variation of photosensitivity and the decrease of concentration, when a photographic photosensitive material is placed in the packaging material of the invention for a long time, in addition to the light-shielding. When the pH of the carbon black is less than 4 or beyond 9, the degradation of photographic properties, such as fogging, the variation of photosensitivity and the decrease of concentration occurs. When the mean particle size is less than 15 μm , carbon black particles aggregate to produce lumps and fish eye problem. While, when the mean particle size is beyond 80 μm , light-shielding ability decreases. Moreover, it is preferable that the free sulfur content is less than 1,000 ppm, because the degradation of photographic properties, such as fogging, the variation of photosensitivity and the decrease of concentration occurs, when the content is beyond 1,000 ppm. The carbon black content is 0.1 to 15 wt. %. When the content is less than 0.1 wt. %, the effect of the carbon black, such as to secure light-shielding, to prevent electrification, and to prevent oxidation, is insufficient. While, when the content is beyond 15 wt. %, the physical strength of the film, particularly tear strength and impact puncture strength, decreases, and heat sealing properties are inferior. Furthermore, the surface strength decreases, and dust is liable to be generated. The dust adheres to photographic photosensitive materials, and causes developing trouble and contamination.

The polyolefin resin film layer contains more than 5 wt. % of an ethylene copolymer resin. The ethylene copolymer resin improves heat sealing properties such as hot tack properties, sealability with other materials, elapsed heat seal strength, heat seal strength and heat seal tolerance, and the generation of pinhole at heat-

sealed portion is prevented. The dispersibility of carbon black is also improved. The ethylene copolymer resin includes EVA resin, EEA resin, EMA resin, EAA resin and L-LDPE resin. L-LDPE resin is preferable in view of improving physical strength, heat sealing properties and the dispersibility of carbon black. The L-LDPE resin is similar to described previously except that the preferable MI is 0.4 to 20 g/10 minutes and the preferable density is 0.87 to 0.95 g/cm³. The content of the ethylene copolymer resin is more than 5 wt. %, preferably 15 to 95 wt. %. When the content is less than 5 wt. %, unless the width of heat seal is increased, heat sealing properties, particularly elapsed heat seal strength and sealability with other materials are inferior, and pinhole is liable to be generated. Moreover, heat-sealed portion is liable to separate. When the ethylene copolymer resin is L-LDPE, the suitable content is 5 to 99.9 wt. %, preferably 10 to 97 wt. %. The polyolefin resin film layer may be oriented or stretched.

The above flexible sheet layers may be laminated according to a known method such as a heat sealing (hot bar sealing, impulse heat sealing, supersonic welding, etc.) or a method using an adhesive (wet laminating, dry laminating, hot melt laminating, extrusion laminating, etc.).

The adhesive is selected by considering both layers to be joined, and includes thermoplastic resin melt adhesives including a polyolefin adhesive, hot melt type gum adhesives and solution type adhesives. The polyolefin adhesives include a homopolymer and a copolymer of an olefin such as various polyethylenes, polypropylenes, polybutenes and ethylene-propylene copolymers and L-LDPE, a copolymer of an olefin and another monomer such as ethylene-vinyl acetate copolymer, ethylene-acrylate ester copolymer, various ionomers ("SURLYN" Dupont, "HIMIRAN" Mitsui Polychemicals Co., Ltd., etc.) and a graft copolymer. The solution type adhesives are divided into adhesives for wet lamination and adhesives for dry lamination. The adhesives for wet lamination are emulsion-type or latex-type. Examples of the emulsion-type adhesives are polyvinyl acetate emulsion, the emulsion of vinyl acetate-ethylene copolymer, the emulsion of vinyl acetate-acrylate ester copolymer, the emulsion of vinyl acetate-maleate ester copolymer, the emulsion of acrylic copolymer and the emulsion of ethylene-acrylic acid copolymer. Examples of the latex-type adhesives are natural rubber latex, styrene-butadiene rubber latex, acrylonitrilebutadiene rubber latex and chloroprene rubber latex. An example of the adhesives for dry lamination is polyurethane adhesive. Adhesives for hot melt lamination containing paraffin wax, microcrystalline wax, ethylene-vinyl acetate copolymer and ethylene-ethylacrylate copolymer, pressure-sensitive adhesives and temperature-sensitive adhesives may also be employed. The melting point of the adhesive employed is preferably more than 5°C below the melting point of the flexible sheet in order to laminate without adverse influences upon the flexible sheet by a thermal melting adhesion.

The thickness of the adhesive layer formed by extrusion laminating using a thermoplastic resin is usually 6 to 50 µm, preferably 10 to 20 µm. However, the thickness is determined based upon cost, rate of application, thickness of the total layers, and etc., and accordingly, the thickness is not limited to the above range.

The adhesive strength of the adhesive layer may be improved by coating an anchor coating agent, physical surface treatment, chemical agent treatment, or etc.

Anchor coating agent is a generic name of adhesive promoter and cross-linking agent used in the field of laminating, and it is also called primer. Representative examples of the anchor coating agent are as follows:

Organic titanate anchor coating agent

Tetrapropyl titanate or tetrabutyl titanate is used as the principal constituent, and tetrasteryl titanate is added as a hydrolysis-adjusting agent.

Polyethyleneimine anchor coating agent

A relatively high polymer of ethyleneimine $\{\text{CH}_2\text{-CH}_2\text{-NH}\}_n$ is used. This agent is particularly preferable because its handling is easy and its pot life is long.

Polyisocyanate anchor coating agent

One-component type;	Polymer having isocyanate group alone
Two-component type;	Combination of a polymer having isocyanate group and a polyester having OH group

A chemical reaction such as a crosslinking reaction occurs in both types, and an adhesive effect appears. Pot life is short, and this coating agent is expensive.

Polyester and urethane anchor coating agent

Saturated polyester resin or urethane resin is dissolved in a solvent such as ethyl acetate or toluene.

5 Polyolefin anchor coating agent

Polybutadiene anchor coating agent

10 The anchor coat layer is preferably made extremely thin. The coating method may be gravure roll coating, kiss roll coating, curtain coating, bar coating, reverse roll coating, direct roll coating, air knife coating or the like.

Representative examples of the physical surface treatment are described below. Two or more kinds of the physical surface treatment may be combined, or the physical surface treatment may be combined with the coating of an anchor coating agent.

15 Flame treatment Running cost is high, and there is the danger of fire.

Plasma treatment Argon gas is converted into plasma, and joining surface is treated with the plasma. The treating strength is several times as much as corona discharge treatment, but the equipment cost for plasma treatment is several tenths higher than corona discharge treatment.

20 Corona discharge treatment Treatable materials are various polymer films and sheets, aluminum foil, aluminum vacuum metallized film, etc. This inexpensive treatment is widely utilized, and the treated effect is large.

Sandblasting treatment Sand such as silica sand is blasted at a high pressure to the joining surface, and the surface is made rough.

25 Representative examples other treatments are as follows:

Chemical agent treatment Treated with a dichromate solution or etc.

Ozone treatment Treated in a box filled with ozone gas. Even though the resin temperature of extrusion laminating is lowered, the adhesive strength is still improved.

30 Preheat treatment The flexible sheet to be conducted with extrusion laminating preheated with a heat drum, hot air or etc.

Ultraviolet irradiation

High-frequency heating

Dielectric heating

Microwave heating, etc.

35 The packaging material of the invention may be used for packaging photosensitive materials such as photographic photosensitive materials, foods, medicines or chemical substances, and it is particularly suitable for packaging silver halide photographic photosensitive materials, diazo photographic photosensitive materials, photofixing-type thermosensitive photosensitive materials, photosensitive resin photosensitive materials, ultraviolet curing-type photosensitive materials, transfer-type heat developing photosensitive materials, direct positive type photographic photosensitive materials, self-developing type photographic photosensitive materials, photosensitive materials for lithographic printing and other photographic materials which is degraded by
40 little amount of moisture, light or gas.

The package form may be conventional, and includes a single-sheet flat bag, a double-sheet flat bag, a self-standing bag, a single-sheet gusset bag, a double-sheet gusset bag, inner lining for a moisture proof box, inner lining for a light room-loading light-shielding box, wrapping paper and a leader paper. The bag-making
45 form may also be conventional, and includes heat sealing, side welding (heat-cut sealing), impulse heat sealing, supersonic sealing and high frequency sealing. The methods of using an adhesive may also be utilized.

In the above packaging material for photographic photosensitive materials, the release of fibers and the picking of paper do not occur from the long fiber paper, and they do not adhere to photographic photosensitive
50 materials as a foreign material. The long fiber paper improves the Young's modulus, heat resistance and drawing ability by writing tools. The aluminum vacuum metallized biaxially stretched thermoplastic resin film layer imparts antistatic property, moistureproofness, gas barrier and light-shielding, and prevents the penetration of harmful substances. The polyolefin resin film layer secures sealing and the carbon black contained therein does not affect the photographic photosensitive materials adversely. The packaging bag formed of the pack-
55 aging material may be a single sheet bag, and is excellent in bag-making ability and packaging workability.

Representative embodiments of the packaging material comprising an aluminum vacuum metallized biaxially stretched thermoplastic resin film layer, a long fiber layer and a polyolefin resin film layer are illustrated in Figures 1 to 4.

The packaging material of Figure 1 is composed of an aluminum vacuum metallized biaxially stretched thermoplastic resin film layer 21 consisting of a biaxially stretched thermoplastic resin film layer 19 and an aluminum vacuum deposition layer 20, a long fiber paper layer 22 laminated on the aluminum vacuum deposition layer 20 as the outer layer, and a light-shielding polyolefin resin film layer 23a on the biaxially stretched thermoplastic resin film layer 19 as the inner layer, each through an adhesive layer 3.

The packaging material of Figure 2 is similar to the packaging material of Figure 1, except that the light-shielding polyolefin resin film layer 23a is replaced by a coextruded multilayer film layer 25a consisting of a light-shielding thermoplastic resin film layer 24a and a light-shielding polyolefin resin film layer 23a.

The packaging material of Figure 3 is similar to the packaging material of Figure 2, except that the aluminum vacuum metallized biaxially stretched thermoplastic resin film layer 21 is turned inside out.

The packaging material of Figure 4 is similar to the packaging material of Figure 1, except that the light-shielding polyolefin resin film layer 23a is directly laminated by the extrusion laminating method.

Figure 5 indicates a comparative packaging material I similar to the packaging material of Figure 2, except that the long fiber paper layer 22 is replaced by a conventional bleached kraft paper layer 26.

EXAMPLES

Examples I and II are examples of the packaging material comprising an aluminum vacuum metallized biaxially stretched thermoplastic resin film layer, a long fiber paper layer and a polyolefin resin film layer.

The packaging material of Example I corresponds to illustrated in Figure 2.

The long fiber paper layer 22 consisted of a bleached kraft paper composed of the fibers having a fiber length of about 4 mm, containing 2.5 wt. % of polyacrylamide resin ("Polystlon", Arakawa Rinsan Kagaku K.K.) as paper reinforcing agent and each less than 500 ppm of harmful substances for photographic photosensitive materials, and having a cool water extracting pH of 4.8, a surface strength of 9, an areal weight of 35 g/m², and a glossy face by Yankee calender, made by using aluminum sulfate as a fixer.

The biaxially stretched thermoplastic resin film 19 of the aluminum vacuum metallized biaxially stretched thermoplastic resin film layer 21 was a biaxially stretched nylon resin film 15 μ m in thickness. The thickness of the aluminum vacuum deposition layer 20 was 400 Å.

The light-shielding polyolefin resin film layer 23a of the coextruded multilayer film layer 25a was composed of 91.75 wt. % of ethylene-4-methylpentene-1 copolymer resin, 5 wt. % of LDPE resin, 3 wt. % of oil furnace carbon black having a pH of 8.0, a mean particle size of 21 m μ and a free sulfur content of 450 ppm and 0.2 wt. % of antioxidant, 0.05 wt. % of oleic acid amide, having a thickness of 40 μ m.

The light-shielding thermoplastic resin film layer 24a was composed of 71.75 wt. % of ethylene-4-methylpentene-1 copolymer resin, 20 wt. % of HDPE resin having a density of 0.954 g/cm³, 5 wt. % of LDPE resin, 3 wt. % of the same oil furnace carbon black as the light-shielding polyolefin resin film layer 23a, 0.2 wt. % of antioxidant and 0.05 wt. % of oleic acid amide having a thickness of 40 μ m.

The adhesive layers 3 were LDPE resin extrusion laminating adhesive layers 13 μ m in thickness.

The laminations of laminated film was carried out in the same process using a tandem laminator.

The packaging material of Example II corresponds to illustrated in Figure 2.

The long fiber paper layer 22 consisted of an unbleached kraft neutral paper composed of the fibers having a fiber length of about 3.5 mm, containing 0.2 wt. % of alkylketene dimer ("Aquapell", Dick Hercules) and 0.5 wt. % of modified starch as paper reinforcing agent and each less than 1,000 ppm of harmful substances for photographic photosensitive materials, and having a cool water extracting pH of 6.8, a surface strength of 8, and an areal weight of 50 g/m², made by using aluminum sulfate as a fixer.

The other layers were the same as Example I.

Comparative packaging material I corresponds to illustrated in Figure 5.

The beached kraft paper layer 26 consisted of a semibleached kraft paper composed of the fibers having a fiber length of 2.5 mm, containing 2.0 wt. % of melamine-formaldehyde resin as paper reinforcing agent and 1870 ppm of formaldehyde adversely affecting photographic photosensitive materials, and having a cool water extracting pH of 4.3, a surface strength of 6 and an areal weight of 50 g/m², made by using aluminum sulfate as a fixer.

The other layers were the same as Example I.

Conventional packaging material I corresponds to illustrated in Figure 6.

The bleached kraft paper layer 26 consisted of a bleached kraft paper composed of the fibers having a fiber length of 2.5 mm, having a cool water extracting pH of 4.5, a surface strength of 5 and an areal weight of 30 g/m², made by using aluminum sulfate as a fixer.

The metal foil layer 27 was aluminum foil 7 μ m in thickness.

The thermoplastic resin film layer 28a was a LDPE resin film 80 μ m in thickness containing 3 wt. % of the

same carbon black as Example I.

The adhesive layers 3 were LDPE resin extrusion laminating adhesive layers 40 μm in thickness.

The laminated film was formed by laminating through twice extrusion laminating processes successively.

Various properties of the above films were measured, and the results are tabulated in Table 1.

Table 1

	Invention		Comparative	Conventional
	I	II	I	I
Layer Composition	Fig. 2	Fig. 2	Fig. 5	Fig. 6
Light-Shielding after Dropping Test	B	B	B	E
Hot Tack Properties	A	A	A	E
Sealability with Other Materials	A	A	A	E
Elapsed Heat Seal Strength	A	A	A	D
Bag Rupture Strength	A	A	A	E
Paper Powder Generation	B	B	D	D
Surface Strength	9	8	6	5
Photographic Properties	B	B	E	B
Tear Strength (MD) (g)	1120	1075	957	286
" (CD) (g)	1230	1186	1051	384

Evaluations in Table 1 were carried out as follows:

A very excellent

B excellent

C practical

D having a problem

E impractical

In the following tests, the packaging bag used was a single-sheet gusset bag, and 4 rolls of color printing paper of 8.9 cm in width x 180 m in length were placed in a corrugated board box in two layers through a corrugated board pad.

Light-Shielding after Dropping Test:

5 After the dropping test of JIS Z-0202 level I, each packaging bag was exposed to 80,000 luxes light for 1 hour. The color printing paper was developed, and the light-shielding was judged.

Hot Tack Properties (Hot-Seal Ability):

10 Two sheets of each exemplified film having 15 mm in width were heat-sealed at 170°C, and just after, the open ends were pulled by the weight of 45 g at the releasing angle of 22.5 degree. This character was estimated by the released length (cm).

Sealability with Other Materials:

15 Each exemplified film was cut in a width of 15 mm, and the cigarette end after smoking was smeared on the heat seal face by using a finger. Thereafter, two sheets of the films were superposed, and heat-sealed at each optional temperature at a sealing pressure of 1 kg/m² for one second. This character was estimated by the load necessary for releasing the sealed portion at 180 degrees.

Elapsed Heat Seal Strength:

Two sheets of each exemplified film having a width of 15 mm were heat sealed at each optimal temperature at a sealing pressure of 1 kg/m² for one second. This character was estimated by the load necessary for releasing the sealed portion at 180 degrees after one month from the heat seal.

20 Bag Rupture Strength:

Judged by the bag rupture state after the dropping test of JIS Z-0202 level I.

Paper Powder Generation:

Judged by the amount of paper powder after the shaking test of JIS Z-0232 level I.

Surface Strength:

25 Measured by the wax method of JIS P-8129, and it is expressed in wax number.

Photographic Properties:

According to a contact test with the uppermost layer.

Teat Strength:

According to JIS P-8116.

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Claims

35 1. A packaging material for photographic photosensitive materials which comprises an aluminum vacuum metallized biaxially stretched thermoplastic resin film layer, a long fiber paper layer, of which more than 50 % of the fibers have a fiber length of longer than 3 mm, containing a paper reinforcing agent and having a PH of 4 to 9 measured by cool water extracting method (JIS P-8133), laminated on one side of the above thermoplastic resin film layer, and a polyolefin resin film layer containing 0.1 to 15 wt. % of carbon black having a pH of 4 to 9 and a mean particle size of 15 to 80 mμ and more than 5 wt. % of an ethylene copolymer resin laminated on the other side.

2. The packaging material of claim 1 wherein the long fiber paper has a surface strength of more than 6 expressed in wax number (according to JIS-P-8129).

45 3. The packaging material of claim 1 wherein the ethylene copolymer resin is L-LDPE resin.

Patentansprüche

50 1. Verpackungsmaterial für photographische lichtempfindliche Materialien, umfassend eine mit Aluminium vakuumbedampfte, biaxial gestreckte thermoplastische Harz-Filmschicht, eine Papierschicht mit langen Fasern, wobei mehr als 50% der Fasern eine Faserlänge von mehr als 3 mm besitzen, die ein Papierverstärkungsmittel enthält und einen pH von 4 bis 9 besitzt, gemessen mit dem Kaltwasser-Extraktionsverfahren (JIS P-8133), auflaminiert auf einer Seite der obengenannten thermoplastischen Harz-Filmschicht, und eine Polyolefinharz-Filmschicht, die 0,1 bis 15 Gew.-% Ruß mit einem pH von 4 bis 9 und einer mittleren Teilchengröße von 15 bis 80 μm und mehr als 5 Gew.-% eines Ethylen-Copolymer-Harzes enthält, auflaminiert auf der anderen Seite.

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2. Verpackungsmaterial nach Anspruch 1, worin das Papier mit langen Fasern eine Oberflächenfestigkeit von mehr als 6 besitzt, ausgedrückt als Wachszahl (entsprechend JIS P-8129).
3. Verpackungsmaterial nach Anspruch 1, worin das Ethylen-Copolymer-Harz ein L-LDPE-Harz ist.

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Revendications

1. Matériel d'emballage pour matériaux photographiques photosensibles, qui comprend une couche de pellicule de résine thermoplastique biaxialement étirée, métallisée sous vide avec de l'aluminium, une couche de papier à fibres longues, dont plus de 50 % des fibres ont une longueur de fibre supérieure à 3 mm, contenant un agent renforçant le papier et ayant un pH de 4 à 9 mesuré par un procédé d'extraction à l'eau fraîche (JIS P-8133), laminée sur un côté de la couche de pellicule de résine thermoplastique ci-dessus, et une couche de pellicule de résine de polyoléfine contenant 0,1 à 15 % en poids de noir de carbone, ayant un pH de 4 à 9 et une taille moyenne de particules de 15 à 80 μm , et plus de 5 % en poids d'une résine de copolymère de l'éthylène laminée sur l'autre côté.
2. Matériau d'emballage selon la revendication 1, dans lequel le papier à fibres longues a une résistance superficielle de plus de 6, exprimée en indice de cire (selon JIS P-8129).
3. Matériau d'emballage selon la revendication 1, dans lequel la résine de copolymère de l'éthylène est la résine L-LDPE.

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FIG. 1

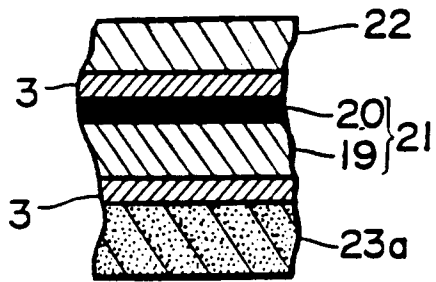


FIG. 2

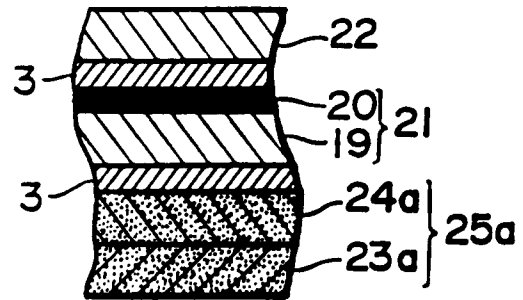


FIG. 3

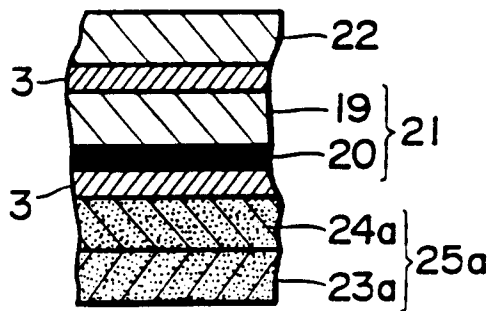


FIG. 4

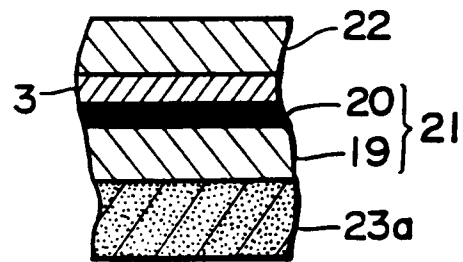


FIG. 5

COMPARATIVE

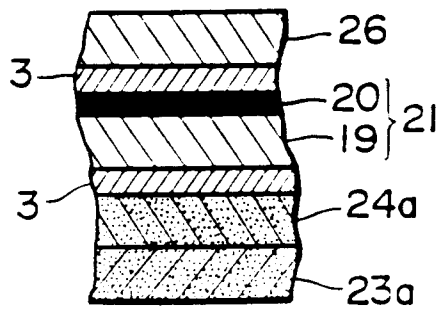


FIG. 6

PRIOR ART

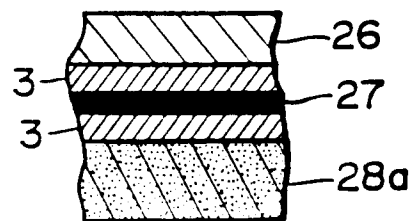


FIG. 7

