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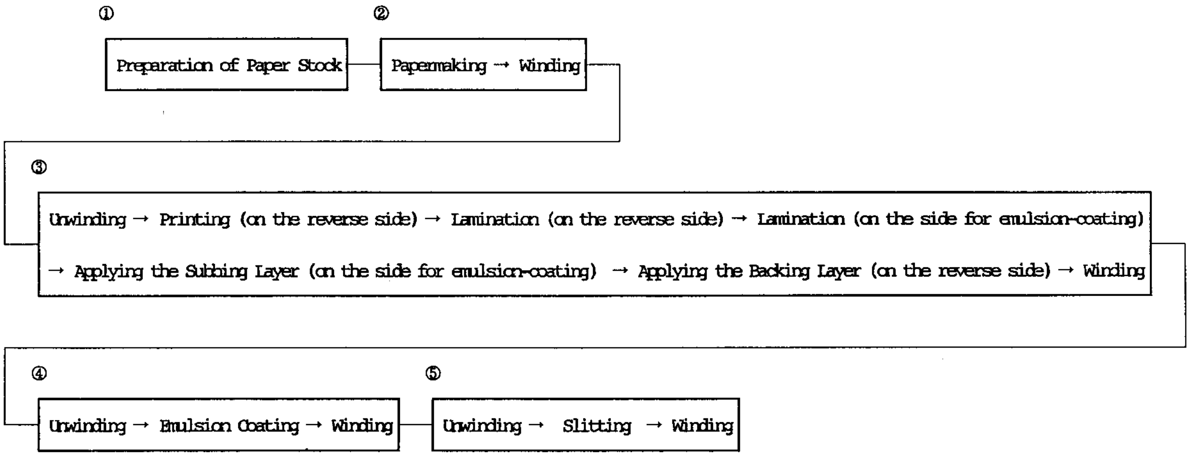
(54) Method of manufacturing photographic printing paper or photographic film.

(57) Disclosed is a method of manufacturing a photographic printing paper or photographic film which consists mainly of a substrate having emulsion layers on one side and a backing layer on the other side, wherein are performed continuously at least two processes comprising the process of applying a subbing layer to the substrate on the side for the emulsion layers and the process subsequent thereto in which the backing layer is applied on the reverse side of the substrate.

Fig. 2



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FIELD OF THE INVENTION

The present invention relates to a method of manufacturing photographic printing papers or photographic films and, more particularly, to a method of continuously manufacturing photographic printing papers or photographic films without requiring any winding processes.

BACKGROUND OF THE INVENTION

Hitherto, there have been arranged independently all the processes required for manufacturing photographic printing papers, including (1) a process of preparing a paper stock, (2) a process of manufacturing a raw paper by making paper and then subjecting the paper successively to drying, sizing and calendering treatments, (3) a process of printing a product name or the like on the raw paper surface to which the application of photographic emulsions is not intended (which is simply called the reverse side of a raw paper, hereinafter), (4) a process of laminating the printed side of raw paper surface with a waterproof resin, (5) a process of laminating the other side of raw paper surface, on which photographic emulsions are to be coated, with a waterproof resin, (6) a process of covering the substrate with a subbing layer on the side where photographic emulsions are to be coated, (7) a process of applying a backing layer on the reverse side of the substrate, (8) a process of applying emulsion layers and protective layer(s) and (9) a process of performing slitting and cutting operations.

In analogy with photographic printing papers, photographic films also have so far been manufactured through independently arranged processes, although the manufacture of photographic films starts from a high molecular resin film instead of the laminated paper prepared going through the processes from (1) to (5).

The aforementioned independent performance of all the processes for manufacturing a photosensitive material has disadvantages in that it not only requires large stock space between every two successive processes but also involves a stock loss, and further causes a systematic loss in the core part of every roll because each process has a winding process inserted thereafter. In addition, it has a drawback of suffering the rising labor costs.

As a result of our intensive studies with the aim of obviating the above-described disadvantages, it has been found out that when the unity in various process speeds is secured by choosing as a unified process speed the speed of the slowest process among the processes required and thereby a continuous through process is realized in the manufacture of photographic printing papers or films not only a stock space can be materially reduced but also a stock loss and a loss ascribed to the roll-core part can be diminished and the workability also can be improved, that is, the productivity can be greatly improved, thereby achieving the present invention.

SUMMARY OF THE INVENTION

Therefore, a first object of the present invention is to provide a method of manufacturing photographic printing papers or photographic films which enables a very considerable reduction in large stock space which conventional manufacturing processes require.

A second object of the present invention is to provide a method of manufacturing photographic printing papers or photographic films which enables a diminution in products loss, including a stock loss and a loss in the roll-core part.

The above-described objects are attained by a method of manufacturing a photosensitive material which consists mainly of a substrate having emulsion layers via a subbing layer on one side and a backing layer on the other side, wherein the photosensitive material is a photographic printing paper or a photographic film and at least two processes comprising the process of applying a subbing layer to the substrate on the side for the emulsion layers and the process subsequent thereto in which the backing layer is applied on the reverse side of the substrate are performed continuously.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a flow chart which illustrates the processes constituting a conventional manufacturing method (See Comparative Example 1).

Fig. 2 is a flow chart which illustrates the processes constituting a manufacturing method according to the present invention (See Example 1).

Fig. 3 is a flow chart which illustrates the processes constituting another manufacturing method according to the present invention (See Example 2).

DETAILED DESCRIPTION OF THE INVENTION

The present invention has no particular restriction as to a substrate, and so there can be used as the substrate a raw paper made mainly from natural pulp, a raw paper made from a mixture containing natural pulp and synthetic fibers or synthetic pulp in an arbitrary ratio, a paper laminated with a waterproof resin on both sides, films or plates of plastics such as polycarbonate, polystyrene, polyacrylate, polymethacrylate, polyethylene terephthalate (PET), etc., metal plates and so on. However, the substrates particularly preferred in the present invention are base papers disclosed, e.g., in JP-A-04-69648 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

As for the natural pulp, wood kraft pulp, such as soft wood kraft pulp, hardwood kraft pulp or soft wood-hardwood mixture kraft pulp, is preferably used. These types of pulp may be prepared using any of the cooking methods, namely polysulfide cooking, batch cooking and continuous cooling methods, or they may be prepared so as to have a proper hardness or Kappa number. Also, they may be prepared by the oxygen pulping method disclosed in JP-B-59-38575 (the term "JP-B" as used herein means an "examined Japanese patent publication").

In particular, it is preferable for the wood kraft pulp used herein to be prepared by the following process: Wood chips are cooked with a muddy liquor containing sodium hydroxide and sodium sulfide as chemical components, and lignin is removed therefrom. Thereafter, in the presence of a defoamer or a foam inhibitor, the resulting matter is separated into pulp fibers and the cooking residue (black liquor), washed and then subjected to a bleaching treatment. The muddy liquor used therein for cooking may additionally contain cooking aids such as salts including sodium carbonate, sodium sulfate, calcium hydroxide, calcium carbonate and the like, sodium borohydride, anthraquinone compounds and so on.

As for the pulp used together with natural kraft pulp, natural pulp is suitable. Especially, wood sulfide pulp such as soft wood sulfide pulp, hardwood sulfide pulp or soft wood-hardwood mixture sulfide pulp is preferred. Also, wood soda pulp and wood dissolving pulp may be used.

The defoamer or foam inhibitor used in the bleaching treatment of pulp can be properly chosen from known ones. For instance, the chemicals containing as the deforming or foam-inhibiting component a higher fatty acid alcohol ester compound, a mineral oil or liquid hydrocarbon oil, a silicone oil or the like, as disclosed in JP-A-54-59404, JP-A-58-220896, JP-A-61-245391, JP-A-61-245319, U.S. Patent 3,923,638 and U.S. Patent 4,107,073, may be used. Of these chemicals, a water-base or oil-base defoamer or foam inhibitor containing a mineral oil or a liquid hydrocarbon oil as a main component is preferred over the others with respect to the defoaming or foam-inhibiting power.

The defoamer or foam inhibitor used herein may contain additional ingredients such as hydrophobic silica, an ethylenebis(higher alkyl amide), a silicone oil and so on. As for the way to make such an defoamer or foam inhibitor be present during the washing process of unbleached kraft pulp, it is desirable to add the defoamer or foam inhibitor to the unbleached kraft pulp slurry or a thickener at any stage of the washing process.

For chlorine bleaching in the natural pulp preparation, chlorine gas or chlorine water is used. Therein, chlorine dioxide may be used together. For alkali treatment or extraction, sodium hydroxide is used to advantage, but calcium hydroxide, ammonia or a mixture thereof may be used. For hypochlorite bleaching, a bleaching powder obtained by making chlorine act on powdery solid of calcium hydroxide or, from an industrial point of view, hypochlorite bleaching liquor prepared by blowing chlorine gas into milk of lime or a dilute sodium hydroxide solution (the so-called calcium-hypo bleaching liquor or sodium-hypo bleaching liquor) is suitable.

For chlorine dioxide bleaching, it is advantageous to use the chloride dioxide prepared by a sulfite process, such as Mathieson process, new Mathieson process, Ersto method, C.I.P. process, etc., or a hydrochloric acid process such as casting process, Nissoh process, Solvay process, etc. As for the peroxides used for peroxide bleaching under an alkaline condition, on the other hand, there can be suitably used inorganic and organic peroxides such as hydrogen peroxide, sodium peroxide, peroxide bleaching liquor (an aqueous mixture containing hydrogen peroxide, sodium hydroxide and sodium silicate, and optionally magnesium sulfate) peracetic acid, 1-butylhydroperoxide and mixtures of two or more thereof. Suitable examples of an alkali used therein include hydroxides of alkali and alkaline earth metals, such as sodium hydroxide, aqueous ammonia, magnesium hydroxide, calcium hydroxide and mixtures of two or more thereof.

The bleaching can be carried out under a condition properly chosen from those described, e.g., in a book entitled "Pulp shori oyobi Hyohaku" (which means "Treatments and Bleaching of Pulp") compiled by Kami Pulp Gijutsu Kyokai (published in January 27, 1968) and JP-B-58-43732.

In preparing stock slurry, various additives can be added in the present invention.

Into the stock slurry, it is especially desirable to incorporate a proper combination of additives which can be chosen from among a sizing agent such as a metal salt of fatty acid and/or a fatty acid, the alkylketene dimer emulsion or the epoxidized higher fatty acid amide disclosed in JP-B-62-7534, alkenyl- or alkylsuccinic acid anhydride emulsions, rosin derivatives, etc.; a dry paper strength reinforcer such as anionic, cationic or amphoteric polyacrylamides, polyvinyl alcohol, cationized starch (as disclosed, e.g., in JP-A-03-171042), vegetable galactomannan, etc.; a wet paper strength reinforcer such as polyaminepolyamide-epichlorohydrin resins, etc.; a filler such as clay, kaoline, calcium carbonate, titanium oxide, etc.; a fixing agent such as water-soluble aluminum salts including aluminum chloride and aluminum sulfate, etc.; a pH modifier such as sodium hydroxide, sodium carbonate, sulfuric acid, etc.; and the colored pigments, the colored dyes and the brightening agents disclosed, e.g., in JP-A-63-204251 and JP-A-01-266537.

Further, other additives including various water-soluble polymers and antistatic agents can be incorporated in the paper stock by means of a spray or a tub size press.

As for the water-soluble polymers which can be added, the starch polymers disclosed in JP-A-01-266537, polyvinyl alcohol polymers, gelatin polymers, polyacrylamide polymers and cellulose polymers are examples thereof. The antistatic agents which can be used are electrically conductive substances, including nonionic surfactants represented by polyoxyethylene glycols, anionic surfactants, cationic surfactants represented by quaternary ammonium salts, amphoteric surfactants, alkylamine derivatives, fatty acid derivatives, various lubricants, carbon black, graphite, metal-coated pigments, metallic powders, metallic flake, carbon fibers, metallic fibers, whiskers (potassium titanate, alumina nitride, alumina) and so on. As specific examples thereof, mention may be made of alkali metal salts such as sodium chloride, potassium chloride, etc,; alkaline earth metal salts such as calcium chloride, barium chloride, etc.; colloidal metal oxides such as colloidal silica, etc.; and organic antistatic agents such as polystyrenesulfonates, etc.

As for the latexes and emulsions which can be added, petroleum resin emulsions and latexes of a styrene-acrylic acid-acrylate copolymer, a styrene-acrylic acid-butadiene copolymer, an ethylene-vinyl acetate copolymer, a styrene-maleic acid-acrylate copolymer and the like are examples thereof. As for the pigments which can be added, clay, kaoline, talc, barium sulfate and titanium oxide are examples thereof. As for the pH modifiers which can be added, hydrochloric acid, phosphoric acid, citric acid and sodium hydroxide are examples thereof. It is desirable for these additives to be added together with other additives properly chosen from the above-cited ones, including colored pigments, colored dyes, brightening agents and so on.

As an especially preferable base paper, a mention may be made of the raw paper which is prepared by making paper from a paper stock containing an epoxidized fatty acid amide and having the pH adjusted to 5.5-6.5, controlling the water content in the paper to 1-4 % by weight and then subjecting the paper to a surface sizing treatment with an alkaline aqueous solution to control the paper surface pH to 7-8.

It is desirable in the present invention that the surface of a substrate be so smooth as to have Bekk smoothness of at least 100 seconds when measured according to JIS P8119. In particular, a substrate having surface smoothness of at least 200 seconds is favored.

The substrate having Bekk smoothness of at least 100 seconds can be prepared generally by using a pulp containing a large proportion of hardwood pulp, which has a tendency to easily make a smooth surface, and beating the pulp with a beater so that the long fibers therein may have the lowest possible content. In this case, it is desirable for the pulp to be beaten so that the beaten pulp may have the fiber length corresponding to 20-45 % in terms of 42-mesh residue and the freeness of 20-350 CSF.

Then, by adopting a proper method for papermaking, such as the method disclosed in JP-A-58-37642, JP-A-61-260240 or JP-A-61-284762, the paper stock slurry to which internal additives have been added is made into paper having uniform formation by means of a generally used paper machine, such as a Fourdrinier paper machine, a cylinder paper machine or so on. The paper obtained is further subjected to a calender treatment with a machine calender, a super calender, a hot calender or the like. Thus, there can be made the base paper having Bekk smoothness of at least 100 seconds.

The raw paper used in the present invention has no particular restriction as to the thickness. However, it is desirable for the raw paper to have a basis weight ranging from 40 g/m^2 to 250 g/m^2 .

On one side (which is the reverse of the side on which photographic emulsions are to be coated) of the thus made raw paper, products name and so on are printed, if needed.

The printing thereon may be performed using any of general printing methods, such as gravure printing, flexographic printing, letterpress printing, offset printing, etc.

Although this printing process may be carried out after the raw paper was once wound into a roll, and that before the covering the raw paper with a waterproof resin layer, it is preferable in view of the reduction in stock space and stock loss that this optional printing process be carried out without inserting a winding process after the papermaking process and be succeeded by the next process so as to be a continuous operation.

Next, the raw paper is covered with a waterproof resin layer on both sides. The covering is carried out by lamination process firstly on the reverse side where the application of emulsions is not intended, and then on the front side to which photographic emulsions are to be applied.

In the covering on the front side, it is desirable that the waterproof resin contain fine grains of titanium dioxide and optionally a bluing agent.

The covering layer may be a single layer or may be constituted of two or more layers. In the latter case, it is preferable to laminate all the constituent layers simultaneously from the viewpoint of the reduction in process number.

As for the waterproof resin which can be used, polyolefins such as polyethylene, polypropylene and ethylene copolymers are suitable examples thereof. In particular, polyethylene is used to advantage. The polyethylene used herein may be high-density polyethylene, low-density polyethylene, linear low-density polyethylene or a mixture thereof. In addition, it is desirable for the polyolefin resins to have in an unprocessed state a melt flow rate (which is abbreviated as "MFR" hereinafter) in the rage of 1.2 g/10 min. to 12 g/10 min. when measured under the condition set forth in Table 1 of JIS K 7210. The expression "MFR of a polyolefin resin in an unprocessed state" as used herein is intended to include MFR of the resin into which neither a bluing agent nor titanium dioxide has not yet been kneaded and MFR of the resin which has not yet been mixed with any resins for dilution.

As for the bluing agent, known pigments such as ultramarine blue, cobalt blue, cobalt phosphate oxide, quinacridone pigments and mixtures of two or more thereof can be contained in the waterproof resin layer. The grain size of a bluing agent has no particular limitation. In general, commercially available bluing agents have a grain size of the order of 0.3 ~ 10 μm. So far as the bluing agent has its grain size in such a range, it is well fit for use. Additionally, different bluing agents may be used in the upper and the lower layers respectively.

When the waterproof resin layer has a multi-layer structure, it is desirable that the content of a bluing agent in the topmost layer be in the range of 0.01 to 0.8 % by weight, preferably 0.05 to 0.6 % by weight, and particularly preferably 0.1 to 0.4 % by weight, and the content in layers disposed on the lower side be in the range of 0 to 0.6 % by weight, preferably 0.01 to 0.45 % by weight, and particularly preferably 0.05 to 0.3 % by weight. The bluing agent is kneaded into a waterproof resin with a kneading machine such as a two-rod roll mill, a three-rod roll mill, a kneader, a Bumbury's mixer or the like, and molded in the form of pellets, which are used as a master batch. The concentration of the bluing agent in the pellets ranges from 1 to 30 % by weight.

As for the titanium dioxide (TiO_2) contained together with a bluing agent in the waterproof resin layer, both anatase-type and rutile-type TiO_2 may be used. However, it is preferable to use anatase-type TiO_2 when priority is given to the achievement of high whiteness; while rutile-type TiO_2 is preferable when priority is given to the achievement of high sharpness. On the occasion both whiteness and sharpness are taken into account, on the other hand, a blend of anatase-type TiO_2 and rutile-type TiO_2 may be used, or the TiO_2-containing layer may be constituted of the upper layer in which which anatase-type TiO_2 is used and the lower layer in which rutile-type TiO_2 is used. The upper and the lower layers may be the same or different in TiO_2 concentration, and the TiO_2 concentrations therein can be arbitrarily chosen from the range of 5 to 20 % by weight.

Prior to the incorporation into the waterproof resin layer, TiO_2 is generally subjected to a surface treatment for the purpose of depressing its activity to inhibit the yellowing phenomenon. Suitable examples of an agent which can be used for such a surface treatment include inorganic materials such as hydrated aluminium oxide, hydrated silicon oxide, etc. and organic materials such as a polyhydric alcohol, a polyamine, a metal soap, an alkyl titanate, a polysiloxane, etc. It is desirable that such a surface treatment agent as cited above be used in a proportion of from 0.2 to 2.0 % by weight to TiO_2 when it is an inorganic material, while when it is an organic material it be used in a proportion of from 0.1 to 1.0 % by weight to TiO_2. Further, it is desirable for the TiO_2 used to have an average grain size of the order of 0.1 to 0.4 μm.

In preparing the pellets of a bluing agent, TiO_2 also can be kneaded into the waterproof resin. For the purpose of helping the dispersion of the bluing agent, a low molecular weight waterproof resin, a metal salt of higher fatty acid, an ester of higher fatty acid, a higher fatty acid amide, a higher fatty acid or so on can be used therein as dispersing aid.

In preparing TiO_2-kneaded pellets separately from the bluing agent-kneaded pellets, TiO_2 is kneaded into a waterproof resin by means of a kneading machine, such as a two-rod roll, a three-rod roll, a kneader, a Bumbury's mixer or the like, wherein a metal salt of higher fatty acid, an ethyl ester of higher fatty acid, a higher fatty acid amide, a higher fatty acid or so on is further used as dispersing aid. In general, the TiO_2 concentration in the thus prepared pellets is in the range of about 30 to about 75 %.

At least the resin layer which covers the raw paper on the side where emulsion layers are to be applied can contain at least one kind of additive chosen from among known antioxidants, lubricants, surfactants, etc.

Of these additives, it is desirable to add an antioxidant for the purpose of preventing the resin from undergoing oxidative decomposition to produce an aldehyde or a ketone which causes the generation of fog and abnormal sensitivity in a photographic film, or from the standpoint of preventing the generation of non-soluble foreign matter and coloration troubles. Representatives of such antioxidants are described below.

(a) Antioxidants of phenol type:

6-t-Butyl-3-methylphenol derivatives, 2,6-di-t-butyl-p-cresol, t-butylphenol, 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 4,4'-butylidenebis(6-t-butyl-m-cresol), 4,4'-thiobis(6-t-butyl-m-cresol), 4,4'-dihydroxydiphenyl-cyclohexane, alkylated bisphenols, styrene-introduced phenols, 2,6-di-t-butyl-4-methylphenol, n-octadecyl-3-(3',5'-di-t-butyl-4'-hydrpoxyphenyl)propionate, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), stearyl-β-(3,5-di-4-butyl-4-hydroxyphenyl)propionate, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzeneand tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]-methane are examples thereof.

(b) Antioxidants of ketone-amine condensate type:

6-Ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, 2,2,4-trimethyl-1, 2-dihydroquinone polymers and trimethyldihydroquinoline derivatives are examples thereof.

(c) Antioxidants of arylamine type:

Phenyl-α-naphthylamine, N-phenyl-β-naphthylamine, N-phenyl-N'-isopropyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-di-β-naphthyl-p-phenylenediamine and N-(3'-hydroxybutylidene)-1-naphthylamine are examples thereof.

(d) Antioxidants of imidazole type:

2-Mercaptobenzimidazole, zinc salt of 2-mercaptobenzoimidazole and 2-mercaptomethylimidazole are examples thereof.

(e) Antioxidants of phosphite type:

Alkylated-aryl phosphites, diphenylisodecyl phosphite, tris(nonylphenyl)phosphite • sodium phosphite, and triphenyl phosphite are examples thereof.

(f) Antioxidants of thiourea type:

Thiourea derivatives such as 1,3-bis(dimethylaminopropyl)-2-thiourea are examples thereof.

(g) Other antioxidants effective against aerial oxidation:

Dilauryl thiodipropionate is an example thereof.

Further, typical examples of commercially available antioxidants are given below.

(1) Antioxidants of phenol type:

Sumilizer series BHT, BP-76, BP-101, GA-80 and WX R (trade names, the products of Sumitomo Chemical Co., Ltd.), Irganox series 565, 1010, 1035, 1076, 1330, 1425WL and 3114 (trade names, the products of Ciba Geigy Co., Ltd.), Mark series AO-20, 30, 50, 60, 80 and 330 (trade names, the products of Adeka Argus Chemical Co., Ltd.), Tominox SS and Tominox TT (trade names, the products of

Yoshitomi Pharmaceutical Industries, Ltd.), Topanol CA and Nonnox WST (trade names, the products of British I.C.I. Co., Ltd.), Santon-OX (trade name, the product of Monsanto Co., Ltd.), Antage Crystal and Antage W-400 (trade names, the products of kawaguchi Kogyo Co. , Ltd.), Nokulizer NS-6 (trade name, the product of Ohuchi Shinko K.K.), Cyanox 1790 (trade name, the product of American ACC Co.) and so on.

(2) Phosphorus-containing antioxidants: Irgafos 168 (trade name, the product of Ciba Geigy Co., Ltd.), Mark 2112, Mark PEP-8, Mark 24G and Mark 36 (trade names, the products of Adeka Argus Chemical Co., Ltd.), Weston 618 and Ultranox 626 (trade name, the products of Vorg-Warner Corp.), HCA (trade name, the product of Sanko K.K.), and so on.

(3) Antioxidants of thioether type:
DLTOP YOSHITOMI, DMTD YOSHITOMI AND DSPT YOSHITOMI (trade names, the products of Yoshitomi Pharmaceutical Industries, Ltd.), Sumilizer series TPL, TPM, TPS and TPD (trade names, the products of Sumitomo Chemical Co., Ltd.), Antiox M and Antiox S (trade name, the products of Nippon Oil & Fats Co., Ltd.), C-Nox 4125 (trade name, the product of Zipro K.K.), Mark series AO-412 S, AO-23, 260, 329K and 522A (trade names, the products of Adeka Argus Chemical Co., Ltd.), Sandstub P-EPQ (trade name, the product of Sandstub Co., Ltd.), Irgafos P-EPQ FF and Irganox 1222 (trade names, the products of Ciba Geigy Co., Ltd.), Weston 399 (trade name, the products of Vorg-Warner Corp.), and so on.

(4) Metal deactivators:
Nougard XL-1 (trade name, the product of Uniroyal K.K), Mark CDA-1 and Mark CDA-6 (trade names, the products of Adeka Argus Chemical Co., Ltd.), Irganox MD-1024 (trade name, the product of Ciba Geigy Co., Ltd.), CU-Nox (trade name, the product of Mitsui Toatsu Chemicals Inc.), and so on.

Of the above-cited ones, the phenol type antioxidants are preferred over the others. Especially, the antioxidants of hindered phenol type are effective.

As for the antioxidants of hindered phenol type, commercial products, e.g., Irganox series produced by Ciba Geigy Co., Ltd. and Sumilizer series, BHT, BH-76, WX-R and BP-101, produced by Simitomo Chemical Co., Ltd. can be used to advantage.

Also, it is effective to use one or more, especially two or more, of an antioxidant chosen from the group consisting of 2,6-di-t-butyl-p-cresol (BHT), the antioxidants of low volatile high-molecular phenol type (those having the trade names, Irganox 1010, Irganox 1076, Topanol CA, Ionox 330, etc.), dilauryl thiodipropionate, distearyl thiopropionate and dialkyl phosphates.

It is desirable that the amount of an antioxidant added (by weight) be in the range of 0 to 8,000 ppm, preferably 20 to 3,000 ppm and particularly preferably 50 to 1,500 ppm.

When the antioxidant is added in an amount greater than 8,000 ppm, it produces bad influences upon photosensitive materials, including photographic films and photographic printing papers, because oxidation-reduction reactions are utilized therein. Specifically, excess addition of antioxidants sometime causes abnormality in photographic properties andtends to deteriorate the adhesiveness of the resin layer to a substrate. Therefore, it is desired that the antioxidant be added in the smallest possible amount so far as it can prevent the troubles of coloration and adhesion and the generation of lamps.

In addition to the above-cited ones, it is possible to use other antioxidants chosen from those described, e.g., in <u>Plastics Data Handbook</u>, pages 794-799, published by KK Kogyo Chosakai, <u>The Data of Additives for Plastics</u>, pages 327-329, published by KK Kagaku Kogyo Limited, and <u>Plastics Age Encyclopedia Advanced Edition 1986</u>, pages 211-212, published by KK Plastics-Age Co., Ltd..

In the present invention, it is desirable to add a lubricant for the purpose of improvement upon kneadabilities of other additives.

Typical representatives of lubricants suitable for use herein are instanced below.

(1) Fatty acid amide type lubricants:

<u>Saturated fatty acid amide type lubricants</u>

① Behenic acid amide lubricants; Dyamid KN (trade name, the product of Nippon Kasei Chemicals Co., Ltd.), and so on.

② Stearic acid amide lubricants; Armide HT (trade name, the product of Lion Fat & Oil Co., Ltd.), Alflow S-10 (trade name, the product of Nippon Oils & Fats Co., Ltd.), Fatty Acid Amide S (trade name, the product of Kao Corporation), Dyamid 200 and Dyamid AP-1 (trade names, the products of Nippon Kasei Chemicals Co., Ltd.), Amide S and Amide T (trade names, the products of Nitto Chemical Industry Co., Ltd.), Newtron-2 (trade name, the product of Nippon Seika K.K.), and so on.

③ Palmitic acid amide lubricants; Newtron S-18 (trade name, the product of Nippon Seika K.K.), Amide C (trade name, the product of Nitto Chemical Industry Co., Ltd.), and so on.
④ Lauric acid amide lubricants; Armide C (trade name, the product of Lion Akuzo Co., Ltd.), Dyamid (trade name, the product of Nippon Kasei Chemicals Co., Ltd.), and so on.

Unsaturated fatty acid amide type lubricants

① Erucic acid amide lubricants; Alflow P-10 (trade name, the product of Nippon Oils & Fats Co., Ltd.), Newtron-S (trade name, the product of Nippon Seika K.K.), Lubrole (trade name, the product of I.C.I. Co., Ltd.), Dyamid L-200 (trade name, the product of Nippon Kasei Chemicals Co., Ltd.), and so on.
② Oleic acid amide lubricants; Armoslip CP (trade name, the product of Lion Akuzo Co., Ltd.), Newtron and Newtron E-18 (trade names, the products of Nippon Seika K.K), Dyamid O-200 and Dyamid G-200 (trade names, the products of Nippon Kasei Chemicals Co., Ltd.), Alflow E-10 (trade name, the product of Nippon Oils & Fats Co., Ltd.), Fatty Acid Amide O (trade name, the product of Kao Corporation), and so on.

Bis(fatty acid) amide type lubricants

① Methylenebis(behenic acid amide) lubricants; Dyamid NK Bis (trade name, the product of Nippon Kasei Chemicals Co., Ltd.), and so on.
② Methylenebis(stearic acid amide) lubricants; Dyamid 200 Bis (trade name, the product of Nippon Kasei Chemicals Co., Ltd.), Armowax (trade name, the product of Lion Akuzo Co., Ltd.), Bisamide (trade name, the product of Nitto Chemical Industry Co., Ltd.), and so on.
③ Methylenebis(oleic acid amide) lubricants; Lubron O (trade name, the product of Nippon Kasei Chemicals Co., Ltd.), and so on.
④ Ethylenebis(stearic acid amide) lubricants; Armoslip EBS (trade name, the product of Lion Akuzo Co., Ltd.), and so on.
⑤ Hexamethylenebis(stearic acid amide) lubricants; Amide 65 (tradename, the product of Kawaken Fine Chemicals, Ltd.), and so on.
⑥ Hexamethylenebis(oleic acid amide) lubricants; Amide 60 (trade name, the product of Kawaken Fine Chemicals, Ltd.), and so on.

(2) Silicone type lubricants:

Dimelthylpolysiloxanes of various grades, modified products thereof and a wide variety of modified products of other silicones (represented by siloxanes) are included therein.

As typical examples thereof, mention may be made of carboxyl-modified silicones, α-methylstyrene-modified silicones, α-oleic acid-modified silicones, polyether-modified silicones, fluorine-modified silicones, specially modified hydrophilic silicones, olefin polyether-modified silicones, epoxy-modified silicones, amide-modified silicones, alcohol-modified silicones, alkyl-modified silicones, alkylaryl-modified silicones, amino-modified silicones and alkyl- and hydrogen-modified silicones (produced by Shin-Etsu Silicone Co., Ltd. and Toshiba Silicone Co., Ltd.).

In particular, the addition of silicones of various types is desirable because they not only have improving effects upon the resin's flowability and lubricity, but also can achieve unexpected effects if a light-shielding material and a coloring material are added together therewith. Specifically, they can have elevating effects upon the dispersibilities of light-shielding and coloring materials, the coloring power of coloring material, and so on.

(3) Nonionic surfactant type lubricants:

Electrostripper TS-2 and TS-3 (trade names, the products of Kao Corporation) and so on are examples thereof.

(4) Hydrocarbon type lubricants:

Liquid paraffin, natural paraffin, micro wax, synthetic paraffin, polyethylene wax, polypropylene wax, chlorinated hydrocarbons, fluorocarbons and the like are examples thereof.

(5) Fatty acid type lubricants:

Higher fatty acids (especially C_{12} fatty acids), oxyfatty acids and the like are examples thereof.

(6) Ester type lubricants:

Lower alcohol esters of fatty acids, polyhydric alcohol esters of fatty acids, polyglycol esters of fatty acids, aliphatic alcohol esters of fatty acids and the like are examples thereof.

(7) Alcohol type lubricants:

Polyhydric alcohols, polyglycols, polyglycerols and the like are examples thereof.

(8) Metal soaps:

The compounds of higher fatty acids, such as lauric acid, stearic acid, ricinolic acid, naphthenic acid, oleic acid, etc., with metals such as Li, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, etc. are examples thereof.

The lubricants as cited above may be used alone, or as a mixture of two or more thereof, if desired. The amount of lubricants added is requested to be minimized, account being taken of the prevention of a smoking phenomenon and their influences upon photographic properties of photographic light-sensitive materials such as photographic printing papers, photographic films and so on. Therefore, the proportion of lubricants added is in the range of generally 0.001 to 5 % by weight, preferably 0.005 to 5 % by weight and particularly preferably 0.01 to 3 % by weight.

Further, it is desirable to use surfactants for the purposes of heightening the dispersibilities of inorganic pigments and other additives in resins and the prevention of electrification.

The surfactants used for such purposes can be chosen properly from nonionic, anionic, cationic and amphoteric surfactants well known to those skilled in the arts.

As typical examples of nonionic surfactants, mention may be made of polyethylene glycol fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene aliphatic alcohol ethers, polyoxyethylene alkylphenyl ethers, polyoxyethylene glycerine fatty acid esters, polyoxyethylene aliphatic amines, sorbitan monofatty acid esters, fatty acid pentaerythritols, ethylene oxide adducts of alipahtic alcohols, ethylene oxide adducts of fatty acids, ethylene oxide adducts of fatty acid amines or fatty acid amides, ethylene oxide adducts of alkylphenols, ethylene oxide adducts of alkylnaphthols, ethylene oxide adducts of partial fatty acid esters of polyhydric alcohols, and the nonionic antistatic agents disclosed in JP-B-63-26697 (at page 120).

As typical examples of anionic surfactants, mention may be made of various metal salts of fatty acids, ricinoleic acid ester sulfate sodium salt, sulfated oleic acid ethylaniline, olefin sulfate salts, oleyl alcohol sulfate sodium salt, alkylsulfate salts, fatty acid ethylsulfonates, alkylsulfonates, alkylnaphthalenesulfonates, alkylbenzenesulfonates, succinic acid ester sulfonates, phosphonic acid ester salts and so on.

As typical examples of cationic surfactants, mention may be made of primary amines, tertiary amines, quaternary ammonium salts, pyridine derivatives and so on.

As typical examples of amphoteric surfactants, mention may be made of carboxylic acid derivatives, imidazoline derivatives, betaine derivatives and so on.

The surfactants as cited above are added in a proportion ranging from 0 to 7.0 % by weight, preferably from 0.005 to 5.0 % by weight and particularly preferably from 0.01 to 3.0 % by weight.

Furthermore, it is desirable to incorporate acid-modified thermoplastic resins, especially acid-modified polyolefin resins, into the resin layer for the purpose of improvement upon the adhesiveness of the resin layer to a base paper.

The term acid-modified polyolefin resins as described above is intended to include the resins obtained by subjecting polyolefin resins to the graft-modification reaction with unsaturated carboxylic acids. Specifically, graft-modified polyethylene resins, graft-modified polypropylene resins and graft-modified ethylene copolymer resins are examples thereof.

The unsaturated carboxylic acids which can be used in the foregoing reaction include their derivatives also. As typical examples of such unsaturated carboxylic acids, mention may be made of acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, tetrahydrophthalic acid, mesaconic acid, angelic acid, citraconic acid, crotonic acid, isocrotonic acid, nagic acid (endocis-bicyclo[2,2,1]hepto -5-ene-2,3-dicarboxylic acid), maleic anhydride, citraconic anhydride, itaconic anhydride, methyl acrylate, methyl methacrylate, ethyl acrylate, ethtyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylate, monoethyl maleate, diethyl maleate, monoethyl fumarate, dimethyl fumarate, diethyl itaconate, acrylic acid amide, methacrylic acid amide, maleic acid monoamide, maleic acid diamide, maleic acid N-monoethylamide, maleic acid N,N-diethylamide, maleic acid N-monobutylamide, maleic acid N,N-dibutylamide, fumaric acid monoamide, fumaric acid diamide, fumaric acid N-monoethylamide, fumaric acid N,N-diethylamide, fumaric acid N-monobutylamide, fumaric acid N,N-diethylamide, fumaric acid N-monobutylamide, fumaric acid N,N-dibutylamide, monomethyl maleate, dimethyl maleate, potassium acrylate, sodium acrylate, zinc acrylate, magnesium acrylate, calcium acrylate, sodium methacrylate, potassium methacrylate, maleimide, N-butylmaleimide, N-phenylmaleimide, malenyl chloride, glycidyl maleate, dipropyl maleate, aconitic acid anhydride, sorbic acid and so on. Of these compounds, acrylic acid, maleic acid, maleic anhydride and nagic acid are preferred over the others. In particular, maleic anhydride is favored. Those unsaturated carboxylic acids may be used as a mixture of two or more thereof.

In preparing the modified polyolefin resins, the present invention does not have any particular restriction as to the method of grafting unsaturated carboxylic acids on polyolefins. Therein, any methods, for instance, the melt kneading method as disclosed in JP-B-43-27421 wherein reactants undergo the reaction in a molten condition, the method as disclosed in JP-B-44-15422 wherein reactants in a state of solution undergo the reaction, the method as disclosed in JP-B-43-18144 wherein reactants in a state of slurry undergo the reaction, the method as disclosed in JP-B-50-77493 wherein the reaction is run in a vapor phase, and so on can be adopted.

Of those methods, the melt kneading method wherein an extruder is used is preferred over the others because it can be performed by simple operations, and that at a low price.

From the standpoint of ensuring adhesion strength for the resin layer, it is desirable that the proportion of unsaturated carboxylic acids used be in the range of 0.01 to 20 parts by weight, preferably 0.2 to 5 parts by weight, to 100 parts by weight of polyolefin resin as the base polymer (e.g., various types of polyethylene resins, including linear low-density polyethylenes, various types of polypropylene reins, and various α-olefin copolymer resins such as ethylene-butene-1 copolymer resin, ethylene-4-methylpentene-1 copolymer resin, etc.).

For the purpose of promoting the reaction of polyolefin resins with unsaturated carboxylic acids, organic peroxides may be used. Specific examples of an organic peroxide which can be used include benzoyl peroxide, lauroyl peroxide, dicumyl peroxide, α,α'-bis(t-butylperoxydiisopropyl)benzene, 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne, di-t-butyl peroxide, cumene hydroperoxide, t-butyl hydroperoxide, t-butyl peroxylaurate, t-butyl peroxybenzoate, 1,3-bis(t-butylperoxyisopropyl)benzene, di-t-butyl-di-peroxyphthalate, t-butyl peroxymaleate, isopropyl percarbonate and so on.

These organic peroxides may be used as combination of two or more thereof. Of those peroxides, particularly preferable peroxides are those having their decomposition temperatures in the range of 170 to 200 °C, namely di-t-butyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne and 1, 3-bis(t-butylperoxyisopropyl)benzene.

These peroxides are not particularly limited in amount to be added. However, it is effective to add them in an amount of 0.005 to 5 parts by weight, preferably 0.01 to 1 part by weight, per 100 parts by weight of polyolefin resin.

Representatives of commercially available acid-modified thermoplastic resins (trade names) are as follows:

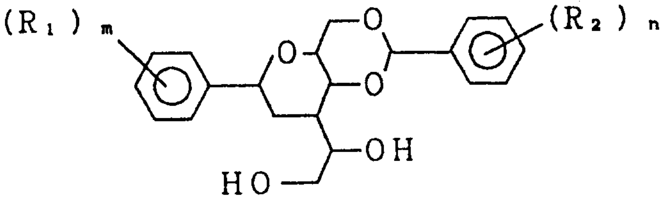
(1) N Polymer (produced by Nippon Peterochemicals Co., Ltd.)
(2) ADMER (produced by Mitsui Petrochemical Industries, Ltd.)
(3) ER RESIN (produced by Showa Denko K.K.)
(4) Novatec-AP (produced by Mitsubishi Chemical Industries, Ltd.)
(5) MODIC (produced by Mitsubishi Petrochemical Co., Ltd.)
(6) NUC-ACE (produced by Nippon Unicar Co., Ltd.)
(7) UBE BOND (produced by Ube Industries, Ltd.)
(8) Bondyne (produced by Sumitomo Chemcial Co., Ltd.)
(9) Melcene M (produced by TOSOH Corporation)
(10) CMPS (produced by Du Pont Mitsui Polychemical Co., Ltd.)

The content of an acid-modified thermoplastic resin in the resin layer is preferably in the range of 0 to 40 % by weight, particularly 10 to 30 % by weight.

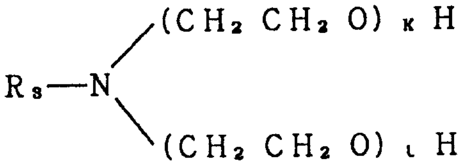
It is also possible to use the acid-modified resins together with other resins. Suitable examples of resins which can serve for the combined use include known various types of polyethylene resins.

Moreover, in view of improvements in crystallization speed, rigidness, transparency, suitabilities for a slitter and a guillotine cutter,mechanical strength and so on, it is desirable to incorporate a nucleating agent into at least one resin layer which covers the base paper on the side where emulsion layers are to be coated. As for the nucleating agent, both organic and inorganic nucleating agents can be used herein. Representatives thereof are described below in detail.

Suitable examples of an organic nucleating agent include carboxylic acids, dicarboxylic acids, salts and anhydrides of those acids, aromatic sulfonic acids and their salts and esters, aromatic phosphinic acids, aromatic phosphonic acids, aromatic carboxylic acids and their aluminum salts, metal salts of aromatic phosphoric acids, alkyl alcohols containing 8 to 30 carbon atoms, condensates of polyhydric alcohols and aldehydes, and alkylamines. More specifically, there can be used aluminum p-t-butylbenzoate, 1,3,2,4-dibenzylidene-sorbitol,disubstituted benzylidenesorbitol compounds represented by the following general formula;



(wherein R_1 and R_2 each represent an alkyl group containing 1 to 8 carbon atoms, an alkoxy group or a halogen atom, and m and n are each an integer of 0 to 3, provided that m + n≧1), calcium, magnesium and like metal salts of stearyllactic acid, N-(2-hydroxyethyl)stearylamine, the compounds represented by the following general formula;



$$R_3-N\begin{cases}(CH_2CH_2O)_kH\\(CH_2CH_2O)_lH\end{cases}$$

(wherein R_3 represents an alkyl group containing 8 to 30 carbon atoms, and k and l are each an integer of 0 to 10, provided that k + l≧1), lithium, sodium, potassium, calcium, magnesium and like metal salts of 1, 2-hydroxystearic acid, alkyl alcohols such as stearyl alcohol, lauryl alcohol, etc., sodium benzoate, benzoic acid, cebacic acid and so on.

Specific examples of an inorganic nucleating agent which can be used include alkali metal hydroxides such as lithium hydroxide, sodium hydroxide, potassium hydroxide, etc., alkali metal oxides such as sodium oxide, etc., alkali metal carbonates such as lithium carbonate, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, etc., alkaline earth metal hydroxides such as calcium hydroxide, magnesium hydroxide, etc., alkaline earth metal oxides such as calcium oxide, etc., and so on.

The nucleating agents which can be used should not be construed as being limited to the above-cited ones, but any known nucleating agents can also be used herein. As a matter of course, those nucleating agents can be used alone or as a mixture of two or more thereof.

The organic nucleating agents set forth below are especially advantageous in that they have great addition effects upon improvements in acceleration of resin crystallization, suitabilities for a slitter and a guillotine cutter, rigidness, transparency (or whiteness when white pigments are contained) and so on without attended by any bad influences on a photographic light-sensitive material, such as a photographic film or a photographic printing paper.

Namely, they are di(o-methylbenzylidene)sorbitol, di(m-methylbenzylidene)sorbitol, di(p-methylbenzylidene)sorbitol, o-methylbenzylidene-p-methylbenzylidenesorbitol, m-methylbenzylidene-o-methylbenzylidenesorbitol, m-methylbenzylidene-p-methylbenzylidene-sorbitol, 1,3-heptanylidenesorbitol, 1,3,2,4-diheptanylidenesorbitol, 1, 3,2,4-di(3-nonyl-3-pentylidene)sorbitol and 1,3-cyclohexanecarbylidene-sorbitol.

In particular, the dibenzylidenesorbitol compounds are preferred over the others.

In addition, for the purpose of neutralizing halogen compounds contained as the residues of polymerization catalysts used or the impurities in the additives used, it is desirable to add metal salts of fatty acids to resin compositions for forming the present resin layers. By adding the metal salt of fatty acids, the purposes of diminishing a bleed-out phenomenon, preventing the organic nucleating agent from scattering and improving the dispersibility of the organic nucleating agent can also be accomplished.

Further, the addition of fatty acid metal salts can bring about improvements in not only dispersibility and moldability of a light-shielding material but also photographic properties because they can neutralize halogen compounds contained in resins, which act adversely on photographic properties of a photographic light-sensitive material, to convert them to harmless compounds.

Specific examples of such fatty acid metal salts include the compounds prepared from higher fatty acids, such as lauric acid, stearic acid, ricinolic acid, naphthenic acid, oleic acid, erucic acid, etc., and metals such as Li, Mg, ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, etc.

With the intention of converting halogen compounds, which are contained in resins and have bad influences on photographic properties, to harmless ones by neutralization, hydrotalcite group compounds can also be used.

The fatty acid metal salts and/or hydrotalcite group compounds are added in a proportion of 0 to 10.0 % by weight, preferably 0.05 to 5. 0 % by weight, to 100 parts by weight of resin component.

With respect to the formation of multiple waterproof resin layers, the foregoing ultramarine and/or titanium dioxide-containing pellets are molten by heating, if necessary, after dilution with other heat-resisting resins, and therewith are laminated the travelling paper or synthetic paper as a raw paper using either a successive lamination method or a simultaneous multilayer lamination method utilizing a multilayer extrusion die of feed block type, multimanifold type or multislot type.

As the lamination method adopted herein does not have any particular restriction as to the shape of multilayer extrusion die, a T-die, a coat hanger die or so on can be generally used. The exit temperature of the waterproof resin lamination by hot melt extrusion is generally in the range of 280 °C to 340 °C, particularly preferably 310 °C to 330 °C. Before a raw paper is covered with a resin, it is also desirable to subject the raw paper to activation treatments such as a corona discharge treatment, a flame treatment, a glow discharge treatment and so on.

The surface of the topmost waterproof resin layer on the side where emulsions are to be coated is subjected to a die embossing treatment of the type which can put thereon a gloss or the fine grain described in JP-A-55-26507 or can render the surface mat or silky. On the other hand, the waterproof resin layer on the reverse side is subjected to a die embossing treatment of the type which makes the surface dull. The process after the die embossing treatment is the same as the process of preparing photographic films using PET or cellulose ester films as base films.

Accordingly, the both-sided resin-laminated raw paper and a base film are called the substrate, hereinafter.

Prior to the application of a subbing layer and a backing layer, it is desirable for the substrate surface to undergo an activation treatment such as a corona discharge treatment, a flame treatment or so.

With respect to the base film, there can be used to advantage the cellulose acetate film containing a plasticizer of phosphate type in which the content of acid impurities is less than 0.0050 mole (JP-A-06-16869) and the copolymerized polyester film which contains polyethylene terephthalate (PET) as a main component and further the metal sulfonate-containing comonomer component in a proportion of 2-7 mole % to the whole ester linkage units and additionally contains a 0.01-2.0 % by weight of antioxidant (JP-A-05-323496).

As for the phosphate plasticizer contained in the cellulose acetate film, it is desirable that the proportion thereof to the cellulose ester be in the range of 5 to 20 % by weight.

In order to achieve excellent applicability and adhesiveness of photographic emulsions to the substrate, a subbing layer is provided on the resin-covered surface of the substrate on the side where photographic emulsions are to be coated, continuously from the activation treatment without winding the substrate into a roll. The subbing layer is constituted of gelatin, a viscosity regulator, a surfactant, a coating aid and so on. The coating composition for forming the subbing layer comprises an aqueous gelatin solution, which may optionally contain a water-soluble organic solvent, a pH regulator, a surfactant, antiseptics, a hardener, a defoamer, a white pigment, a viscosity regulator and so on.

In forming the subbing layer, any of well-known coating methods, such as dip coating, air knife coating, curtain coating and roller coating methods, may be adopted.

After applying the foregoing subbing layer and before coating emulsions, a backing layer aiming at improvements in, e.g., antistatic, writing and slipping properties is provided on the resin-covered surface on the side opposite to the subbing layer.

The backing layer as described above is important from the viewpoints of improving writing properties and preventing a curling phenomenon, especially in the case of photographic printing paper. In this backing layer, there can be incorporated a combination of ingredients properly chosen from the inorganic antistatic agents, the organic antistatic agents, the hydrophilic binders, the latexes, the water dispersions, the hardeners, the pigments, the surfactants and so on as disclosed, e.g., in JP-B-52-18020, JP-B-57-9059, JP-B-57-53940, JP-B-58-56859, JP-A-59-214849, JP-A-58-184144, JP-A-62-6256, JP-A-03-206440 and JP-A-04-34138. As for the coating method, the same methods as applied to the subbing layer can be used for the backing layer.

In the present invention, it is desirable that all the aforementioned processes be embodied in a continuous through process without interposing any winding processes. In particular, it is preferable for the continuous through process to be extended into the next emulsion-coating process.

In application of silver halide emulsions on the subbing layer, the silver halide emulsions used are those which have already undergone physical ripening, chemical ripening and spectrally sensitizing steps. Additives usable for these steps are described in Research Disclosure , No. 17643, No. 18716 and No. 307105. A list of the additives and the places at which they are described in those references respectively are shown below as Table 1.

Table 1

Kind of Additive		RD 17643	RD 18716	RD 307105
1	Chemical Sensitizer	p. 23	p. 648, right column	p. 866
2	Sensitivity Elevat		p. 648, right	
3	ing Agent Spectral Sensitizer and Supersensitizer	pp. 23-24	column p. 648, right column, to p. 649, right column	pp. 866-868
4	Brightening Agent	p. 24	p. 647, right column	p. 868
5	Antifoggant and Stabilizer	pp. 24-25	p. 649, right column	pp. 868-870
6	Light Absorbent, Filter Dye and UV Absorbent	pp. 25-26	p. 649, right column, to p. 650, left column	p. 873
7	Stain Inhibitor	p. 25, right column	p. 650, right to left column	p. 872
8	Dye Image Stabilizer	p. 25	p. 650, left column	p. 872
9	Hardener	p. 26	p. 651, left column	pp. 874-875
10	Binder	p. 26	p. 651, left column	pp. 873-874
11	Plasticizer and Lubricant	p. 27	p. 650, right column	p. 876
12	Coating Aid and Surfactant	pp. 26-27	p. 650, right column	pp. 875-876
13	Antistatic Agent	p. 27	p. 650, right column	pp. 876-877
14	Matting Agent			pp. 878-879

In the present photosensitive materials, two or more of light-sensitive silver halide emulsions which differ from one another in at least one characteristic, namely grain size, grain size distribution, halide composition, grain form or sensitivity, can be used as a mixture in the same layer.

For instance, the surface-fogged silver halide grains disclosed in U.S. Patent 4,082,553, the interior-fogged silver halide grains disclosed in U.S. Patent 4,626,498 and JP-A-59-214852, colloidal silver and the like can be desirably used for a light-sensitive silver halide emulsion layer and/or a substantially light-insensitive hydrophilic colloid layer.

The expression "interior-fogged or surface-fogged silver halide grains" describes the silver halide grains of the kind which can be uniformly (non-imagewise) developed, whether they are present in the exposed area or the unexposed area of a photosensitive material. The preparation methods of the interior- or surface-fogged silver halide grains are described in U.S. Patent 4,626,498 and JP-A-59-214852. The silver halides which constitute the core part of interior-fogged silver halide grains having a core/shell structure may be the same or different in halide composition.

To the interior- or surface-fogged silver halide grains, any of silver halides including silver chloride, silver chlorobromide, silver iodobromide and silver chloroiodobromide can be applied. These fogged silver halide grains don't have any particular limitation on the grain size. However, it is desirable that they have an average grain size in the range of 0.01 to 0.75 µm, especially 0.05 to 0.6 µm. Also, those grains has no particular restriction as to the grain form. They may have a regular crystal form or not. Further, although the emulsions prepared may be polydisperse emulsions, it is preferable for them to be monodisperse emulsions (such that at least 95 % by weight or by number of the silver halide grains have their grain sizes within ± 40 % of the average grain size).

It is effective to control the silver coverage to no greater than 6.0 g/m^2, particularly no greater than 4.5 g/m^2.

On the emulsion layers, as usual, protective layer(s) are provided. The thus obtained material is slitted and cut, thereby manufacturing finished products. In the present invention, it is desirable that all the manufacturing processes, including the protective layer application process and up to the slitting-and-cutting process, be embodied in a continuous through process.

Although the present manufacturing method for photographic printing papers and photographic films has a disadvantage in that it is required of the processes embodied in a continuous through process to have the same process speed that the slowest process among them has, the advantages drawn from the present continuous through process which makes winding processes unnecessary, that is, reduction in stock space and stock loss as well as labor saving, far outweigh the disadvantage which it entails. Accordingly, the present manufacturing method is extremely useful for improving the production efficiency.

Now, the present invention will be illustrated in more detail by reference to the following examples, but it should be understood that these examples are not be construed as limiting the scope of the invention in any way.

EXAMPLES 1 AND 2, AND COMPARATIVE EXAMPLE 1

A conventional manufacturing method (Comparative Example 1) is shown in Fig. 1, and manufacturing methods according to the present invention are shown in Fig. 2 and Fig. 3 respectively.

Operations for each of the processes which constitute each manufacturing method are described below in detail.

Pulp (LBKP: 100%) was beaten with a double disk refiner so as to have a freeness of 200± 50 ml C.S.F., and then admixed with dry broke in a proportion of 20 % by weight at the most. Thereto were further added as internal sizing agents 0.5~2.0 % by weight of polyacrylamide, 0.5~ 2.0 % by weight of sulfate band, 0.05 ~ 1.0 % by weight of polyamidepolyamine epichlorohydrin, 0.1~1 % by weight of alkylketene dimer and 0.5 % by weight of epoxidized fatty acid amide. The thus obtained slurry was adjusted to pH 7 ± 0.5 by the addition of sodium hydroxide, and once stored in a chest. This paper stock was admixed with wet broke in a proportion of 60 % by weight at the most, and then discharged from a head box with a J/W ratio set to 0.8~1.2 in order to make paper.

In making paper from the foregoing paper stock; the plastic wire was continued to be shaken in a shaking width of 10 ~ 40 mm and with the frequency of 2 ~ 6 Hz and, at the same time, the water was squeezed successively with a foil, a suction box, a vacuum foil box and a table roller and further the wet paper surface was conditioned by turning a dandy roll at a speed of + 1~5 m/min relative to the wire speed.

In the press part, the water was further squeezed out by being nipped 2~6 times under the linear pressure of 20 ~ 100 N/mm. Thereafter, the drying operation was performed at a surface temperature of 40~135 °C by means of 15 ~ 30 drum dryers. Then, the resulting paper was nipped under linear pressure of 50 ~ 120 N/mm by means of a calender (1~3 steps), and further coated with the coating solution described below at a coverage rate of 10 ~ 100 cc/mm^2 in the size press or gate roll coater part, followed by the drying operation at a surface temperature of 40~135 °C by means of 4~10 drum dryers.

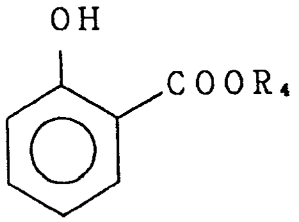
The coating solution used therein was prepared by dissolving in water 0.5~10 % of PVA, 1~5 % of calcium chloride, 0.1~1.0 % of a brightening agent and 0.001~0.01 % of a fatty acid ester.

Furthermore, the resulting paper was nipped under pressure of 100 ~250 N/mm by means of a calender (1~4 steps) and, wound up under press pressure of 300~900 N/mm by means of a single drum Pope type reel. These papermaking processes were carried out at one continuous operation. The thus made raw paper had a basis weight of 60 ~ 200 g/m^2, a thickness of 60 ~ 200 μm and a water content of 5~9 %.

On the reverse surface of the thus made raw paper (or the surface to which the application of photographic emulsions were not intended), some marks were printed with a flexographic printing machine or a gravure printing machine wherein printing ink having a specific gravity of 0.8~1.2 and a viscosity of 1~30 cp was used, and then dried with hot air of 30 ~ 100 °C. A resin mixture of a high density polyethylene (HDPE) and a low density polyethylene (LDPE) wherein a HDPE/LDPE ratio was chosen from the range of 1/9 to 9/1 was laminated on the thus printed surface using a melt-extrusion technique at a head temperature of 250~340 °C so as to have a coverage rate of 10~50 g/m^2, and then die-embossed with an embossing roller through which 5 ~ 30 °C cooling water was circulated at a flow rate of 1,000-6,000 ml/min.

Then, LDPE containing 5~ 40 % by weight of TiO_2 and 0~4 % by weight of ultramarine blue was laminated on the raw paper surface to which photographic emulsions were to be applied using a melt-extrusion technique at a head temperature of 250 ~ 340 °C, and then die-embossed with an embossing roller through which 5~ 30 °C cooling water was circulated at a flow rate of 1,000-6,000 ml/min.

The drying air having a dew point of 5 ~ -15 °C was blown onto the embossing roller. Then, a subbing layer was supplied on the emulsion-side of the substrate with a solution prepared by adding to water 1 ~ 10 % by weight of gelatin, 0.05 ~ 0.5 % by weight of benzoic acid or a derivative thereof represented by the following formula;



(wherein R_4 represents a hydrogen atom or a hydrocarbon group containing 1 to 5 carbon atoms), 1 ~ 5 % by weight of a water-soluble high molecular compound, such as sodium polystyrenesulfonate, polyethylene glycol, polyacrylic acid or a salt thereof, etc., 100 ~ 300 % by weight of an alcohol, such as methanol, ethanol, isopropanol, etc., and 0.05 ~ 0.5 % by weight of potassium polystyrenesulfonate. Herein, a gravure coater (gravure mesh: 100-400) was used as a coating means.

Next, a solution prepared by adding to water 1 ~ 5 % by weight of silicone dioxide having a grain size of 10 ~ 1,000 nm, 0.5 ~ 3.0 % by weight of alumina sol having a grain size of 10~1,000 nm, 0.01~0.05 % by weight of PVA or carboxyl-modified PVA and 5~20% by weight of an alcohol, such as methanol, ethanol, isopropanol, etc., or a solution prepared by adding to water 2~10 % by weight of colloidal silica,3~15 % by weight of an styreneacrylic acid ester polymerized in the presence of a water-soluble high molecular compound, 1~5 % by weight of at least one compound selected from a group consisting of carboxyl- or sulfo-containing water-soluble high molecular compounds, the salts thereof and hydrophilic organic high molecular colloid and 5 ~ 20 % by weight of an alcohol, such as methanol, ethanol, isopropanol, etc., was coated by means of a bar coater on the reverse surface to which the application of photographic emulsions were not intended, and then dried with drying air of 40 ~ 120 °C, thereby forming a backing layer.

Further, the thus obtained paper (web) was cooled with 1 ~ 3 cooling drums through which cooling water of 15 ~ 30 °C was circulated so that the web temperature before winding might be lowered to 20 ~ 60 °C, and then wound into a roll using a winder equipped with a press roll (linear pressure: 50 ~ 300 N/m).

The constitution of a photographic printing paper prepared according to the foregoing processes is shown in Table 2.

Table 2

Raw Paper	LBKP, basis weight: 180 g/m^2
Resin Layer on Emulsion -coated Side	LDPE, coverage rate: 35 g/m^2
Resin Layer on Side opposite to Emulsion -coated Side	LDPE + HDPE, coverage rate: 30 g/m^2
Subbing Layer	gelatin, coverage rate: 5 cc/m^2 (wet)
Backing Layer	antistatic agent + matting agent, coverage rate: 5 cc/m^2 (wet)
Emulsion Layer	gelatin + silver halides, thickness: 10 µm

According to conventional methods, the processes described above were performed at separate operations as shown in Fig. 1. This case is named "Comparative Example 1", hereinafter.

In accordance with the present invention, on the other hand, the foregoing processes were performed at one or two continuous operations as shown in Fig. 2 (Example 1) or Fig. 3 (Example 2) respectively.

The manufacturing processes, Example 1, Example 2 and Comparative Example 1, were examined for the stock space required thereof, the regular loss caused by the winding operation and the days required for manufacturing photographic printing paper as the finished goods, from the preparation of paper stock till the completion of finishing. The comparison of these examination results are shown in Table 3.

Table 3

	Stock Space	Regular Loss	Days for Manufacturing Finished Goods
Comparative Example 1	3,000 m^2	8 %	9 days
Example 1	2,400 m^2	4 %	6 days
Example 2	1,600 m^2	3 %	4 days

The results shown in Table 3 have proved that the present manufacturing methods were effective in saving resources and labor, and the effectiveness thereof was greater the more the number of processes performed continuously was increased (that is, the greater the reduction in number of winding processes was).

Claims

1. A method of manufacturing a photosensitive material which consists mainly of a substrate having emulsion layers via a subbing layer on one side and a backing layer on the other side, wherein the photosensitive material is a photographic printing paper or a photographic film, and wherein are performed continuously at least two processes comprising the process of applying the subbing layer to the substrate on the side for the emulsion layers and the process subsequent thereto in which the backing layer is applied on the reverse side of the substrate.

2. A method of manufacturing a photosensitive material as described in Claim 1, wherein the process of applying the backing layer is followed continuously by a process of applying the emulsion layers and protective layer(s) to the subbing layer.

3. A method of manufacturing a photosensitive material as described in Claim 2, further comprising a slitting process.

4. A method of manufacturing a photosensitive material as described in Claim 1, 2 or 3, wherein the substrate consists of a raw paper and a waterproof resin laminated on both sides of the raw paper.

5. A method of manufacturing a photosensitive material as described in Claim 4, wherein the substrate is a material prepared from a raw paper in a continuous through process which comprises, in the order of performance, a step of printing on one side of the raw paper, a step of laminating the raw paper with a waterproof resin on the printed side, and a step of laminating the raw paper with a waterproof resin on the other side.

6. A method of manufacturing a photosensitive material as described in Claim 5, wherein the raw paper is a paper which has been made from a prepared paper stock and has undergone successively to drying, sizing and calendering treatments and the paper is fed to the printing step subsequently to the calendering treatment.

7. A method of manufacturing a photosensitive material as described in Claim 1, 2 or 3, wherein the substrate is a high molecular resin film.

8. A method of manufacturing a photosensitive material as described in Claim 7, wherein the high molecular resin film undergoes a surface treatment prior to the process of applying the subbing layer.

9. A method of manufacturing a photosensitive material as described in Claim 8, wherein the surface treatment of the high molecular resin film and the process of applying the subbing layer are performed continuously.

10. A method of manufacturing a photosensitive material as described in Claim 4, wherein the waterproof resin is a resin containing as a main component a polyolefin resin having a melt flow rate of from 1.2 g/10 min. to 12 g/10 min. when it is measured by JISK 7210.

11. A method of manufacturing a photosensitive material as described in Claim 10, wherein the waterproof resin laminated on one side of the raw paper contains as additives titanium oxide fine grains, a bluing agent, a lubricant and a surfactant.

12. A method of manufacturing a photosensitive material as described in Claim 11, wherein the waterproof resin further contains as additives an antioxidant, an acid-modified thermoplastic resin and a nucleating agent.

Fig. 1

PRIOR ART

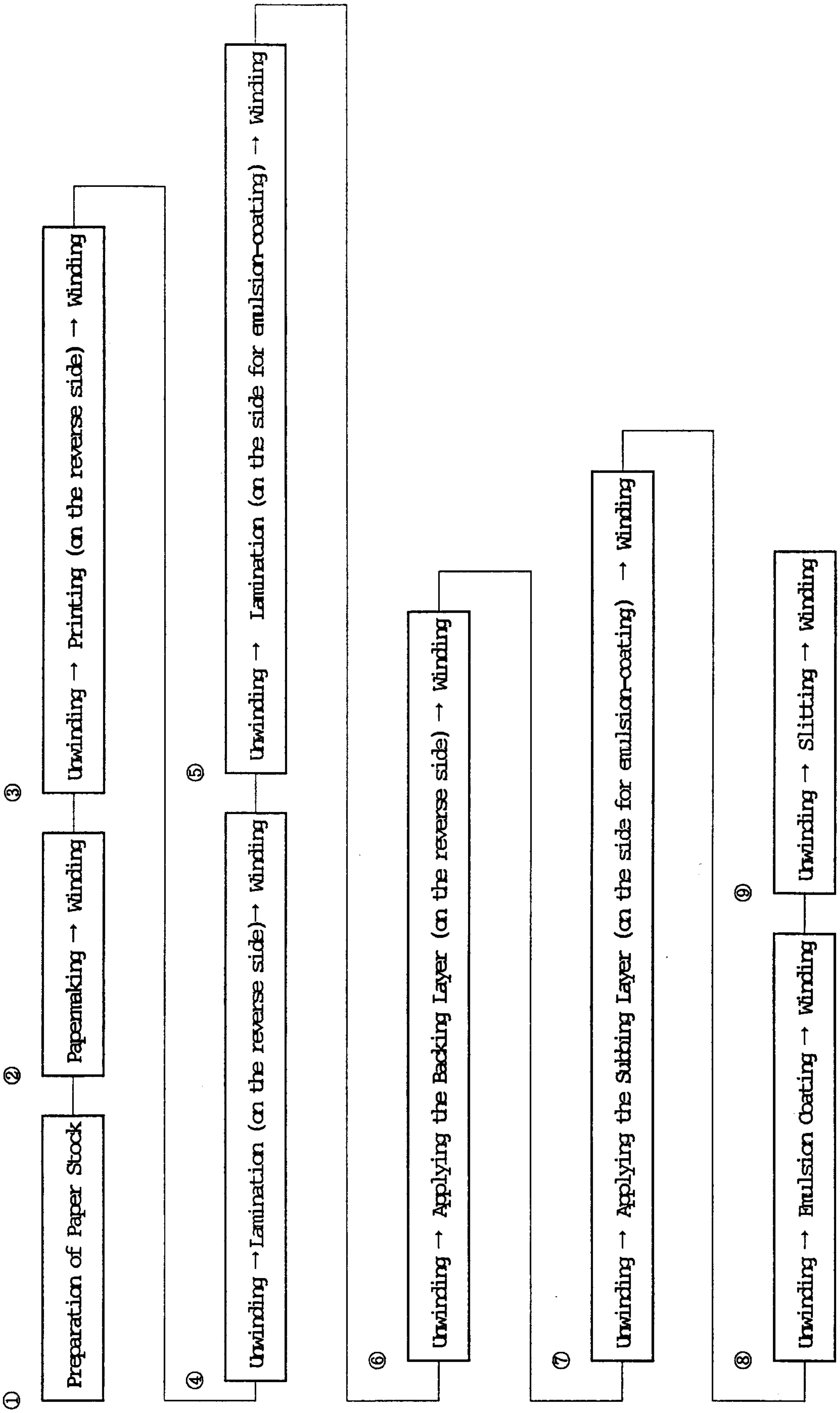


Fig. 2

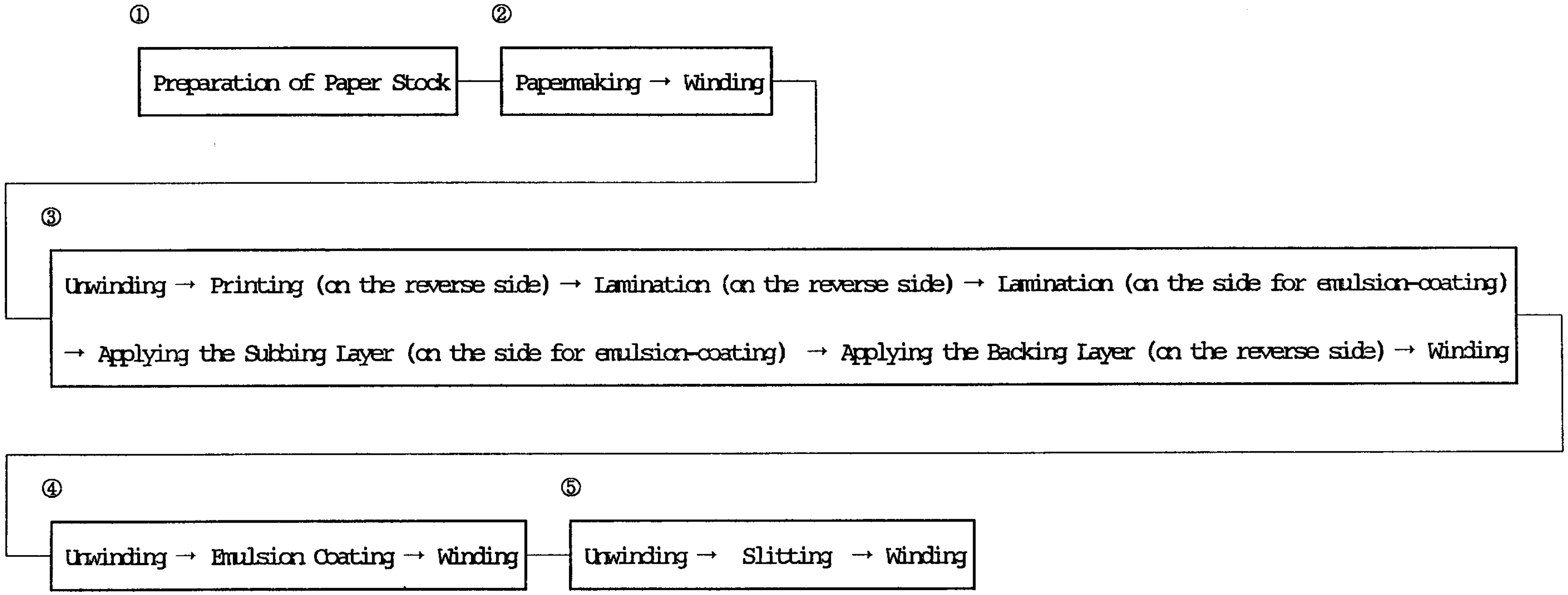
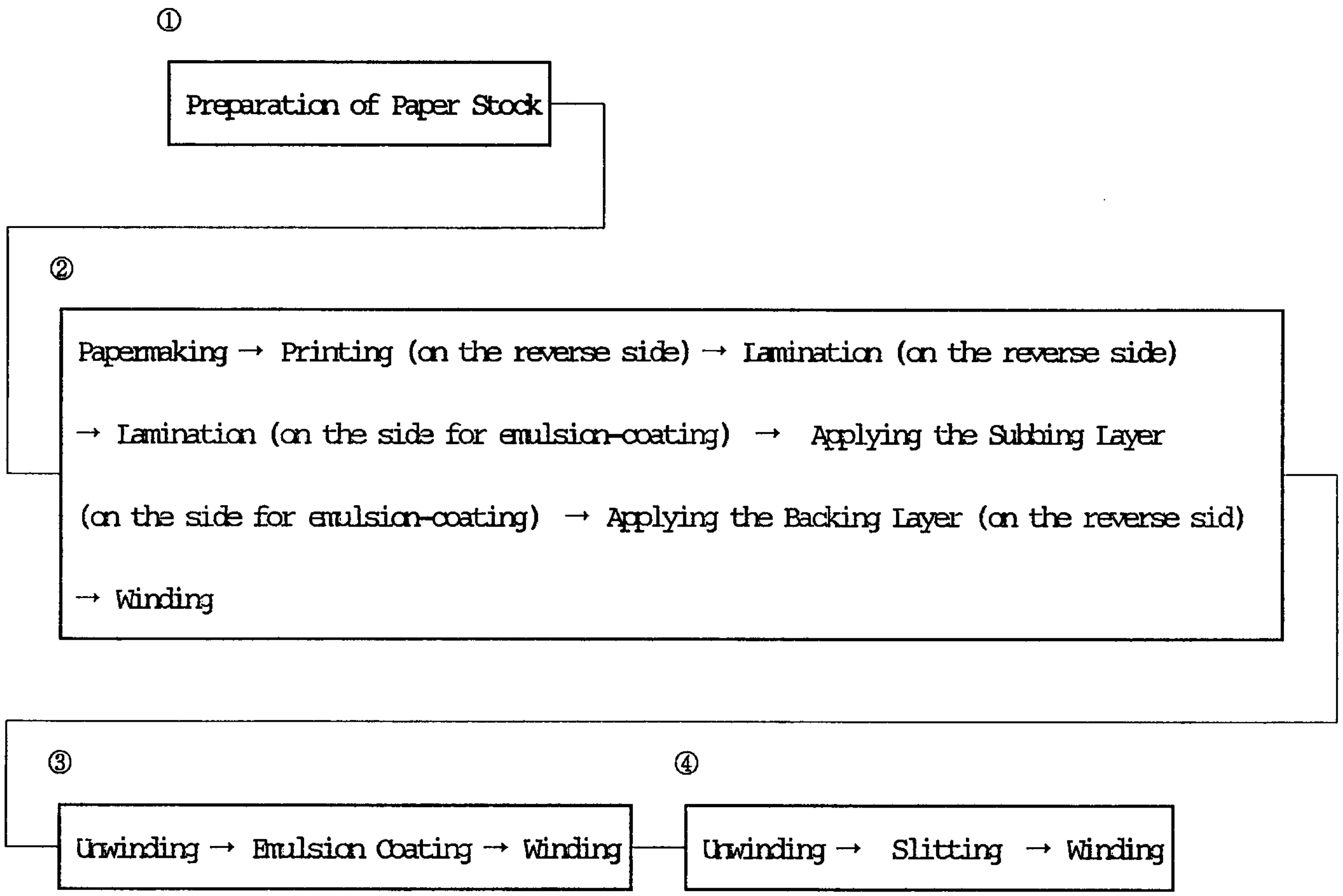

①
Preparation of Paper Stock
②
Papermaking → Winding
③
Unwinding → Printing (on the reverse side) → Lamination (on the reverse side) → Lamination (on the side for emulsion-coating)
→ Applying the Subbing Layer (on the side for emulsion-coating) → Applying the Backing Layer (on the reverse side) → Winding
④
Unwinding → Emulsion Coating → Winding
⑤
Unwinding → Slitting → Winding

Fig. 3


①
Preparation of Paper Stock
②
Papermaking → Printing (on the reverse side) → Lamination (on the reverse side)
→ Lamination (on the side for emulsion-coating) → Applying the Subbing Layer
(on the side for emulsion-coating) → Applying the Backing Layer (on the reverse sid)
→ Winding
③
Unwinding → Emulsion Coating → Winding
④
Unwinding → Slitting → Winding