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⑦① Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma Minamiashigara-shi
Kanagawa-ken, 250-01(JP)

⑦② Inventor: **Tamagawa, Shigehisa**
No. 200, Onakazato
Fujinomiya-shi, Shizuoka(JP)

⑦④ Representative: **Patentanwälte Dr. Solf & Zapf**
Zeppelinstrasse 53
D-8000 München 80(DE)

⑤④ **Photographic printing paper support.**

⑤⑦ A support for use in photographic printing paper which comprises a base paper covered on both sides with a polyolefin coating, wherein the base paper has undergone calender treatment between a metal roll and a synthetic resin roll which produces a photographic printing paper support having good surface smoothness.

PHOTOGRAPHIC PRINTING PAPER SUPPORT

FIELD OF THE INVENTION

The present invention relates to a support for use in photographic printing paper, and more particularly,
5 it is concerned with a photographic printing paper support having a good surface smoothness.

BACKGROUND OF THE INVENTION

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In recent years, water-resistant photographic printing paper supports which consist of a base paper covered on both sides with a coating of a polyolefin such as polyethylene, have been frequently used for the rapid development of photographic printing paper.

Such photographic printing paper supports consisting of a base paper covered on both sides with a
15 polyolefin coating include ones which have glossy surfaces, ones having matte surfaces, and ones whose surfaces have patterns such as a silk texture. Most advantageously employed of those are supports having smooth and glossy surfaces with no patterns, and particularly preferred are ones in which both surfaces have very few fine irregularities to give a mirror-like smoothness.

In obtaining such supports having a good surface smoothness, various papers have been proposed as a
20 base for the supports. For example, JP-A-60-67940 discloses a base paper prepared by use of a pulp in which the content of voids not larger than 0.4 μm in diameter is 0.04 ml/g or more (The term "JP-A" as used herein means an "unexamined published Japanese patent application"); JP-A-60-69649 discloses a base paper prepared by use of a wood pulp having an average fiber length of 0.4-0.9 mm, an average fiber width of 13.5 μm or more, and an average fiber thickness of 4 μm or less; JP-A-61-275752 discloses a
25 base paper prepared by use of a fiber mixture composed of a natural pulp and 5 to 60% hydrophobic fibers; and JP-A-61-284762 discloses a base paper prepared by a method in which when a wet web is obtained from a pulp slurry by means of a twin-wire paper machine, dehydration is effected under specific conditions. Furthermore, there is also employed a method in which a base paper is subjected to calender treatment between a metal roll and a second metal roll at an increased machine calender pressure, thereby
30 to densify the base paper which is used in a photographic printing paper support. On the other hand, for the coating of base papers with a polyolefin such as polyethylene, there generally is employed an extrusion coating process, in which a molten polyolefin is extruded at a high temperature over the surface of the base paper thereby to apply a coating. In order to improve the smoothness of the photographic printing paper supports, the above extrusion coating is performed in such an improved manner that the thickness of the
35 polyolefin coating is increased or the pressure applied when the polyolefin coating is formed is increased.

However, the above improvements in the polyolefin coating process are not very effective and are also disadvantageous in regard to cost. Moreover, the above-described method to densify the base paper by means of machine calender treatment is also disadvantageous in that appearance defects such as blacking and cockles are apt to result therefrom. Accordingly, the above known methods cannot produce photo-
40 graphic printing paper supports having satisfactorily smooth surfaces, because of the presence of irregularities on the base paper. This applies of course to a base paper having irregularities on its front side, and also applies to a base paper having irregularities on its back side with the front side being smooth; in the latter case, the irregularities on the back side affect the polyolefin covering being extrusion-coated on the front side, depending upon the degree of the back side's irregularities.

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SUMMARY OF THE INVENTION

50 The present inventor conducted intensive studies in order to solve the above drawbacks. As a result, he found that there are two kinds of irregularities on base paper; that is, wavelike large irregularities having wavelengths of around 5 mm (hereinafter referred to as "undulation") and dot-like small irregularities having wavelengths of around 0.5 mm (hereinafter referred to as "fine roughness"). Further studies were made based on this finding and, as a result, it has turned out that even if base paper is subjected only to machine calender treatment between a metal roll and a second metal roll, the "fine roughness" is difficult to remove

without the occurrence of blacking etc., although the "undulation" can be removed, whereas just the supercalender treatment of base paper between a metal roll and a cotton roll cannot sufficiently remove the "undulation", although the "fine roughness" can be eliminated.

Furthermore, supercalendering is disadvantageous in regard to cost, because the rolls are prone to suffer damage so that the on-machine use (continuous running) of supercalenders is difficult.

Treatment with a calender employing a synthetic resin roll was tried by the present inventor in place of the conventional supercalendering described above, and as a result, it has been found that such specific calender treatment can greatly diminish the "fine roughness" and is also very effective in reducing the "undulation" as compared with supercalendering. This invention has been completed based on the above.

Accordingly, it is an object of the present invention to provide a support for use in photographic printing paper which has not only sufficient smoothness but is free from blacking and cockles and also advantageous in regard to production cost.

The above and other objects of the present invention are accomplished with a support for use in photographic printing paper which support comprises a base paper covered on both sides with a polyolefin coating, the base paper being one which has undergone calender treatment between a metal roll and a synthetic resin roll.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be explained below in detail.

The base paper to be employed in the photographic printing paper support according to the present invention can be obtained by forming a paper sheet from a pulp slurry which may comprise a natural pulp, as the base material, which is selected from among coniferous wood pulps, deciduous wood pulps, and others, and also comprises chemical additives which will be described later.

As the pulp slurry, a synthetic pulp, which is made, for example, of polyethylene or polypropylene, may be used in place of the natural pulp, or a base material which consists of a mixture of a natural pulp and a synthetic pulp in arbitrary proportions may be used. It is preferable that the deciduous wood pulp, which has short fibers, constitute 60% by weight or more of the base material.

For more effectively producing the desired effects of this invention, it is preferable that a pulp having an α -cellulose content of at least 90 % constitute 25 % by weight or more, more preferably 50 % by weight or more, of the base material in the pulp slurry.

Further, the degree of beating of the pulp is preferably from 200 to 500 cc C.S.F., more preferably from 250 to 350 cc C.S.F.

The chemicals to be added to the pulp may include fillers such as clay, talc, calcium carbonate, and urea resin fine particles; sizing agents such as rosin, alkylketene dimers, salts of higher fatty acids, paraffin wax, and alkenylsuccinic acids; paper-strength improvers such as polyacrylamide; and fixing agents such as aluminum sulfate and aluminum chloride.

If necessary, other additives may be incorporated such as dyes, fluorescent dyes, slime control agents, and defoamers. If desired and necessary, a softening agent selected from those described below may further be incorporated, whereby the effects of the invention can be brought about more effectively.

A description of softening agents is given in, for example, "Shin Kami Kako Binran (New Paper Processing Handbook)" (edited by Shigyo Times Company), pp. 554-555, published in 1980. Particularly preferred softening agents are ones having a molecular weight of 200 or more, and specifically, ones which contain a hydrophobic group having 10 or more carbon atoms and also contain an amine salt or quaternary ammonium salt which have the property of self-fixing on cellulose. Examples of such softening agents include a product of the reaction of a maleic anhydride copolymer with a polyalkylene polyamine, a product of the reaction of a higher fatty acid with a polyalkylene polyamine, a product of the reaction of an urethane alcohol with an alkylating agent, and a quaternary ammonium salt of a higher fatty acid. Particularly preferred of these is the product of the reaction of a maleic anhydride copolymer with a polyalkylene polyamine and the product of the reaction of an urethane alcohol with an alkylating agent.

The base paper may be surface-sized with a film-forming polymer such as gelatin, starch, carboxymethyl cellulose, polyacrylamide, polyvinyl alcohol, or modified polyvinyl alcohol. Such modified polyvinyl alcohols include, for example, carboxyl-modified polyvinyl alcohol, silanol-modified polyvinyl alcohol, and a copolymer of vinyl alcohol with acrylamide. The preferred film-forming polymer used in the present invention is polyvinyl alcohol or carboxyl-modified polyvinyl alcohol. Where surface-sizing treatment with a film-forming polymer is performed, the film-forming polymer may be applied at a coating weight of from

about 0.1 to 5.0 g/m², preferably from 0.5 to 2.0 g/m². If necessary, an antistatic agent, a fluorescent brightener, a pigment, an anti-foaming agent, etc. may be incorporated into the film-forming polymer to be used in the surface sizing.

The base paper may be produced by forming a wet paper sheet from a pulp slurry comprising the above-described pulp and additives, and added thereto if necessary, a filler, a sizing agent, a paper-strength improver, a fixing agent, etc. by means of a paper machine such as a wire paper machine, subsequently drying the wet sheet, and then reeling up the dry sheet. Either before or after the drying, the above-described surface-sizing treatment may be performed, while calender treatment may be effected between the drying and the reeling. In the case where the surface-sizing treatment is performed after the drying, the calender treatment may be conducted either before or after the surface-sizing treatment. It is, however, preferable that the calender treatment according to this invention be performed at the final finishing stage after the other various treatments, so as to effectively accomplish the objects of the present invention.

The calender treatment according to the present invention includes a soft calender treatment of the base paper, which is performed between a metal roll and a synthetic resin roll, and machine calender treatment, which may be performed if necessary between a metal roll and a second metal roll prior to the soft calender treatment.

If machine calender treatment only is performed in place of the above-described soft calender treatment or a combination of the machine calender and soft calender treatments until the density of the base paper becomes not lower than about 1.06 g/cm³ so as to obtain sufficient smoothness, blacking occurs to impair the appearance of the base paper obtained. If the calender treatment is performed in such a manner that the density of the base paper is not increased to about 1.06 g/cm³, the aforementioned "fine roughness" cannot be eliminated, so that a photographic printing paper having good surface smoothness which is an object of this invention cannot be obtained. Furthermore, if supercalender treatment only is performed, base papers which can be subjected to the supercalendering are limited in thickness and the "undulation" cannot be removed, so that the objects of the present invention cannot be accomplished.

In contrast thereto, the calender treatment employing a synthetic resin roll according to the present invention has the effect of removing both "undulation" and "fine roughness". However, in order to attain more effective thickness control and elimination of the "undulation", the calender treatment between a metal roll and a second metal roll may be performed prior to the calender treatment between a metal roll and a synthetic resin roll.

As a metal roll employed according to the invention, known metal rolls, preferably a hard chromium-plated metal roll having 0.5 μ m or less of surface roughness, can be used. The surface temperature of the metal roll is preferably from 50 to 250 °C, more preferably from 100 to 200 °C.

The synthetic resin roll employed according to the invention is one composed of a metal roll and a synthetic resin covered thereon. Examples of the synthetic resin include a urethane type, ebonite type, nylon type, aramid type, isocyanurate type, polyether type, or rubber type.

The coating thickness of the synthetic resin constituting the synthetic resin roll may be about 5 to 50 mm, preferably 10 to 30 mm and the diameter (r) of the synthetic resin roll may be about 200 to 1,000 mm, preferably 300 to 800 mm. The hardness of the synthetic resin may be from about 60 to 98, preferably from 75 to 93, in terms of Shore D hardness. In performing the calender treatment, the moisture content of the base paper being subjected to the calendering is preferably from 6.0 to 9.0%, and the surface temperature of the synthetic resin roll is preferably from 50 to 250 °C, more preferably from 70 to 150 °C.

With respect to the density control for the base paper, it is preferable that the calender treatment between a metal roll and a second metal roll be performed so as to give a paper density in the range of from about 0.90 to 1.05 g/cm³ and then the subsequent calender treatment between a metal roll and a synthetic resin roll be performed such that the final density of the base paper is in the range of from about 1.00 to 1.20 g/cm³.

Through the above-described calender treatment, the thickness of the base paper to be employed in the photographic printing paper support of this invention is finally regulated at about 50 to 250 μ m, preferably 80 to 200 μ m.

The base paper thus obtained is then covered on both sides with a polyolefin coating, thereby giving a photographic printing paper support of this invention.

Such polyolefin resins include, for example, homopolymers of α -olefins, such as polyethylene and polypropylene, and mixtures of various polymers of the above kind. Particularly preferred polyolefins are high-density polyethylene, low-density polyethylene, and mixtures thereof. These polyolefins are not particularly limited in molecular weight as long as they can be extrusion-coated. Generally, however, a polyolefin having a molecular weight in the range of from about 20,000 to 200,000 is employed.

The thickness of the polyolefin resin coating is not particularly limited and it can be fixed in accordance with the thicknesses of the polyolefin resin coatings in conventional printing paper supports. In general, the preferred range of the thickness thereof is from 15 to 50 μm , preferably 20 to 40 μm .

The polyolefin resin coating may contain a white pigment, a coloring pigment, or other known additives such as a fluorescent brightener, an antioxidant, etc. It is preferable that a white pigment and a coloring pigment be incorporated particularly in the polyolefin coating on the base paper's front side to which a photographic emulsion is to be applied.

As apparatuses for use in extrusion-coating the polyolefin, an extruder and an laminator which are ordinarily employed with polyolefins may be used.

The photographic printing paper support of the present invention is further coated on one side with a photographic emulsion layer, which is then dried, thus giving a photographic printing paper. However, various modifications can be made to the photographic printing paper support. For example, a print storage layer of the type disclosed in JP-A-62-6256 may be provided on the other side of the support opposite the emulsion layer.

According to the present invention, since the base paper to be used in a photographic printing paper support has sufficiently smooth surfaces from which various irregularities, including large and small ones, have been removed, a photographic printing paper support excellent in surface smoothness can be easily obtained by coating the base paper on both sides with a polyolefin thin layer. The photographic printing paper support thus obtained has smooth surfaces free from blacking and cockles and has no cost problems and, therefore, it can be advantageously used in glossy photographic printing paper.

The present invention will now be explained in more detail by reference to the following Example, which should not be construed to be limiting the scope of the invention.

Unless otherwise specified, all percents, ratios, parts, etc. are by weight.

EXAMPLE

Sample No.1 (present invention)

A wood pulp composed of 25 parts of LBKP (Laubholz Bleached Kraft Pulp) having an α -cellulose content of 92 % and 75 parts of LBKP having an α -cellulose content of 86 % was beaten to 290 cc Canadian freeness by means of a disk refiner. Thereto were added 1.0 part of sodium stearate, 1.0 part of anionic polyacrylamide, 1.5 parts of aluminum sulfate, and 0.3 part of polyamide-polyamine-epichlorohydrin, each amount being relative to 100 parts by oven-dry weight of the wood pulp. From the resulting pulp slurry, a paper sheet having a basis weight of 180 g/m² was formed by means of a wire paper machine. Calendering was performed on this base paper under the following conditions. The base paper was first subjected to machine calender treatment to increase the density of the paper to 0.98 g/cm³ and then subjected to soft calender treatment (employing a urethane resin roll) so that the final density thereof became 1.06 g/cm³. The moisture content of the base paper being subjected to the calendering was 8.0 %. The surface temperature of the metal roll was 130 °C and that of the resin roll was 70 °C. The hardness of the used resin roll was 91.

Sample No.2 (present invention)

A wood pulp composed of 50 parts of LBKP having an α -cellulose content of 92 % and 50 parts of LBKP having an α -cellulose content of 86 % was beaten to 300 cc Canadian freeness by means of a disk refiner. Thereto were added the same internal chemical additives as those used for Sample No.1, and then a paper sheet was formed from the resulting pulp slurry in the same manner as for Sample No.1. Calendering was performed on this base paper under the following conditions. The base paper was first subjected to machine calender treatment to increase the density of the paper to 1.01 g/cm³ and then subjected to soft calender treatment so that the final density thereof became 1.07 g/cm³. The moisture content of the base paper being subjected to the calendering was 7.8 %. The surface temperature of the metal roll was 150 °C and that of the resin roll was 60 °C. The hardness of the used resin roll was 91.

Sample No.3 (present invention)

To the same beaten pulp as that used in preparing Sample No.2 were added 0.5 part of anionic polyacrylamide, 0.5 part of cationic polyacrylamide, 0.5 part of an alkylketene dimer, 0.5 part of an epoxidized resin acid amide, and 0.5 part of polyamide-polyamine-epichlorohydrin, each amount being relative to 100 parts by oven-dry weight of the wood pulp. A paper sheet was formed from the resulting pulp slurry in the same manner as for Sample No.1. Calendering was performed on this base paper under the following conditions. The base paper was first subjected to machine calender treatment to increase the density of the paper to 0.99 g/cm³ and then subjected to soft calender treatment so that the final density thereof became 1.06 g/cm³. The moisture content of the base paper being subjected to the calendering was 8.1 %. The surface temperature of the metal roll was 150 °C and that of the resin roll was 70 °C. The hardness of the used resin roll was 89.

Sample No.4 (comparative example)

Sample No.4 as a comparative paper sample was prepared in the same manner as that for Sample No.1 except that the calendering conditions were modified as follows. That is, the base paper was subjected only to machine calender treatment to increase the density of the paper to 1.06 g/cm³. As a result, blacking occurred on the base paper, impairing the appearance of the paper.

Sample No.5 (comparative example)

Sample No.5 was prepared in the same manner as that for Sample No.4 except that the base paper was subjected only to supercalender treatment (employing a cotton roll) in place of the machine calender treatment, to increase the density of the paper to 1.05 g/cm³.

With respect to each of the above-described five papers, the center plane average roughness ($SRa = 1 S_M \int_0^{L_x} \int_0^{L_y} |f(X,Y)| dx dy$, in which $S_M = L_x L_y$) in the wavelength range of from 0.2 to 1.6 mm and the center plane average roughness in the wavelength range of from 1.6 to 6.4 mm were measured with surface roughness analyzer SE-3AK employing a feeler with a tip of $R = 2\mu m$ and manufactured by Kosaka Laboratory, Japan.

Further, the above-obtained samples, No.1 to No.5, were extrusion-coated with the same polyethylene by means of the same laminators, thereby preparing five kinds of water resistant supports. The density of the polyethylene coated was 0.920 g/cm³ on the side of a photographic emulsion and 0.958 g/cm³ on the other side, and the polyethylene coated on the photographic emulsion side contains TiO₂ (ultramarine). In each support, the thickness of the polyethylene layer on either side was 28 microns. From those supports, glossy supports were obtained, with the surface of the cooling roll in the laminator for polyethylene-laminating the side on which a photographic emulsion was to be applied being used as a mirror surface. The glossy supports thus obtained were coated with a gelatin-silver halide photographic emulsion for general use. The printing papers thus prepared were exposed to light and then developed, and the smoothness of the printed surfaces were visually evaluated and compared. The evaluation results were graded into five ranks; wherein 5 means best and 1 means worst, and 2 or smaller are of no commercial value. The results obtained are shown in the Table.

Table

Sample No.	Center Place Average Roughness at Each Wave Length		Smoothness of Printed Surface
	0.2-1.6mm	1.6-6.4mm	
No. 1 (the invention)	0.69 μ m	0.61 μ m	4.5
No. 2 (do)	0.64 μ m	0.57 μ m	5
No. 3 (do)	0.57 μ m	0.50 μ m	5
No. 4 (c. example)	1.01 μ m	0.58 μ m	2.5
No. 5 (do)	0.65 μ m	1.21 μ m	2

The results in Table 1 show that the printing papers employing the photographic printing paper supports according to the present invention have extremely good smoothness.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A support for use in photographic printing paper which comprises a base paper covered on both sides with a polyolefin coating, said base paper being one which has undergone calender treatment between a metal roll and a synthetic resin roll.

2. The support for use in photographic printing paper as claimed in claim 1, wherein said calender treatment has been performed under conditions in which the moisture content of the base paper is from 6.0 to 9.0 % and the surface temperature of the synthetic resin roll is from 50 to 250 °C.

3. The support for use in photographic printing paper as claimed in claim 1, wherein said base paper undergoes calender treatment between a metal roll and a second metal roll before undergoing said calender treatment between a metal roll and a synthetic resin roll.

4. A process for producing a photographic printing paper comprising a base paper covered on both sides with a polyolefin coating, which comprises using a base paper which has undergone calender treatment between a metal roll and a synthetic resin roll.