(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 507 489 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **92302540.7**

(51) Int. Cl.[5] : **G03C 1/95**

(22) Date of filing : **25.03.92**

(30) Priority : **27.03.91 JP 89983/91**
05.11.91 JP 317433/91

(43) Date of publication of application :
07.10.92 Bulletin 92/41

(84) Designated Contracting States :
DE GB NL

(71) Applicant : **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma Minami Ashigara-shi
Kanagawa (JP)

(72) Inventor : **Miyoshi, Takahito, c/o Fuji Photo Film Co., Ltd.**
No. 200, Onakazato
Fujinomiya-shi, Shizuoka (JP)
Inventor : **Okutu, Toshimitu, c/o Fuji Photo Film Co., Ltd.**
No. 200, Onakazato
Fujinomiya-shi, Shizuoka (JP)
Inventor : **Tada, Sugihiko, c/o Fuji Photo Film Co., Ltd.**
No. 200, Onakazato
Fujinomiya-shi, Shizuoka (JP)
Inventor : **Sato, Takanori, c/o Fuji Photo Film Co., Ltd.**
No. 200, Onakazato
Fujinomiya-shi, Shizuoka (JP)

(74) Representative : **Diamond, Bryan Clive et al**
Gee & Co., Chancery House, Chancery Lane
London WC2A 1QU (GB)

(54) Photographic paper supports coated with a polyester.

(57) A paper sheet is coated by melt extrusion with a coating of (a) a mixture of (1) polyethylene terephthalate or a copolymer thereof, optionally with up to 50 wt% of other polymers and (2) titanium oxide particles, or (b) (1) a polyester, which is a homo- or copolymer or mixture thereof, e.g. polyethylene terephthalate, (2) a polyolefin, preferably polyethylene, and (3) titanium dioxide particles.

The weight ratio of the polymer(s) to the TiO_2 is preferably 98 :2 to 50 :50. The weight ratio of (a) the polyester to the polyolefin is generally 70 :30 to 99.9 :0.2.

The mixture is coated on at least one surface ; a polyolefin can be coated on the back surface ; on the coating a photographic emulsion is then coated.

EP 0 507 489 A1

This invention relates to a photographic paper support. More particularly, it relates to a photographic paper support which has excellent water resistance, whiteness and glossiness.

In a conventional method for improving water resistance and reflection efficiency of photographic papers, the raw paper surface to be coated with a photographic emulsion is pre-coated with a polyolefin layer wherein titanium oxide is kneaded and dispersed; this titanium oxide contributes to the improvement in image qualities by increasing the whiteness of the photographic paper. However, the titanium oxide also impairs the flatness of the photographic paper surface.

The most commonly employed method for improving the appearance of an image on a glossy photographic paper has been to further improve the flatness and glossiness of the surface of the photographic paper.

It is an object of the present invention to provide a photographic paper support which has in particular an improved glossiness, and also excellent water resistance, whiteness and surface smoothness.

We have now found that good results can be achieved by replacing the polyolefin with a polymer mainly comprising polyethylene terephthalate. The employment of the polyethylene terephalate coating causes no disadvantage from the viewpoint of production cost, since polyethylene terephthalate, which is superior to polyolefin in toughness and fineness, can be formulated into a thinner coating film. We have further found that the suitability of the photographic paper for production can be improved by mixing polyethylene terephthalate with a polyolefin.

According to the present invention a photographic paper support comprises a raw paper having a composition comprising (a) (1) polyester containing polyethylene terephthalate as the main component and (2) titanium oxide, or (b) a composition comprising (1) polyester, (2) polyolefin and (3) titanium oxide coated on at least one surface of the raw paper.

The polyester comprising polyethylene terephthalate as the main component to be used in the present invention may include polyethylene terephthalate alone, mixtures of polyethylene terephthalate together with other polyester(s) in amount of less than 50% by weight based on the total weight of polyester, and polymers prepared by copolymerizing polyethylene terephthalate, employed as the main component, with dibasic acid components other than terephthalic acid (for example, isophthalic acid) and glycol components other than ethylene glycol (for example, neopentyl glycol, triethylene glycol, butanediol and bisphenol A-ethylene oxide adduct). The molecular weight of these polymers, including polyethylene terephthalate homopolymer, preferably ranges from 30,000 to 50,000.

The polyester to be used together with the polyolefin may be selected from polyester homopolymers or copolymers, which are obtained by condensation-polymerizing a known dibasic acid with a known diol, and mixtures thereof. Polyethylene terephthalate is preferred in particular. From the viewpoints of water resistance, flatness and glossiness, the molecular weight of the polyester preferably ranges from 30,000 to 50,000. Examples of the abovementioned dibasic acid include terephthalic acid, isophthalic acid, sulfonate group-containing isophthalic acid and adipic acid. Examples of the above-mentioned diol include ethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol and bisphenol A-ethylene oxide adduct.

The polyolefin to be used in the present invention may be selected from known polyolefins, with polyethylene being preferred. Either high-density polyethylene or low-density polyethylene may be used. The average molecular weight of the polyolefin preferably ranges from 10,000 to 100,000.

The mixing ratio of the polyester and the optional polyolefin may vary depending on the polyester and polyolefin employed. In order to sustain the inherent glossiness of the polyester and to impart the desired Barus effect due to the polyolefin to the polyester so as to improve production suitability, control of the weight ratio of polyester: polyolefin to generally within a range of from 70:30 to 99.8:02, preferably from 80:20 to 99:1 and still preferably from 90:10 to 99:1, is necessary.

The titanium oxide to be used in the present invention may be either of anatase type or rutile type. Its particle size may preferably range from 0.1 to 1.0 μm, still preferably from 0.2 to 0.6 μm.

The mixing ratio (by weight) of the polyester comprising polyethylene terephthalate as the main component or the polyester/polyolefin mixture to the titanium oxide may preferably range from 98:2 to 50:50, more preferably from 95:5 to 70:30, most preferably 90:10 to 80:20. When the titanium oxide content is less than 2% by weight, only an insufficient whiteness is achieved. When the titanium oxide content exceeds 50% by weight, on the other hand, flatness and glossiness become poor.

The polyester comprising polyethylene terephthalate as the main component or the polyester/polyolefin mixture may be blended with titanium oxide in any conventional manner. The order of the addition of the polyester, polyolefin and titanium oxide and the mixing method are not particularly restricted. In general, the polyester is first mixed with the polyolefin and then titanium oxide is added thereto, in accordance with a conventional method.

In the production of the photographic paper support of the present invention, the mixture of polyester comprising polyethylene terephthalate as the main component with titanium oxide or the mixture of polyester,

polyolefin and titanium oxide thus obtained is then applied by melt extrusion at least onto one surface of raw paper to be coated with emulsion.

The above-mentioned mixture may further contain, for example, organic polymer grains such as styrene-acrylic type cross-linked polymer grains, if required.

As the raw paper used herein, any raw paper commonly used as a photographic paper may be employed. The thickness of the coating layer of the mixture of polyester comprising polyethylene terephthalate as the main component with titanium oxide or the mixture of polyester, polyolefin and titanium oxide on the raw paper may range from 5 to 100 μm, preferably from 10 to 80 μm, and still preferably from 10 to 50 μm. When the thickness of the coating layer is less than 5 μm, the whiteness and surface smoothness thus achieved are insufficient. On the other hand, a coating layer exceeding 100 μm in thickness is disadvantageous from an economic viewpoint.

In the above-mentioned mixture, the polyolefin gives a Barus effect to the polyester. Thus, the die-swell of the composition upon melt extrusion can be improved, and the occurrence of neck-in can be prevented.

In general, a polyester is harder and stiffer than the conventionally employed polyolefin. Therefore, the polyester coating can achieve good results in surface smoothness and glossiness, even in the case of a thinner coating film, as compared with a polyolefin coating.

In the present invention, the surface of the raw paper may be pre-treated by, for example, corona discharging or undercoating, prior to the coating of the raw paper with the above-described composition.

Next, a photographic emulsion may be applied onto the coating layer of the support thus obtained, as widely known in the art, so as to produce a photographic paper which has excellent water resistance, whiteness and glossiness. The back surface may be also coated with polyolefin, as is done conventionally.

The support of the present invention, wherein the surface of the raw paper is coated with a polyester resin mainly comprising polyethylene terephthalate which is essentially superior to polyolefin in surface smoothness, has improved surface smoothness and excellent glossiness, while water resistance and whiteness are retained. When polyolefin is admixed, the die-swell of the polyester is improved and thus neck-in scarcely occurs during the melt extrusion step. Thus, production suitability is improved.

To further illustrate the present invention in greater detail, and not by way of limitation, the following Examples are provided. Unless otherwise indicated herein, all parts and percentages are by weight.

EXAMPLES 1 TO 4 AND COMPARATIVE EXAMPLE 1

Each of the titanium oxide-containing polymers listed in Table 1 was laminated onto the surface of a raw paper having a thickness of 150 μm by melt extrusion so as to produce a polymer layer of a thickness of 30 μm. Then the glossiness of the surface and the stiffness of the support thus obtained were evaluated. Table 1 shows the results. Glossiness was determined by measuring reflecting light at 60° by using a gloss meter (product of Suga Shikenki K.K.) in accordance with JIS B0601. Then, the average centerline roughness (Ra) was calculated by referring the length thus measured as to 0.25 mm. The stiffness was determined by measuring the force required for bending the end portion (length: 1.0 cm) of a long strip sample (width: 1.5 cm) by 4 mm.

Table 1

	Example 1	Comparative Example 1	Example 2	Example 3	Example 4
Polymer	PET*	PE**	PET*	PET*	PET*
Average particle size of TiO_2 (μm)	0.4	0.4	0.4	0.4	0.4
TiO_2 cont. (wt%)	20	20	10	20	20
Polymer/ TiO_2 film thickness (μm)	20	20	20	10	50
Glossiness	101	87	110	100	105
Ra cut off 0.25 mm (μm)	0.020	0.100	0.015	0.023	0.015
Stiffness	B	C	B	B	A

[Note]

PET*: polyethylene terephthalate.

PE**: polyethylene.

A: excellent (not less than 50 g)

B: good (more than 25 g but less than 50 g)

C: poor (not more than 25 g)

EXAMPLES 5 TO 12 AND COMPARATIVE EXAMPLE 1

Each of the polyethylene terephthalate (PET), polyethylene (PE) and titanium oxide mixture compositions listed in Table 2 were applied to the surface of a raw paper having a thickness of 175 μm by melt extrusion so as to produce a polymer layer of a thickness of 30 μm. Each of the above-mentioned compositions contained 10 % by weight of titanium oxide.

Neck-in and die-swell observed during the above-mentioned production process and the glossiness of the coated surface of the support were evaluated. Table 2 shows the results.

The evaluation was conducted as follows:

Neck-in: The width of sagging film extruded from a T-die of a width of 20 cm at 300°C was measured at a point 5 cm below the discharge opening of the T-die, and the value obtained was divided by 20 cm and then expressed in %. Die-swell: The diameter of polymer yarn extruded from an orifice of a diameter of 1 mm at 300°C was measured at a point 5 mm below the discharge opening.

Glossiness: Reflected light at 60° was measured by using a Handy Gloss Meter MODEL HG-246 (product of Suga Shikenki K.K.).

Table 2

	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comparative Example 1
PET (parts)	65	70	80	90	97	98	99	100	-
PE (parts)	35	30	20	10	3	2	1	-	100
Neck-in (%)	83	80	79	77	75	73	71	55	85
Die-swell (mm)	1.55	1.50	1.45	1.40	1.30	1.29	1.28	1.07	1.90
Glossiness	81	84	90	92	93	98	99	100	80

Claims

1. A photographic paper support comprising a paper sheet having a composition comprising (1) a polyester comprising polyethylene terephthalate as the main component and (2) titanium oxide coated on at least one surface of the paper.

2. A photographic paper support, comprising a paper sheet having a composition comprising (1) a polyester, (2) a polyolefin and (3) titanium oxide coated on at least one surface of the paper.

3. A photographic paper support as claimed in Claim 2, wherein said polyolefin is polyethylene.

4. A photographic paper support as claimed in Claim 2 or 3, wherein the weight ratio of said polyester to said polyolefin is from 70:30 to 99.8:2.

5. A photographic paper support as claimed in Claim 4, where the weight ratio of said polyester to said polyolefin is from 80:20 to 99:1.

6. A photographic paper support as claimed in Claim 5, wherein the weight ratio of said polyester to said polyolefin is from 90:10 to 99:1.

7. A photographic paper support as claimed in any preceding claim, wherein the weight ratio of said polyester component (1) to said titanium oxide is from 98:2 to 50:50.

8. A photographic paper support as claimed in any of Claims 2 to 7, wherein said polyester is polyethylene terephthalate.

9. A photographic paper support as claimed in Claim 8, wherein said polyester comprising polyethylene terephthalate as the main component and said titanium oxide are present in a ratio of from 95:5 to 70:30 by weight.

10. A photographic paper support as claimed in any preceding claim, wherein the thickness of said coated layer is 5 to 100 μm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 2540

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 389 266 (KONICA CORPORATION) 26 September 1990 * page 2, line 3 - page 2, line 6 * * page 2, line 58 - page 4 *	1-10	G03C1/95
X	WORLD PATENTS INDEX Week 7818, Derwent Publications Ltd., London, GB; AN 78-32846A & JP-A-53 031 125 (FUJI PHOTO FILM KK) 24 March 1978 * abstract *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	02 JULY 1992	MARKOWSKI V.F.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)