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(54) Polyester photographic film support

(57) The present invention is a photographic film base including a polyester support. Superposed on the polyester support is a polymer layer superposed having a photoreactive moiety and a gelatin reactive moiety. A gelatin subbing layer is attached to the polymer layer. The present invention includes a photographic element having at least one light sensitive silver halide emulsion layer on the described photographic film base. The present invention also includes a process for producing a film base which includes providing a polyester support, exposing the polyester support to an energy treatment, applying a polymer coating to the polyester support, the polymer coating having a photoreactive moiety and a gelatin reactive moiety, and applying a gelatin subbing layer to the polymer coating.

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DescriptionFIELD OF INVENTION

5 This invention relates to a method for modifying the surface properties of polymer substrates. More particularly, the present invention relates to applying photoreactive polymers to an irradiated polyester substrate. After irradiation of the polyester substrate the photoattachable polymer is applied and subsequently coated with a gelatin subbing layer.

BACKGROUND OF INVENTION

10 In photographic film manufacture, a gelatin layer containing the photographic chemicals is deposited onto a polymer film which provides support and mechanical integrity to the final product. Cellulosic or polyester supports, such as poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate)(PEN), are typically employed. Polyesters have many desirable properties including high mechanical strength, dimensional stability, durability, optical clarity, and resistance to attack by most chemicals. However, the chemical inertness of PET and PEN also results in difficulty in obtaining acceptable adhesion of polar materials, such as gelatin-based photographic emulsions, to PET and PEN substrates.

15 To obtain acceptable adhesion of the light-sensitive emulsion layer to the support, intermediate anchoring layers are applied to the polyester film support prior to the orientation and crystallization of the support. Adhesion of the anchoring, or subbing, layer is promoted by a variety of methods, including the use of chlorine-containing copolymers, the application of the adhesive layer prior to the orientation and heat setting or crystallization of the polyester, and the addition of organic solvents which attack the polyester film surface. In addition, a subsequent gelatin-containing layer is often required prior to photographic emulsion coating.

20 Disadvantages of the above described approaches include the requirement of organic solvents, such as chlorophenol and resorcinol, which pose an environmental problem, and the use of chlorinated materials which degrade at elevated temperature and therefore cannot be recycled in the polyester extrusion process, causing economic and environmental problems. In addition, it is often necessary to apply a subbing layer to a polyester film which is already biaxially oriented and heat set. It is more difficult to obtain adhesion to biaxially oriented polyester support as compared to unoriented polyester. Solvents used to attack the polyester surface are less effective on the oriented support. In this case, polymer surface treatments, such as corona discharge (CDT), ultraviolet (UV), and glow discharge (GDT) treatments, are used to promote adhesion through introduction of specific functional groups which interact with subsequent coating layers as described in US Patent Nos. 4,695,532, 4,689,359, 4,933,267, 5,098,818, and 5,407,791. CDT provides sufficient adhesion improvements for many subbing applications, as demonstrated in US Patent Nos. 4,695,532 and 5,102,734, and is performed at atmospheric conditions so is inexpensive relative to other surface treatment methods. GDT provides more dramatic surface modification and rearrangement which is often necessary to obtain the desired adhesion. However, GDT is a vacuum technique so is quite expensive, requiring either very large vacuum chambers (for batch treatment) or expensive interlocks for air-to-air in-line treatment. UV treatment is preferred because it provides the necessary surface modification and can be conducted at atmospheric conditions so is less expensive than GDT.

25 UV treatment, as an approach to polyester surface treatment, is referred to in, for example, US Patent Nos. 5,407,791, 3,892,575, 4,824,699, and 5,098,818. In US Patent 5,407,791, a gel sub with high chlorophenol levels was used to obtain adhesion to UV treated PEN. In US Patent No. 3,892,575, a polymer/gelatin blend was grafted to polyester using UV radiation. Grafting of monomers to polymer surfaces for surface modification and adhesion improvement (not for photographic applications) is described in US Patent Nos. 4,267,202, 5,209,849, 3,977,954, 4,278,703, JP Kokoku Patent Hei[1991]-6225, and EP Patent Application 521 605 A2.

30 US patent application No. 08/595,613, filed on April 19, 1996 provides a means for obtaining excellent adhesion of photographic emulsion to oriented polyester support, without the need for phenolic solvents, chlorinated polymers, or expensive GDT processes. However, the subbing layer contains a reactive monomer, such as maleic anhydride, which may be disadvantageous for health and safety reasons. Additionally, monomeric materials may migrate through the emulsion layers resulting in sensitometric keeping problems.

35 In the present invention, the monomer of U.S. patent application No. 08/595,613 is replaced with a photo-attachable polymer, which would not exhibit the problems described for monomer-containing subbing materials described.

PROBLEM TO BE SOLVED BY THE INVENTION

40 Thus, there is a continuing need for polyester photographic film supports to which subsequently applied layers will readily adhere.

Further, there exists a need to provide a means for obtaining excellent adhesion of photographic emulsion to oriented polyester support.

SUMMARY OF INVENTION

The present invention is a photographic film base including a polyester support. Superposed on the polyester support is a polymer layer superposed having a photoreactive moiety and a gelatin reactive moiety. A gelatin subbing layer is attached to the polymer layer. The present invention includes a photographic element having at least one light sensitive silver halide emulsion layer on the described photographic film base.

The present invention also includes a process for producing a film base which includes providing a polyester support, exposing the polyester support to an energy treatment, applying a polymer coating to the polyester support, the polymer coating having a photoreactive moiety and a gelatin reactive moiety, and applying a gelatin subbing layer to the polymer coating.

ADVANTAGEOUS EFFECT OF THE INVENTION

The present invention provides a silver halide photographic element which exhibits excellent adhesion between an emulsion layer and an oriented polyester support.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention contemplates a polyester photographic support having; a polymer layer containing a photoreactive moiety and gelatin reactive moiety; and a gelatin layer attached to the polymer layer. Further the present invention contemplates photographic elements having at least one light-sensitive silver halide emulsion layer on the exposed surface of the gelatin layer. In addition, the present invention contemplates a method of making a photographic support and element wherein radiation treatment is used to modify the surface of polyester support, followed by coating with a photoreactive, gelatin reactive polymer and a gelatin layer. The radiation treatment can be conducted before coating the polymer layer, after coating the polymer layer, or both before and after coating the polymer layer.

Any suitable polyester may be employed in the practice of this invention as the photographic film support, including polyethylene terephthalate, polyethylene naphthalate, polyethylene isothalate, polybutylene terephthalate, polyethylene cyclohexane dimethylterephthalate, polyethanol codimethanol cyclohexane naphthalate, polycarbonates, copolymers and blends thereof and the like.

Any suitable radiation treatment for the polyester support may be employed such as, for example, corona discharge treatment, flame treatment, high energy visible light treatment, ultraviolet light, high frequency wave treatment, glow discharge treatment, active plasma treatment, laser treatment and the like. Ultraviolet light is the preferred radiation source. Ultraviolet radiation in the range of 170 nm to 400 nm is most preferred. This can be obtained by utilizing a quartz UV lamp. A preferred intensity of UV radiation is from 100 to 5000 mJ/cm² per pass under the lamp at 30 ft/min, and most preferably from 800 to 2400 mJ/cm² per pass under the lamp at 30 ft/min as measured by a UVICURE high energy UV integrating radiometer produced by Electronic Instrumentation and Technology, Inc., Sterling, VA. The number of passes under the UV lamp is in the range of 1 to 10, most preferably between 3 and 6.

Photo-reactive monomers incorporated into the polymer of the subbing layer include any monomer with an abstractable hydrogen. Photo-reactive monomers of this invention include, but are not limited to, vinylidene chloride, vinyl chloride, styrene, butadiene, acrylonitrile, acrylates, hydroxy esters, urethanes, ureas, and vinyl ethers. Gelatin-reactive monomers incorporated into the polymer include all monomers containing carboxylic acid, anhydride, or primary amine groups. Such monomers include, but are not limited to, acrylic acid, itaconic acid, maleic anhydride, itaconic anhydride, acrylamide, methacrylamide, and aminoethyl esters. Examples of polymers which are suitable for this photo-reactive layer include a terpolymer of vinylidene chloride, acrylonitrile, and acrylic acid (VNA); a terpolymer of vinylidene chloride, methylacrylate, and itaconic acid (VMI); and a terpolymer of butylmethacrylate, 2-methyl-2-aminoethyl ester of propenoic acid, and 2-methyl-2-hydroxyethyl ester of propenoic acid (BAmH).

In the invention, the polyester support is exposed to radiation, preferable UV radiation in the range of 170 nm to 400 nm. This is obtained using, for example, a quartz UV lamp. A preferred intensity of UV irradiation ranges per pass under the lamp is from 50 to 5000 mJ/cm², and more preferably from 800 mJ/cm² to 2400 mJ/cm² per pass, as measured by a UVICURE high energy UV integrating radiometer (UV A spectrum, 320 - 390 nm) produced by Electronic Instrumentation and Technology, Inc., Sterling, VA. 1-10 passes under the lamp at 30 ft/min are used to obtain adhesion, preferably between 3 and 6 passes at 30 ft/min. In addition, the treatment may be conducted before coating the polymer, after coating the polymer layer, or both before and after coating the polymer layer.

The polymer, typically a latex polymer, is then coated onto the radiated support using a suitable surfactant to obtain sufficient wetting of the coating. Such surfactants could include, but are not limited to, sodium lauryl sulfonate, dioctyl sodium sulfosuccinate, sodium octylphenylpolyether sulfonate, saponin and the like.

The polymer is typically coated at solution concentrations between 0.5 and 20% by weight, to obtain a dry coverage of from 0.2 to 10 mg/dm², preferably between 0.5 and 5 mg/dm². The coating is then dried at an appropriate tempera-

ture to remove the water or solvent and coalesce the latex polymer if necessary. Typical conditions are in the temperature range of 50°C to 120°C, preferably between 60°C and 100°C, for times ranging between 10 s and 20 min, preferable between 1 min and 5 min.

Polymer coatings described above may contain photosensitizers including, but not limited to, α -diketones as described in US patent 3,933,607 and free radical producers such as benzoin ethers and azobisisobutyronitrile, triplet state sensitizers such as benzophenone, photo-redox photosensitizers, and dye-reduction photosensitizers, as described in US Patent 4,267,202.

A gelatin-based subbing layer is then coated over the polymer layer. The gelatin-based layer is preferably a hydrophilic colloid layer in which gelatin or modified gelatin is contained as a main ingredient. The gelatin-based layer is typically coated from 0.5-2% solutions to obtain a dry coverage of 0.5 - 5 mg/dm². Additionally, the gelatin-based layer may contain an antistatic agent, a matting agent, a surface active agent, a crosslinking agent, and/or a dye. The gelatin-based is then dried at a temperature ranging from 80°C to 140°C, preferably between 100°C and 140°C for a period of 10 s to 10 min, preferably between 1 min and 5 min.

The polymer and gelatin subbing layer can be coated by any suitable coating process well known in the art, for example, dip coating, air knife coating, curtain coating, roller coating, wire bar coating, relief edge knife coating, gravure coating, or extrusion, utilizing a hopper as described in U.S. Patent 2,681,294. When two or more layers are coated they can be applied sequentially or simultaneously according to the processes described in U.S. Patents 2,761,791; 3,508,947; 2,941,898 and 3,526,528.

The polymer and gelatin subbing layer may be applied to the polyester at any suitable point in the preparation of the polyester. For example, the polymer layer and gelatin subbing layer may be applied after extrusion of the polyester into a sheet before any orientation of the polymer sheet is carried out, it may be applied after orientation in a first direction such as, for example, in the machine direction or it may be applied after the biaxial orientation is completed, for example, should the polyester first be subjected to a machine direction stretching and subsequently to a transverse direction stretching, the polymer layer or gelatin subbing layer may be applied at any point in the procedure.

The subbed support is then coated with a photographic emulsion. Subsequent to the application of the gelatin based subbing layer to the polyester support, the layer is coated with a photosensitive layer or layers that contain photographic silver halide emulsion. The invention is applicable to both negative and reversal silver halide elements. For reversal films, the emulsion layers as taught in U.S. Patent 5,236,817, especially Examples 16 and 21 are particularly suitable. Any of the known silver halide emulsion layers, such as those described in Research Disclosure, Vol. 176, December 1978, Item 17643 and Research Disclosure Vol. 225, January 1983, Item 22534 are useful in preparing photographic elements in accordance with this invention. Generally, one or more layers comprising a dispersion of silver halide crystals in an aqueous solution of gelatin are applied to the substrate subsequent to the gelatin based subbing layer. The coating process can be carried out on a continuously operating machine wherein a single layer or a plurality of layers are applied. For multicolor elements, layers can be coated simultaneously on the composite support film as is described in U.S. Patent Nos. 2,761,791 and 3,508,947. Additional useful coating and drying procedures are described in Research Disclosure, Vol. 176, December 1978, Item 17643. Suitable photosensitive image forming layers include those which provide color or black and white images.

The invention will be further illustrated by the following examples. Each of the elements are then coated with a photographic emulsion containing silver halide and an image coupler.

The adhesion of the emulsion coated support is measured as follows:

Dry adhesion test:

The emulsion surface of the green sample (before development) or dry sample (after development) was cross-hatched with a razor at 5 mm intervals to make nine squares. An adhesive tape (3M 610 tape) was adhered thereto and rapidly stripped off at a peel angle of 180°. The adhesion was evaluated according to the estimated percent removal of the emulsion.

Wet adhesion test:

A 35 mm x 12.7 cm strip of the coating is soaked at 37.8°C. for 3 min. 15 sec. in Kodak Flexicolor Developer Replenisher. The strip is then scored with a pointed stylus tip across the width of the strip and placed in a small trough filled with a developer solution. A weighted (900 g) filled natural rubber pad, 3.49 cm diameter, is placed on top. The pad is moved back and forth across the strip 100 times. The amount of emulsion removal is then assessed in units of % removed. The lower the value the better the wet adhesion of the system.

Post-Process Dry adhesion test:

The sample is run through the standard C41 development process. Dry adhesion is then measured as in the Dry Adhesion Test described above.

EXAMPLES

Adhesion test results for the following examples are in Table 1.

Invention Example 1

Irradiation of 100 mm poly(ethylene naphthalate) (PEN) manufactured by Imperial Chemicals Incorporated (ICI) was conducted using the Fusions F300 curing system with model LC-6 benchtop conveyor (Fusions UV Curing Systems, 7600 Standish Place, Rockville, MD 20855-2798). The uncoated PEN sample was passed under the lamp three times at a conveyor speed of 30 fpm. The lamp was the D bulb (emission from 200 nm to 450 nm, with major output between 350 nm and 390 nm) with an output of 120 W/cm. The energy density of one pass under the lamp at 30 fpm is approximately 1.5 J/cm² as measured by the UVICURE high energy UV integrating radiometer (UV A spectrum, 320 - 390 nm) described previously. A photo-reactive, gelatin-reactive polymer of the following formulation was then coated on a room temperature coating block to obtain a total dry coverage of 2 mg/dm²:

Formulation A

Component 1: 1.0 weight percent BAmH polymer
 Component 2: 0.1 weight percent saponin surfactant
 balance: deionized water

The coated samples was then dried for 10 min at 60°C in a standard convection oven. The coated sample was then overcoated on a 30°C coating block with a gelatin-containing subbing layer of the following formulation to obtain a dry coverage of 1 mg/dm²:

Formulation B

Component 1: 1.0 weight percent gelatin
 Component 2: 0.01 weight percent saponin
 Component 3: 0.01 weight percent potassium chromium sulfate
 balance: deionized water

The overcoated sample was then dried 5 min at 120°C, and subsequently coated with an emulsion layer.

Invention Example 2

Irradiation of 100 mm PEN was conducted using the Fusions F300 curing system described in example 1. The uncoated PEN sample was passed under the lamp four times at a conveyor speed of 30 fpm. The lamp used was the H+ bulb, which has major emissions between 215 nm and 315 nm, and at 365 nm. The energy density of one pass under the lamp at 30 fpm is approximately 50 mJ/cm² as measured by the UVICURE high energy UV integrating radiometer (UV C spectrum, 240 - 270 nm) described previously. A photo-reactive, gelatin-reactive polymer of the following formulation was then coated on a room temperature coating block to obtain a total dry coverage of 6 mg/dm²:

Formulation C

Component 1: 3.0 weight percent VNA polymer
 Component 2: 0.1 weight percent saponin surfactant
 balance: deionized water

The coated samples was then dried for 3 min at 120°C in a standard convection oven. The coated PEN sample was passed under the lamp six times at a conveyor speed of 30 fpm prior to coating and drying the gelatin subbing layer and emulsion layer as described in Ex. 1 (Formulation B).

Comparison Example 2

The procedure in example 2 was repeated, but the UV irradiation steps were eliminated.

5 Invention Example 3

The procedure of Invention Example 2 was repeated with the following exceptions. The following polymer formulation was used:

10 Formulation D

Component 1: 5.0 weight percent VNA polymer

Component 2: 0.1 weight percent saponin surfactant

Component 3: 0.05 weight percent resorcinol

15 balance: deionized water

The uncoated PEN sample was passed under the D bulb two times at a conveyor speed of 30 fpm prior to coating Formulation D and 3 times at 30 fpm after coating Formulation D. The coating was dried 5 min at 140°C. Subsequently Formulation B and emulsion were coated as in Example 2.

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Invention Example 4

The procedure of Invention Example 3 was repeated using VMI for the polymer (component 1) in Formulation D.

25 Invention Example 5

The procedure of Invention Example 4 was repeated using the H+ bulb rather than the D bulb.

30 Invention Example 6

The procedure of Invention Example 3 was repeated, except that the uncoated PEN sample was passed under the D bulb one times at a conveyor speed of 30 fpm prior to coating Formulation D and six times at 30 fpm after coating Formulation D. The coating was dried 5 min at 90°C.

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Table 1

Wet and Dry Adhesion Results for Invention and Comparison Examples			
Sample	Cross hatch dry tape adhesion	Post-process dry tape adhesion	Wet Adhesion
Invention Ex. 1	A	A	A
Invention Ex. 2	A	A	A
Comparison Ex. 2	D	D	D
45 Invention Ex.3	A	A	A
Invention Ex. 4	A	A	A
Invention Ex.5	A	A	A
50 Invention Ex. 6	A	A	A
Definition of codes: Cross hatch dry tape adhesion and wet adhesion - A: 0-5% removed, B: 5-20% removed, C: 20-50% removed, D: 50-100% removed.			

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Claims

1. A photographic film base comprising;

a polyester support;
a polymer layer superposed on said support, said polymer having a photoreactive moiety and a gelatin reactive moiety; and
a gelatin subbing layer attached to the polymer layer.

2. The film base according to claim 1 wherein said polymer having a photoreactive moiety and a gelatin reactive moiety is selected from the group consisting of terpolymers of vinylidene chloride, acrylonitrile, and acrylic acid; terpolymers of vinylidene chloride, methylacrylate, and itaconic acid; terpolymers of butylmethacrylate, 2-methyl-2-aminoethyl ester of propenoic acid; and 2-methyl-2-hydroxyethyl ester of propenoic acid.
3. The film base according to claim 1 wherein said polymer layer further comprises a phenol type material.
4. The film base according to claim 1 wherein the polyester support is selected from the group consisting of polyethylene terephthalate, polyethylene naphthalate, polyethylene isophthalate, polybutylene terephthalate, polyethylene cyclohexane dimethylterephthalate, polyethanol codimethanol cyclohexane naphthalate, polycarbonates, and copolymers thereof.
5. The film base according to claim 1 wherein said gelatin subbing layer further comprises an antistatic agent.
6. The film base according to claim 1 wherein said gelatin subbing layer further comprises a matting agent.
7. The film base according to claim 1 wherein said gelatin subbing layer further comprises a surface active agent.
8. The film base according to claim 1 wherein said gelatin subbing layer further comprises a surfactant.
9. The film base according to claim 1 wherein said gelatin subbing layer further comprises a cross-linking agent.
10. The film base according to claim 1 wherein said gelatin subbing layer further comprises a dye.



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EUROPEAN SEARCH REPORT

Application Number
EP 97 20 3830

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.6)
X	US 4 135 932 A (MANN DAVID R) * column 1, line 50 - line 58 * * column 2, line 9 - line 19 * * column 3, line 22 - line 36 * * column 4, line 5 - line 22 * * column 4, line 60 - line 63 * * column 5, line 45 - line 47 * * claims 1,3,10,12; examples 11,14 * ---	1-10	G03C1/93 G03C1/91 C08J7/04
X	US 2 698 235 A (FRANK E SWINDELLS) * claims 1,6; figure 2; examples 10-17 * ---	1-10	
X	US 3 488 195 A (HUNTER CLARENCE S) * column 2, line 65 - column 3, line 18; examples 1,2 * ---	1-10	
X	US 3 502 475 A (KANE WILLIAM PAUL) * column 5, line 58 - line 65 * ---	1,2,4	
X	US 3 988 157 A (VAN PAESSCHEN AUGUST JEAN ET AL) * abstract; claims 1-6; example 3 * ---	1	
A	US 3 892 575 A (WATTS RONALD E ET AL) * abstract; claims 1-6 * ---	1-10	
A	GB 1 549 317 A (KONISHIROKU PHOTO IND) * claims 1-10; example 3 * ---	1	
A	EP 0 477 670 A (KONISHIROKU PHOTO IND) * page 11, line 6 - line 37 * -----	1,2	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 2 April 1998	Examiner Bolger, W
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	

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