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Polymers containing 4,4'-bis (5-methyl-2-benzoxazolyl) stilbene as sole optical brightener.

A polymer comprising 4,4'-bis(5-methyl-2 benzoxazolyl) stilbene as the sole optical brightener.

This invention relates to polymers comprising an optical brightener and the use of such polymers in photographic elements.

Polymers containing optical brighteners have many commercial uses. To make polymer products attractively white, optical brighteners are used to mask the inherent yellowness of the polymers and to brighten their white appearance. Such polymers find use in, for example, photographic supports and elements comprising a paper base material having thereon a polyolefin coating containing a white pigment and an optical brightener. These supports are particularly useful in photographic elements such as color prints because they exhibit good brightness and excellent dimensional stability and are highly resistant to the action of aqueous acid and alkaline photographic processing solutions. The polyolefin coating provides a very smooth surface which is desirable when thin layers, such as silver halide emulsion layers, are to be coated thereover. US-A-3,411,908 described such a support which has achieved widespread commercial acceptance.

The purpose of the optical brightener is to make the white areas of the support appear even brighter. The optical brightener fluoresces upon irradiation with UV (ultraviolet) light, emitting visible light, usually bluish in hue, thus enhancing the brightness of the support. Optical brighteners for use in photographic print materials must absorb UV light, especially in the region from the brightness of the print, and have the desired brightening power.

Moreover, the optical brightener must be nonmigrating so that it remains in the polyolefin coating and does not exude as a surface film on the polyolefin. Such exudation not only can give rise to a nonuniform brightness of the reflection surface of the support, but also readily transfers to any other surface contacted with it. For example, brightener transferred nonuniformly to the back side of the adjacent layer of support results in visual imperfections. Brightener when migrated to the surface of the front side, can when would in roll form, adversely affect subsequent coating and finishing operations and, in consequence, the quality and performance of the final element.

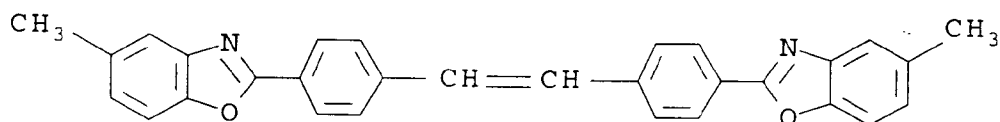
US-A-4,794,071 discloses a photographic element containing a fluorescent bis(benzoxazolyl) stilbene optical brightener mixture. The support in the disclosed element is comprised of a paper base material having thereon a polyolefin coating containing a white pigment and a mixture of optical brighteners, such mixture comprising certain fluorescent bis(benzoxazolyl)stilbenes.

While the elements described in US-A-4,794,071 have found commercial acceptance further improvements in resistance to brightener exudation and increased optical brightening power is desired. Moreover it would be advantageous to eliminate the need to prepare a mixture of optical brighteners and the cost associated with the manufacture and use of three different compounds.

The present invention provides a polymer comprising 4,4'-bis(5-methyl-2 benzoxazolyl) stilbene as the sole optical brightener. The use of a single optical brightener from the mixture unexpectedly provides improvements in resistance to exuding and improved optical brightening.

The invention further provides a photographic element comprising a paper support having at least one side thereof and a polymer coating containing a white pigment and 4,4'-bis(5-methyl-2 benzoxazolyl) stilbene as the sole optical brightener.

The 4,4'-bis(5-methyl-2 benzoxazolyl) stilbene has the structure:



The amount of the brightener which is used in the polymer is an amount effective to brighten the reflective layer. Such amounts of the mixture can be from 0.01 percent to 0.25, preferably 0.04 to 0.10, percent by weight based on the total weight of the polymer, including the white pigment. One employs an amount of brightener sufficient to give the increase in brightness desired.

The polymer can be any polymer, especially polyolefins and polyvinyl chloride. Representative of these materials are polyethylene, polypropylene, polystyrene, polybutylene, and copolymers thereof. Polyethylene of low, medium or high density is preferred. The polyolefin can be copolymerized with one or more copolymerizable monomers including vinyl stearate, vinyl acetate, acrylic acid, methyl acrylate, ethyl acrylate, acrylamide, methacrylic acid, methylmethacrylate, ethyl methacrylate, metacrylamide, butadiene, isoprene, and vinyl chloride. The polymers can be copolymers with polyesters, such as polyethylene terephthalate, polysul-

phones, polyurethanes, polyvinyls, polycarbonates, cellulose esters, such as cellulose acetate and cellulose propionate, and polyacrylates. Preferred polyolefins are film forming and adhesive to paper. Polyethylene having a density in the range of from 0.910 g/cm³ is particularly preferred.

5 The optical brightener can be incorporated into the polymer by conventional methods. Preferred are methods so that the brightener is uniformly dispersed within a polyolefin. Such methods include a melt extrusion process, a kneader extruder, a roll mill, a high shear mixer, or a twin-screw compounder.

The white pigment incorporated in the polymer layer can be, calcium carbonate, titanium dioxide, zinc oxide, zinc sulfide, zirconium dioxide, white lead, lead sulfate, lead chloride, lead aluminate, lead phthalate, antimony trioxide, white bismuth, tin oxide, white manganese, white tungsten and combination thereof. The pigment is used in any form that is conveniently dispersed within the polymer. The preferred pigment is titanium dioxide. The titanium dioxide preferably is anatase, rutile or combinations of these forms. Enhanced image resolution in a photographic element can be obtained by the addition of functional amounts of such highly white-light reflective pigments to the polyolefin layer. Preferably, the white pigment is used in the range from 3 to 35 percent, more preferably 5 to 25 percent by weight based on the total weight of the polyolefin coating. Titanium dioxide at levels of 5 to 20 percent is particularly useful.

In addition to the brightener and the white pigment, the polymer coating can contain, if desired, a variety of additives including antioxidants such as 4,4'-butylidene-bis(6-tert-butyl-meta-cresol), dilauryl-3,3'-thiodipropionate, N-butylated-p-aminiphenol, 2,6-ditert-butyl-p-cresol, 2,6-di-tert-butyl-4-methylphenol, N,N-disalicydene-1,2-diaminopropane, tetra(2,4-di-tert-butylphenyl)-4,4'-diphenyldiphenyldiphosphonite, octadecyl 3-(3'',5'-di-tert-butyl-4'-hydroxyphenyl propionate), combinations of the above, and the like; heat stabilizers, such as higher aliphatic acid metal salts such as magnesium stearate, calcium stearate, zinc stearate, as magnesium stearate, calcium palmitate, sodium palmitate, zirconium octylate, sodium laurate, and salts of benzoic acid such as sodium benzoate, calcium benzoate, magnesium benzoate and zinc benzoate; additional optical brighteners; antistatic agents; dispersing agents; UV stabilizers, coating aids; slip agents; lubricants; dyes; and the like, as is well known to those skilled in the art. Additionally, emulsion side resins can contain one or more pigments, such as the blue, violet or magenta pigments described in US-A-3,501,298, or pigments such as barium sulfate, colloidal silica, calcium carbonate and the like.

The paper base material employed in accordance with the invention can be any paper base material which as heretofore been considered useful for photographic support. The weight and thickness of the support can be varied depending on the intended use. A preferred weight range is from 20 g/m² to 500 g/m². Preferred thicknesses are 20 mm to 500 mm. It is preferred to use a paper base material calendered to a smooth surface. The paper base material can be made from any suitable paper stock preferably comprising hard or softwood. Either bleached or unbleached pulp can be utilized as desired. The paper base material can also be prepared from partially esterified cellulose fibers or from a blend of wood cellulose and a suitable synthetic fiber such as a blend of wood cellulose and polyethylene fiber.

As is known to those skilled in the art, the paper base material can contain, if desired, agents to increase the strength of the paper such as wet strength resins, for example, the amino-aldehyde or polyamideepichlorohydrin resins, and dry strength agents, for example, starches, including both ordinary starch and cationic starch, or polyacrylamide resins. In a preferred embodiment of this invention, the amino-aldehyde, polyamideepichlorohydrin and polyacrylamide resins are used in combination as described in US-A-3,592,731. Other conventional additives include water soluble gums, for example, cellulose ethers such as carboxymethyl cellulose, sizing agents, for example, a ketene dimer, sodium stearate which is precipitated onto the pulp fibers with a polyvalent metal salt such as alum, aluminum chloride or aluminum sulfate; fluorescing agent; antistatic agents; filters, including clays or pigments such as titanium dioxide; dyes; and so forth.

45 It is to be understood that although paper is a preferred support, the nature of the support is not a critical feature of the invention. Thus for example the paper support may be substituted by a synthetic paper or a plastic film.

The coating of the paper base material with the polyolefin preferably is by extrusion from a hot melt as is known in the art. The paper base material preferably is treated with corona discharge to obtain good adhesion before the polyolefin coating is extruded thereon, as described in US-A-3,411,908. The invention can be practiced within a wide range of extrusion temperatures, for example, 150°-350°C., and speeds for example, 60 m/min. to 460 m/min., depending on the particular intended application of the support. For many applications, preferred extrusion temperatures are 310°-330°C. The optical brightener is stable to such temperatures. Under these conditions, the aforescribed polyolefin coating, over which the silver halide emulsion is applied, is coated onto the paper base material in a coverage of 1 to 100 g/m², at a uniform thickness ranging from 1 to 100 mm. About the same coverage of clear polyethylene coating preferably is applied to the side of the paper base material opposite to the pigmented polyolefin coating. As such, the polyolefin coatings are particularly effective in preventing acid and alkaline photographic processing solutions from penetrating to the paper base.

As noted, photographic elements in accordance with this invention comprise the above-described optically brightened photographic support and at least one silver halide emulsion layer. Any of the known silver halide emulsion layers, such as those described in *Research Disclosure*, Vol. 176, December 1978, Item 7643 and *Research Disclosure*, Vol. 225, January 1983, Item 22534, the disclosures of which are hereby incorporated by reference in their entirety, are useful in preparing photographic elements in accordance with this invention. Generally, the photographic element is prepared by coating the support with one or more layers comprising a dispersion of silver halide crystals in an aqueous solution of gelatin, and optionally, one or more stubbing layers, and so forth. The coating process is generally carried out on a continuously operating machine wherein a single layer or a plurality of layers are applied to the support. For multilayer elements, layers are generally coated simultaneously on the support as described in US-A-2,761,791, and US-A-3,508,947. Additional useful coating and drying procedures are described in *Research Disclosure*, Vol. 176, December 1978, Item 17643.

The following examples illustrate the unexpected improvements obtainable through use of the present invention.

Example 1

Evaluation of 4,4'-Bis(5-methyl-2-benzoxazolyl)stilbene as sole optical brightener in TiO₂-pigmented polyethylene-coated paper.

A mixture of 60% polyethylene, 31% TiO₂, 7.5% ZnO, 1.25% calcium stearate, 0.25% antioxidant, 0.15% optical brightener and low level of red and blue colorants was blended extruded at 200°C and pelletized. This was labeled Blend A

Various levels of optical brightener in polyethylene were prepared by diluting Blend A with a calculated amount of polyethylene. These mixtures were then used to produce a 1 mil (0.0254 mm) thick coating on one side of a 6.5 mil (0.1651 mm) thick paper. To the other side of the paper, a 1 mil (0.0254 mm) thick coating of neat polyethylene was extrusion coated to provide curl control.

Coated paper samples were tested for color properties on the optical brightener side of the paper using a Pacific-Standard Spectrogard Spectrophotometer. CIELAB b* values, as specified by the CIELAB 1976 colorimetry measurement system, were obtained in two different measurement modes: (1) UVI (ultraviolet portion of the spectrum included in the incident light beam) and (2) UVO (ultraviolet portion of the spectrum filtered out of the incident beam). A measure of the effectiveness of the optical brightener was obtained by subtracting the value of b* at UVO conditions from b* at UVI conditions. This calculates the contribution to the blueness of the support by the included optical brightener. The larger the negative number for this value, called delta b*, the larger the optical brightening effect.

Coated paper samples were also tested for optical brightener migration. This was accomplished by placing stacks of 4-inch (0.1016 mm) wide by 12-inch (0.3048 mm) long strips in an oven controlled to a specific temperature and relative humidity. Samples were periodically withdrawn, examined under UV light and given a visual rating based on the amount of the optical brightener present at the surface of the polyethylene coating. The number of days needed to reach a severe level of migration was recorded. A severe level of migration had perhaps 20% or more of the surface coated with the optical brightener (visible as yellowness on the surface, due to its inability to fluoresce once it crystallizes at the surfaces).

Test Results

OB	Wt%	Delta b*	Days of Migration	
			110°F/50% RH	140°F/50% RH
I	0.04	-4.34	>42	>42
	0.06	-4.78	>42	>42
	0.08	-5.29	>42	>42
	0.10	-5.48	>42	>42
II	0.08	-5.00	22	20
	0.10	-5.34	20	9
OB-1	0.08	-4.49	<3	<3
	0.10	-4.62	<3	<3
OB-t-Bu	0.05	-3.58	16	3
	0.06	-3.59	7	<2
OB-Oct	0.16	-4.56	<2	<2
Host KS	0.08	-4.84	>42	>42
	0.10	-5.17	>42	>42
	0.12	-5.20	42	20

*I 4,4'-Bis(5-methyl-2-benzoxazolyl)stilbene.
 II 4,4'-Bis(5-ethyl-2-benzoxazolyl)stilbene.
 OB-1 4,4'-Bis(2-benzoxazolyl)stilbene.
 OB-t-Bu 4,4'-Bis(5-t-butyl-2-benzoxazolyl)stilbene.
 OB-t-Oct 4,4'-Bis(5-t-octyl-2-benzoxazolyl)stilbene.
 Host KS Hostalux KS, product of Hoechst Celanese, a mixture of compound I, OB-1, and 4-(5-methyl-2-benzoxazolyl)-4'-(2-benzoxazolyl)stilbene disclosed in U.S. Patent 4,794,071.

These test results show that Compound I gives more intense fluorescence (larger negative delta b* values) than all other 4,4'-bis(2-benzoxazolyl)stilbenes, as well as mixtures of such compounds that include compound I, at equivalent concentrations, and Compound I shows least migratory among all other stilbenes with equivalent fluorescence. Indeed compound I is unexpectedly better than the mixture Host KS that includes compound I. This is synergistic in that brightening and migration inhibition of compound I alone is better than the mixture. These results also show that this invention is unobvious in view of the poor results obtained with structurally similar compounds and mixtures of such compounds. Thus compositions free of other optical brighteners provide improved results.

Example 2

Evaluation of 4,4'-Bis(5-methyl-2-benzoxazolyl)stilbene as sole optical brightener in Polyvinyl chloride.

A mixture of PVC (100 parts per hundred) (Geon 300, 100 phr), Dioctyl phthalate (40 parts per hundred), heat stabilizer comprising a mixture of zinc, barium and cadmium carboxylates (1.5 parts per hundred), TiO₂ (2 parts per hundred), and optical brightener (0.01 and 0.01 parts per hundred) were blended, dispersed, hot two-roll milled at 160-165°C and pressed into 30-mil (0.735 mm) flexible film. The yellowness of these film samples were determined by using a Gardner color difference meter and described as b-values

Test Results

OB	Whitening Effect/b-Value	
	0.01%	0.02%
None	2.58	
I	-0.30	-0.61
OB-1	0.17	0.03
OB-t-Bu	0.45	-0.43
*OB-4	0.15	-0.60
*U-OB	1.19	0.17
*H-KCB	0.44	-0.11

*OB-4 A mixture of compound I, OB-1 and 4-(5-methyl-2-benzoxazolyl)-4'-(2-benzoxazolyl)stilbene.

U-OB Uvitex OB, product of Ciba Geigy, 2,5-bis(5-t-butyl-2-benzoxazolyl)thiophene.

H-KCB Hostalux KCB, product of Hoechst Celanese, 1,4-bis(5-t-butyl-2-benzoxazolyl)naphthalene.

Compound I is the most effective fluorescent whitening agent for PVC among all optical brighteners tested, including mixtures of optical brighteners that include compound I.

Claims

1. A polymer comprising 4,4'-bis(5-methyl-2 benzoxazolyl) stilbene as the sole optical brightener.
2. The polymer of claim 1 also containing a white pigment.
3. The polymer of claim 1 wherein the optical brightener is present in the polymer at a concentration of 0.04 to 0.10 weight percent.
4. The polymer of claim 2 wherein the polymer is selected from the group consisting of polyolefins and polyvinyl chlorides.
5. The polymer of claim 4 wherein the polyolefin is polyethylene.
6. The polymer of claim 2 wherein the pigment is titanium dioxide.
7. A photographic element comprising a paper support having at least one side thereof a polymer coating containing a white pigment and 4,4'-bis(5-methyl-2 benzoxazolyl) stilbene as the sole optical brightener.
8. The element of claim 7 wherein the optical brightener is present in the polymer at a concentration of 0.04 to 0.10 weight percent.
9. The element of claim 8 wherein the polymer is a polyolefins.
10. The element of claim 9 wherein the polyolefin is polyethylene.
11. The element of claim 7 wherein the pigment is titanium dioxide.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 42 0123

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-A-5 075 206 (NODA TOURU ET AL) 24 December 1991 * column 29, line 29 - line 36 * * column 29, line 58 - column 30, line 12; examples *	1-11	C08K5/353 G03C1/815
X	--- CHEMICAL ABSTRACTS, vol. 113, no. 26, 24 December 1990 Columbus, Ohio, US; abstract no. 241360, * abstract * & JP-A-02 071 256 (MITSUBISHI PAPER MILLS, LTD.) 9 March 1990	1-11	
X	--- CHEMICAL ABSTRACTS, vol. 114, no. 18, 6 May 1991 Columbus, Ohio, US; abstract no. 174874, * abstract * & JP-A-02 168 249 (MITSUBISHI PAPER MILLS, LTD.) 28 June 1990	1-11	
A	--- US-A-5 198 330 (MARTIC PETER A ET AL) 30 March 1993 * claims * -----	1-11	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Place of search THE HAGUE		Date of completion of the search 9 August 1995	Examiner DE LOS ARCOS, E
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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