

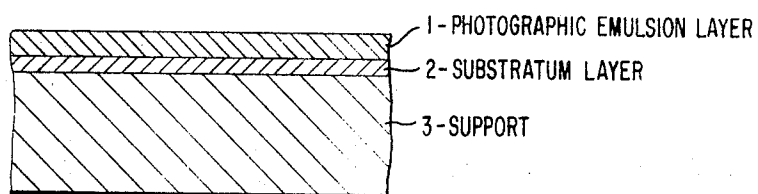
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PHOTOGRAPHIC LIGHT SENSITIVE ELEMENTS

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PHOTOGRAPHIC LIGHT SENSITIVE ELEMENTS
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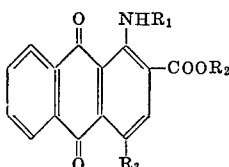
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2 Claims

ABSTRACT OF THE DISCLOSURE

Photographic light sensitive element comprising a cellulose ester support, at least one substratum layer, and at least one gelatino-silver halide emulsion layer, at least one of said support and substratum containing at least one anthraquinone dye having the following general formula:



wherein R₁ represents a member selected from the group consisting of a hydrogen atom and an alkyl group; R₂ represents a member selected from the group consisting of an alkyl group, a cyclohexyl group and an alkoxyalkyl group; and R₃ represents a member selected from the group consisting of a hydroxy group, an amino group and an NHR group (where R represents a member selected from the group consisting of an alkyl group, a cycloalkyl group, an alkoxyalkyl group, a phenyl group, an alkyl-substituted phenyl group, an alkoxy-substituted phenyl group, and a halogen-substituted phenyl group); the total carbon atom number of the aliphatic portions contained in said R₁, R₂ and R₃ being less than 12.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates generally to a photographic light-sensitive element and more particularly to a photographic light-sensitive element having a substratum or a support dyed by an anthraquinonic dye.

Description of the prior art

Usually a photographic light-sensitive element comprises fundamentally, as shown in the accompanying drawing, a support 3 of, e.g. a cellulose ester, a substratum 2 and a gelatino silver halide light-sensitive emulsion layer 1. As a substratum for improving the adhesive property between a support and a gelatino silver halide emulsion layer in the case of employing a cellulose triacetate film as the support, a substratum is known which is prepared by applying to the support a dispersion of a hydrophilic high molecular weight material, such as, gelatin, in a mixture of an organic acid, such as, acetic acid or salicylic acid, and an organic solvent, such as, acetone, methyl alcohol, methylene chloride and the like (U.S. Patent 2,852,378). Also known is a substratum prepared by applying a dilute cellulose nitrate solution to a support, and then applying a gelatin-containing liquid to the thus formed layer.

In photographic light-sensitive elements, various additives which are used for the preparation thereof must be ones by which the photographic properties and the physical properties of the photographic light-sensitive elements are not reduced.

That is, it is necessary that the sensitivity and the for-

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mation of gamma and fog are not influenced when the additives are added to a gelatino-silver halide emulsion, the dispersivity of the dispersion of gelatin and the like must be maintained stably for a long period of time when the additives are added to a substratum, and the adhesive property of the substratum must not be affected when the substratum containing the additives is formed on the support. Moreover, it is necessary that when the additives are added to a viscous dope used for the preparation of the support, the properties of the dope are not changed and a band or a drum on which the dope is applied is not attacked or influenced by the dope. Among such additives, there are dyes which are added to the support or substratum for photographic light-sensitive elements.

It is necessary to prevent the formation of halation by absorbing light having long wave length which will tend to form halation, that is, light in red region and near infrared region in a negative light-sensitive element in which a negative silver halide emulsion layer is formed on a support (antihalation effect). It is also necessary to prevent the entrance of light having a long wave length, since such light tends to enter the inside of the photographic light-sensitive film from the edge of the film which is withdrawn from a magazine. Furthermore, it is desirable that the absorption of light in a short wave length region (400–500 mμ) be less by the support for a photographic light-sensitive element which has been developed and dried. One such fault arises from the fact that if the support absorbs light in this region, a filter desensitizing action occurs and photographs having turbidity, such as, yellow fog, are obtained upon printing a light-sensitive positive element, such as, a printing paper or an X-ray film, since the light sensitive element has its light-sensitive region in the short wave length region. This also occurs upon photographing a light-sensitive element for X-ray photography.

For the reasons mentioned above, the support for photographic light-sensitive elements is usually colored in blue or cyan and the dyes used for the purpose are usually the following ones which have the following faults. For example, Nigrosine Sprit Jet (color index No. 50,415) or Grasoil Fast Black G has very large desensitizing power and corrosive power, and Sudan Black S gives no protective action for photographic light-sensitive elements in the near infrared region.

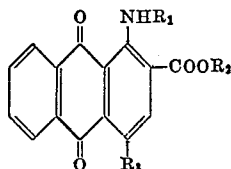
Further, 1,4-di-[para-(β-hydroxyethoxyethoxyethoxy)-phenyl]-amino - 5,8 - di-hydroxyanthraquinone or 1,5-di-[para-(β-hydroxyethoxyethoxyethoxy) phenyl]amino - 4,8-di-hydroxyanthraquinone (U.S. Patent No. 2,622,026) is undesirable, since such a dye absorbs light in a short wave length region (about 400–500 mμ). Further the dye affects the properties of the photographic emulsion. Considering the chemical structure, the dye has a group similar to a hydroquinone nucleus, a phenylenediamine nucleus or para-aminophenol nucleus, since the hydrogen atom of the amino group or the hydroxyl group remaining at the 5,8-position (or the 4,8-position) of the dye is in a free state, although the oxygen atom of the anthraquinone forms a hydrogen bridge with the hydrogen atom of a 1,4-position or 1,5-position substituted amino group or hydroxyl group. Thus, it is surmised that the dye provides a desensitizing action and fog forming property to the silver halide emulsion, since these three nuclei usually have basic or reducing properties. Furthermore, a blue-green dye, 1,8-di-hydroxy-5-nitro-4-hydroxyethyl-phenyl-amino-anthraquinone (U.S. Patent No. 2,641,602) tends to give a desensitizing action to a silver halide emulsion, perhaps caused by the oxidizing property of the 5-nitro group.

Thus, an object of this invention is to provide a photographic light-sensitive element having an antihalation effect

and filter effect as well as having improved photographic properties.

SUMMARY OF THE INVENTION

The object of this invention can be attained according to the present invention by incorporating in a substratum, present between a cellulose ester support and a silver halide emulsion layer, or in the support itself, an anthraquinone dye having the following general formula:



wherein R_1 represents a hydrogen atom or an alkyl group; R_2 represents an alkyl group, a cyclohexyl group or an alkoxyalkyl group; and R_3 represents a hydroxy group, an amino group or an NHR group (where R represents an alkyl group, a cyclohexyl group, an alkoxyalkyl group, a phenyl group or a phenyl group substituted by an alkyl group, an alkoxy group or a halogen atom); the total number of carbon atoms of the aliphatic portions contained in said R_1 , R_2 and R_3 is less than 12.

Since the photographic light-sensitive element containing the anthraquinone dye has good photographic properties as well as the properties of absorbing light having long wave length, including the near infrared regions, and absorbing almost no light having short wave length, as mentioned above, it has a very excellent antihalation effect and filter effect. Thus, by using the anthraquinone dye of this invention, a photographic film base is obtained which has a high brightness and color purity owing to a lower absorption of the desirable spectra. That is, since the anthraquinone dye of this invention has a carboxylic acid ester at the 2-position of the anthraquinone nucleus, the basic property or the reducing property of the amino group or hydroxyl group substituted at the 1-position and 4-position is reduced. Hence, the dye does not have a bad influence on the silver halide emulsion. Also, it is considered that by the incorporation of the anthraquinone dye, the absorption of the photographic light-sensitive element is shifted to a longer wave side, due to the introduction of the carboxylic acid ester group at the 2-position. At the same time the absorption of light in the short wave length region is almost removed.

DETAILED DESCRIPTION OF THE INVENTION

Specific practical examples of the anthraquinone dyes of this invention are shown in the following table.

	R_1	R_2	R_3
Number:			
1.....	H	C_8H_{17}	$NHCH_3$
2.....	H	C_8H_{11}	$NHCH_3$
3.....	H	C_8H_9	$NHCH_3$
4.....	H	C_2H_5	$NHCH_3$
		C_4H_9 CHCH ₃	
5.....	H	C_4H_9	NHC_4H_9
6.....	H	C_4H_9	$NH(CH_2)_3OCH_3$
7.....	H	C_8H_7	$NHC_4H_9(iso)$
8.....	H	$C_4H_9(iso)$	NH
9.....	H	C_8H_{17}	NH
10.....	H	C_8H_{17}	NH
11.....	H	C_8H_{17}	NH
12.....	H	C_2H_5	NH

TABLE.—Continued

	R_1	R_2	R_3
5	13..... CH_3	C_2H_5	NH
	14..... CH_3	C_8H_{17}	$NHCH_3$
	15..... CH_3	C_8H_{11}	$NHCH_3$
	16..... CH_3	C_8H_7	$NHC_4H_9(iso)$
	17..... CH_3	$C_2H_5O-CH_2CH_3$	$NHC_4H_9(iso)$
10	18..... H		$NHC_4H_9(iso)$
	19..... C_2H_5	C_4H_9	$NHCH_3$
	20..... H	C_8H_{17}	NH_2
	21..... H	C_8H_{17}	OH
15	22..... CH_3	CH_3	OH

The chemical names of dyes included in the above table, by number, are as follows:

Number Dye	Name
1.....	1-amino-4-methylaminoanthraquinone-2-carboxylic acid octylester.
2.....	1-amino-4-methylaminoanthraquinone-2-carboxylic acid amylester.
3.....	1-amino-4-methylaminoanthraquinone-2-carboxylic acid butylester.
25	4..... 1-amino-4-methylaminoanthraquinone-2-carboxylic acid (2-ethyl)hexylester.
5.....	1-amino-4-butylaminoanthraquinone-2-carboxylic acid butylester.
6.....	1-amino-4-γ-methoxypropylaminoanthraquinone-2-carboxylic acid butylester.
7.....	1-amino-4-isobutylaminoanthraquinone-2-carboxylic acid propylester.
30	8..... 1-amino-4-cyclohexylaminoanthraquinone-2-carboxylic acid isobutylester.
9.....	1-amino-4-p-toluidinoanthraquinone-2-carboxylic acid octylester.
10.....	1-amino-4-(4'-methoxy)phenylaminoanthraquinone-2-carboxylic acid octylester.
35	11..... 1-amino-4-(3'-chloro)phenylaminoanthraquinone-2-carboxylic acid octylester.
12.....	1-amino-4-anilinoanthraquinone-2-carboxylic acid ethylester.
13.....	1-methylamino-4-p-toluidinoanthraquinone-2-carboxylic acid ethylester.
14.....	1,4-bis-methylaminoanthraquinone-2-carboxylic acid octylester.
40	15..... 1,4-bis-methylaminoanthraquinone-2-carboxylic acid amylester.
16.....	1-methylamino-4-isobutylaminoanthraquinone-2-carboxylic acid propylester.
17.....	1-methylamino-4-isobutylaminoanthraquinone-2-carboxylic acid ethoxyethylester.
18.....	1-amino-4-isopropylaminoanthraquinone-2-carboxylic acid cyclohexylester.
19.....	1-ethylamino-4-methylaminoanthraquinone-2-carboxylic acid butylester.
45	20..... 1,4-diaminoanthraquinone-2-carboxylic acid octylester.
21.....	1-amino-4-hydroxyanthraquinone-2-carboxylic acid octylester.
22.....	1-methylamino-4-hydroxyanthraquinone-2-carboxylic acid methylester.

Such a dye may be prepared, e.g., as shown in Japanese Patent 14,315/65, by the esterification of 1-amino-4-amino(or hydroxy)-anthraquinone-2-carboxylic acid with toluenesulfonic acid ester. Or, the dye may also be prepared, as shown in British Patent 790,728, by the esterification of the same anthraquinone-2-carboxylic acid with an alcohol or by converting the 1-position of the 4-position, when the product contains a nitrogroup or a halogen atom at the 1-position or the 4-position into an amino group.

Examples of this invention are explained below.

EXAMPLE 1

Coloring of support

A solution of 10 g. of 1-amino-4-methylaminoanthraquinone-2-carboxylic acid octylester (Dye No. 1 in the above table), 900 g. of ethylene chloride and 100 g. of methanol was mixed uniformly with a solution of 33 kg. of triacetyl cellulose ester, 153 kg. of methylene chloride, 5 kg. of methanol, and 5 kg. of triphenyl phosphate (a plasticizer). The dope thus obtained was cast in a sheet of 0.2 mm. in dry thickness. Thereby there is obtained a blue-dyed film support uniformly absorbing light having from about 600 $m\mu$ to about 690 $m\mu$ but scarcely absorbing short wave length light of from about 400 $m\mu$ to about

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590 $m\mu$. The optical absorption coefficient of the support in the long wave length region was about 0.23. By applying to the support a substratum and then a gelatino silver halide X-ray emulsion followed by drying there is provided a light-sensitive element for X-ray photography.

When the light-sensitive element was developed after light exposure, the photographic properties, such as, desensitization, fog, gamma, and spot, were uninfluenced. Further, since the support had almost no absorption in the short wave length region, a blue X-ray photograph having an improved color purity was obtained.

EXAMPLE 2

Coloring of substratum

By dissolving 2 g. of 1-amino-4-methylaminoanthraquinone-2-carboxylic acid amylester (Dye No. 2) into 98 g. of methylene chloride, a 2% solution of the dye was prepared. The resulting solution (1.5 g.) was mixed with a gelatin dispersion consisting of 1 g. of gelatin, 2 g. of water, 0.5 g. of acetic acid (or 1 g. of salicylic acid), 30 g. of methanol, 60 g. of acetone and 10 g. of methylene chloride to provide a substratum coating composition. When the substratum coating composition was stored for 7 days, no coagulation of gelatin occurred and the dispersion of the gelatin was maintained very stably. The substratum coating composition was applied to the opposite surfaces of a support of a transparent triacetyl cellulose film and dried to provide a film base having dyed substratums. The film thus prepared could absorb, almost smoothly, light in a long wave length region of about 600 to about 690 $m\mu$, and the optical extinction coefficient was about 0.11. By applying a gelatino silver iodobromide X-ray emulsion to the opposite surfaces of the film base having thereon the dyed substratums and drying, a photographic light-sensitive film was obtained. When the light-sensitive film was developed, after exposure, the results were as good as in Example 1.

EXAMPLE 3

Coloring of support

The same procedure as in Example 1 was repeated using 10 g. of 1-amino-4-methylaminoanthraquinone-2-carboxylic acid butyl ester (Dye No. 3) and 5 g. of 1-methylamino-4-hydroxyanthraquinone-2-carboxylic acid methyl ester (Dye No. 22). In this example, however, the thickness of the support formed was 0.15 mm.

By the procedure, a blue violet dyed film base absorbing, almost smoothly, light having a wave length of from about 550 to about 690 $m\mu$, but absorbing almost no light in a short wave length region of from 400 to 500 $m\mu$ was obtained. The optical extinction coefficient of the film base in a long wave length region was about 0.17. Other results were the same as in Example 1, except that the color of the X-ray photography was blue-purple.

EXAMPLE 4

Coloring of substratum

Into 98 g. of methylene chloride was dissolved 2 g. of 1-amino-4-butylaminoanthraquinone-2-carboxylic acid butyl ester (Dye No. 5) to provide a 2% solution of the dye (Solution A). On the other hand, 2 g. of 1-amino-4-anilinoanthraquinone (Color Index No. 61110) was dissolved into 98 g. of methylene chloride to provide a 2% solution of the dye (Solution B).

Using a mixed dye solution of 1.1 g. of Solution A and 2 g. of Solution B, the same procedure as in Example 2 was repeated. The substratum coating composition thus prepared could be stored stably for a long period of time and by the procedure a film base having the substratums colored in blue-violet was obtained. The film absorbed almost no light in a short wave length region of from about 400 to about 500 $m\mu$ and absorbed, almost smoothly, light in a region of from about 550 to about 690 $m\mu$. The extinction coefficient of the film was about 0.15.

A gelatino silver iodobromide X-ray emulsion was ap-

plied to the opposite surfaces of the film base having thereon the substratums colored in blue-violet to provide a photographic light-sensitive X-ray film. When the light-sensitive film was exposed and developed, desensitization and fog formation were not increased and a clear photographic X-ray image was obtained. When the image was observed through it, the eyes were not fatigued. Furthermore, when a pancromatic gelatino silver iodobromide X-ray emulsion was applied to one surface of a film base having a substratum of the same composition, almost the same antihalation and filtering effects were obtained as in the aforesaid case of applying to the opposite surfaces.

EXAMPLE 5

Coloring of support

The same procedure as in Example 1 was repeated using 4 g. of 1,4-bis-methylaminoanthraquinone-2-carboxylic acid amylester (Dye No. 15), 6 g. of 1-amino-4-(4'-methoxy)phenylaminoanthraquinone-2-carboxylic acid octyl ester (Dye No. 10) and 5 g. of 1-amino-4-hydroxyanthraquinone-2-carboxylic acid octylester (Dye No. 21) instead of Dye No. 1 in the same example.

By the procedure, a film base colored in blue-violet was obtained, absorbing, almost smoothly, light in a region of from about 550 to about 695 $m\mu$ but absorbing almost no light in a short wave length region. The extinction coefficient of the film in a long wave length region was about 0.22. By applying a substratum coating composition to the film base and thereafter coating a gelatino silver iodobromide panchromatic negative emulsion thereon followed by drying a lightsensitive film for photographic negative film was obtained. During the preparation of the film, the rolling pressure and the weight of the rolled film were applied to the silver halide emulsion layer, but no bad influence on the photographic properties by pressure, such as, the formation of fog and the like were observed. The film showed also an excellent antihalation effect in a long wave length region.

EXAMPLE 6

Coloring of substratum

Into 958 g. of methylene chloride were dissolved 22 g. of 1-methylamino-4-paratoluidinoanthraquinone-2-carboxylic acid ethylester (Dye No. 13) and 20 g. of o-toluene-azo-o-toluene-azo- β -naphthol (Color index No. 26105; e.g., Oil Red RR made by Orient Co.). The resulting solution (32 g.) was mixed with a gelatin dispersion consisting of 11 g. of gelatin, 20 g. of water, 11 g. of salicylic acid, 250 g. of methanol, 600 g. of acetone and 150 g. of ethylene chloride to provide a colored substratum coating composition. When the substratum coating composition was stored for 7 days, no precipitation and no coagulation of gelatin occurred and the composition was maintained very stably for a long period of time. The substratum coating composition was applied to a surface of a transparent triacetyl cellulose film and dried.

The results showed that the adhesive strength between the substratum and an emulsion layer to be applied to the substratum was as good as the case of adding no dyes. The film base having the substratum colored in blue-violet absorbed, almost smoothly, light in a region of from about 500 to about 700 $m\mu$. The optical extinction coefficient of the film in the long wave region was about 0.13. A gelatino silver iodobromide emulsion for negative photographic film was applied to the surface of the substratum on the film and dried to provide a light-sensitive film for negative photographic film. When the light-sensitive film was developed after exposure, no bad influences on the photographic properties were observed and also the light-sensitive film had a good antihalation effect.

EXAMPLE 7

Coloring of support and substratum

The same procedures as in Example 1 and Example 2 were repeated by using the following dyes individually

instead of using Dye No. 1 and Dye No. 2 in the examples.

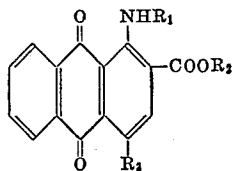
By using dyes of from No. 3 to No. 12 and Dye No. 18, blue film bases having the same absorption properties as in Example 1 and Example 2 were obtained respectively.

By using dyes of from No. 13 to No. 17 and Dye No. 19, cyan-colored film bases absorbing light in a region of from about 610 to about 700 m μ were obtained.

By using Dye No. 20, a blue-violet film base was obtained and by using Dye No. 21 and Dye No. 22, violet film bases were obtained respectively. These film bases thus prepared showed almost no absorption of light in a region of from about 400 to about 550 m μ (from about 400 to about 500 m μ in the case of using Dye 21 and Dye 22) and the photographic properties thereof were better.

What is claimed is:

1. A photographic light-sensitive element comprising a cellulose ester support, at least one substratum, selected from the group consisting of gelatin and cellulose nitrate, and at least one gelatino silver halide emulsion layer, at least one of said substratum and said support containing at least one anthraquinone dye having the following general formula:



wherein R₁ represents a member selected from the group consisting of a hydrogen atom and an alkyl group; R₂ represents a member selected from the group consisting of an alkyl group, a cyclohexyl group and an alkoxyalkyl group; and R₃ represents a member selected from the group consisting of a hydroxy group, an amino group and an NHR group (where R represents a member selected from the group consisting of an alkyl group, a cycloalkyl group, an alkoxyalkyl group, a phenyl group, and a halogen-substituted phenyl group; the total carbon atom number of the aliphatic portions contained in said R₁, R₂ and R₃ being less than 12.

2. The photographic light-sensitive element according to claim 1 wherein said anthraquinone dye is selected from the group consisting of 1-amino-4-methylamino-anthraquinone-2-carboxylic acid octylester, and 1-methyl-amino-4-hydroxyanthraquinone-2-carboxylic acid methyl-ester.

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