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[54] PHOTOGRAPHIC PAPER FOR RAPID STABILIZING PROCESS

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[58] **Field of Search** 96/61, 95, 137

[56] **References Cited**

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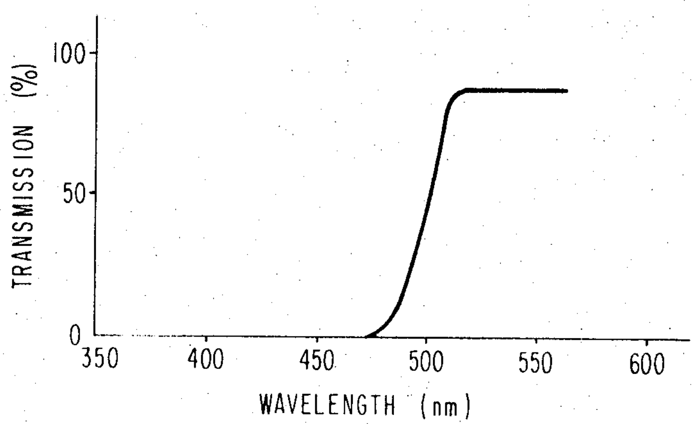
[57] **ABSTRACT**

A photographic paper for a rapid stabilizing process coated with a silver halide photographic emulsion containing a specific carboxyalkyl-containing sensitizing dye is disclosed. This specific dye is highly sensitive to green light in flash exposure, and does not remain unbleached after stabilization with a stabilizing solution containing a sulfurous acid radical-containing compound or sulfite adduct of formaldehyde. The photographic paper is especially useful for high speed transmission and recording of information.

5 Claims, 1 Drawing Figure



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PHOTOGRAPHIC PAPER FOR RAPID STABILIZING PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a photographic paper for a rapid stabilizing process. More specifically, this invention relates to a photographic paper for a rapid stabilizing process which has a high sensitivity to green light in flash exposure and a reduced amount of dye remaining after the stabilization treatment. The terms "flash exposure" and "remaining of dye" will be defined later on.

2. Description of the Prior Art

With the advent of the age of information, various systems for the rapid transmission of information have been developed. They include, for example, a press facsimile system for transmitting a newspaper manuscript rapidly to a remote locality, a high speed phototypesetting system for rapidly setting up a form, and a cathode ray tube display system which immediately transforms the information produced by an electronic computer into letters or figures. Exposure for a time as short as less than one one-hundred thousandth of a second, especially about one one-millionth of a second, is frequently used in the equipment for these rapid information transmitting systems. In recent years, there has been a very brisk demand for photographic materials for use on such equipment.

Two types of light sources, a xenon flash lamp and a cathode ray tube, are used in such equipment. As the cathode ray tube, those generally known to be used for flying spot which have a fluorescent substance of a short afterglow time are used. For example, fluorescent substances such as those called "**P-11**," "**P-15**," "**P-16**," and "**P-24**" are used. It is known that in an emission spectroscopic energy distribution, a peak exists at **460** nm for **P-11**, and at **385** nm for **P-16**. Since such a distribution corresponds to the spectral sensitivity area inherent to a photosensitive silver halide, the spectral sensitization of photographic materials to be exposed to these fluorescent substances is not particularly necessary. On the other hand, "**P-15**" is known to have a peak at 505 nm in its emission spectroscopic energy distribution, and "**P-24**," at 520 nm. Sensitivity to green light needs to be imparted to photographic materials for recording images on such cathode ray tubes.

The xenon lamp emits light of a relatively wide range of wavelength. Radiation leaving the light source converges through a condenser lens, a negamatrix, a main lens, a prism, a reflector, or a special lens or prism for letter deformation or other purposes, and forms an image on the light-sensitive surface of a photographic material. Because of the optical system provided in the path of this light, radiation of shorter wavelengths is absorbed to a greater extent, and the light which has reached the light-sensitive surface contains a reduced proportion of radiation in a range from the ultraviolet to blue, and a larger proportion of green light or radiation of longer wavelengths. For this reason, it is essential to subject the photographic material to green color sensitization so that its overall sensitivity will be increased.

As previously stated, the afterglow time of the luminescence of a cathode ray tube is as short as one ten-millionth of a second to one one-hundred thousandth of a second. The xenon flash lamp used in the above-described information transmitting systems also has an afterglow time much the same as this. The term "flash exposure," as used in the present specification, generally refers to such a short time exposure to these light sources.

Photographic papers used in these information transmitting systems should desirably be subjected to a rapid processing corresponding to the rapidity of the systems. Thus, instead of the conventional processing including development, stopping, fixation, rinsing and drying (or ferrotype finishing) which has previously been practiced in processing photographic paper, a rapid processing based on an activator development-stabilization processing system is frequently used.

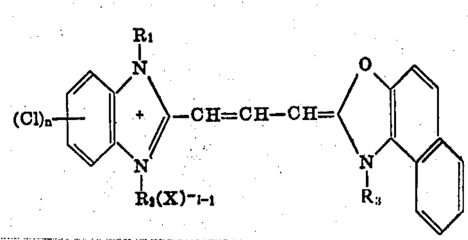
In rapid development using an activator, the use of a silver halide emulsion containing silver chloride, such as a pure chloride emulsion, chlorobromide emulsion, iodochloride emulsion or chloroiodobromide emulsion, is preferred in order to increase the rate of the development. Such an emulsion is poor in spectral sensitization efficiency in comparison with a pure silver bromide emulsion or silver iodobromide emulsion. Furthermore, conventional sensitization dyes have a tendency to reduced efficiency of spectral sensitization in flash exposure.

When a photographic material is rapidly stabilized in a stabilization bath, the sensitization dye of the material frequently remains unbleached or is not washed out, in comparison with a photographic material processed through fixation and rinsing steps. It is desired therefore that the sensitization dye used on such a photographic material should be rapidly destroyed and bleached in a stabilization or activator bath. In the present specificaton, the term "remaining of dye" refers to the phenomenon in which the sensitization dye remains unbleached after completion of the processing, coloring the surface of a photographic paper.

An object of the present invention is to provide a photographic paper for a rapid stabilizing process, using a specific sensitizing dye which imparts to the photographic paper a high sensitivity to green light and hardly remains unbleached after the stabilization processing of the photographic paper.

SUMMARY OF THE INVENTION

The object of this invention can be achieved by using a carboxy-alkyl-containing sensitizing dye expressed by the general formula (I)



wherein R_1 and R_3 each represent an alkyl group such as a methyl group, an ethyl group, an iso-propyl group or an n-propyl group, R_2 is a carboxyalkyl group such as a carboxymethyl group, a β-carboxyethyl group, a γ-carboxypropyl group, a δ-carboxybutyl group, or an ω-carboxypentyl group, n is 1 or 2, X^- represents an anion, and l is 1 or 2, in which where l is 1, this dye forms an intramolecular salt. A photographic paper coated with a silver halide emulsion containing this sensitizing dye is developed, and then is stabilized with a stabilizing solution containing a sulfurous acid radical or sulfite addition product.

DESCRIPTION OF THE INVENTION

The characteristic feature of the chemical structure of the sensitizing dye used in the invention consists in the substituent R_2. As will be shown later in the Examples, the compound of the formula (III) in which R_2 is an alkyl group imparts good spectral sensitivity to the emulsion but remains to a great extent on photographic paper after the stabilization processing. On the other hand, the compound of the formula IV in which R_2 is a sulfoalkyl group hardly remains after completion of the processing but has a reduced spectral sensitivity. Only when R_2 is a carboxyalkyl group can satisfactory results be obtained both in spectral sensitization and remaining of dye.

The sensitizing dyes of this invention exhibit a strong green sensitizing effect not only on a gelatin-silver halide emulsion but also on one not containing silver chloride. This effect is the same in flash exposure. When a photographic material containing such a dye is developed and then stabilized, the color is bleached, and the resulting image has good whiteness.

The sensitizing dyes used in the invention enable silver halide photographic emulsions containing them to be sensitized spectrally. Such dyes are particularly useful for widening the spectral sensitive area of a gelatin-silver halide emulsion, but also can sensitize fully photographic emulsions containing a water-permeable colloid, such as a water-soluble cellulose derivative, polyvinyl alcohol, or other hydrophilic synthetic or natural resin or polymer instead of gelatin.

A photographic emulsion used for the photographic paper of the invention may be prepared by adding one or several dyes to a photographic emulsion using customary methods. It is the general practice to add the dyes as a solution in a suitable solvent. The concentration of the dye in the emulsion may be varied over a wide range, for example, from 1 to 200 mg per kilogram of the emulsion according to the effect desired. Conventional additives, such as stabilizers, toning agents, hardening agents, wetting agents, antifoggants, plasticizers, development accelerators, and fluorescent whitening agents, may be added further to the emulsion using customary methods in the preparation of the photographic emulsion used in the invention. A developing agent for activator development, for example, hydroquinone, may also be added to the emulsion using customary methods.

The photographic emulsion so prepared may be coated on a suitable paper support, such as a photographic raw paper, a baryta paper, a resin soaked paper or a resin-coated paper, using customary methods.

According to the present invention, there can be obtained a photographic paper which is especially suitable for high speed transmitting and recording of information, which has a high sensitivity in an orthochromatic spectral region of green light and a sufficiently low sensitivity to red light, and in which the sensitizing dye is readily bleached by the stabilization processing and the resulting image after the processing is free from the remaining of the dye. The photographic paper of the invention should desirably be subjected to the rapid

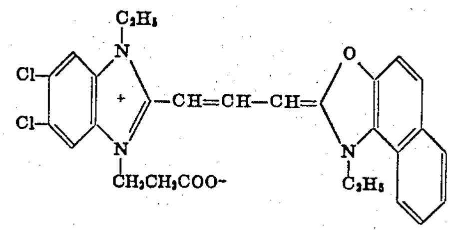
activator development in view of its uses, but may also be developed in the usual manner.

The stabilizing processing solution used in the invention contains a thiosulfate or thiocyanate usually employed and also a sulfite salt or sulfite addition product (e.g., an adduct of formaldehyde with sulfurous acid). The sensitizing dye expressed by the general formula (I) may be prepared by a known method based on the disclosure appearing in Belgian Patent No. 693,303, for example.

An example of the synthesis of the sensitizing dye used in the invention is given briefly below.

SYNTHESIS EXAMPLE

Five grams of 2-(β-acetoanilide vinyl)-3-ethyl-naphtho[1,2-d]oxazolium iodide, 5 g of 3-(β-carboxyethyl)-5, 6-dichloro-1-ethyl-2-methyl-benzimidazolium bromide, and 4 ml of triethylamine were reacted in 100 ml of ethanol by heating for 1 hour. The solvent was concentrated, and the crystals precipitated were recovered by filtration. Recrystallization of the crystals from methanol gave a dye of the following formula (II) having a melting point of 214°C in an amount of 2.4 g. It had a maximum spectral absorption at 505 nm (in methanol).



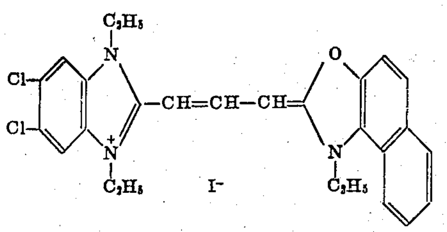
(II)

The invention will be specifically described by reference to the following Examples which are presented for illustrative purposes and not intended in any way to limit the invention.

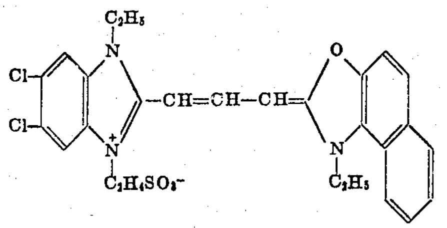
EXAMPLE 1

A methanol solution of 0.005 milligram equivalent of the dye having the structure expressed by the formula (II) above was added to 100 g of a photographic emulsion containing a silver halide composed of 50 mole percent silver chloride and 50 mole percent silver bromide (containing 23 milligram equivalents of silver and 12 grams of gelatin). Saponin (0.06 g) as a wetting agent and 0.27 g of formaldehyde as a hardener were further added. The resulting coating solution was coated on a polyethylene-coated paper (the amount of silver coated 1.4 mg/dm²).

To prepare samples for comparison purposes, three photographic emulsions of the same composition as above each weighing 100 g were prepared, and 0.005 milligram equivalent of the dye having the formula (III) was added to one of these emulsions and 0.005 milligram equivalent of the dye having the formula (IV) to another of these emulsions. The same additives as used above were added to each of the three emulsions in the same manner as set forth above. Each of the resulting coating solutions was applied to a polyethylene-coated paper as described above.



(III)



(IV)

Each of the samples was exposed for one one-hundredth of a second and one one-millionth of a second, respectively, through a V–Y 50 color glass filter (product of Tokyo Shibaura Electric Co., Ltd., Japan), and an optical wedge using a Mark VII sensitometer (EG & G Company, U.S.A.). The accompanying drawing is a graphical representation showing the relationship of the transmittance of the V–Y 50 color glass filter used in the Examples to wavelength of light. As shown in the drawing, this filter absorbs light of wavelengths corresponding to the sensitivity region inherent to silver halide, and allows the transmission of light of wavelengths above about 500 nm which corresponds to the spectral sensitivity region.

The exposed sample was developed for 2 minutes at 20°C in a developing solution of the following formulation.

N-Methyl para-aminophenol	2 g
Anhydrous Sodium Sulfite	30 g
Hydroquinone	7 g
Sodium Carbonate Monohydrate	53 g
Potassium Bromide	1.5 g
Water to make	1 liter

The developed sample was stabilized by immersion for 5 seconds in a stabilizing solution of the following formulation.

Ammonium Thiocyanate	250 g
Sodium Bisulfite	125 g
Acetic Acid to adjust the pH to	5.0
Water to make	1 liter

The reflection density of the image obtained was measured. The sensitivity value was expressed as the reciprocal of the amount of light which gives a density of 0.5. This sensitivity value was a relative value since an absolute amount of light through the filter was not measured. But in Table 1 below, the sensitivity for a given exposure time could be compared.

As to the remaining of dye, the reflection density through a green filter set down by the ASA standard in the densitometry of a color photographic paper was measured. The reflection density of the control sample was set at 0.

The results obtained are shown in Table 1.

TABLE 1

	Green Light Sensitivity at Exposure for 1/100th Second (relative values)	Green Light Sensitivity at Exposure for 1/1,000,000th Second (relative values)	Remaining of Dye
Control Sample	Not Sensitive	Not Sensitive	0.00
Sample Containing Dye (II)	421	220	0.03
Sample Containing Dye (III)	423	205	0.15
Sample Containing Dye (IV)	406	170	0.02

These results demonstrate that dye (II) of the invention has a high sensitivity to green light in flash exposure and little remains after processing.

EXAMPLE 2

One hundred grams each of four photographic emulsions (silver content 45 milligrams equivalent, gelatin content 12 g) containing a silver halide composed of 29 mole percent silver chloride, 70 mole percent silver bromide and 1 mole percent silver iodide were prepared. To three of them, 0.012 milligram equivalent each of the three dyes (II), (III) and (IV) was added respectively. Sodium benzinesulfinate (0.2 g) as an antioxidant, 2.3 g of hydroquinone as a developing agent for activator development, 0.25 g of 4(N,N-diethylamino)-2,6-xylenol hydrochloride as a development accelerator, 0.06 g of saponin as a wetting agent, and 0.24 g of formaldehyde as a gelatin hardener were further added to each of the emulsions. The resulting coating solution was coated on baryta paper (the amount of silver coated 1.6 milligram equivalents/dm^2).

The photographic paper so produced was exposed in the same manner as set forth in Example 1, and processed by Industrial Processor C–230 (Fuji Photographic Film Co., Ltd.) using a sodium hydroxide solution having a pH of 13.3 as an activator and a solution containing 250 g/liter of ammonium thiocyanate, and 160 g/liter of an adduct of formaldehyde with sodium bisulfite as a stabilizer.

The sensitivity to green light and the remaining of dye were determined in the same way as set forth in Example 1 from the reflection density of the resulting image.

The results obtained are shown in Table 2.

TABLE 2

	Green Light Sensitivity at Exposure for 1/100th Second (relative values)	Green Light Sensitivity at Exposure for 1/1,000,000th Second (relative values)	Remaining of Dye
Control Sample	Not Sensitive	Not Sensitive	0.00
Sample Containing Dye (II)	352	370	0.05
Sample Containing Dye (III)	350	360	0.16
Sample Containing Dye (IV)	237	246	0.03

The results demonstrate that dye (II) of the invention has a high sensitivity to green light in flash exposure and remains little after processing.

EXAMPLE 3

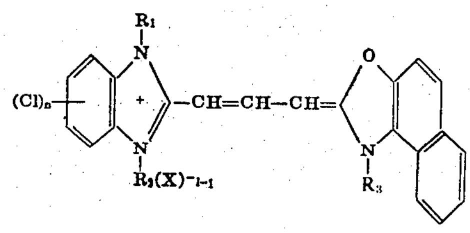
The procedure of Example 2 was repeated using photographic emulsions containing a silver halide composed of 98 mole percent silver bromide and 2 mole percent silver iodide (containing 45 milligram equivalents of silver and 15 grams of gelatin per 100 grams of the emulsion). The results obtained are shown in Table 3 below.

TABLE 3

	Green Light Sensitivity at Exposure for 1/100th Second (relative values)	Green Light Sensitivity at Exposure for 1/1,000,000th Second (relative values)	Remaining of Dye
Control Sample	Not Sensitive	Not Sensitive	0.00
Sample Containing Dye (II)	545	530	0.03
Sample Containing Dye (III)	550	515	0.14
Sample Containing Dye (IV)	380	350	0.04

What is claimed is:

1. A photographic paper capable of being stabilized with a stabilizing solution containing a sulfurous acid radical-containing compound or a sulfite addition product after exposure and development, comprising a photographic paper coated with a silver halide emulsion containing a sensitizing dye having the following general formula



wherein each of R_1 and R_3 is an alkyl group, R_2 is a carboxyalkyl group, *n* is 1 or 2, X^- is an anion, and *l* is 1 or 2.

2. The photographic paper according to claim 1, wherein R_1 and R_3 are ethyl groups, R_2 is a β-carboxyethyl group, *n* is 2 and wherein the chlorine atoms are at the 5- and 6-positions of the benzene ring, and *l* is 1.

3. In a process for processing an exposed photographic paper which comprises developing said paper and stabilizing said developed paper, the improvement which comprises said paper being the photographic paper of claim 1 and wherein said stabilizing is with a solution containing a stabilizing member selected from the group consisting of a sulfurous acid radical-containing compound and a sulfite addition product.

4. The process of claim 3, wherein said stabilizing member is sodium bisulfite.

5. The process of claim 3, wherein said stabilizing member is an adduct of formaldehyde with sodium bisulfite.

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