

[54] LIGHT-SENSITIVE COLOR
PHOTOGRAPHIC MATERIAL

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[58] Field of Search **96/84 UV; 252/300**

[56] **References Cited****UNITED STATES PATENTS**

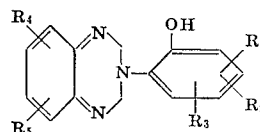
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[57] **ABSTRACT**

A light-sensitive silver halide color photographic material comprising one or more layers. At least one layer constituting the photographic material contains a dispersion in a difficulty water-soluble high boiling organic solvent, either singly or in admixture with a low boiling organic solvent, of two or more compounds represented by the general formula



wherein R₁, R₂ and R₃ are individually a hydrogen or halogen atom or a cycloalkyl, alkoxy, aryl, carbalkoxy or alkylsulfone group having one to six carbon atoms and at least one of the groups R₁, R₂ and R₃ is not hydrogen; R₄ and R₅ are individually a hydrogen or halogen atom or an alkyl, cycloalkyl, alkoxy, aryl, carbalkoxy or alkylsulfone group having one to six carbon atoms; and the sum of the carbon atoms of R₁, R₂ and R₃ is 8 or less, provided that in case the sum of the carbon atoms of R₁, R₂ and R₃ is 8, each of R₁, R₂ and R₃ has less than four carbon atoms.

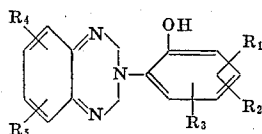
5 Claims, No Drawings

LIGHT-SENSITIVE COLOR PHOTOGRAPHIC MATERIAL

CROSS RELATED APPLICATION

This application is a continuation of application Ser. No. 889,298 filed Dec. 30, 1969 and now abandoned.

The present invention relates to light-sensitive color photographic materials containing ultraviolet ray absorbers. More particularly, the invention pertains to light-sensitive color photographic materials having incorporated in at least one of the layers constituting the photographic materials a solvent dispersion containing two or more compounds represented by the general formula



wherein R_1 , R_2 and R_3 are individually a hydrogen or halogen atom or cycloalkyl, alkoxy, aryl, carbalkoxy or alkylsulfone group having one to six carbon atoms, and at least one of said R_1 , R_2 and R_3 is not hydrogen; R_4 and R_5 are individually a hydrogen or halogen atom or an alkyl, cycloalkyl, alkoxy, aryl, carbalkoxy or alkylsulfone group having one to six carbon atoms; and the sum of the carbon atoms of R_1 , R_2 and R_3 is 8 or less, provided that in case the sum of the carbon atoms of R_1 , R_2 and R_3 is 8, each of R_1 , R_2 and R_3 has less than four carbon atoms.

It is well known that ultraviolet rays have detrimental effects on photographic images. Particularly in the case of a light-sensitive color photographic material which forms, by color development, a dye image on its light-sensitive emulsion layer, the said dye image is unstable to ultraviolet rays and hence is liable to be decolorized or discolored when subjected to the action of ultraviolet rays. Further, there is the fear that after formation of said dye image, a coupler remaining in the light-sensitive emulsion layer of the color photographic material brings about, due to the action of ultraviolet rays, a cause for contamination of the dye image.

In order to protect photographic images from such action of ultraviolet rays, various processes have been proposed heretofore. Among these, the most common process is such that a ultraviolet ray absorber is incorporated into a layer constituting a light-sensitive photographic material, e.g. silver halide emulsion layer, protective layer, inter layer or the like. However, light-sensitive photographic materials according to the prior art processes are not satisfactory in protection of photographic images from ultraviolet rays, and have such drawbacks that they are inferior in photographic properties or become unstable in properties when stored for a long period of time.

In view of such circumstances as mentioned above, the present inventors made various studies for years to find that a light-sensitive color photographic material, which is obtained by incorporating an organic solvent dispersion containing two or more compounds represented by the aforesaid general formula into at least one of the layers constituting the light-sensitive photographic material, is markedly excellent in protection of

the photographic image from ultraviolet rays and is storage stable for a long period of time without being deteriorated in photographic properties.

The compounds represented by the aforesaid general formula are excellent ultraviolet ray-absorbing agents when effectively absorb ultraviolet rays without absorbing visible rays, are substantially colorless, and are so stable to ultraviolet rays that they are not injured in photographic properties or contaminated even when irradiated with ultraviolet rays. However, such excellent characteristics are not exhibited if said compounds are incorporated into layers constituting a light-sensitive photographic material by the Fischer's method (a method carried out by introducing a soluble group such as carboxyl or sulfone group into a ultraviolet ray-absorbing agent, which has been made non-diffusible, to form a water-soluble alkali metal salt thereof and then incorporating said alkali metal salt in a hydrophilic colloid layer). Further, if only one compound represented by the aforesaid general formula is applied to a light-sensitive photographic material by adoption of the solvent dispersion method (a method carried out in such a manner that a non-diffusible ultraviolet ray-absorbing agent having an oleophilic group is dissolved in an organic solvent and is immediately dispersed in an aqueous gelatine solution), crystals of said compound deposit to greatly injure the photographic properties of the material, because the compounds of the aforesaid general formula are extremely low in solubility in organic solvents. If, in the above case, the amount of the solvent is so increased as not to deposit the crystals of the compound, a large amount of the organic solvent is necessarily incorporated into the layers constituting the photographic material, whereby the penetration of other treating liquids into said layers is inhibited or physical properties of said layers are undesirably deteriorated.

In contrast thereto, when two or more of the compounds represented by the aforesaid general formula are subjected, according to the present invention, to the solvent dispersion method, the compounds show markedly excellent solubility for the organic solvent employed in said method, as is clear from the test Example set forth later. This has not been anticipatable heretofore.

Typical examples of the compounds represented by the aforesaid general formula, which are used in the present invention, are set forth below together with the absorption maximum wave lengths thereof in methanol (λ_{max}^{MeOH}), but it is needless to say that compounds usable in the present invention are not limited thereto.

1. 2-(2'-Hydroxyphenyl-5'-*t*-butoxyphenyl)-benzotriazole
 λ_{max}^{MeOH} 335 m μ
2. 2-(2'-Hydroxy-5'-ethoxyphenyl)-benzotriazole
 λ_{max}^{MeOH} 338 m μ
3. 2-(2'-Hydroxy-5'-methoxyphenyl)-benzotriazole
 λ_{max}^{MeOH} 350 m μ
4. 2-(2'-Hydroxy-5'-cyclohexoxyphenyl)-benzotriazole
 λ_{max}^{MeOH} 340 m μ
5. 2-(2'-Hydroxy-5'-phenylphenyl)-methoxybenzotriazole
 λ_{max}^{MeOH} 340 m μ
6. 2-(2'-Hydroxy-5'-cyclohexylphenyl)-benzotriazole
 λ_{max}^{MeOH} 338 m μ
7. 2-(2'-Hydroxy-5'-phenylphenyl)-benzotriazole
 λ_{max}^{MeOH} 340 m μ

8. 2-(2'-Hydroxy-5'-methoxyphenyl)-5,6-dimethylbenzotriazole

λ_{max}^{MeOH} 342 m μ

9. 2-(2'-Hydroxy-5'-methoxyphenyl)-5-methylbenzotriazole

λ_{max}^{MeOH} 350 m μ

10. 2-(2'-Hydroxy-5'-phenylphenyl)-5-butoxybenzotriazole

λ_{max}^{MeOH} 345 m μ

11. 2-(2'-Hydroxy-5'-methoxyphenyl)-benzotriazole-5-ethylsulfone

λ_{max}^{MeOH} 350 m μ

12. *t*-Butyl-2-(2'-hydroxy-5'-methoxyphenyl)-benzotriazole-5-carboxylate

λ_{max}^{MeOH} 340 m μ

13. 2-(2'-Hydroxy-5'-chlorophenyl)-5-chlorobenzotriazole

λ_{max}^{MeOH} 335 m μ

14. 2-(2'-Hydroxy-5'-phenylphenyl)-5-chlorobenzotriazole

λ_{max}^{MeOH} 342 m μ

15. 2-(2'-Hydroxy-5'-cyclohexylphenyl)-5-chlorobenzotriazole

λ_{max}^{MeOH} 342 m μ

16. 2-(2'-Hydroxy-4', 5'-dichlorophenyl)-benzotriazole

λ_{max}^{MeOH} 334 m μ

17. *t*-Butyl 2-(2'-hydroxy-5'-ethoxyphenyl)-benzotriazole-5-carboxylate

λ_{max}^{MeOH} 342 m μ

18. 2-(2'-Hydroxy-3',5'-dichlorophenyl)-5-methoxybenzotriazole

λ_{max}^{MeOH} 350 m μ

19. 2-(2'-Hydroxy-4',5'-dichlorophenyl)-5-methylbenzotriazole

λ_{max}^{MeOH} 348 m μ

20. *t*-Butyl-2-(2'-hydroxy-4'-methoxyphenyl)-benzotriazole-5-carboxylate

λ_{max}^{MeOH} 347 m μ

21. 2-(2'-Hydroxy-4'-butoxyphenyl)-benzotriazole-5-ethylsulfone

λ_{max}^{MeOH} 351 m μ

The following test example shows the fact that when two or more of the above-mentioned compounds are used in combination, they interact each other to exhibit markedly excellent solubility in organic solvents.

TEST EXAMPLE

Two or more of the compounds represented by the aforesaid general formula were mixed with each other in the proportions as shown in Table 1, and the mixture was dissolved at 65°C. in a mixed solvent comprising 1 ml. of tri-*o*-cresyl phosphate and 2 ml. of ethyl acetate and was dispersed in 10 ml. of a 5 percent gelatine solution containing 0.1 g. of saponin. Thereafter, the dispersion was added to 100 ml. of a silver chlorobromide emulsion, was coated onto a photographic baryta paper, and was then dried to prepare a sample. Each sample prepared in the above manner was microscopically observed in dispersed state of the ultraviolet ray-absorbing agent to obtain the results as set forth in the right hand column of Table 1.

The amounts of the tri-*o*-cresyl phosphate necessary for individual dispersion of the exemplified compounds (2), (9), (18) and (19) were 7 ml., 6.5 ml., 5 ml. and 4 ml., respectively. Further, the amount of ethyl acetate employed in the above case was 2 ml., and no influ-

ence on dispersibility was observed even when said amount was varied.

TABLE 1

Exemplified compound Run No.	(2)	(9)	(18)	(19)	Deposition
1	1.0				Great
2		1.0 g			Great
3			1.0 g		
4				1.0 g	Great
5	0.5	0.5			None
6	0.5		0.5		None
7	0.5			0.5	None
8		0.5	0.5		None
9		0.5		0.5	None
10			0.5	0.5	None
11	0.33	0.33	0.33		None
12	0.33	0.33		0.33	None
13	0.33		0.33	0.33	None
14		0.33	0.33	0.33	None
15	0.25	0.25	0.25	0.25	None

From the above test example, it is clear that when used in combination of two or more in accordance with the present invention, the compounds represented by the aforesaid general formula, which have substituents less in molecular weight in view of the fundamental structure for ultraviolet ray-absorbing characteristics, are greatly increased in solubility in organic solvents employed in the solvent dispersion method to make it possible to attain successfully far higher ultraviolet ray-absorbing efficiencies than those of the conventional ultraviolet ray-absorbing agents. Accordingly, the light-sensitive color photographic materials in accordance with the present invention have such advantages that the dye images obtained are greatly inhibited from decoloration, discoloration or contamination due to irradiation of ultraviolet rays, and are not colored or contaminated by the ultraviolet ray-absorbing agents themselves. Further, they are free from the fear that the photographic properties thereof would be injured, because of the decrease in amount of organic solvents dispersed in layers of the photographic materials, and stably maintain excellent photographic properties.

When specifically used in combination, the ultraviolet ray-absorbing agents employed in the present invention become soluble in a markedly small amount of organic solvent, as mentioned above. Accordingly, the incorporation of said agents into layers of light-sensitive photographic materials may be effected according to the conventional solvent dispersion method, whereby they can be dispersed uniformly and stably in a finely-divided non-crystalline form into any one of the layers constituting light-sensitive photographic materials. For example, there may be adopted such procedures that a mixture of two or more members selected from the above-mentioned ultraviolet ray-absorbing agents is dissolved in an organic solvent employed in the solvent dispersion method and is then dispersed in an aqueous gelatine solution by use of a suitable mixing

means, and the resulting dispersion, when desired to be added to a silver halide emulsion, is added thereto after completion of the second ripening, and when desired to be incorporated into an auxiliary layer, e.g. a protective layer or an inter layer, is added to a coating liquid which is the component of said layer. As the coating liquids which are the components of the silver halide emulsion layer and auxiliary layers constituting light-sensitive photographic materials, there may be used those which have been employed heretofore, and the ultraviolet ray-absorbing agents used in the present invention do not show any detrimental interactions with various photographic additives present in said coating liquids. Further, the organic solvent solutions of the above-mentioned ultraviolet ray-absorbing agents may be incorporated with couplers, contamination-preventing agents, fluorescent whitening agents, etc. Ordinarily, the total amount of the ultraviolet-ray-absorbing agents is preferably 1-10 mg per 100 cm² of the area to be coated. In the above case, the mixing proportions of the ultraviolet ray-absorbing agents used in combination are equal proportions. However, the mixing proportions are, of course, not limited thereto and are variable according to the object of application.

The amount of organic solvent necessary for dispersing 1 g. of a mixture of the ultraviolet ray-absorbing agents is adequately about 0.5 ml. to 3 ml., though the amount varies depending on the combination and mixing proportions of the ultraviolet ray-absorbing agents employed and on the kind of the organic solvent. The organic solvent employed in the above case may be any of those which have heretofore been used in the solvent dispersion method. For example, there is used a difficulty water-miscible high boiling solvent having a boiling point of more than 150°C. such as di-n-butyl phthalate, triphenyl phosphate, tri-o-cresyl phosphate or the like, either singly or in combination with a low boiling solvent such as methyl acetate, ethyl acetate, propyl acetate, n-butyl acetate, ethyl propionate, carbon tetrachloride, chloroform, methanol, ethanol, dimethylformamide, dioxane, methyl cellosolve acetate or the like.

The light-sensitive color photographic materials of the present invention, which are produced in the above-mentioned manner, have such advantages that the ultraviolet ray-absorbing agents contained therein do not crystallize and deposit during the production and storage of the photographic materials and photographic properties can be stably maintained even when they are irradiated with ultraviolet rays.

The present invention is illustrated in detail below with reference to examples.

EXAMPLE 1

Onto a photographic baryta paper was applied a red color-sensitive silver chlorobromide gelatine emulsion containing a cyan coupler. Thereafter, a gelatine protective layer containing one or more of the exemplified compounds (2), (9), (18) and (19) in such proportions as set forth in Table 2 was applied so that the amount of the ultraviolet ray-absorbing agent became 2.8 mg/100 cm², followed by drying. In the above manner, there were prepared samples 1-9 of which sample 1 was a so-called blank sample containing no ultraviolet ray-absorbing agent.

In the application of the above-mentioned gelatine protective layer, there was used a liquid formed by dis-

solving at 65°C. 3 parts of the ultraviolet ray-absorbing agent(s) in a mixed solvent comprising 6 parts of ethyl acetate and 3 parts of tri-o-cresyl phosphate, adding the resulting solution to 60 parts of a 10 percent aqueous gelatine solution containing saponin, dispersing the mixed solution by means of a colloid mill and then adding 40 parts of water to the resulting dispersion.

The above-mentioned samples were exposed to light, were subjected to color development, stopping, film hardening-fixing, bleaching-fixing and water-washing treatments, and were then dried. The red color densities of cyan images of these samples and the contamination densities (measured on the basis of blue color densities) of non-image portions thereof were measured before and after exposure to direct sunlight for 50 hours to calculate the red color density lowering ratios and contamination densities of the samples. The results were as set forth in Table 3.

TABLE 2

Exemplified compound Sample No.	(2)	(9)	(18)	(19)	Total amount
1					0 g
2	3				3
3		3			3
4			3		3
5				3	3
6	1.5		1.5		3
7	1.5			1.5	3
8	1		1	1	3
9		1	1	1	3

TABLE 3

Sample No.	Red color density lowering ratio (%)	Contamination density Before test	After test
1	60	0.04	0.18
2	58	0.04	0.18
3	55	0.04	0.17
4	57	0.04	0.16
5	51	0.04	0.15
6	13	0.04	0.06
7	10	0.04	0.05
8	11	0.04	0.04
9	10	0.04	0.05

From Table 3, it is understood that in the case of samples 2-5 prepared by independent use of the exemplified compounds (2), (9), (18) and (19), the ultraviolet ray-absorbing agents had crystallized and deposited, and hence were lowered in ultraviolet ray-absorbing ability to inhibit only slightly the discoloration of color images and the generation of contamination. On the other hand, in the case of the samples 6-9 in accordance with the present invention, the discoloration of cyan dyes and increase of contamination were greatly inhibited.

EXAMPLE 2

Onto a photographic baryta paper was applied a samples color-sensitive silver chlorobromide gelatine emulsion layer containing a magenta coupler, which layer had been incorporated according to the same procedure as in Example 1 with a liquid containing one or more of the exemplified compounds (1), (8), (11) and

(20) in such proportions as set forth in Table 4, so that the amount of the ultraviolet ray-absorbing agent(s) became 8.2 mg/100 cm², followed by drying. In the above manner, there were prepared samples 1-8, of which sample 1 was a blank sample.

The green color densities of image portions of these samples and the contamination densities (measured on the basis of blue color densities) of white grounds thereof were measured before and after exposure to Fade-Ometer to calculate green color density lowering ratios and contamination densities of the samples. The results were as set forth in Table 5.

TABLE 4

Exemplified compound No.	(1)	(8)	(11)	(20)	Total amount
1					0 g
2	1				1
3		1			1
4			1		1
5				1	1
6	0.25	0.25	0.25	0.25	1
7	0.33	0.33	0.33		1
8	0.5	0.5			1

TABLE 5

Sample No.	Green color density lowering ratio (%)	Contamination density Before test	After test
1	19	0.04	0.11
2	17	0.04	0.10
3	17	0.04	0.11
4	15	0.04	0.09
5	16	0.04	0.10
6	4	0.04	0.05
7	4	0.04	0.05
8	5	0.04	0.06

From Table 5, it is understood that in the case of the samples 6-8 in accordance with the present invention, the discoloration of magenta dye and the increase of contamination were greatly inhibited.

EXAMPLE 3

Onto a photographic baryta paper were applied a red color-sensitive silver chlorobromide emulsion layer containing a cyan coupler, and a green color-sensitive silver chlorobromide emulsion layer containing a magenta coupler. Further, a gelatine inter layer containing one or more of the exemplified compounds (2), (7), (15) and (21) in such proportions as shown in Table 6 was applied thereon so that the amount of the ultraviolet ray-absorbing agent(s) became 0.4 mg/100 cm². In addition, a blue color-sensitive silver chlorobromide emulsion layer containing a yellow coupler, which layer had been incorporated with one or more of the exemplified compounds (2), (7), (15) and (21) in the proportions as shown in Table 6, was applied so that the amount of the ultraviolet ray-absorbing agent(s) became 1.0 mg/100 cm², and then a gelatine protective layer was applied, followed by drying. In the above manner, there were prepared samples 1-9, of which sample 1 was a blank sample.

The gelatine layer and the blue color-sensitive silver chlorobromide emulsion layer containing the exempli-

fied compounds (2), (7), (15) and (21) in such proportions as shown in Table 6 were prepared individually by dissolving at 65°C. 4 parts of one or more of the ultraviolet ray-absorbing agents in a mixed solvent comprising 3 parts of triphenyl phosphate and 10 parts of butyl acetate, adding the resulting solution to 100 parts of a 10 percent solution containing saponin, dispersing the mixed solution by means of an ultrasonic emulsifier, and then adding the dispersion to 40 parts of water or to 200 parts of a blue color-sensitive silver chlorobromide emulsion.

The above-mentioned samples 1-9 were exposed, were subjected to color development, stopping, film hardening, fixing, bleaching fixing and water-washing treatments, and were then dried. The blue, green and red color densities of image portions of these samples and the contamination densities (measured on the basis of blue color densities) of white grounds thereof were measured before and after exposure to direct sunlight for 6 hours to calculate individual color density lowering ratios and contamination densities. The results were as set forth in Table 7.

TABLE 6

Exemplified compound Sample No.	(2)	(7)	(15)	(21)	Total amount
1					0 g
2	4				4
3		4			4
4			4		4
5				4	4
6	2		2		4
7	2			2	4
8			2	2	4
9	1	1	1	1	4

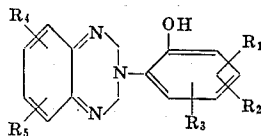
TABLE 7

Sample No.	Blue color	Density lowering ratio (%) Green color	Red color	Contamination density Before test	After test
1	41	50	63	0.09	0.23
2	40	50	60	0.09	0.23
3	38	49	60	0.09	0.23
4	38	47	58	0.09	0.21
5	35	47	56	0.09	0.19
6	3	5	8	0.09	0.10
7	3	6	7	0.09	0.10
8	2	4	5	0.09	0.11
9	1	4	8	0.09	0.09

As is clear from Table 7, the samples 6-9 in accordance with the present invention are markedly less in discoloration of individual color densities and in increase of contamination.

What we claim is:

1. A light-sensitive silver halide color photographic material comprising one or more layers wherein at least one layer constituting the photographic material contains a dispersion in a difficultly water-soluble high boiling organic solvent, either singly or in admixture with a low boiling organic solvent, of 2 or more compounds represented by the general formula



wherein R_1 , R_2 and R_3 are individually a hydrogen or halogen atom or a cycloalkyl, alkoxy, aryl, carbalkoxy or alkylsulfone group having one to six carbon atoms and at least one of the groups R_1 , R_2 and R_3 is not hydrogen; R_4 and R_5 are individually a hydrogen or halogen atom or an alkyl, cycloalkyl, alkoxy, aryl, carbalkoxy or alkylsulfone group having one to six carbon atoms; and the sum of the carbon atoms of R_1 , R_2 and R_3 is 8 or less, provided that in case the sum of the carbon atoms of R_1 , R_2 and R_3 is 8, each of R_1 , R_2 and R_3 has less than four carbon atoms.

2. A photographic material as in claim 1 wherein R_1 is methoxy, ethoxy, *n*-butoxy, *t*-butoxy, phenyl, cyclo-

hexyl or chloro, R_2 , R_3 and R_5 are hydrogen or chloro and R_4 is hydrogen, methyl, ethyl sulfonyl, chloro, methoxy, or carbo-*t*-butoxy.

3. A photographic material as claimed in claim 1 wherein said material comprises equal amounts of 2-(2'-hydroxy-5-cyclohexoxyphenyl) benzotriazole and 2-(2'-hydroxy-5' tert-butoxyphenyl) benzotriazole.

4. A photographic material as claimed in claim 1 wherein said material comprises equal amounts of 2-(2'-hydroxy-3',5' - dichlorophenyl)-5-methoxybenzotriazole and 2-(2'-hydroxy-5'-phenylphenyl)-5-chlorobenzotriazole.

5. A photographic material as claimed in claim 1 wherein said material comprises equal amounts of 2-(2'-hydroxy-5' - cyclohexoxyphenyl)-benzotriazole, 2-(2'-hydroxy-5' tert-butoxyphenyl) benzotriazole, 2-(2'-hydroxy-5'-phenylphenyl)-5-chlorobenzotriazole and 2-(2'-hydroxy-5'-cyclohexoxyphenyl)-benzotriazole.

* * * * *

25

30

35

40

45

50

55

60

65