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Hayashi et al.

[11] **3,713,828**

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[54] **MULTI-LAYER COLOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS**

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[52] **U.S. Cl.**....................**96/74,** 96/139

[51] **Int. Cl.**....................**G03c 1/76,** G03c 3/00

[58] **Field of Search**....................96/139, 74

[56] **References Cited**

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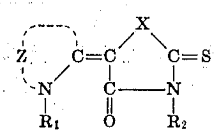
Primary Examiner—J. Travis Brown

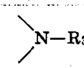
Attorney—Sughrue, Rothwell, Mion, Zinn and Macpeak

[57] **ABSTRACT**

A multi-layer type color photographic light-sensitive material characterized in that a merocyanine dye having the following general formula I



wherein X is selected from the group consisting of a sulfur atom, a selenium atom, an oxygen atom, and



wherein each of R_1, R_2 and R_3 is selected from the group consisting of a hydrogen atom, an alkyl group, a substituted alkyl group, an aryl group, and a substituted aryl group; and wherein Z represents an atomic group necessary to complete a heterocyclic ring, which may be substituted, is incorporated in at least one layer of the multi-layer type color photographic light-sensitive material, said multi-layer type color photographic light-sensitive material having on a support at least two silver halide photographic emulsion layers is disclosed.

10 Claims, No Drawings

MULTI-LAYER COLOR PHOTOGRAPHIC SILVER HALIDE LIGHT-SENSITIVE MATERIALS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a multi-layer color photographic light-sensitive material showing improved color contrast due to the interimage effect.

2. Description of the Prior Art

In a multi-layer color photographic light-sensitive material having on a support a red-sensitive emulsion layer, a green-sensitive emulsion layer and a blue-sensitive emulsion layer, the dye formed by the reaction of the oxidation product of an aromatic primary amino color developing agent and a color former or a coupler has the property of absorbing to some extent light other than that to be absorbed. For instance, a magenta dye absorbs blue light and red light to some extent in addition to the green light to be absorbed. Similarly, a yellow dye and cyan dye absorb to some extent light other than blue light and red light respectively. This undesirable and unnecessary absorption by the dye tends to reduce the color contrast and hence tends to darken the color obtained and to reduce the saturation.

The reduction of the saturation of color by this unnecessary absorption of the dye may be improved to some extent by the inter-image effect. The interimage effect is a phenomenon wherein the formation of a dye image in one photographic emulsion layer influences the formation of the dye image in other photographic emulsion layers in a multi-layer color photographic light-sensitive material. With the interimage effect the color contrast can be increased.

The interimage effect increasing the color contrast can be explained as follows. A silver halide emulsion sensitive to red light and designed to give an image of a cyan dye after development is applied to a film base and then a silver halide emulsion sensitive to blue light and designed to give an image of a yellow dye after development is further applied to the red-sensitive emulsion layer. The sample thus obtained is cut into two parts. One (Sample I) of the parts is wedge exposed to red light only, while the other part (Sample II) is exposed to red light at the same exposure amount and then to blue light giving the same photographic effect as above. Thereby a wedge image is formed in only the lower red-sensitive emulsion layer of Sample I and also a wedge image is formed in the upper blue-sensitive layer and the lower red-sensitive layer of Sample II. After development the contrasts of the cyan dye images formed in the red-sensitive layers of Sample I and Sample II are evaluated by measuring their densities. When the contrast of the cyan dye image of Sample I is higher than the contrast of the cyan dye image of Sample II, the interimage effect has occurred. In a multi-layer color photographic light-sensitive material having a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer on a support, the contrasts of the yellow dye image and the magenta dye image can also be increased by these interimage effects. The term "interimage effect" as used in the instant specification is intended to encompass the interimage effect of increasing the color contrast as described above.

This interimage effect is a well known phenomenon in color photography. For instance, W. T. Hanson & C.A. Horton in Journal of the Optical Society of America, 42 663–669 (1952) and A. Thiels, in Zeitschrift fur Wissenschaftliche Photographie, Photophysik and Photochemie, 47 106–118 and 246–255 (1952), described that the color contrast obtained in exposing a multi-layer color photographic light-sensitive material to a monochromatic light is higher than that obtained in exposing the material to white light and thus the color saturation in the former case is higher than in the latter case.

It is known that the interimage effect is important for increasing the color contrast, but the manner of increasing this interimage effect is not well known. For instance, although it is known that this interimage effect is caused by using a coupler capable of releasing a development inhibiting material on coupling, such as a benztriazole or a mercapto compound or a compound such as hydroquinone capable of releasing an inhibiting material on development, such as iodine ions or a mercapto compound, such compounds are generally unstable, are readily decomposed or cause great desensitization, which limits their selection. Accordingly, it has hitherto been considered difficult to increase the contrast by the interimage effect without adversely influencing the photographic properties.

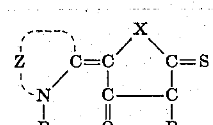
An object of this invention is to provide a color photographic image in which the unnecessary absorption of the dye is corrected by the interimage effect.

Another object of this invention is to provide a color photographic image having a high color saturation unaccompanied with any reduction in sensitivity.

SUMMARY OF THE INVENTION

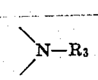
As a result of the inventors' investigations, the inventors have found that the interimage effect occurs markedly by incorporating a merocyanine dye in at least one photographic emulsion layer of a multi-layer color photographic light-sensitive material having at least two silver halide photographic emulsion layers.

The merocyanine dye used in this invention has the general formula [I]



[I]

wherein X represents a sulfur atom, a selenium atom, an oxygen atom or

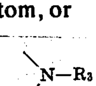


wherein R_1, R_2 and R_3 each represents a hydrogen atom, an unsubstituted alkyl radical or an unsubstituted or substituted aryl radical; and wherein Z represents the atomic group necessary for forming a heterocyclic ring, which may be substituted.

DETAILED DESCRIPTION OF THE INVENTION

The merocyanine dye represented by the above formula will be explained now in greater detail.

In general, in formula [I], X is a sulfur atom, a selenium atom, an oxygen atom, or



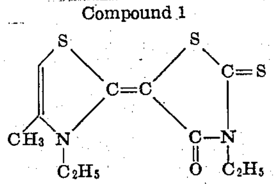
and each of R_1, R_2 and R_3 is a hydrogen atom; an alkyl group, such as a methyl group, an ethyl group, an n-propyl group, an n-butyl group, an iso-butyl group, an n-amyl group, and the like; a substituted alkyl group such as a 2-methoxyethyl group, a 2-hydroxyethyl group, an allyl group (or a vinylmethyl group), a benzyl group, a phenethyl group, a carboxymethyl group, a carboxyethyl group, a sulfomethyl group, a sulfopropyl group, a sulfobutyl group, a 4-carboxyphenethyl group, a 4-sulfophenethyl group, and the like; an aryl group such as a phenyl group; or a substituted aryl group such as a 4-carboxyphenyl group, a 4-sulfophenyl group, and the like.

Also, Z is an atomic group necessary to complete a heterocyclic ring. Suitable such heterocyclic rings are thiazolines such as 4-methylthiazoline, 4-phenylthiazoline, and the like; thiazoles such as thiazole, 4-methylthiazole, 4-phenylthiazole, 5-methylthiazole, 4,5-dimethylthiazole, and the like; benzthiazoles such as benzthiazole, 4-chlorobenzthiazole, 5-chlorobenzthiazole, 6-chlorobenzthiazole, 7-chlorobenzthiazole, 5-methylbenzthiazole, 6-bromobenzthiazole, 5-phenylbenzthiazole, 5-methoxybenzthiazole, 6-methoxybenzthiazole, 5-iodobenzthiazole, 5-ethoxybenzthiazole, 6-hydroxybenzthiazole, 5-carboxyethylbenzthiazole, 6-sulfobenzthiazole, and the like; naphthothiazoles, such as naphtho[1,2]c[2,1]-thiazole, 5-methoxynaphtho[2,1]-thiazole, 7-sulfoethyl-naphtho[1,2]-thiazole, and the like; oxazoles, such as 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, and the like; benzoxazoles, such as benzoxazole, 5-chlorobenzoxazole, 5-methylbenzoxazole, 5-phenylbenzoxazole, 5,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-hydroxybenzoxazole, 6-sulfobenzoxazole, 6-carboxyethylbenzoxazole, and the like; naphthoxazoles, such as naphtho [1,2]oxazole, naphtho[2,1] oxazole, and the like; selenazoles, such as 4methylselenazole, 4-phenylselenazole, and the like; benzselenazoles, such as benzselenazole, 5-chlorobenzselenazole, 5-methoxybenzselenazole, 5-hydroxybenzselenazole, tetrahydrobenzselenazole, and the like; naphthoselenazoles, such as naphtho[1,2] selenazole, naphtho[2,1]cselenazole, and the like; indolenines such as 3,3-dimethylindolenine, 3,3-diethylindolenine, 3,3,7-trimethylindolenine, and the like; benzimidazoles, such as 3-ethylbenzimidazole, 3-phenylbenzimidazole, 5-chlorobenzimidazole, 1,3-diethyl-5,6-dichlorobenzimidazole, and the like; naphthoimidazoles, such as 3-ethylnaphtho[2,1]imidazole, 3-phenylnaphtho[1,2]imidazole, and the like; 2-quinolines, such as quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 6-methoxyquinoline, 6-hydroxyquinoline, and the like; and 2-pyridines, such as pyridine, 5-methylpyridine, and the like.

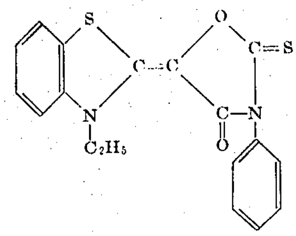
The merocyanine dyes used in this invention are illustrated by the following examples given below but they are not to be limited thereby.

Compound (1)

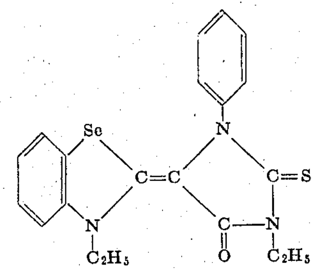
Compound 1



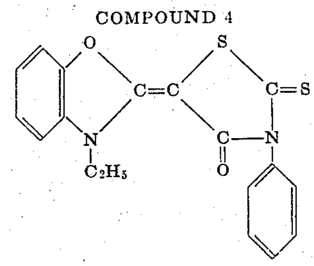
Compound 2



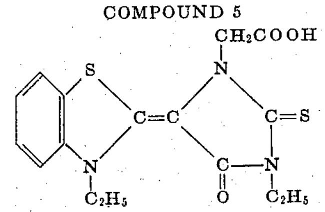
COMPOUND 3



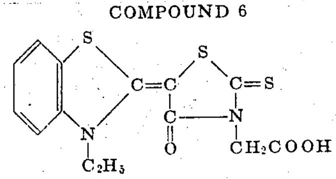
COMPOUND 4



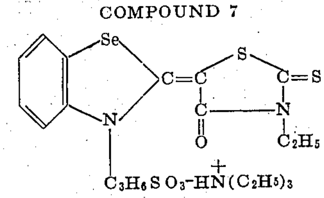
COMPOUND 5



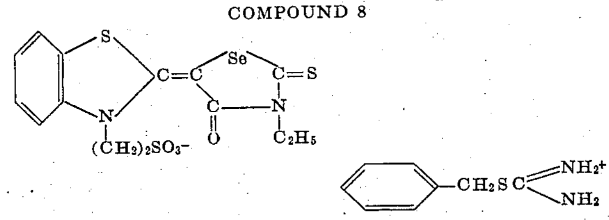
COMPOUND 6



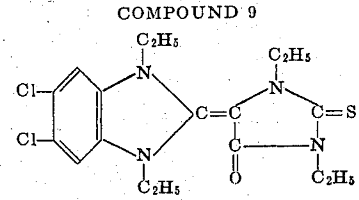
COMPOUND 7



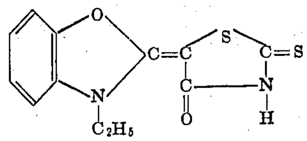
COMPOUND 8



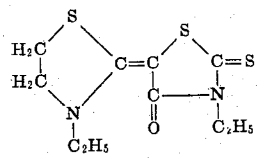
COMPOUND 9



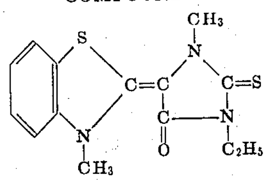
COMPOUND 10



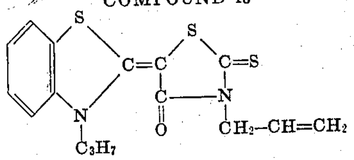
COMPOUND 11



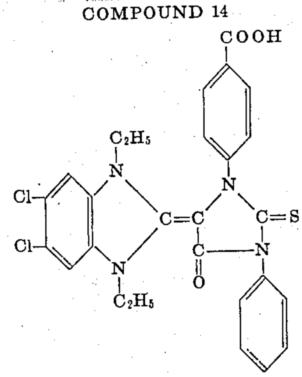
COMPOUND 12



COMPOUND 13

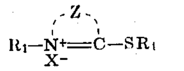


COMPOUND 14



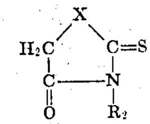
The merocyanine dyes shown above can be synthesized by the well known methods.

For example, the merocyanine dye represented by the general formula [I] shown above can be produced by reacting under heating a quaternary ammonium salt shown by the following general formula [II]



[II]

wherein R_1 and Z have the same meanings as described above in regard to the general formula [I]; R_4 represents an alkyl group or an aryl group and X^- represents an acid anion; and a ketomethylene compound represented by the following general formula [III]



[III]

wherein X and R_2 have the same meanings as described above in regard to the general formula [I] in the presence of an organic base, such as triethylamine, in an alcoholic solvent.

For instance, the merocyanine dyes used in this invention can be readily synthesized by referring to the description in F.M. Famer, The Cyanine Dyes and Related Compounds, p. 511; John Wiley & Sons Co., as well as in the specifications of U.S. Pat. Nos. 2,493,748 and 2,519,001.

The merocyanine dye of this invention can be incorporated in a multi-layer color photographic light-sensitive material by incorporating the dye in at least one of layers consisting of the silver halide emulsion layers of the color photographic light-sensitive material and the layers adjacent to the silver halide emulsion layers, such as a yellow filter layer, an antihalation layer, an intermediate layer, or a protective layer.

The amount of the merocyanine dye used in this invention depends upon the nature of the multi-layer color photographic light-sensitive material and the manner used in developing the material but where the merocyanine dye is incorporated in a silver halide emulsion layer of multilayer color photographic light-sensitive material, the amount of the dye is suitably from 6 to 600 mg per mol of silver halide and where the merocyanine dye is incorporated in an emulsion layer adjacent to the silver halide emulsion layer, the amount of the dye is suitably from 6 to 600 mg per 100 g of gelatin. However, it is to be understood that variance from these amounts can be made where desired. As the solvent for the merocyanine dye suitable solvents are those which do not adversely influence silver halide photographic emulsions, such as water, methanol, and acetone.

For obtaining the interimage effect in this invention the multilayer color photographic light-sensitive material is processed at an ordinary temperature, i.e., from 20° to 30°C, but the material may be processed at a higher temperature, i.e., at from 30° to 80°C or temperatures higher than that if desired.

The merocyanine dye of this invention can be utilized in any of the processed providing color photographic images, i.e., in any of the processes of forming dye images corresponding to the proportion of silver reduced from silver halide by developing a multi-layer color photographic light-sensitive material having at least two photographic emulsion layers, each containing a silver halide dispersion in a hydrophilic colloidal medium. For instance, the merocyanine dye of this invention is effectively used in a reversal color photographic process, i.e., a process for obtaining a positive color image by exposing a multi-layer color photographic light-sensitive material having at least two silver halide photographic emulsion layers, each having a sensitivity in a different wavelength region, developing the light-sensitive material in a black and white developer solution to form a negative silver image and thereafter developing the silver halide emulsion particles at the areas which have not been developed by the black and white developing solution to form a positive color image.

Reversal color photography is classified into two systems, i.e., "a coupler-in-developer type color photographic system" and "a coupler-in emulsion layer color photographic system." In the former the dye images are obtained by developing successively an exposed color photographic light-sensitive material in color developer solutions, each of the solutions containing a diffusible coupler to be coupled in each of the different color layers. In the latter each layer contains a diffusion resisting coupler to be coupled in each of the different color layers incorporated in a multi-layer type color photographic light-sensitive material with the dye images being obtained by processing the light-sensitive material in a color developer solution containing no couplers.

The merocyanine dye of this invention can be applied with good results to both types of the reversal color photographic systems.

The merocyanine dye of the present invention also can be used in a system in which a multi-layer type color photographic light-sensitive material, having at least two layers of a silver halide photographic emulsion, each containing a diffusion resisting coupler and each sensitized to a different wave length region, is exposed and then immediately color-developed to provide a negative color image.

Furthermore, the merocyanine dye of this invention can be used in a color photographic diffusion transfer process, in which the diffusion of a developing solution, couplers, and dyes in conformity with the image from the light-sensitive layer to a reception layer when the light-sensitive layer is contacted closely with the reception layer during development, as described in the specifications of U.S. Pat. Nos. 2,559,643, 2,698,798; and 3,227,551.

Still further, the merocyanine dye of this invention can be used in a silver dye bleaching color photography in which a dye image is obtained by bleaching the dye at the areas where the silver is present, as disclosed in the specifications of U.S. Pat. Nos. 2,020,775 and 2,410,025.

In the multi-layer type color photographic light-sensitive material of this invention, it is desirable to apply a red-sensitive silver halide photographic emulsion, a green-sensitive silver halide emulsion, and a blue-sensitive silver halide emulsion to a support in this order.

Also, in the multi-layer type color photographic light-sensitive material of this invention, it is desirable to form the cyan, magenta and yellow images in the red-sensitive, green-sensitive, and blue-sensitive silver halide emulsion layers, respectively, after development.

However, systems other than those stated above can be employed in this invention.

The silver halide emulsion used in the present invention can be photographic emulsions containing silver bromide, silver iodide, silver chloride, silver chlorobromide, silver iodobromide, or silver chloroiodobromide. In particular, when a photographic emulsion layer contains silver chloroiodide, silver iodobromide or silver chloro-iodobromide having an iodine content of from 1 to 10 mol percent, better results can be obtained.

Moreover, the silver halide photographic emulsion of this invention can be chemically sensitized using methods well known in the art, for example, using a compound containing an unstable sulfur, such as sodium thiosulfate, allylthiocarbazide, and the like; a gold compound such as a gold (I) complex salt of thiocyanate; a polyalkyleneoxide derivative, or a combination thereof. Furthermore, the silver halide photographic emulsion used in this invention can be spectrally sensitized using a cyanine dye such as 1,1′-diethylcyanine iodide, 1,1′-diethyl-9-methylcarbocyanine bromide, anhydro-5,5′-diphenyl-9-ethyl-3,3′-di(2-sulfoethyl)-benzoxazolocarbocyanine hydroxide, and the like, or a combination thereof. Still further, the silver halide photographic emulsion used in this invention can contain a developing agent capable of releasing a development inhibitor such as 2-iodo-5-pentadecylhydroquinone, 2-methyl-5-(1-phenyl-5-tetrazolylthio)-hydroquinone, and the like; a stabilizer such as 4-hydroxy-6-methyl-1,3,3a-7-tetraazaindene, benzimidazole, 1-phenyl-5-mercaptotetrazole, and the like; a hardening agent such as formaldehyde, mucobromic acid, and the like, and a wetting agent such as saponine, sodium alkylbenzenesulfonate, and the like.

The invention will now be explained in greater detail by reference to the following examples. In the following examples, two types of color photographic systems were employed. That is to say, the so-called coupler-in-developer color photographic system in which couplers are supplied from color developer solutions and the so-called coupler-in-emulsion layer type color photographic system in which couplers are incorporated in the photographic emulsion layers of color photographic light-sensitive materials, were employed.

In the examples of the present invention shown below, a multilayer type color photographic light-sensitive material having the following compositions was employed in the coupler-in-developer type color photographic system.

COUPLER-IN-DEVELOPER TYPE COLOR PHOTOGRAPHIC SYSTEM

On a cellulose triacetate film base were coated the following different types of layers in the following order.

First Layer (lowermost layer)

The red-sensitive silver halide emulsion layer; a layer formed by coating a high speed gelatino silver iodobromide emulsion containing no coupler and having red sensitivity due to a sensitizing dye so that the silver content was 15 mg/100 cm^2.

Second Layer

The green-sensitive silver halide emulsion layer; a layer formed by coating a high speed gelatino silver iodobromide emulsion containing no coupler and having green-sensitivity due to a sensitizing dye so that the silver content was 15 mg/100 cm^2.

Third Layer

The yellow filter layer; a layer formed by coating a yellow colloidal silver dispersion prepared by dispersing colloidal silver in gelatin so that the silver content was 2.5 mg/100 cm^2.

Fourth Layer

The blue-sensitive gelatino silver halide emulsion layer; a layer formed by coating a high speed silver iodobromide emulsion containing no coupler so that the silver content was 20 mg/100 cm^2.

In the examples shown below relating to the coupler-in-developer type color photographic system, the multi-layer type color photographic light-sensitive materials were subjected to the following developing procedures:

Process	Time (min.)
1. Hardening	1
2. Water Washing	2
3. Negative Development	4
4. Water Washing	3
5. Reversal Red Flash Exposure	
6. Cyan Color Development	4
7. Water Washing	3
8. Reversal Blue Flash Exposure	
9. Yellow Color Development	4
10. Water Washing	3
11. Reversal White Exposure	
12. Magenta Color Development	4
13. Water Washing	3
14. Silver Bleaching	3
15. Fixing	3
16. Water Washing and Drying	

The temperature of the processing baths used above was 27°C. The compositions of the baths were as follows:

Hardening Bath	
Sodium Hexametaphosphate	2.0 g
Sodium Bisulfite	5.0 g
Sodium Pyrophosphate (10 H_2O)	15.0 g
Sodium Sulfate	100.0 g
Potassium Bromide	2.0 g
Sodium Hydroxide	0.1 g
37% Formaldehyde	17.0 cc
Water added to make the total volume to 1000 cc.	
Negative Developer Solution	
N-Methyl-p-aminophenol Sulfate	5.0 g
Sodium Sulfite	79.0 g
Hydroquinone	2.0 g
Sodium Hydroxide	1.0 g
Sodium Carbonate (1 H_2O)	41.0 g
0.1% Potassium Iodide	12.5 cc
Potassium Bromide	3.6 g
Sodium Hydroquinone Monosulfonate	4.0 g
Potassium Thiocyanate	2.0 g
0.5% 6-Nitrobenzoindazole Nitrate	5.0 cc
Water added to make the total volume to 1000 cc.	
Cyan Color Developer Solution	
Potassium Bromide	2.9 g
1% 6-Nitrobenzoimidazole Nitrate	3.0 cc
0.1% Potassium Iodide	11.0 cc
Sodium Sulfite	10.0 g
Sodium Sulfate	60.0 g
Potassium Thiocyanate	1.2 g
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline Sulfate	2.5 g
Sodium Hydroxide	3.4 g
1-Hydroxy-N-(2-propionamidophenethyl)-2-naphthamide	1.5 g
2,4-Dichloro-1-naphthol	0.2 g
2-Methyl-2,4-pentandiol	10.0 cc
Polyoxyethylene-methylphenyl Ether	0.5 g
Monobenzyl-p-aminophenol Hydrochloride	0.4 g
P-Aminophenol Hydrochloride	0.12 g
Water added to make the total volume to 1000 cc.	
Yellow Color Developer Solution	
Sodium Sulfite	10.0 g
Potassium Bromide	0.65 g
0.1% Potassium Iodide	29.0 cc
1-%6-Nitrobenzoimidazole	10.0 cc
Sodium Sulfate	64.0 g
N,N-Diethyl-p-phenylenediamine Hydrochloride	3.0 g
Sodium Hydroxide	2.4 g
2-Methyl-2,4-pentandiol	20.0 cc
2-Benzoyl-2'-methoxyacetanilide	1.8 g
Diethylhydroxylamine	0.3 cc
Polyoxyethylene-methylphenyl Ether	0.8 g
Water added to make the total volume to 1000 cc.	
Magenta Color Developer Solution	
Concentrated Sulfuric Acid	2.0 cc
Trisodium Phosphate (12 H_2O)	40.0 g
Sodium Sulfite	5.0 g
Potassium Thiocyanate	1.2 g
0.1% Potassium Iodide	7.5 cc
Potassium Bromide	0.6 g
4-Amino-3-methyl-N-(β-methylsulfonamidoethyl) aniline Sulfate	2.0 g
Ethylenediamine	6.0 cc
Sodium Hydroxide	0.3 g
1-(2,4,6-Trichlorophenyl) 3-(4-nitroanilino)-5-pyrazolone	1.7 g
2-Methyl-2,4-pentandiol	10.0 cc
Sodium Sulfate	50.0 g
Polyoxyethylene-methylphenyl Ether	0.5 g
Water added to make the total volume to 1000 cc.	
Bleaching Solution	
Potassium Ferricyanide	100.0 g
Potassium Bromide	30.0 g
Water added to make the total volume to 1000 cc.	
Fixing Solution	
Sodium Thiosulfate	125.0 g
Sodium Sulfite	9.0 g
Water added to make the total volume to 1000 cc.	

In the examples shown below relating to the so-called coupler-in-emulsion layer type color photographic system, a multi-layer type color photographic light-sensitive material having the following composition was used.

COUPLER-IN-EMULSION LAYER COLOR PHOTOGRAPHIC SYSTEM

On a cellulose triacetate film were coated the following different kinds of layers in the following order:

First Layer: (Lowermost Layer)

The antihalation layer; a layer formed by coating a gray colloidal silver dispersion prepared by dispersing colloidal silver in gelatin so that the silver content was 3 mg/100 cm².

Second Layer

An intermediate layer; a layer formed by coating a gelatin solution so that the content of the gelatin was 3.4 mg/100 cm².

Third Layer

The red-sensitive silver halide emulsion layer; a layer formed by coating a high speed gelatino silver iodobromide emulsion having red sensitivity due to a sensitizing dye and containing a cyan coupler (a coupler emulsion prepared by dispersing in gelatin a solution of 1-hydroxy-4-chloro-N-dodecyl-2-naphthamide in tricresyl phosphate) so that the silver content was 10 mg/100 cm².

Fourth Layer

An intermediate layer; a layer formed by coating a gelatin solution so that the gelatin content was 13.4 mg/100 cm².

Fifth Layer

The green-sensitive gelatino silver halide emulsion layer; a layer formed by coating a high speed silver bromide emulsion having green sensitivity due to sensitizing dye and containing a magenta coupler (a coupler emulsion prepared by dispersing in gelatin a solution of 1-(2,6-dichloro-4-methoxyphenyl)-3-[3- α-(2. 4-di-tert-amylphenoxy)propionamido benzamido]-5-pyrazolone in dibutylphthalate) so that the silver content was 15 mg/100 cm².

Sixth Layer

The yellow filter layer; a layer prepared by coating a yellow colloidal silver dispersion formed by dispersing colloidal silver in gelatin so that the silver content was 2.5 mg/100 cm².

Seventh Layer

The blue-sensitive silver halide emulsion layer; a layer formed by coating a high speed gelatino silver iodobromide emulsion containing a yellow coupler (a coupler emulsion prepared by dispersing in gelatin a solution of 2-benzoyl-2'-chloro-5'-tridecanoyloxyacetanilide in dibutylphthalate) so that the silver content was 15 mg/100 cm².

Eight Layer

A protective layer; a layer formed by coating a gelatin solution so that the gelatin content was 8.9 mg/100 cm^2.

In the examples relating to the coupler-in-emulsion layer type color photographic system, the multi-layer type color photographic light-sensitive materials were subjected to the following developing procedures:

Process	Time (min.)
Hardening	1
Water Washing	1
First Development	3
Water Washing	0.5
Reversal Exposure	
Second Development	4
Water Washing	1
Bleaching	1
Water Washing	0.5
Fixing	1
Water Washing	1

The temperature of the above processing baths was 30°C The compositions of the baths used were as follows:

Hardening Bath	
Sulfuric Acid (1:1)	5.4 cc
Sodium Sulfate	150.0 g
Sodium Acetate	20.0 g
30% Pyruvaldehyde	40.0 cc
37% Formaldehyde	20.0 cc
Water added to make the total volume to 1000 cc.	
First Developer Solution	
N-Methyl-p-aminophenol Sulfate	2.0 g
Sodium Sulfite	90.0 g
Hydroquinone	8.0 g
Sodium Carbonate (1 H_2O)	52.5 g
Potassium Bromide	5.0 g
Potassium Thiocyanate	1.0 g
Water added to make the total volume to 1000 cc.	
Second Developer Solution	
Benzyl Alcohol	5.0 cc
Sodium Sulfite	5.0 g
Hydroxylamine Hydrochloride	2.0 g
3-Methyl-4-amino-N-ethyl-N-(β-methylsulfonamidoethyl)aniline Sulfate	1.5 g
Potassium Bromide	1.0 g
Trisodium Phosphate	30 g
Sodium Hydroxide	0.5 g
Ethylenediamine (70% aqueous solution)	7 cc
Water added to make the total volume to 1000 cc.	
Bleaching Solution	
Ferricyanide	100 g
Sodium Acetate	40 g
Glacial Acetic Acid	20 g
Potassium Bromide	30 g
Water added to make the total volume to 1000 cc.	
Fixing Solution	
Sodium Thiosulfate	150 g
Sodium Acetate	70 g
Sodium Sulfite	10 g
Potassium Alum	20 g
Water added to make the total volume to 1000 cc.	

EXAMPLE 1

According to the above descriptions, two types of multi-layer type color photographic light-sensitive materials of the coupler-in-developer type color photographic system were prepared. One of them was used as a control sample and in another sample, Compound 11 shown hereinbefore, was added to the three silver halide emulsion layers (first layer, second layer and fourth layer) in the amount of 40 mg per 1 mol of silver halide.

Each of the multi-layer type color photographic light-sensitive materials thus prepared was subjected to the following two types of sensitometrie exposures, i.e., exposed to red light and to white light (red light + green light + blue light). In the above exposures, the

amount of exposure of red light was the same in both cases and the amount of exposure of the green and blue components in the white light was adjusted so that they formed the same photographic effect as the red exposure.

The samples thus exposed were developed using the above-described developing procedures. After development, the density of the cyan dye in the samples was obtained as a function of the amount of exposure of the red light. From the ratio of the gamma valves of the characteristic curves of the cyan dye images in the case of exposure to red light alone and in the case of exposure to white light (γ_R/γ_W; where γ_R is the gamma value of the cyan dye image when exposed to red light and γ_W is the gamma value when exposed to white light), the interimage effect was evaluated. Also, the interimage effect could be evaluated using the difference in the sensitivity obtained at a density D=0.6, that is to say, Δ log$E$ [Δlog$E$= (log E at D=0.6 of the cyan dye image when exposed to white light) - (log E at D=0.6 of the cyan dye image when exposed to red light)]. In other words, as the interimage effect to the cyan dye image is larger, the ratio γ_R/γ_W becomes larger and also Δ log E becomes larger. The results obtained are shown in Table 1.

TABLE 1

Compound	Amount [mg. mol of silver halide (each of the three layers)]	γ_R/γ_W	Δ Log E
Control	0	1.25	0.21
Compound II	40	1.65	0.48

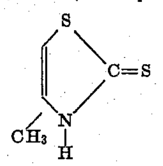
As can be seen from the above table, it is clear that with the incorporation of Compound II, the ratio γ_R/γ_W and Δ log E were increased and hence the interimage effect was increased.

EXAMPLE 2

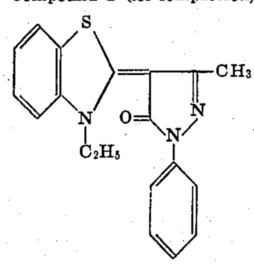
Using the above-described procedure, 37 types of multi-layer type color photographic light-sensitive materials of the coupler-in-developer type were prepared. One of the samples was used as a control sample, while other samples were produced by incorporating each of the compounds shown in Table 2 below in the amount shown into each of the blue-sensitive silver halide photographic emulsion layers (fourth layers) of the light-sensitive materials.

The multi-layer type color photographic light-sensitive materials thus obtained were subjected to exposure and development as in Example 1 and also the density was measured as in Example 1, whereby the ratio γ_R/γ_W was obtained. On the other hand, in order to determine the influence of the compounds shown in Table 2 on the sensitivity of the blue-sensitive layer, the multi-layer type color photographic light-sensitive material was sensitometrically exposed to blue light. Thereafter each of the light-sensitive materials was processed in accordance with the developing procedures of the coupler-in-developer type color photographic system and the density of the yellow dye image was measured. From the change in the sensitivity value S (expressed as a relative value with the control sample being assumed to be 100) obtained at D=0.6, the extent of the sensitivity of the blue layer reduced by adding the compound thereto was determined. That is to say, a lower sensitivity value shows the incorporated compound reduced the sensitivity of the blue-sensitive emulsion layer to a greater extent. The γ_R/γ_W values and sensitivity values S thus obtained are shown in Table 2, in which the results obtained in using the following compounds for comparison are shown.

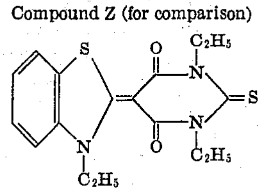
Compound X (for comparison)



Compound Y (for comparison)



Compound Z (for comparison)



In Table 2, the developing procedures were conducted separately in Experiment Nos. 1–3. In order that Experiment Nos. 1–3 could be compared with each other, a control experiment was added to each of the experiments (the results obtained in the control experiment are shown at the beginning of each experimental group). Since each of the control experiments in these experimental groups have essentially the same results, these experimental groups could be directly compared with each other.

TABLE 2

Compound	Amount (mg/mol of silver halide of blue-sensitive layer)	γ_R/γ_W	S (Relative sensitivity of blue-sensitive layer)
Experimental Group 1			
Control	0	1.15	100
1.	6	1.20	102
"	60	1.45	100
"	200	1.68	97
"	600	1.80	99
2.	100	1.28	95
"	200	1.35	90
3.	100	1.32	91
"	200	1.50	72
4.	100	1.31	95
"	200	1.59	85
5.	100	1.30	90
"	200	1.45	75
Experiment Group 2			
Control	0	1.18	100
6.	100	1.35	98
"	200	1.62	100
7.	100	1.28	105
"	200	1.39	108
8.	100	1.20	101
"	200	1.32	96
9.	100	1.25	80
"	200	1.38	65
10.	100	1.30	92
"	200	1.60	78
11.	100	1.58	96
"	200	1.75	93
Experiment Group 3			
Control	0	1.13	100
12.	100	1.28	92
"	200	1.41	78
13.	100	1.30	99
"	200	1.55	96
14.	100	1.30	78
"	200	1.53	66
X	100	1.28	55
"	200	1.35	21
Y	100	1.10	103
"	200	1.12	96
Z	100	1.18	100
"	200	1.14	98

From Table 2 it can be seen that by incorporating compounds 1 to 14 of the present invention, the value of γ_R/γ_W could be increased without reducing the sensitivity S and hence the interimage effect was increased.

When compound X was used, the value of γ_R/γ_W was increased similarly but the sensitivity was greatly reduced. Also, when the merocyanine dyes Y and Z were used, the values of γ_R/γ_W were essentially the same as that of the control experiment and hence compounds Y and Z do not show the effect of increasing the interimage effect as in this invention. As described above, compounds 1 to 14 in this invention have the advantages that the interimage effect was increased without greatly reducing the sensitivity.

EXAMPLE 3

According to the above-described procedures, 16 types of multilayer color photographic light-sensitive materials of the coupler-in-emulsion layer type color photographic system were prepared. One of the samples was used as a control sample and the other samples were prepared by incorporating compound 1 or compound 7 in the protective layer (the eighth layer), the blue-sensitive silver halide emulsion layer (the seventh layer), the yellow filter layer (the sixth layer), or the intermediate layer (the fourth layer) in the amount shown in Table 3 below.

The multi-layer type color photographic light-sensitive materials thus obtained were sensitometrically exposed to the following four different kinds of light, respectively. That is to say, each of the light-sensitive materials were exposed to red light, green light, blue light, or white light (red light + green light + blue light) separately. The amount of exposure of the red component, the green component or the blue component of the white light was the same as that of the exposure to red light, the exposure to green light, or the exposure to blue light alone and the amount of exposure to each of the red light, green light and blue light was so adjusted that the same photographic effect was obtained.

The samples thus exposed were developed using the developing process of the coupler-in-emulsion type color photographic system as described hereinbefore. After development, the ratio of the gamma values γ_R/γ_W of the characteristic curves of the cyan dye images when exposed to red light and when exposed to white light, the gamma value ratio γ_G/γ_W of the characteristic curves of the magenta dye images when exposed to green light and when exposed to white light, and the gamma value ratio of γ_B/γ_W of the characteristic curves of the yellow dye images when exposed to blue light and when exposed to white light were measured. The results obtained are shown in Table 3. From these results, it can be seen that by incorporating Compound 1 or Compound 7 the ratios γ_R/γ_W, γ_G/γ_W and γ_B/γ_W were greatly increased, that is to say, the interimage effects were increased.

TABLE 3

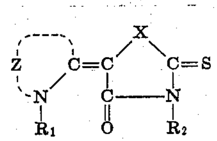
Layer Containing Compound	Compound	Amount	γ_R/γ_W	γ_G/γ_W	γ_B/γ_W
	Control	0 1/	1.25	1.18	1.05
	1	6	1.28	1.21	1.05
Eighth Layer: Protective Layer	"	60	1.41	1.29	1.08
	"	200	1.50	1.30	1.11
	"	600	1.65	1.31	1.15
	7	100	1.40	1.25	1.12
Seventh Layer: Blue-sensitive Layer	1	100 2/	1.38	1.33	1.12
	"	200	1.57	1.35	1.11
	7	100	1.31	1.25	1.08
	"200		1.48	1.29	1.10
Sixth Layer: Yellow Filter Layer	1	100 1/	1.35	1.24	1.07
	"	200	1.51	1.27	1.13
	7	100	1.32	1.21	1.07
	"	200	1.43	1.27	1.09
Fourth Layer: Intermediate Layer	1	100	1.39	1.22	1.07
	"	200	1.49	1.25	1.08

1/ mg/100 g gelatin.
2/ mg/mol AgX

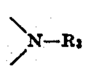
With other merocyanine dyes of the general formula [I] than those described in Examples 1, 2 and 3 mentioned above, essentially similar results were obtained. Also, with other development processes than those described in the Examples, essentially the same results were obtained.

What is claimed is:

1. A multi-layer type color photographic light-sensitive material characterized in that a merocyanine dye having the following general formula [I]



wherein X is a member selected from the group consisting of a sulfur atom, a selenium atom, an oxygen atom, and a



group; wherein each of R_1, R_2 and R_3 is a member elected from the group consisting of a hydrogen atom, an alkyl group, a substituted alkyl group, whose substituents are selected from the group consisting of an alkoxy group, a hydroxy group, a vinyl group, an aryl group, a carboxy group, and a sulfo group, an aryl group, and a substituted aryl group, whose substituents are selected from the group consisting of a carboxy group and a sulfo group; and wherein Z represents an an atomic group necessary to complete a heterocyclic ring selected from the group consisting of thiazolines, thiazoles, benzthiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles, benzselenazoles naphthoselenazoles, benzimidazoles, naphthoimidazoles, 2-quinolines, 2-pyridines, and indolenines, is incorporated in at least one layer of said multi-layer type color photographic light-sensitive material, said multi-layer type color photographic light-sensitive material comprising, in order,

1. a support,
2. a subbing layer,
3. a red sensitive silver halide emulsion layer,
4. a green sensitive silver halide emulsion layer,
5. a blue sensitive silver halide emulsion layer,

the silver halide in at least one of the aforementioned silver halide emulsion layers containing a silver iodide content of from 1 to 10.0 mole percent, and

The silver halide in at least one of the silver halide emulsion layers being a member selected from the group consisting of AgclI, AgIBr and AgClIBr, whose concentration ranges from 1 to 10.0 mole percent, the remaining silver halide emulsion layers containing a silver halide selected from the group consisting of AgBr, AgI, AgCI, AgClBr, AgClI, AgIBr and AgClIBr.

2. The multi-layer type color photographic light-sensitive material as claimed in claim 1 wherein each of R_1, R_2 and R_3 is selected from a group consisting of a hydrogen atom, a methyl group, an ethyl group, an n-propyl group, an n-butyl group, an iso-butyl group, an n-amyl group, a 2-methoxyethyl group, a 2-hydroxyethyl group, an allyl group, a benzyl group, a phenyl group, a carboxymethyl group, a carboxyethyl group, a sulfomethyl group, a sulfopropyl group, a sulfobutyl group, a 4-carboxyphenethyl group, a 4-sulfophenethyl group, a phenyl group, a 4-carboxyphenyl group, and a 4-sulfophenyl group.

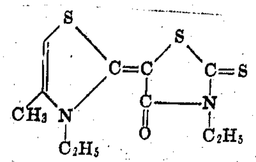
3. The multi-layer type color photographic light-sensitive material as claimed in claim 1 wherein the heterocyclic ring completed by Z is selected from the group consisting of the thiazolines, thiazoles, benzthiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles, benzselenazoles, naphthoselenazoles, indolenines, benzimidazoles, naphthoimidazoles, 2-quinolines and 2-pyridines.

4. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye is incorporated in at least one of the layers consisting of the silver halide emulsion layers and the layers adjacent to the silver halide emulsion layers.

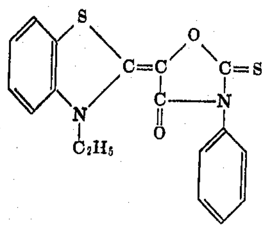
5. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein, after development, cyan, magenta, and yellow images are formed in the red-sensitive, the green-sensitive, and the blue-sensitive silver halide emulsion layers, respectively.

6. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein the silver halide is selected from the group consisting of silver bromide, silver iodide, silver chloride, silver chlorobromide, silver iodobromide, and silver chloro-iodobromide.

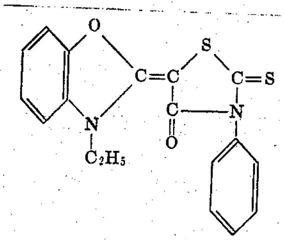
7. The multi-layer type color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye has the formula



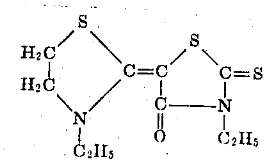
8. The multi-layer color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye has the formula



9. The multi-layer color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye has the formula



10. The multi-layer color photographic light-sensitive material as claimed in claim 1, wherein said merocyanine dye has the formula



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