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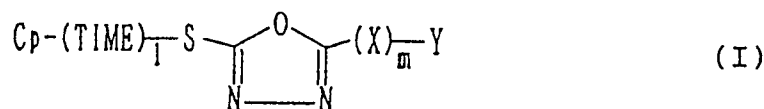
㉖ Applicant : **KONICA CORPORATION**
26-2, Nishishinjuku 1-chome, Shinjuku-ku
Tokyo 160 (JP)

㉗ Inventor : **Sugita, Shuichi**
c/o Konica Corporation, No. 1, Sakura-machi
Hino-shi, Tokyo 191 (JP)
Inventor : **Kida, Shuji**
c/o Konica Corporation, No. 1, Sakura-machi
Hino-shi, Tokyo 191 (JP)

㉘ Representative : **Ellis-Jones, Patrick George**
Armine et al
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5LX (GB)

㉙ **Silver halide photographic material.**

㉚ The improved silver halide photographic material contains a compound of the general formula (I) which is capable of releasing a development restrainer upon reaction with the oxidation product of a developing agent :



where Cp is a coupler residue that is capable of entering into a coupling reaction with the oxidation product of a color developing agent ; TIME is a timing group bound to Cp at the coupling site ; X is 0 or 1 ; X is a linkage group ; Y is a hydrolyzable group ; and m is 0 or 1.
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SILVER HALIDE PHOTOGRAPHIC MATERIAL

BACKGROUND OF THE INVENTION

This invention relates to a silver halide photographic material more particularly to a silver halide color photographic material having improved photographic characteristics and keeping quality.

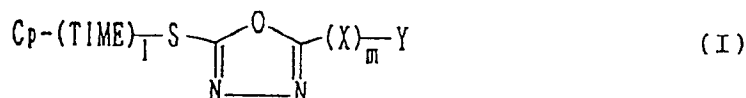
The development of color photographic materials having high sensitivity, good sharpness and high fidelity of color reproduction is one of the objectives in modern photographic industry. A known method of improving sharpness is to use DIR compounds which release development restrainers upon reaction with the oxidation product of color developing agents. As is well known, incorporating these DIR compounds in emulsions is effective for enhancing the sharpness of color image by the edge effect and further for improving the fidelity of color reproduction by the interimage effect. However, the conventional DIR compounds have the disadvantage that development restrainers released during color development dissolve and diffuse from photographic materials into the developing solution which will eventually exhibit a development inhibiting action in the presence of accumulated restrainers.

With a view to solving this problem, improved methods have been proposed in JP-A-57-151944 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-58-205150, JP-A-60-218644, JP-A-60-221750, JP-A-61-11743 and U.S. Patent No. 4,782,012. The methods described in these patents are based on using couplers that exhibit a development inhibiting action when leaving groups are eliminated from the coupling site of a coupler and which, when released into the developing solution, will be decomposed into compounds that cause no adverse effects on the photographic performance of the light-sensitive material in which they are used. As a matter of fact, light-sensitive materials using those couplers could be subjected to continuous processing in large quantities with smaller reduction in sensitivity and with the contamination of the developing solution being markedly reduced. However, the light-sensitive material containing those couplers experience not only increased fog but also deterioration in sensitivity, sharpness and color reproduction during storage. Further, the couplers themselves are not considered to be satisfactory from the viewpoint of achieving the edge effect and the interimage effect at the same time.

SUMMARY OF THE INVENTION

An object, therefore, of the present invention is to provide a color light-sensitive material that achieves good sharpness and high fidelity of color reproduction and which also is improved in storage stability.

This object of the present invention can be attained by a silver halide photographic material containing a compound of the following formula (I) which is capable of releasing a development restrainer upon reaction with the oxidation product of a developing agent :



where Cp is a coupler residue that is capable of entering into a coupling reaction with the oxidation product of a color developing agent ; TIME is a timing group bound to Cp at the coupling site ; Ω is 0 or 1 ; X is a linkage group ; Y is a hydrolyzable group ; and m is 0 or 1.

DETAILED DESCRIPTION OF THE INVENTION

The coupler residue represented by Cp in the general formula (I) may either be a residue that generates a yellow, magenta or cyan dye or a residue that generates a substantially colorless product. Typical examples of the yellow coupler residue represented by Cp are described in U.S. Patent Nos. 2,298,443, 2,407,210, 2,875,057, 3,048,194, 3,265,506, 3,447,928, and Farbkuppler eine Literaturübersicht Agfa Mitteilung (Band II), pp. 112-126, 1961, etc. Among the compounds described in these references, acyl acetanilides such as benzoyl acetanilide and pivaloyl acetanilide are preferred.

Typical examples of the magenta coupler residue represented by Cp are described in U.S. Patent Nos. 2,369,489, 2,343,703, 2,311,182, 2,600,788, 2,908,573, 3,062,653, 3,152,896, 3,519,429, 3,725,067, 4,540,654, JP-A-59-162548, Agfa Mitteilung (Band II), *ibid*, pp. 126-156, 1961, etc. Among the compounds des-

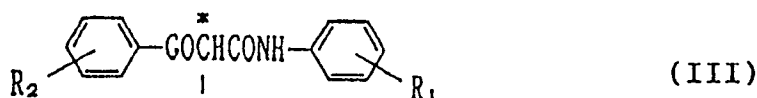
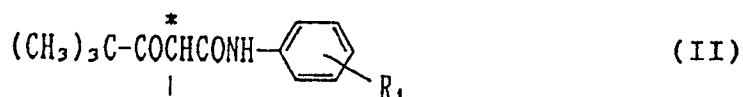
cribed in these references, pyrazolones and pyrazoloazoles (e.g. pyrazoloimidazole and pyrazolotriazole) are preferred.

5 Typical examples of the cyan coupler residue represented by Cp are described in U.S. Patent Nos. 2,367,531, 2,423,730, 2,474,293, 2,772,162, 2,395,826, 3,002,836, 3,034,892, 3,041,236, 4,666,999 and Agfa Mitteilung (Band II), *ibid*, pp. 156-175, 1961. Among the compounds described in these references, phenols and naphthols are preferred.

10 Typical examples of the coupler residue represented by Cp which forms a substantially colorless product are described in U.K. Patent No. 861,138, U.S. Patent Nos. 3,632,345, 3,928,041, 3,958,993, 3,961,959, etc. Among the compounds described in these patents, cyclic carbonyl compounds are preferred.

15 Typical examples of the timing group represented by TIME include those which release photographically useful groups by an intramolecular nucleophilic substitution reaction as described in U.S. Patent No. 4,248,962 and JP-A-57-56837, as well as those which release photographically useful groups by an electron transfer reaction along conjugated chains as described in JP-A-56-114946 and JP-A-57-154234. Other examples of the timing group are described in JP-A-57-188035, JP-A-58-98728, JP-A-59-206834, JP-A-60-7429, JP-A-60-214358, JP-A-50-225844, JP-A-60-229030, JP-A-60-233649, JP-A-60-237446, and JP-A-60-237447.

Preferred examples of the yellow coupler residue represented by Cp in the general formula (I) are represented by the following general formulas (II) and (III) :

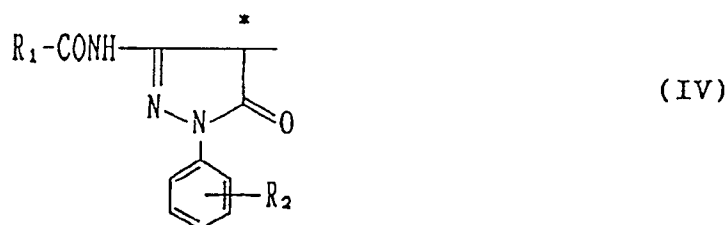


where R_1 and R_2 each represents an alkyl group, a cycloalkyl group, an aryl group, a hetero ring or a halogen atom, with the alkyl, cycloalkyl, aryl and hetero ring being optionally bound via at least one member of the group consisting of an oxygen atom, a nitrogen atom and a sulfur atom ; the alkyl, cycloalkyl, aryl and hetero ring may also be bound via one or more of the following bonding groups, namely, acylamino, carbamoyl, sulfonamido, sulfamoyl, sulfamoylcarbonyl, carbonyloxy, oxycarbonyl, ureido, thioureido, thioamide, sulfone, sulfonyloxy, etc.

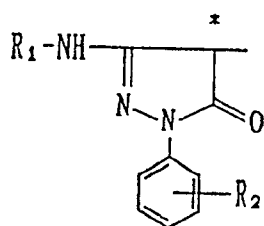
35 The alkyl, cycloalkyl, aryl and hetero ring may further contain one or more of the following substituents, namely, a halogen atom, nitro, cyano, alkyl, alkenyl, cycloalkyl, aryl, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl, carboxy, sulfo, sulfamoyl, carbamoyl, acylamino, ureido, urethane, sulfonamido, hetero ring, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, anilino, hydroxyl, imido, acyl, etc.

When more than one each of R_1 and R_2 is present, two or more R_1 's or R_2 's may be the same or different.

45 Preferred examples of the magenta coupler residue represented by Cp in the general formula (I) are those represented by the following general formulas (IV), (V), (VI) and (VII) :



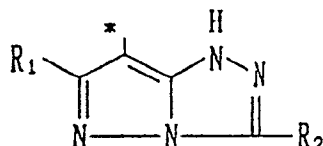
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(V)

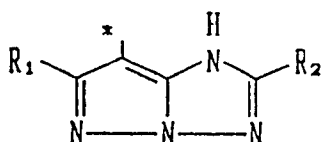
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(VI)

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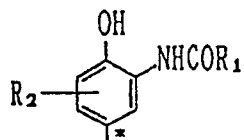
(VII)

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where R_1 and R_2 are the same as defined for R_1 and R_2 in the general formulas (II) and (III).

Preferred examples of the cyan coupler residue represented by Cp in the general formula (I) are those represented by the following general formulas (VIII), (IX) and (X) :

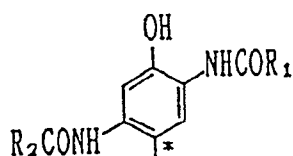
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(VIII)

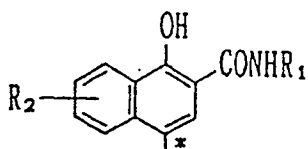
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(IX)

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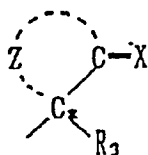
(X)

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where R_1 and R_2 are the same as defined for R_1 and R_2 in the general formulas (II) and (III).

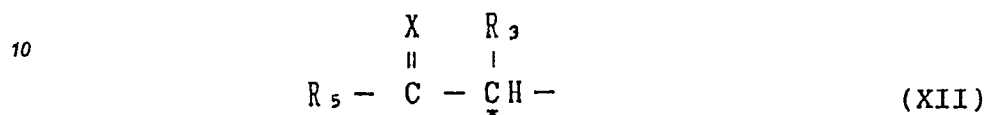
Preferred examples of the coupler residue which forms a substantially colorless product as represented by Cp in the general formula (I) are those represented by the following general formulas (XI) - (XIV) :

55



(XI)

where R₃ may be a hydrogen atom, an alkyl group, an aryl group, a halogen atom, an alkoxy group, an acyloxy group or a heterocyclic group ; X is an oxygen atom or =NR₄ (where R₄ is an alkyl group, an aryl group, a hydroxyl group, an alkoxy group or a sulfonyl group) ; and Z is the nonmetallic atomic group necessary to form a 5- to 7-membered carbon ring (e.g. indanone, cyclopentanone or cyclohexanone) or a 5- to 7-membered hetero ring (e.g. piperidone, pyrrolidone or hydrocarbostyryl) ;



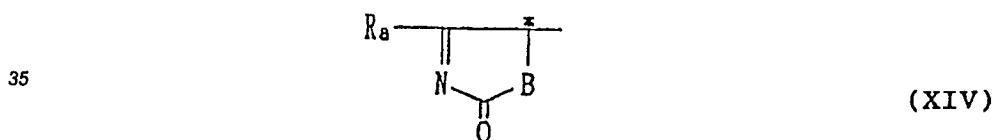
where R₃ and X are the same as defined for R₃ and X in the general formula (XI) ; R₅ is an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, an alkoxy group, an aryloxy group, a heterocycloxy group, an alkylamino group, a dialkylamino group or an anilino group ;



20 where R₆ and R₇ which may be the same or different each represents an alkoxycarbonyl group, a carbamoyl group, an acyl group, a cyano group, a formyl group, a sulfonyl group, a sulfinyl group, a sulfamoyl group, an ammoniumyl group or

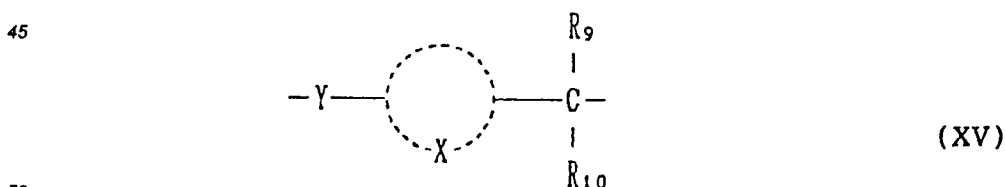


(where A is nonmetallic atomic group necessary to form, taken together with the nitrogen atom, a 5- to 7-membered hetero ring such as phthalimido, triazole or tetrazole) :



where R₈ is an alkyl group, an aryl group, an anilino group, an alkylamino group or an alkoxy group ; and B is
40 an oxygen atom, a sulfur atom or a nitrogen atom.

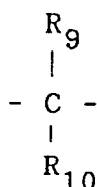
Examples of TIME useful in the present invention include, but are not limited to, those which are represented by the following general formulas (XV), (XVI) and (XVII) :



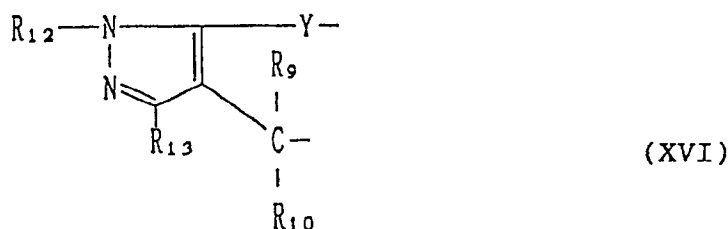
where X is the atomic group necessary to form an optionally substituted benzene or naphthalene ring ; Y is -O-, -S- or



and is bound at the coupling site to the coupler residue represented by Cp in the general formula (I) ; R_9 , R_{10} and R_{11} are each a hydrogen atom, an alkyl group or an aryl group ; and

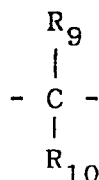


which is substituted in the position ortho or para to Y is bound to the sulfur atom in the development restraining group ;



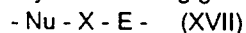
where Y, R_9 and R_{10} are each the same as defined for Y, R_9 , and R_{10} in the general formula (XV) ; R_{12} may be a hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfonyl group, an alkoxy carbonyl group or a heterocyclic residue ; and R_{13} is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic residue, an alkoxy group, an amino group, an acid amido group, a sulfonamido group, a carboxyl group, an alkoxy carbonyl group, a carbamoyl group or a cyano group.

As in the general formula (XV), the timing group TIME is bound via Y to the coupling site of the coupler residue represented by Cp in the general formula (I), or via



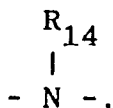
to the sulfur atom in the development restraining group.

An example of the timing group that releases a development restraining group by an intramolecular nucleophilic substitution reaction is represented by the following general formula (XVII) :



where Nu is a nucleophilic group having an electron-rich oxygen, sulfur or nitrogen atom and it is bound at the coupling site to the coupler residue represented by Cp in the general formula (I) ; E is an electrophilic group having an electron-lean carbonyl, thiocarbonyl, phosphinyl or thiophosphinyl group and it is bound to the sulfur atom in the development restraining group ; X is a bonding group that sterically relates Nu and E and which, after Nu is released from the coupler residue represented by Cp in the general formula (I), undergoes an intramolecular nucleophilic reaction involving the formation of a 3- to 7-membered ring to thereby release a development restrainer.

In the general formula (I), X represents alkylene, cycloalkylene, phenylene, alkenylene,



-O-, -S- (where R_{14} may be a hydrogen atom, an alkyl group, a cycloalkyl group or an aryl group) or combinations of these groups. Among these, alkylene,



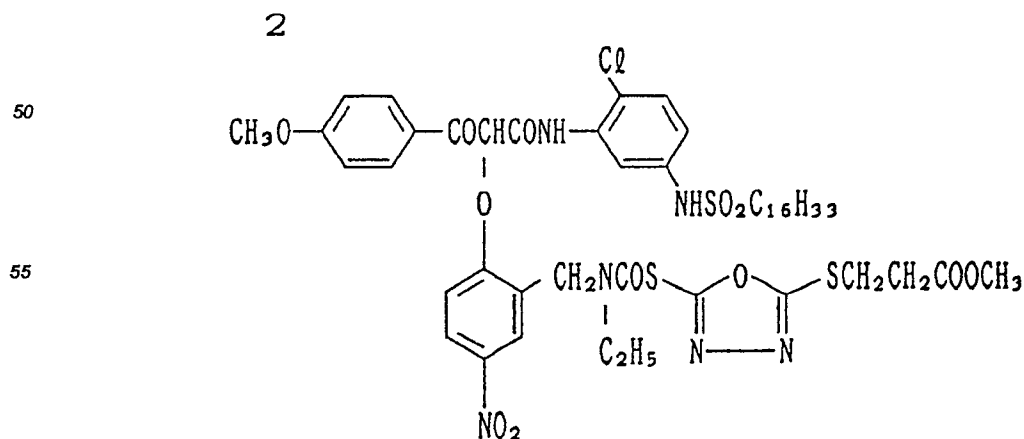
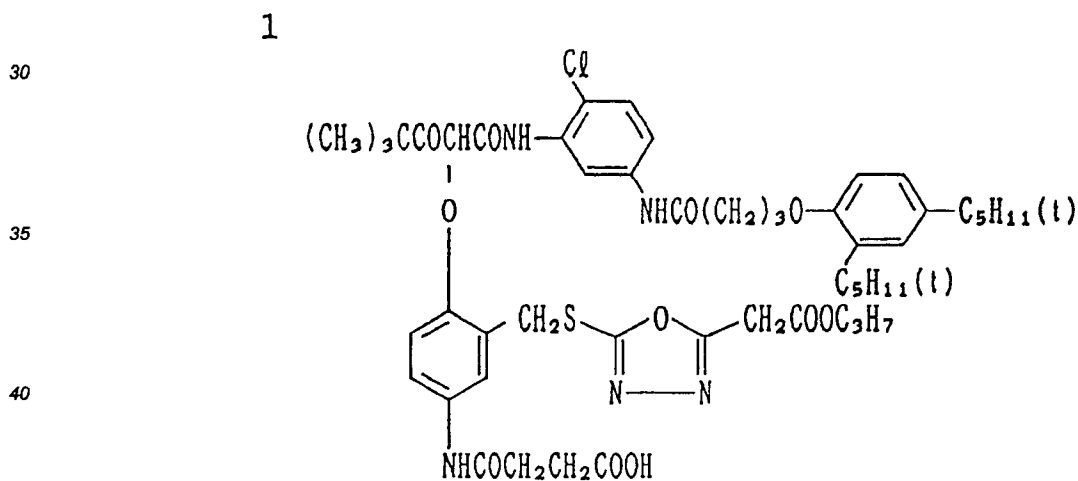
and combinations of these groups are preferred.

10 Examples of the hydrolyzable group represented by Y in the general formula (I) include $-\text{COOR}_{15}$, $-\text{OCOR}_{15}$, $-\text{OSO}_2\text{R}_{15}$ and

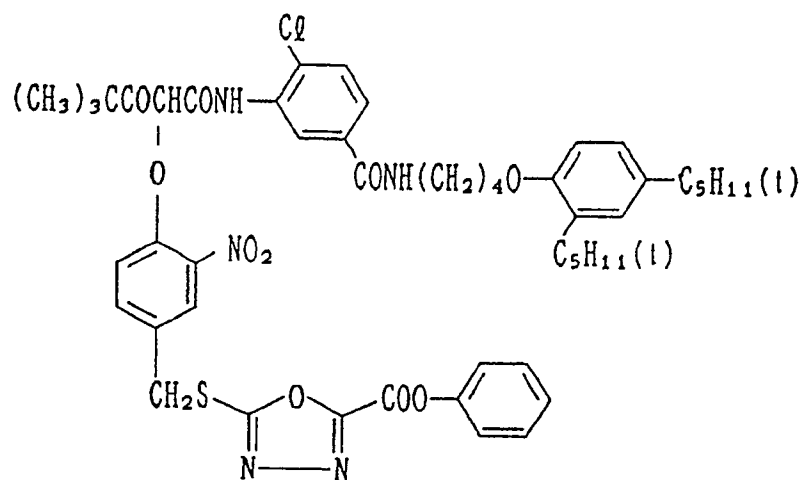


with $-\text{COOR}_{15}$ being preferred. Examples of the group represented by R_{15} include an alkyl group (e.g. methyl, ethyl, propyl, isopropyl, butyl, sec-butyl or n-hexyl), a cycloalkyl group (e.g. cyclopentyl or cyclohexyl), an aryl group (e.g. phenyl or naphthyl), and a heterocyclic group (e.g. pyridinyl, imidazolyl or pyrrolyl). These groups may have substituents such as a halogen atom, nitro, cyano, alkyl, alkenyl, cycloalkyl, aryl, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl, carboxyl, sulfo, sulfamoyl, carbamoyl, acylamino, ureido, urethane, sulfonamido, hetero ring, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, anilino, hydroxyl, imido and acyl.

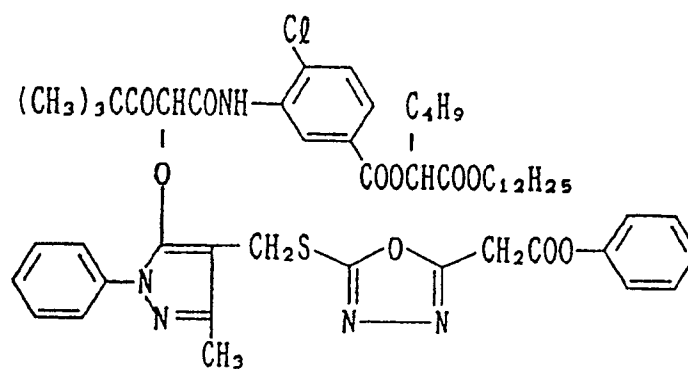
25 A substituted alkyl group and an aryl group are preferred for R_{15} , with aryl being more preferred. Typical examples of the compound of the general formula (I) are listed below but it should be understood that the present invention is by no means limited to these examples.



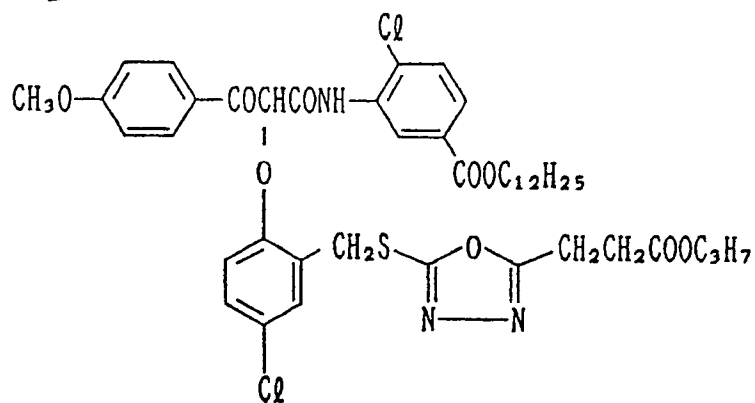
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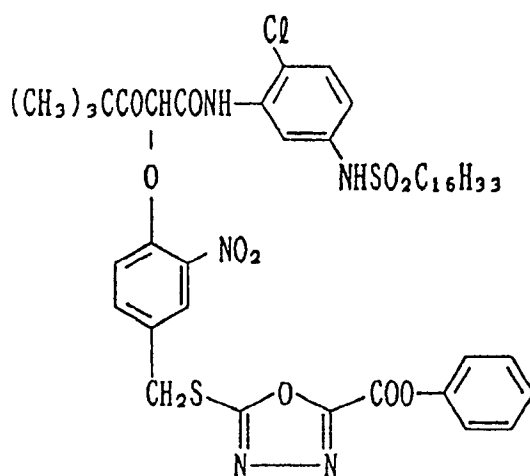
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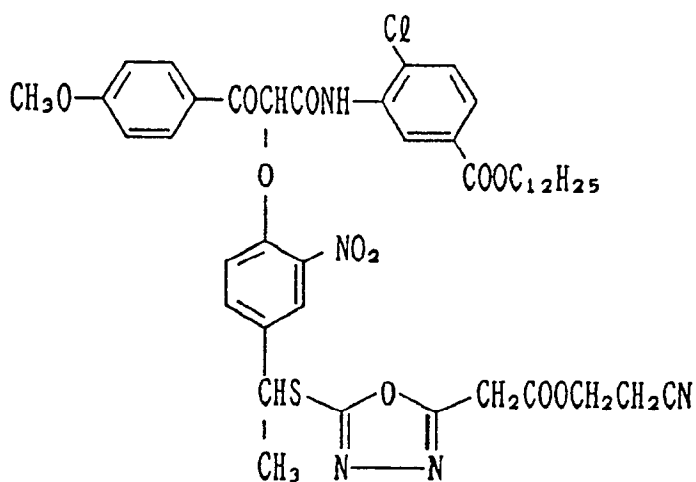
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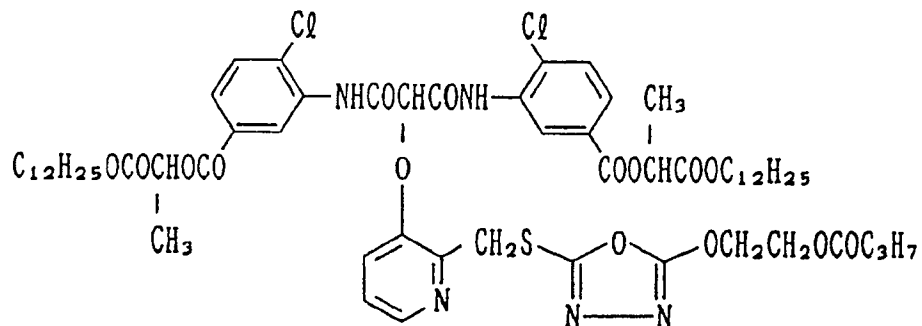
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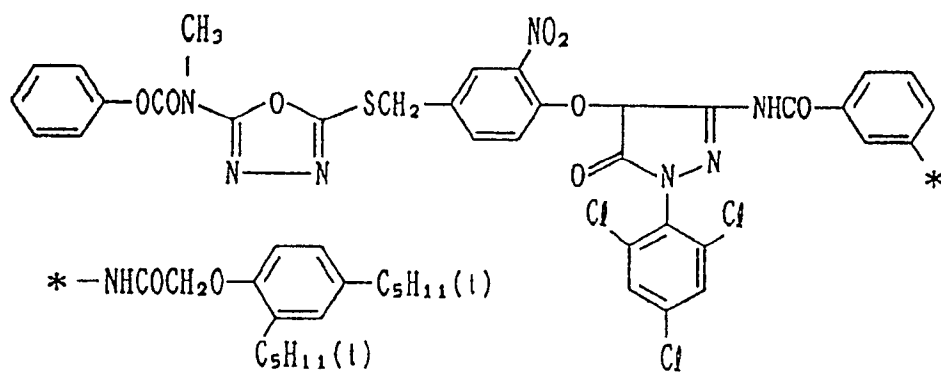
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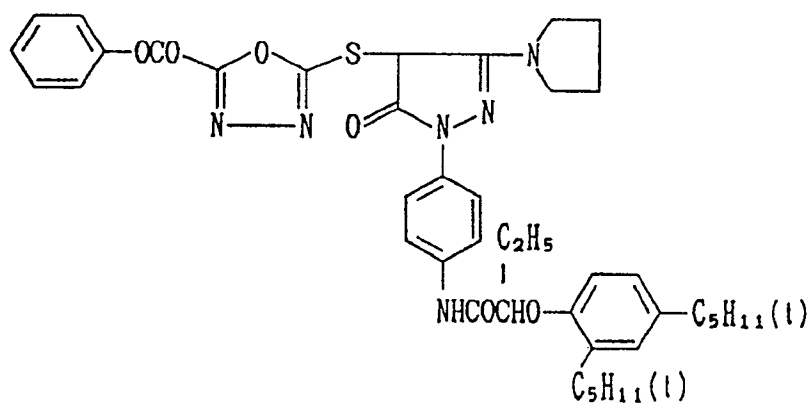
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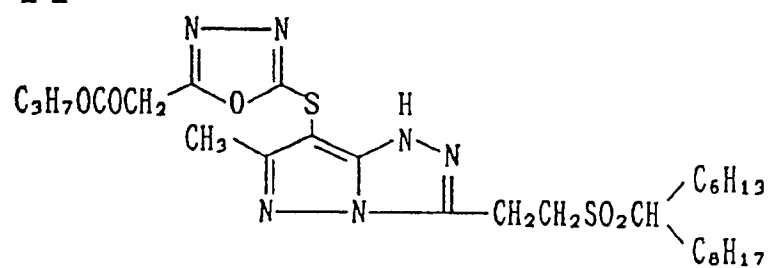
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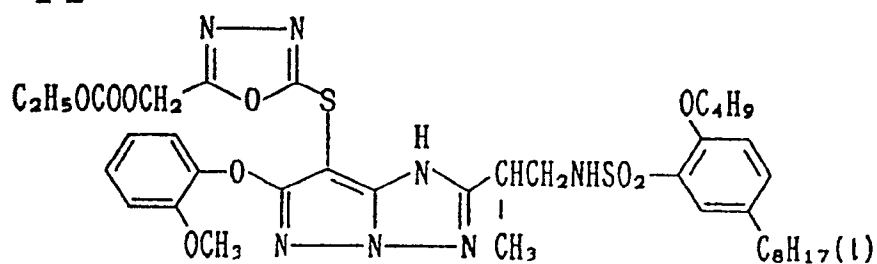
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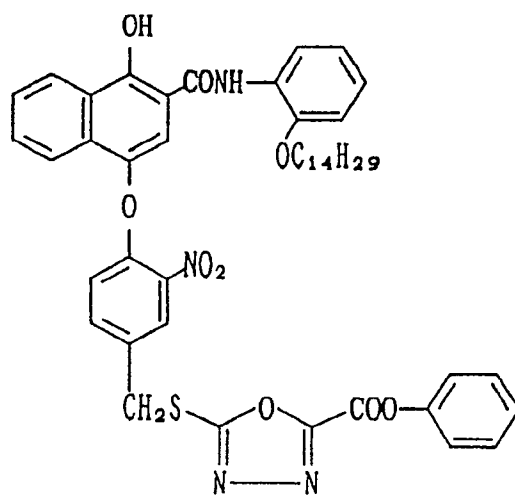
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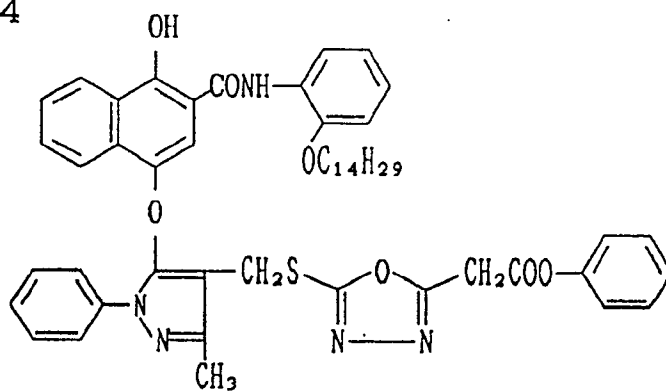
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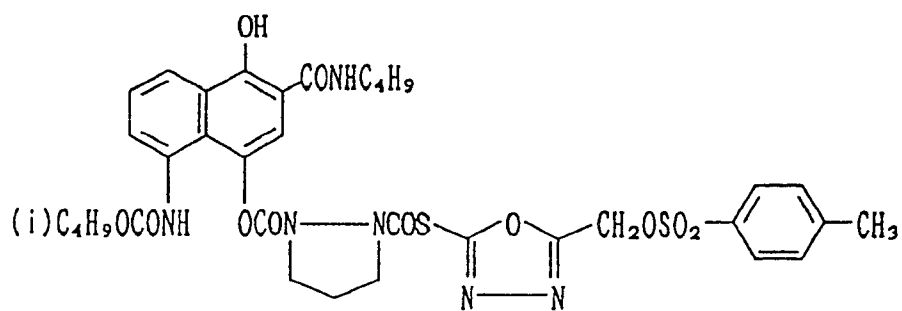
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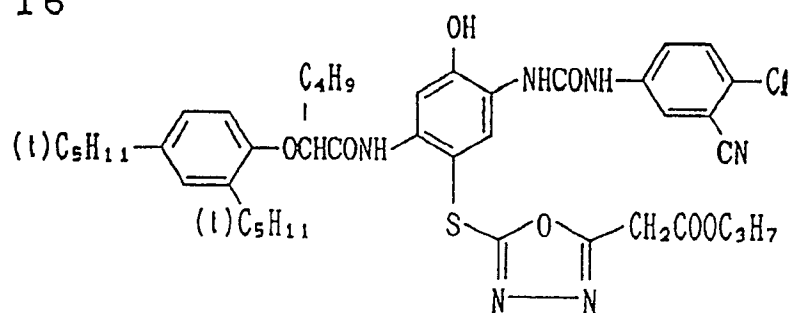
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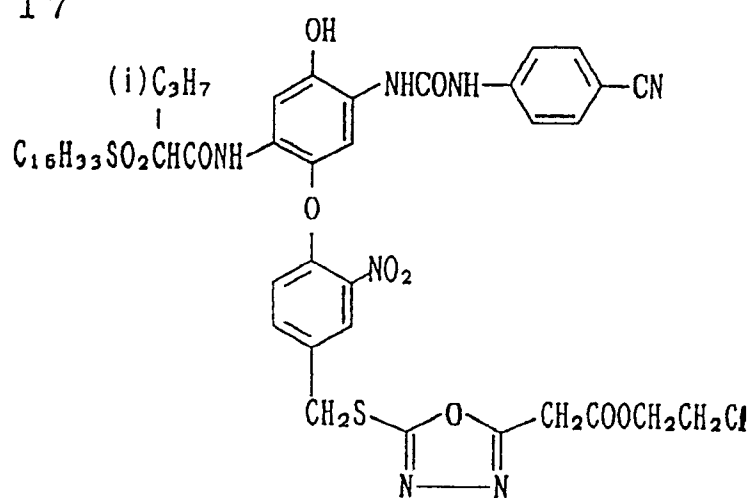
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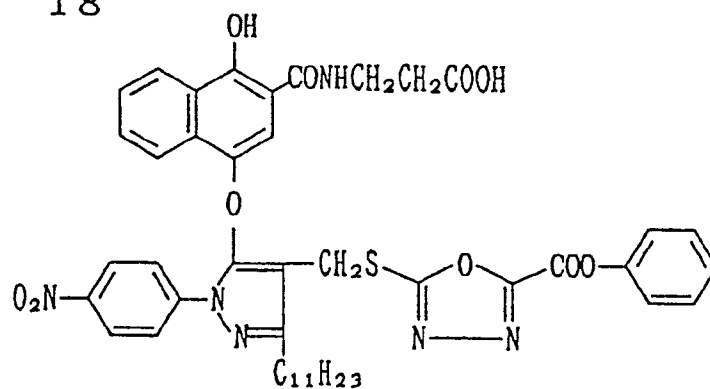
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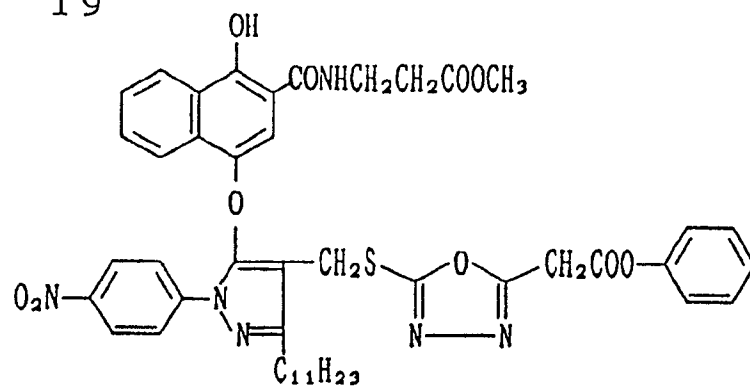
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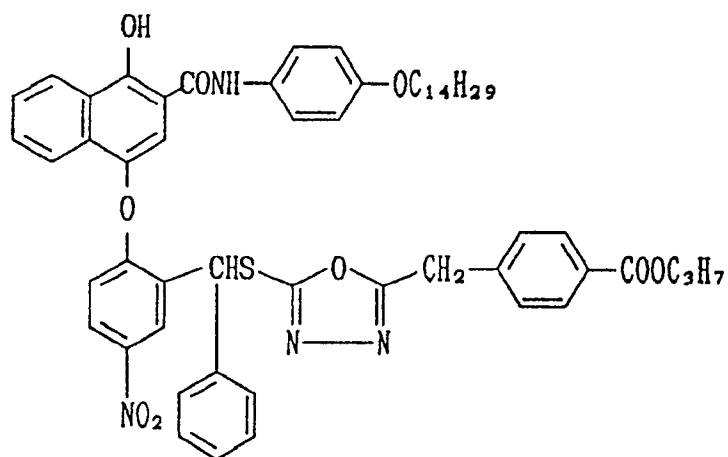
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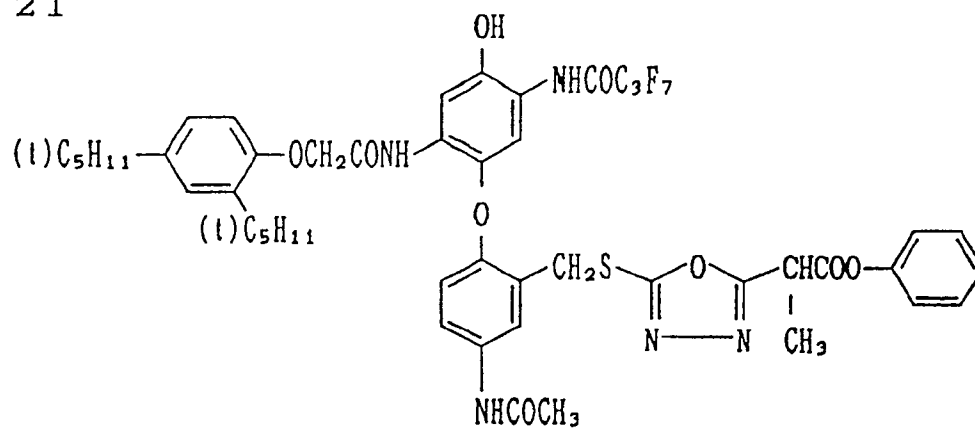
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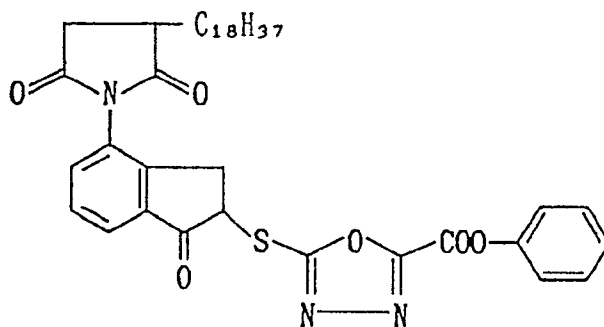
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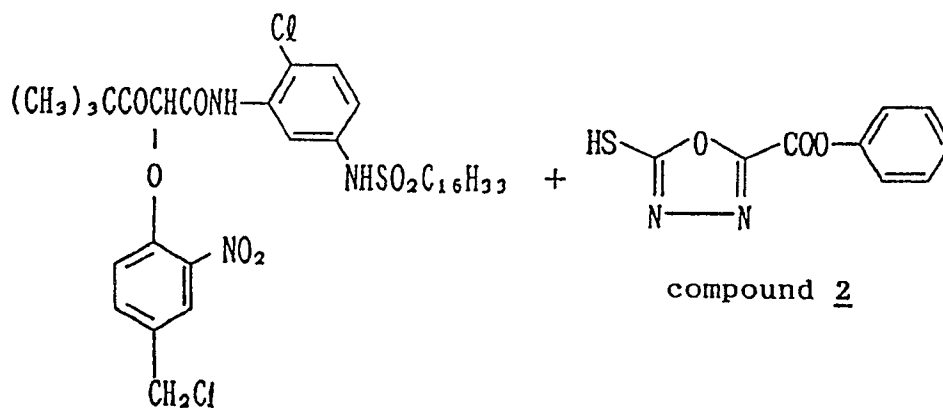


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Two examples of the synthesis of compounds represented by the general formula (I) are described below.

Synthesis 1 (synthesis of illustrative compound 6)

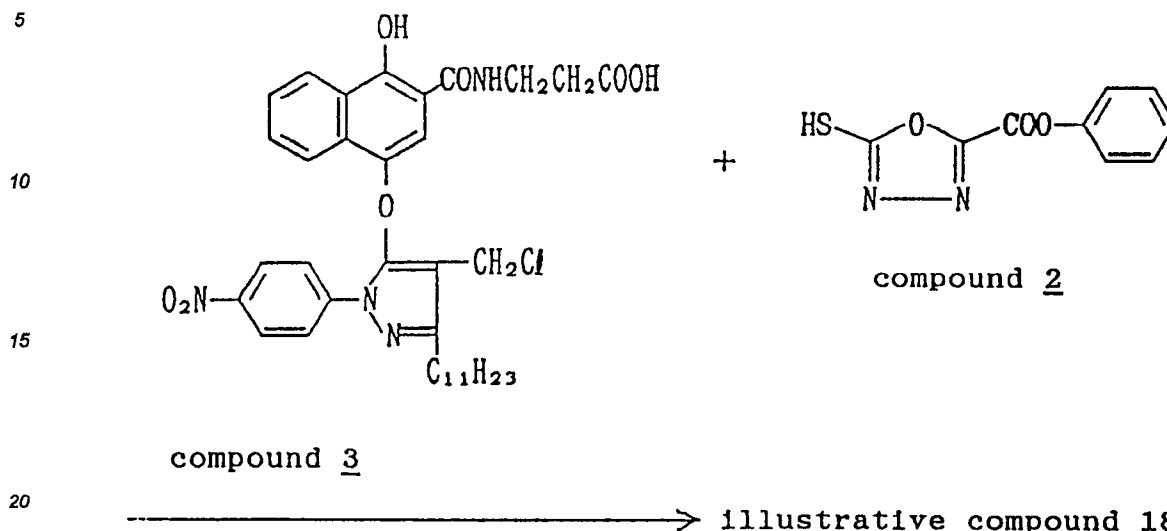


compound 1

illustrative compound 6

Compound 1 (7.4 g), compound 2 (2.2 g) and triethylamine (2.0 g) were dissolved in 20 ml of methylene chloride and the solution was stirred for 2 h. The reaction solution was washed with 50 ml of 1 N HCl and 150 ml of water, followed by concentration under vacuum. The residue was recrystallized from methanol to obtain 7.0 g of illustrative compound 6.

Synthesis 2 (synthesis of illustrative compound 18)



Compound 3 (3.3 g) and compound 2 (1.1 g) were dissolved in 20 ml of methylene chloride. The resulting solution was mixed with a solution of 0.42 g of sodium bicarbonate and 0.1 g of tetrabutylammonium bromide in 20 ml of water, and the mixture was stirred for 24 h.

The methylene chloride layer was separated, washed with water and concentrated under vacuum. The residue was recrystallized from a solvent system composed of ethyl acetate and hexane, whereby illustrative compound 18 was obtained in an amount of 2.7 g.

In both syntheses, the compounds obtained were identified as the desired products by taking NMR, MS and IR spectra.

The compound represented by the general formula (I) (which is hereinafter sometimes referred to as the "DIR coupler" of the present invention) may be incorporated in any layers, such as silver halide emulsion layers and/or non-light-sensitive hydrophilic colloidal layers, in a photographic material. Preferably, the DIR coupler is incorporated in silver halide emulsion layers. More preferably, the DIR coupler of the present invention is incorporated in a blue-sensitive silver halide emulsion layer and/or a red-sensitive silver halide emulsion layer.

The DIR couplers of the present invention may be incorporated in hydrophilic colloidal layers in a color photographic material by the following procedure: the DIR couplers, taken either individually or in combination, are dissolved in a mixture of a known high-boiling point solvent such as dibutyl phthalate, tricresyl phosphate or dinonyl phenol and a known low-boiling point solvent such as butyl acetate or propionic acid; the solution is then mixed with an aqueous gelatin solution containing a surfactant, followed by dispersion using a high-speed rotary mixer, a colloid mill or an ultrasonic disperser, with the resulting dispersion being directly added to a silver halide emulsion; alternatively, the dispersion is allowed to set, shredded into noodles, which are then washed with water and added to a silver halide emulsion.

The DIR couplers of the present invention are used in amounts that preferably range from 0.005 ~ 10 mol%, more preferably from 0.01 ~ 5 mol% of silver halide. The DIR couplers of the present invention may be used either individually or as admixtures.

Any customary silver halide emulsions may be used in the photographic material of the present invention. Such emulsions may be chemically sensitized in the usual manner, or they may be optically sensitized with spectral sensitizers to have sensitivity in a desired wavelength region.

Antifoggants, stabilizers, etc. may be added to silver halide emulsions. Gelatin is advantageously used as a binder for silver halide emulsions.

Emulsion layers and other hydrophilic colloidal layers may be hardened. Plasticizers or dispersions (latices) of synthetic polymers that are either insoluble or slightly soluble in water may also be contained in emulsion layers and other hydrophilic colloidal layers.

Couplers are used in emulsion layers in a color photographic material. Also usable are colored couplers which are capable of color correction, competing couplers, as well as those compounds which, upon coupling with the oxidation product of developing agents, release photographically useful fragments such as a development accelerator, a bleach accelerator, a developing agent, a silver halide solvent, a toning agent, a hardener, a foggant, an antifoggant, a chemical sensitizer, a spectral sensitizer and a desensitizer.

The photographic material of the present invention may have a filter layer, an anti-halo layer, an anti-

irradiation layer, etc. These layers and/or emulsion layers may contain dyes that will dissolve out of the photographic material during photographic processing or which are bleachable.

The photographic material of the present invention may also contain a matting agent, a lubricant, an image stabilizer, a surfactant, an anti-color fog agent, a development accelerator, a development retarder or a bleach accelerator.

Supports that can be used in the present invention include paper laminated with a resin such as polyethylene, a polyethylene terephthalate film, baryta paper, a triacetyl cellulose film, etc.

In order to produce dye image using the photographic material of the present invention, it may be subjected to known procedures of color photographic processing.

The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting. In the following examples, the amounts of components or additives in silver halide photographic materials are based on one square meter unless otherwise noted. The amounts of silver halides and colloidal silver are calculated for silver.

Example 1

Multi-layered color photographic material (sample 1) was prepared by forming the following layers in the order written on a triacetyl cellulose film base.

Sample 1 (comparison) :

First layer : Anti-halo layer (HC-1)
Gelatin layer containing black colloidal silver

Second layer : Intermediate layer (IL)
Gelatin layer containing an emulsified dispersion of 2,5-di-t-octylhydroquinone

Third layer : Less red-sensitive silver halide emulsion layer (RL-1)
Monodispersed emulsion (emulsion I)
composed of AgBrI grains (6 mol% AgI) having an average grain

size ($\bar{r}$) of 0.30 μm

1.8 g

Spectral sensitizer I

6×10^{-5} moles

per mole of
silver

5	Spectral sensitizer II	1×10^{-5} moles per mole of silver
10	Cyan coupler (C-1)	0.06 moles per mole of silver
15	Colored cyan coupler (CC-1)	0.003 moles per mole of silver
20	DIR compound (D-1)	0.0035 moles per mole of silver
25		
	Fourth layer : Highly red-sensitive silver halide emulsion layer (RH-1) Monodispersed emulsion (emulsion II) composed of AgBrI grains (7.0 mol% AgI) having an average grain size	
30		
35	$(\bar{r})$ of 0.5 μm	1.3 g
	Spectral sensitizer I	3×10^{-5} moles per mole of silver
40		
45	Spectral sensitizer II	1.0×10^{-5} moles per mole of silver
50		
55		

5	Cyan coupler (C-1)	0.02 moles per mole of silver
10	Colored cyan coupler (CC-1)	0.0015 moles per mole of silver
15	DIR compound (D-1)	0.001 mole per mole of silver
20	Fifth layer : Intermediate layer (IL) Sixth layer : Same gelatin layer as the second layer Less green-sensitive silver halide emulsion layer (GL-1)	
25		
	Emulsion I	1.5 g
30	Spectral sensitizer III	2.5×10^{-5} moles per mole of silver
35	Spectral sensitizer IV	1.2×10^{-5} moles per mole of silver
40		
45	Magenta coupler (M-1)	0.050 moles per mole of silver

50

55

5	Colored magenta coupler (CM-1)	0.009 moles per mole of silver
10	DIR compound (D-1)	0.0010 mole per mole of silver
15	DIR compound (D-3)	0.0030 moles per mole of silver
20		
	Seventh layer : Highly green-sensitive silver halide emulsion layer (GH-1)	
25	Emulsion II	1.4 g
	Spectral sensitizer III	1.5×10^{-5} moles per mole of silver
30		
	Spectral sensitizer IV	1.0×10^{-5} mole per mole of silver
35		
	Magenta coupler (M-1)	0.020 moles per mole of silver
40		
	Colored magenta coupler (CM-1)	0.002 moles per mole of silver
45		
50		
	DIR compound (D-3)	0.0010 mole per mole of silver
55		

Eighth layer : Yellow filter layer (YC-1)
Gelatin layer containing yellow colloidal
silver and an emulsified dispersion of

5	Ninth layer :	2,5-di-t-octylhydroquinone Less blue-sensitive silver halide emulsion layer (BL-1) Monodispersed emulsion (emulsion III) composed of AgBrI grains (6 mol% AgI) having an average grain size of	
10		0.48 μm	0.9 g
15		Spectral sensitizer V	1.3×10^{-5} moles per mole of silver
20		Yellow coupler (Y-1)	0.29 moles per mole of silver
25	Tenth layer :	Highly blue-sensitive silver halide emulsion layer (BH-1) Monodispersed emulsion (emulsion IV) composed of AgBrI grains (15 mol% AgI) having an average grain size	
30		of 0.8 μm	0.5 g
35		Spectral sensitizer V	1×10^{-5} moles per mole of silver
40		Yellow coupler (Y-1')	0.08 moles per mole of silver
45		DIR compound (D-2)	0.0015 moles per mole of silver
50			
55	Eleventh layer :	First protective layer (Pro-1) Gelatin layer containing silver iodobromide grains (1 mol% AgI ; $\bar{r} = 0.07 \mu\text{m}$ silver deposit, 0.5 g), as well as uv absorbers UV-1 and UV-2	
	Twelfth layer :	Second protective layer (Pro-2) Gelatin layer containing polymethyl methacrylate particles (diameter, 1.5 μm) and formaldehyde scavenger (HS-1)	

Besides the compounds mentioned above, a gelatin hardener (H-1) and a surfactant were also added to each layer.

5 The following compounds were incorporated in the respective layers of sample 1.

Spectral sensitizer I : Anhydro-5,5'-dichloro-9-ethyl-3,3'-
di(3-sulfopropyl)thiacarbocyanine
hydroxide

10 Spectral sensitizer II : Anhydro-9-ethyl-3,3'-
di(sulfopropyl)-4,5,4',5'-
dibenzothiacarbocyanine hydroxide

Spectral sensitizer III : Anhydro-5,5'-diphenyl-9-ethyl-
3,3'-di(3-sulfopropyl)
oxacarbocyanine hydroxide

15 Spectral sensitizer IV : Anhydro-9-ethyl-3,3'-
di(3-sulfopropyl)-5,6,5',6'-
dibenzoxacarbocyanine hydroxide

Spectral sensitizer V : Anhydro-3,3'-di(3-sulfopropyl)-4,5-
benzo-5'-methoxythiacyanine
hydroxide

20 (The remaining space is left blank.)

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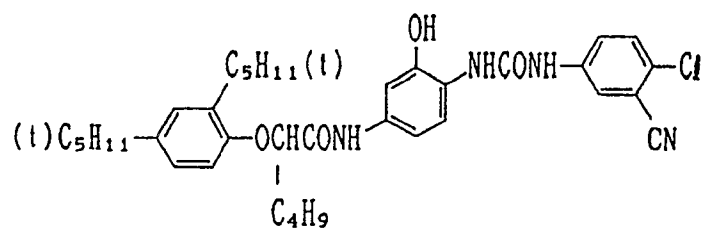
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C - 1

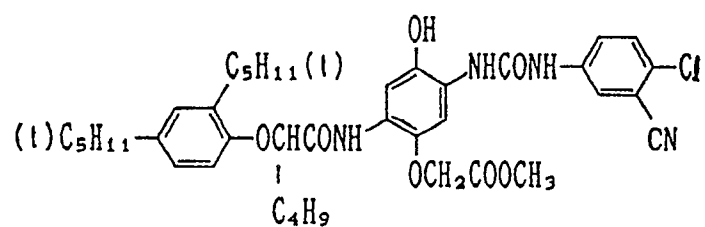
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15

C - 2

20

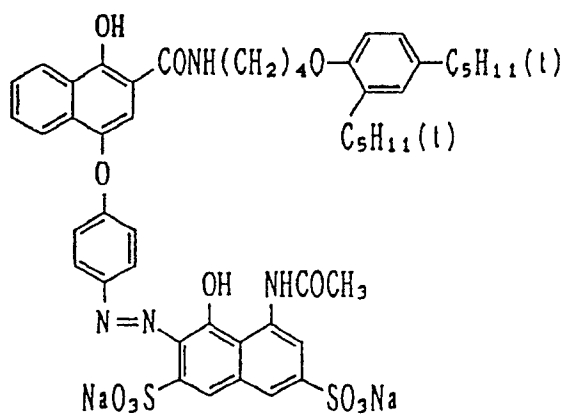


25

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C C - 1

35



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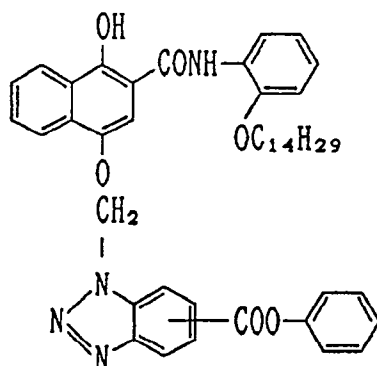
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D-1

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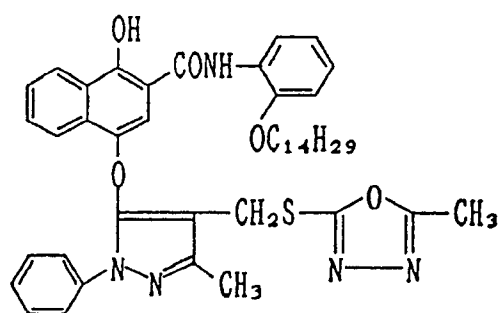
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D-2

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30



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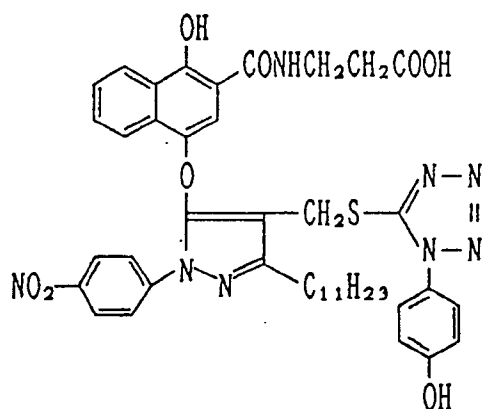
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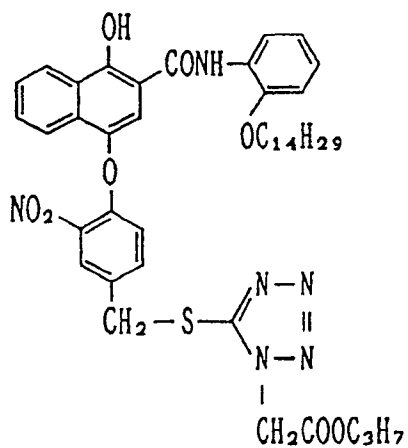
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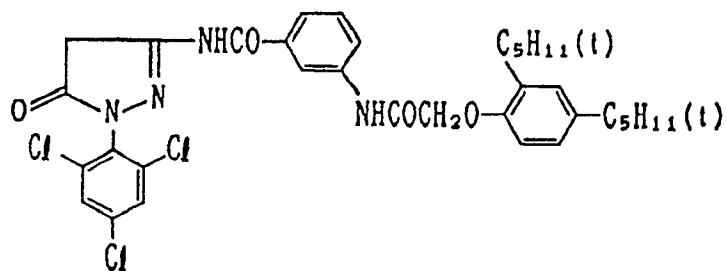
D-3



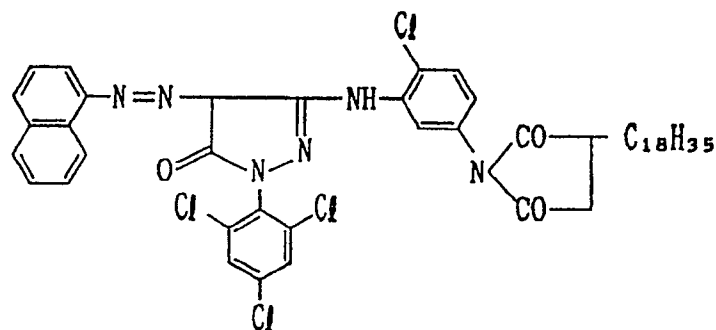
D-4



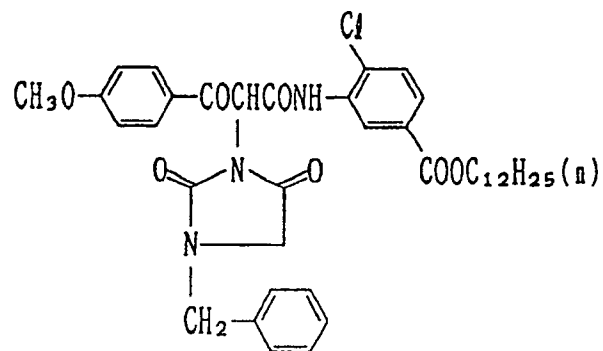
M-1



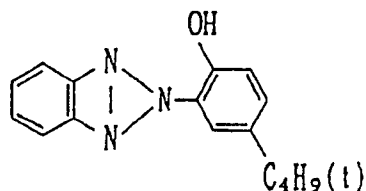
CM-1



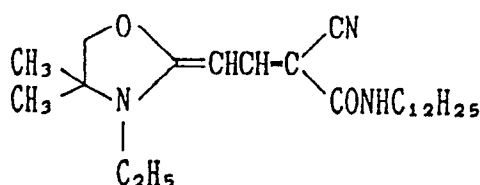
Y-1



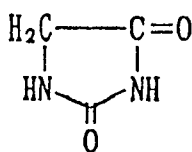
UV-1



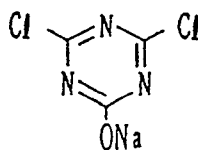
UV-2



HS-1



H-1



Samples 2 - 5 were prepared by replacing the DIR compound (D-1) in the third and fourth layers of sample 1 with equimolar amounts of the compounds shown in Table 1 below.

Each of the thus prepared samples 1 - 5 was divided into two lots, one of which was left to stand at 55°C for 7 days at 20% r.h. before exposure. The samples including the untreated lots were exposed to white light through an optical wedge and processed by the scheme shown below. The sensitivity of the red-sensitive layers and the fog that occurred were measured. At the same time, the sharpness of image was also measured and the results were shown in terms of the relative values of MTF at a resolution of 30 lines/mm, with the value for sample 1 taken as 100. The results of the measurements are shown in Table 1 below.

Processing scheme (38°C)

Color development	3 min and 15 sec
Bleaching	6 min and 30 sec
Washing with water	3 min and 15 sec
Fixing	6 min and 30 sec
Washing with water	3 min and 15 sec

Stabilization 1 min and 30 sec

Drying

5 The processing solutions used in the color developing, bleaching, fixing and stabilizing steps had the following compositions.

Color developing solution

10	4-Amino-3-methyl-N-ethyl-N-	
	(β -hydroxyethyl)aniline sulfate	4.75 g
	Anhydrous sodium sulfite	4.25 g
15	Hydroxylamine hemisulfate	2.0 g
	Anhydrous calcium carbonate	37.5 g
20	Sodium bromide	1.3 g
	Nitrilotriacetic acid trisodium salt	
	(monohydrate)	2.5 g
25	Potassium hydroxide	1.0 g
	Water	to make 1,000 ml

30 Bleaching solution

	Ethylenediaminetetraacetic acid iron (III)	
35	ammonium salt	100 g
	Ethylenediaminetetraacetic acid diammonium	
	Salt	10.0 g
40	Ammonium bromide	150.0 g
	Glacial acetic acid	10 ml
45	Water	to make 1,000 ml
	pH	adjusted to 6.0 with aqueous ammonia

Fixing solution

50	Ammonium thiosulfate	175.0 g
	Anhydrous sodium sulfite	8.6 g
	Sodium metasilicate	2.3 g
	Water	to make 1,000 ml
55	pH	adjusted to 6.0 with acetic acid

Stabilizing solution

5	Formaldehyde (37% aq. sol.)	1.5 ml
	Konidax (product of Konica Corp.)	7.5 ml
10	Water	to make 1,000 ml

Table 1

15	Sample No.	DIR compound in layers 3 and 4	Untreated		Treated at 55°C		Sharpness
20			specific sensitivity	fog	specific sensitivity	fog	
25	1 (comparison)	D-1	100	0.16	92	0.30	100
30	2 (comparison)	D-4	99	0.16	93	0.31	101
35	3 (invention)	13	101	0.15	99	0.20	113
40	4 (invention)	14	100	0.15	99	0.21	112
	5 (invention)	20	100	0.15	98	0.22	110

As is clear from Table 1, the samples prepared in accordance with the present invention were markedly improved in image sharpness and further they experienced less thermal fogging and reduction in sensitivity during storage. Reduction in sensitivity was also negligible even when the samples of the present invention were subjected to continuous processing.

Example 2

A basic sample was prepared by coating multiple layers in superposition on a triacetate base in the order indicated below.

- (1) Red-sensitive silver halide emulsion layer containing 0.5 g of cyan coupler (C-2), 2.4 g of gelatin and 1.6 g of silver halide ;
- (2) Intermediate gelatin layer containing 0.5 g of gelatin and 0.1 g of 2,5-di-t-octylhydroquinone ;
- 55 (3) Blue-sensitive silver iodobromide emulsion layer containing 1.70 g of yellow coupler (Y-1), 2.4 g of gelatin and 1.6 g of silver halide ; and
- (4) Protective layer containing 0.8 g of gelatin.

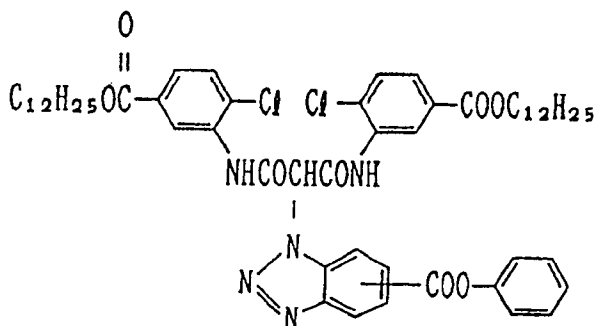
Five additional samples 6 - 10 were prepared by adding specific DIR couplers (see Table 2) to the yellow coupler containing third layer in an amount of 3.0×10^{-4} mol/m². Each of these samples was divided into two lots, one being exposed to white light through an optical wedge and the other exposed to red light through an

optical wedge. Each lot of the samples were then processed as in Example 1. Gamma values were determined from the characteristic curves of cyan dye as obtained for each sample by color development and the gamma by exposure to red light (r_R) was divided by the gamma by exposure to white light (r_W). The results are shown in Table 2 below.

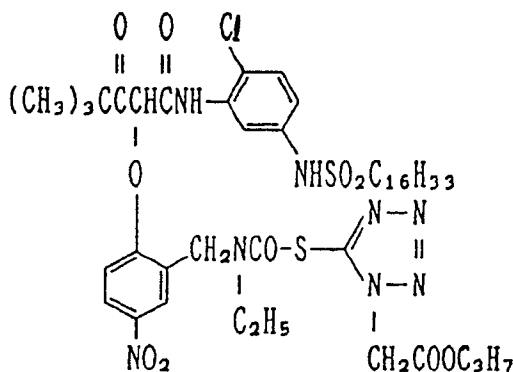
Table 2

Sample No.	DIR compound	r_R/r_W
6 (comparison)	D - 5	1.20
7 (comparison)	D - 6	1.22
8 (invention)	3	1.55
9 (invention)	5	1.47
10 (invention)	18	1.52

D-5:



D-6:



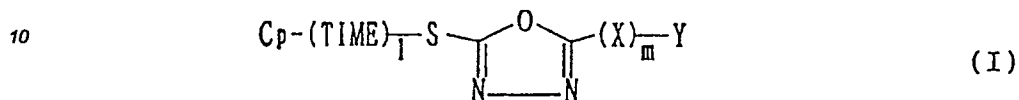
As is clear from Table 2, the samples using the DIR compounds of the present invention provided large r_R/r_W values and obviously produced a greater interimage effect than when the conventional DIR couplers were used.

The advantage of the present invention is that it provides a silver halide color photographic material that achieves good sharpness and high fidelity of color reproduction and which is also improved in storage stability.

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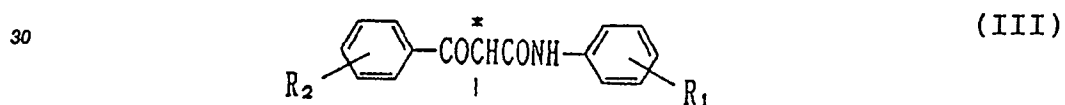
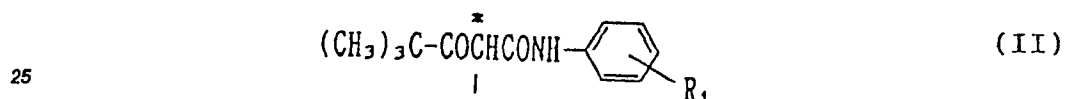
Claims

1. A silver halide photographic material containing a compound of the following general formula (I) which is capable of releasing a development restrainer upon reaction with the oxidation product of a developing agent :



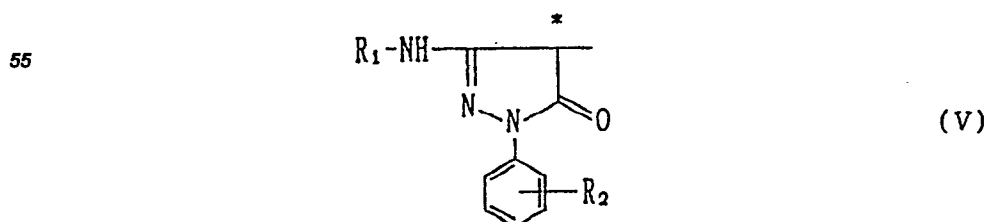
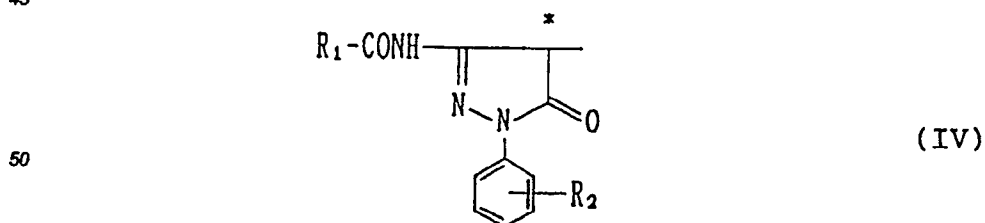
where Cp is a coupler residue that is capable of entering into a coupling reaction with the oxidation product of a color developing agent ; TIME is a timing group bound to Cp at the coupling site ; I is 0 or 1 ; X is a linkage group ; Y is a hydrolyzable group ; and m is 0 or 1.

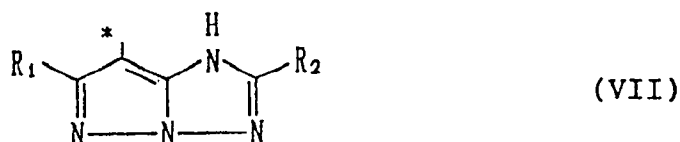
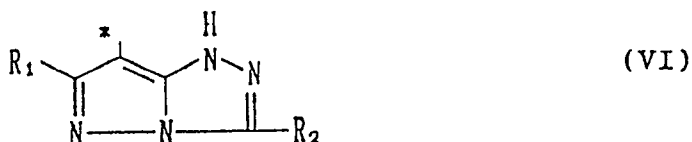
2. A silver halide photographic material according to claim 1 wherein the coupler residue represented by Cp in the general formula (I) is a yellow coupler residue represented by the following general formula (II) or (III) :



where R_1 and R_2 each represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group or a halogen atom, provided that the alkyl, cycloalkyl, aryl or heterocyclic group may be bound via at least one member of the group consisting of an oxygen atom, a nitrogen atom, a sulfur atom, an acylamino group, a carbamoyl group, a sulfonamido group, a sulfamoyl group, a sulfamoylcarbonyl group, a carbonyloxy group, an oxycarbonyl group, a ureido group, a thioureido group, a thioamido group, a sulfone group and a sulfonyloxy group.

3. A silver halide photographic material according to claim 1 wherein the coupler residue represented by Cp in the general formula (I) is a magenta coupler residue represented by either one the following general formulas (IV) - (VII) :

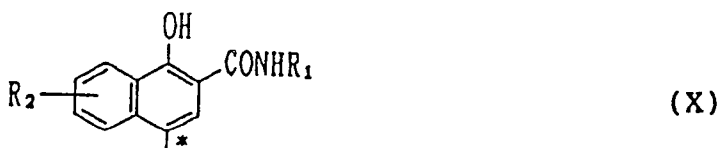
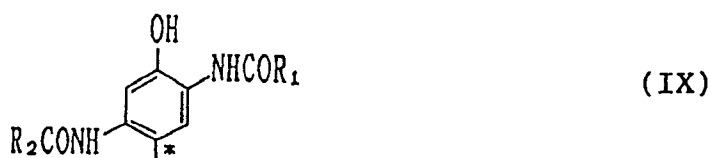




15 where R_1 and R_2 each represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group or a halogen atom, provided that the alkyl, cycloalkyl, aryl or heterocyclic group may be bound, via at least one member of the group consisting of an oxygen atom, a nitrogen atom, a sulfur atom, an acylamino group, a carbamoyl group, a sulfonamido group, a sulfamoyl group, a sulfamoylcarbonyl group, a carbonyloxy group, an oxycarbonyl group, a ureido group, a thioureido group, a thioamido group, a sulfone group and a sulfonyloxy group.

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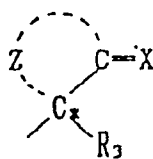
4. A silver halide photographic material according to claim 1 wherein the coupler residue represented by Cp in the general formula (I) is a cyan coupler residue represented by either one of the following general formulas (VIII) - (X) :
- 25



50 where R_1 and R_2 each represents an alkyl group, a cycloalkyl group, an aryl group, a heterocyclic group or a halogen atom, provided that the alkyl, cycloalkyl, aryl or heterocyclic group may be bound via at least one member of the group consisting of an oxygen atom, a nitrogen atom, a sulfur atom, an acylamino group, a carbamoyl group, a sulfonamido group, a sulfamoyl group, a sulfamoylcarbonyl group, a carbonyloxy group, an oxycarbonyl group, a ureido group, a thioureido group, a thioamido group, a sulfone group and a sulfonyloxy group.

- 55 5. A silver halide photographic material according to claim 1 wherein the coupler residue represented by Cp in the general formula (I) is a coupler residue that forms a substantially colorless product and which is represented by either one of the following general formulas (XI) - (XIV) :

5

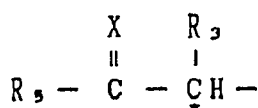


(XI)

10

where R_3 is a hydrogen atom, an alkyl group, an aryl group, a halogen atom, an alkoxy group, an acyloxy group or a heterocyclic group ; X is an oxygen atom or $=NR_4$ (where R_4 is an alkyl group, an aryl group, a hydroxyl group, an alkoxy group or a sulfonyl group) ; and Z is the non-metallic atomic group necessary to form a 5- to 7-membered carbon ring ;

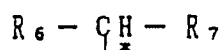
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(XII)

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where R_3 and X are the same as defined for R_3 and X in the general formula (XI) ; R_5 is an alkyl group, an aryl group, a heterocyclic group, a cyano group, a hydroxyl group, an alkoxy group, an aryloxy group, a heterocycloxy group, an alkylamino group, a dialkylamino group or an anilino group ;



(XIII)

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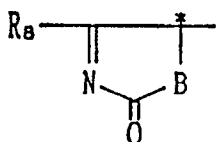
where R_6 and R_7 which may be the same or different each represents an alkoxycarbonyl group, a carbamoyl group, an acyl group, a cyano group, a formyl group, a sulfonyl group, a sulfinyl group, a sulfamoyl group, an ammoniumyl group or

30



(where A is the non-metallic atomic group necessary to form, taken together with the nitrogen atom, a 5- to 7-membered hetero ring) ; and

35



(XIV)

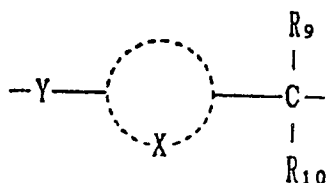
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where R_8 is an alkyl group, an aryl group, an anilino group, an alkylamino group or an alkoxy group ; and B is an oxygen atom, a sulfur atom or a nitrogen atom.

45

6. A silver halide photographic material according to claim 1 wherein TIME in the general formula (I) is a group represented by either one of the following general formulas (XV) - (XVII) :

50

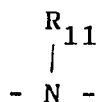


(XV)

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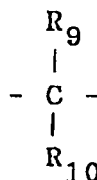
where X is the atomic group necessary to form a benzene or naphthalene ring ; Y is $-O-$, $-S-$ or

5



and is bound at the coupling site to the coupler residue represented by Cp in the general formula (I) ; R_9 , R_{10} and R_{11} are each a hydrogen atom, an alkyl group or an aryl group ; and

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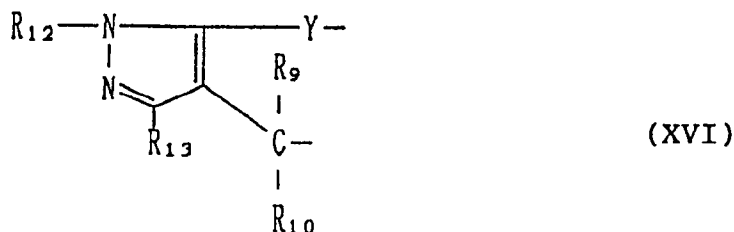


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which is substituted in the position ortho or para to Y is bound to the sulfur atom in the development restraining group ;

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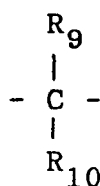


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where Y, R_9 and R_{10} are each the same as defined for Y, R_9 and R_{10} in the general formula (XV) ; R_{12} is a hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfonyl group, an alkoxy carbonyl group or a heterocyclic residue ; R_{13} is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic residue, an alkoxy group, an amino group, an acid amido group, a sulfonamido group, a carboxyl group, an alkoxy carbonyl group, a carbamoyl group or a cyano group ; and Y is bound to the coupling site of the coupler residue represented by Cp in the general formula (I) ; and

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is bound to the sulfur atom in the development restraining group ;

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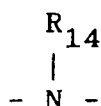


where Nu is a nucleophilic group having an electron-rich oxygen, sulfur or nitrogen atom and it is bound at the coupling site to the coupler residue represented by Cp in the general formula (I) ; E is an electrophilic group having an electron-lean carbonyl, thiocarbonyl, phosphinyl or thiophosphinyl group and it is bound to the sulfur atom in the development restraining group ; X is a bonding group that sterically relates Nu to E.

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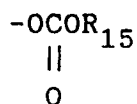
7. A silver halide photographic material according to claim 1 wherein the linkage group represented by X in the general formula (I) is an alkylene group, a cycloalkylene group, a phenylene group, an alkenylene group,

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(where R_{14} is a hydrogen atom, an alkyl group, a cycloalkyl group or an aryl group). -O-, -S- or a combination thereof.

8. A silver halide photographic material according to claim 1 where the hydrolyzable group represented by Y in the general formula (I) is $-\text{COOR}_{15}$, $-\text{OCOR}_{15}$, $-\text{OSO}_2\text{R}_{15}$ or



(where R_{15} is an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group).

9. A silver halide photographic material according to claim 1 wherein the compound represented by the general formula (I) is incorporated in a silver halide emulsion layer.
10. A silver halide photographic material according to claim 1 wherein the compound represented by the general formula (I) is incorporated in either a blue-sensitive silver halide emulsion layer or red-sensitive silver halide emulsion layer or both.
11. A silver halide photographic material according to claim 1 wherein the compound represented by the general formula (I) is contained in an amount of 0.005 ~ 10 mol% of silver halide.
12. A silver halide photographic material according to claim 1 wherein the compound represented by the general formula (I) is contained in an amount of 0.01 ~ 5 mol% of silver halide.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 0752

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X, Y	EP-A-0252376 (FUJII) * page 8, lines 39 - 51 * * page 11, line 40 - page 13, line 45; claims 1, 7, 8, 13 * ---	1-12	G03C7/305
Y	EP-A-0175311 (KONISHIROKU) * page 8, line 16 - page 12, line 11 * * page 35, line 1 * * page 42, line 2 * -----	1-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 APRIL 1991	Examiner MAGRIZOS S.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons & : member of the same patent family, corresponding document			

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