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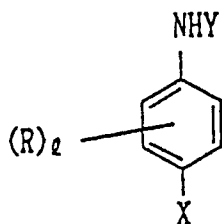
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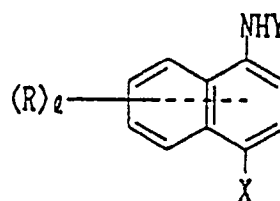
54 A novel cyan coupler.

57 There are disclosed a novel cyan dye-forming coupler and a silver halide photographic light-sensitive material containing the novel coupler represented by the following Formulas I to V:

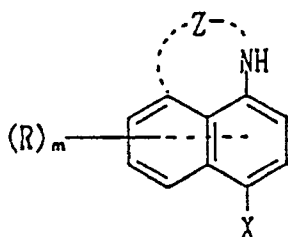
Formula I



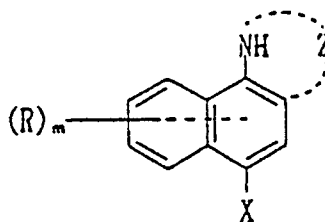
Formula II



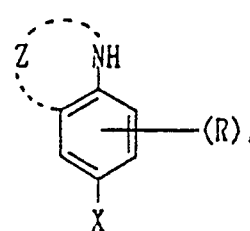
Formula III



Formula IV



Formula V



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wherein R represents a substituent; Y represents a substituent having a Hammett's substituent constant σ_p

of not less than 0.3 and not more than 1.5; Z represents the group of atoms necessary to form a 5 to 7-membered nitrogen-containing heterocyclic ring; l , m and n are the integers of 0 to 4, 0 to 5 and 0 to 3, respectively; and X represents a hydrogen atom or a substituent capable of splitting off upon a reaction with an oxidation product of a developing agent.

A NOVEL CYAN COUPLER

FIELD OF THE INVENTION

5 The present invention relates to a novel photographic coupler which is used as a color photographic component material, and more particularly to a photographic coupler for the formation of a dye image having an excellent fastness against heat, moisture and light.

BACKGROUND OF THE INVENTION

10

Where an exposed silver halide photographic light-sensitive material is processed in a color developer, an oxidation product of a color developing agent reacts with a dye-forming coupler to produce a dye, whereby a color image is formed.

15 In the photographic method, color reproduction is generally carried out by a subtractive color process to form a color image composed of yellow, magenta and cyan dyes.

A photographic coupler used for the formation of a yellow dye image includes acylacetanilide couplers; a magenta color image-forming coupler includes pyrazolone, pyrazolobenzimidazole, pyrazolotriazole and indazolone couplers; and cyan color image-forming coupler includes phenol and naphthol couplers.

20 Dye images formed by these couplers are requested to cause no fading and discoloration even when exposed to light over a long period of time and stored under high temperature/moisture conditions.

However, the phenol and naphthol couplers that have so far been used for the formation of cyan dyes still have the insufficient spectral absorption characteristics and heat, moisture and light resistances of the dye image formed therefrom. To improve the characteristics of a cyan dye image, various attempts
25 including introduction of substituents have been made to date, but no compounds having wholly improved characteristics are yet available.

SUMMARY OF THE INVENTION

30

It is an object of the present invention to provide a novel photographic coupler which is used as a color photographic component material.

35 The other object is to provide a photographic coupler used for the formation of a cyan dye image that undergoes no discoloration attributable to heat, moisture and light.

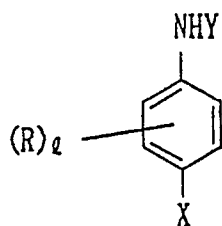
The above objects of the invention is accomplished by photographic couplers represented by the following Formulas I to V:

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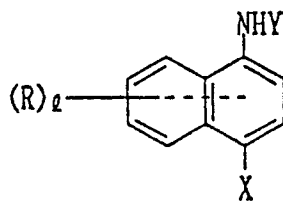
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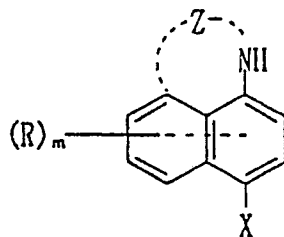
Formula I



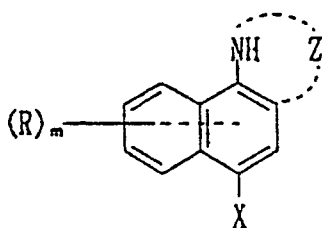
Formula II



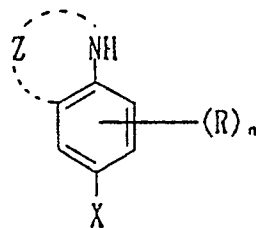
Formula III



Formula IV



Formula V



wherein R represents a substituent: 1 is an integer of zero to 4; m is an integer of zero to 5; n is an integer of zero to 3, provided that when 1, m or n is 2 or more, R's may be the same or different; Y is a substituent whose Hammett's substituent constant σ_p is not less than 0.3 and not more than 1.5; Z is a group of atoms necessary to form a 5- to 7-member nitrogen-containing heterocyclic ring; and X is a hydrogen atom or a substituent which splits off upon reaction with an oxidation product of a color developing agent.

In Formulas I through V, the substituent represented by R includes an alkyl group, an aryl group, an anilino group, an acylamino group, a sulfonamido group, an alkylthio group, an arylthio group, an alkenyl group, a cycloalkyl group, a halogen atom, a cycloalkenyl group, an alkynyl group, a heterocyclic group, a sulfonyl group, a sulfinyl group, a phosphoryl group, an acyl group, a carbamoyl group, a sulfamoyl group, a cyano group, an alkoxy group, a sulfonyloxy group, an aryloxy group, a heterocyclic-oxy group, a siloxy

group, an acyloxy group, a carbamoyloxy group, an amino group, an alkylamino group, an imido group, a ureido group, a sulfamoylamino group, an alkoxy-carbonylamino group, an aryloxy-carbonylamino group, an alkoxy-carbonyl group, an aryloxy-carbonyl group, a heterocyclic-thio group, a thioureido group, a carboxyl group, a hydroxy group, a mercapto group, a nitro group, a sulfonic acid group, a spiro compound residue and a bridged hydrocarbon compound residue.

In the above substituents, the alkyl group has preferably 1 to 32 carbon atoms.

The aryl group is preferably phenyl.

The acylamino group is preferably an alkylcarbonyl amino or arylcarbonylamino group.

The sulfonamido group is preferably an alkylsulfonylamino or arylsulfonylamino group.

The alkyl and aryl components of the alkylthio and arylthio groups are the above alkyl and aryl groups.

The alkenyl group has preferably 2 to 32 carbon atoms, and the cycloalkyl group has preferably 3 to 12 carbon atoms, more preferably 5 to 7 carbon atoms.

The cycloalkenyl group has preferably 3 to 12 carbon atoms, more preferably 5 to 7 carbon atoms.

The sulfonyl group is an alkylsulfonyl or arylsulfonyl group.

The sulfinyl group is an alkylsulfinyl or arylsulfinyl group.

The phosphonyl group is an alkylphosphonyl, arylphosphonyl, alkoxyphosphonyl or aryloxyphosphonyl group.

The acyl group is an alkylcarbonyl or arylcarbonyl group.

The carbamoyl group is an alkylcarbamoyl or arylcarbamoyl group.

The sulfamoyl group is an alkylsulfamoyl or arylsulfamoyl group.

The acyloxy group is an alkylcarbonyloxy or arylcarbonyloxy group.

The carbamoyloxy group is an alkylcarbamoyloxy or arylcarbamoyloxy group.

The ureido group is an alkylureido or arylureido group.

The sulfamoylamino group is an alkylsulfamoylamino or arylsulfamoylamino group.

The heterocyclic group is preferably 5- to 7-member ring such as 2-furyl, 2-thienyl, 2-pyrimidinyl, 2-benzothiazolyl, 1-pyrrolyl and 1-tetrazolyl.

The heterocyclic-oxy group is preferably a 5- to 7-member ring, such as 3,4,5,6-tetrahydropyran-2-yl and 1-phenyltetrazole-5-yl.

The heterocyclic-thio group is preferably a 5- to 7-member ring such as 2-pyridylthio, 2-benzothiazolylthio and 2,4-diphenoxy-1,3,5-triazole-6-thio.

The siloxy group is trimethylsiloxy, triethylsiloxy or dimethylbutylsiloxy.

The imido group is succinic acid imido, 3-heptadecylsuccinic acid imido, phthalimido or glutarimido.

The spiro compound residue is preferably spiro[3.3]heptane-1-yl.

The bridged hydrocarbon compound residue is bicyclo[2.2.1]heptane-1-yl, tricyclo[3.3.1.1^{3,7}]decane-1-yl, or 7,7-dimethyl bicyclo[2.2.1]heptane-1-yl.

Preferred among the above substituents represented by R are the alkyl, aryl, carboxyl, oxycarboxyl, cyano, hydroxy, alkoxy, aryloxy, amino, amido and sulfonamido groups and halogen atom.

l is an integer of zero to 4; m is an integer of zero to 5; and n is an integer of zero to 3; provided that when l, m or n is 2 or more, R's may be either the same or different.

R's may combine with each other to form a ring, and the formed ring is preferably a 5- to 8-member ring such as a pyridine ring and a quinoline ring.

The above groups may have further a substituent of a non-diffusible group such as a long-chain hydrocarbon group and a polymer residue.

The groups represented by X are a halogen atom, an alkoxy group, an aryloxy group, a heterocyclic-oxy group, an acyloxy group, a sulfonyloxy group, an alkoxy-carbonyloxy group, an aryloxy-carbonyl group, an alkyloxyloxy group, an alkoxyoxyloxy group, an alkylthio group, an arylthio group, a heterocyclicthio group, an alkyloxythiocarbonylthio group, an acylamino group, a sulfonamido group, a nitrogen-containing heterocyclic group which has a reactive site at the N atom, an alkyloxy-carbonylamino group, an aryloxy-carbonylamino group, and a carboxyl group.

In Formulas I and II, the substituent represented by Y have the Hammett's substituent constant ρ of not less than 0.3 and not more than 1.5, of which examples are a cyano group, a nitro group; a sulfonyl group such as octylsulfonyl, phenylsulfonyl, trifluoromethylsulfonyl and pentafluorophenylsulfonyl; a β -carboxyvinyl group; a sulfinyl group such as t-butylsulfinyl, tolylsulfinyl, trifluoromethylsulfinyl and pentafluorophenylsulfinyl; a β,β -dicyanovinyl group; a halogenated alkyl group such as trifluoromethyl, perfluorooctyl and ω -hydroperfluorododecyl; a formyl group, a carboxyl group; a carbonyl group such as acetyl, pivaloyl, benzoyl and trifluoroacetyl; alkyl- and aryloxy-carbonyl groups such as ethoxycarbonyl and phenoxycarbonyl; a 1-tetrazolyl group, a 5-chloro-1-tetrazolyl group; a carbamoyl group such as dodecylcarbamoyl and phenylcarbamoyl; and a sulfamoyl group such as trifluoromethylsulfamoyl, phenylsulfamoyl and ethylsulfamoyl.

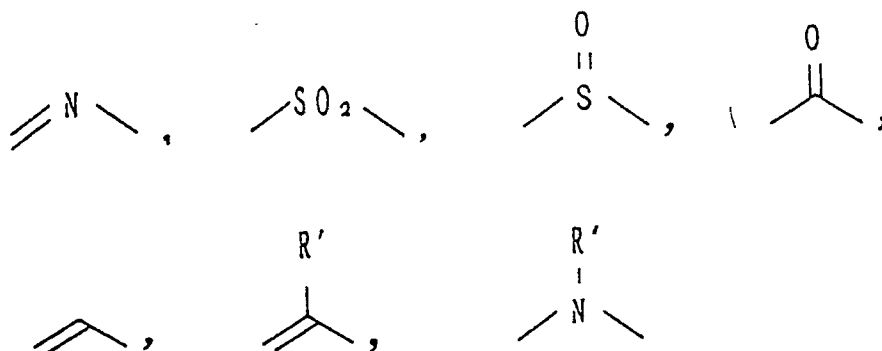
Preferred among these groups are the cyano, sulfonyl and sulfamoyl groups.

As follows are shown the σ_p values of some substituents falling within the scope of the invention.

Substituent	σ_p value
-CN	0.66
-SO ₂ CH ₃	0.72
-SO ₂ CF ₃	0.93
-SO ₂ Ph	0.70

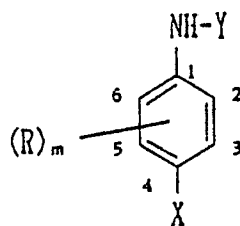
Provided that the σ_p value of the substituent represented by Y in Formula II is less than 0.3, the coupler does not substantially develop color, while the σ_p value more than 1.5 makes it substantially impossible to synthesize the coupler.

In Formulas III to V, Z is preferably a group of non-metallic atoms, and more preferably a group of non-metallic atoms containing the following units:

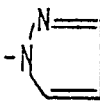
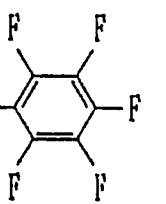
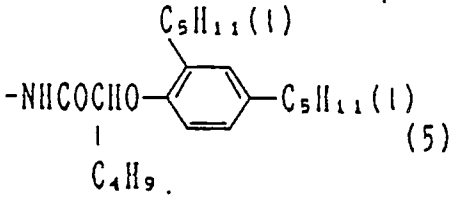


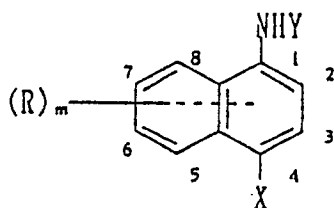
wherein R' and R'' each represent the same substituents as those represented by the foregoing R. The above units may be contained in combination.

The following are typical examples of the compounds usable in the invention:

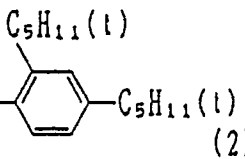
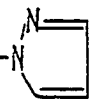
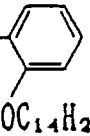
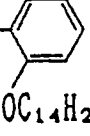
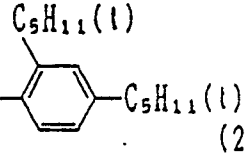


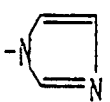
Cpd. No.	R	m	Y	X
I - 1	_____	0	-CN	-H
I - 2		1	-CN	-Cl
I - 3	-(1) C_4H_9 (2), -(1) C_4H_9 (5)	2	-CN	-H
I - 4	-(1) C_5H_{11} (2), -(1) C_4H_9 (5)	2	-CN	- SCH_2CH_2 - * *-COOH
I - 5	-(1) C_5H_{11} (2), -(1) C_4H_9 (5)	2	-CN	-O-* *-COOCH ₃
I - 6		3	-CN	-Cl

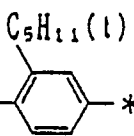
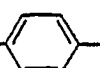
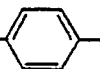
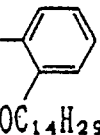
Cpd. No.	R	m	Y	X
I - 7	$-(1)C_4H_9(2), -(1)C_4H_9(5)$	2	$-SO_2CF_3$	$-H$
I - 8	$-(1)C_4H_9(2), -(1)C_4H_9(5)$	2	$-SO_2$ 	$-Cl$
I - 9	_____	0	$-SO_2C_{16}H_{33}$ (sec)	$-H$
I - 10	$-(1)C_5H_{11}(2), -(1)C_5H_{11}(5)$	2	$-SO_2C_{12}H_{25}$	$-H$
I - 11	$-(1)C_5H_{11}(2), -(1)C_5H_{11}(5)$	2	$-SO_2C_{12}H_{25}$	
I - 12	$(1)C_5H_{11}-(2), (1)C_5H_{11}-(5)$	2	$-SO_2C_{12}H_{25}$	$-OCH_2CH_2OH$
I - 13	$-NHCO$  (2)  (5) C_4H_9	2	$-SO_2C_{12}H_{25}$	$-Cl$



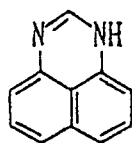
Cpd. No.	R	m	Y	X
II - 1	_____	0	- C N	-H
II - 2	-NHCOC ₁₄ H ₂₉ (5)	1	- C N	-H
II - 3	$ \begin{array}{c} \text{C}_5\text{H}_{11}(1) \\ \\ \text{-NHCOCO-} \text{C}_6\text{H}_4 \text{-C}_5\text{H}_{11}(1) \text{ (5)} \\ \\ \text{C}_4\text{H}_9 \end{array} $	1	- C N	- C I
II - 4	-NHCOC ₁₆ H ₃₃ (sec) (5)	1	- C N	-SCH ₂ CH ₂ COOH
II - 5	-NHCONHC ₁₆ H ₃₃ (sec) (5)	1	- C N	-H
II - 6	-NHCONHC ₁₆ H ₃₃ (sec) (5)	1	- C N	$ \text{-O-C}_6\text{H}_4\text{-*} $ * -COOCH ₃
II - 7	$ \begin{array}{c} \text{C}_5\text{H}_{11}(1) \\ \\ \text{-CONH(CH}_2)_4\text{O-C}_6\text{H}_4\text{-C}_5\text{H}_{11}(1) \\ \text{(2)} \end{array} $	1	- C N	-H

Cpd. No.	R	m	Y	X
II - 8	$\text{-CONH(CH}_2\text{)}_4\text{O-}$  $\text{C}_5\text{H}_{11}(\text{l})$ (2)	1	-CN	-Cl
II - 9	-CONHC ₁₆ H ₃₃ (sec) (2)	1	-CN	
II - 10	$\text{-CONHC}_8\text{H}_{17}(\text{l})$ (2) $\text{-NHCOC}_{12}\text{H}_{25}$ (5)	2	-CN	-H
II - 11	-CONH-  $\text{OC}_{14}\text{H}_{29}$ (2), -NHCOCH_3 (5)	2	-CN	-Cl
II - 12	-CONH-  $\text{OC}_{14}\text{H}_{29}$ (2), -NHCOCH_3 (5)	2	-CN	-SCH ₂ CH ₂ COOH
II - 13	$\text{-CONH(CH}_2\text{)}_4\text{O-}$  $\text{C}_5\text{H}_{11}(\text{l})$ (2) $\text{-NHCONHC}_2\text{H}_5$ (5)	2	-CN	-Cl
II - 14	-NHCOC ₁₆ H ₃₃ (sec) (8)	1	-CN	-H

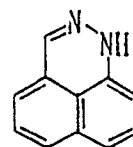
Cpd. No.	R	m	Y	X
II-15	—	0	-SO ₂ C ₁₄ H ₂₉	-H
II-16	$ \begin{array}{c} \text{C}_5\text{H}_{11}(1) \\ \\ -\text{CONH}(\text{CH}_2)_4\text{O}-\text{C}_6\text{H}_4-* \\ *-\text{C}_5\text{H}_{11}(1) \quad (2) \end{array} $	1	-SO ₂ CF ₃	-H
II-17	-CONHC ₁₄ H ₂₉ (2)	1	-SO ₂ - 	-Cl
II-18	-CONHC ₁₆ H ₃₃ (sec)(2)	1	-SO ₂ CH ₃	
II-19	$ \begin{array}{c} \text{C}_5\text{H}_{11}(1) \\ \\ -\text{NHCOCHO}-\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11}(1) \\ \quad (5) \\ \text{C}_2\text{H}_5 \end{array} $	1	$ \begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{SO}_2-\text{C}_6\text{H}_2-\text{F} \\ \quad \\ \text{F} \quad \text{F} \end{array} $	-H
II-20	$ \begin{array}{c} \text{C}_5\text{H}_{11}(1) \\ \\ -\text{NHCOCHO}-\text{C}_6\text{H}_4-\text{C}_5\text{H}_{11}(1) \\ \quad (5) \\ \text{C}_4\text{H}_9 \end{array} $	1	-SO ₂ CH ₃	-Cl
II-21	-NHCOC ₁₄ H ₂₉ (5)	1	-SO ₂ C ₄ H ₉	-SCH ₂ CH ₂ OH

Cpd. No.	R	m	Y	X
II - 22	$\text{-CONH(CH}_2)_4\text{O-}$  $\text{-NHCOC}_{14}\text{H}_{29}(5)$ $\text{* -C}_5\text{H}_{11}(1) (2)$	2	$\text{-SO}_2\text{-}$ 	-H
II - 23	-CONH-  $\text{-OC}_4\text{H}_9(2)$ $\text{-NHCOC}_{14}\text{H}_{29}(5)$	2	$\text{-SO}_2\text{CF}_3$	$\text{-OCH}_2\text{COOH}$
II - 24	-CONH-  $\text{-OC}_4\text{H}_9(2)$ $\text{-NHCOC}_{14}\text{H}_{29}(5)$	2	$\text{-SO}_2\text{C}_2\text{H}_5$	-Cl
II - 25	$\text{-NHCOC}_{16}\text{H}_{33}(8)$	1	$\text{-SO}_2\text{-}$ 	-H
II - 26	$\text{-NHCOCH}_3(8)$	1	$\text{-SO}_2\text{C}_{14}\text{H}_{29}$	-Cl
II - 27	-CONH-  (2)	1	$\text{-SO}_2\text{NHC}_2\text{H}_5$	-H
II - 28	$\text{-NHCOC}_{10}\text{H}_{21}(5)$	1	$\text{-SO}_2\text{NH-}$ * - 	-Cl

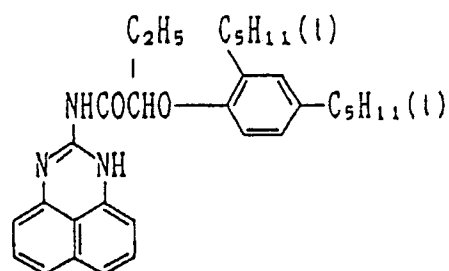
III - 1



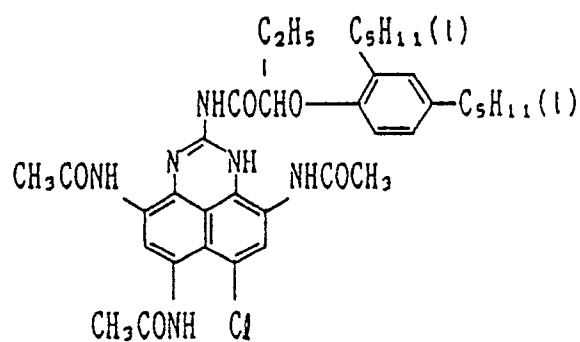
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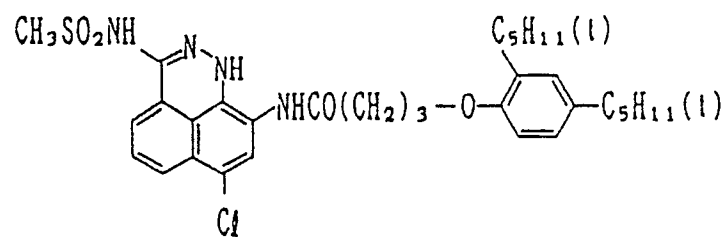
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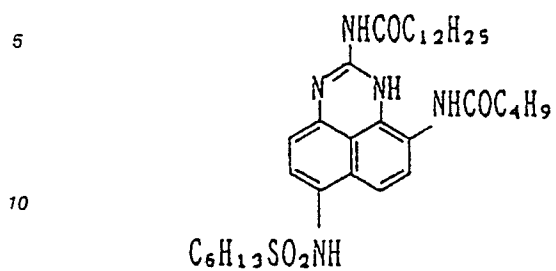
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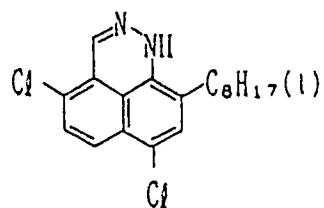
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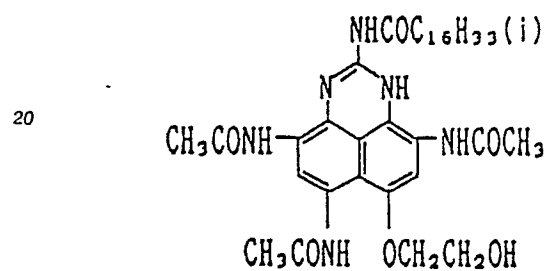
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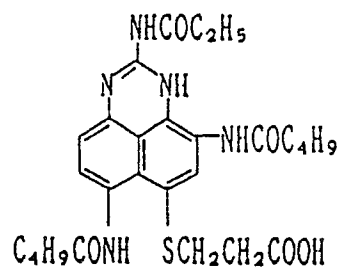
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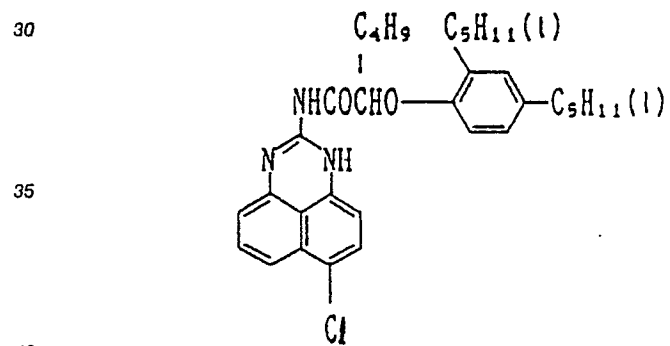
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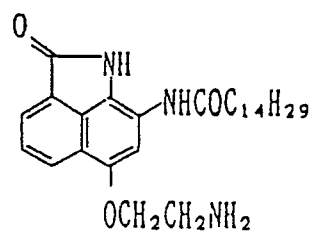
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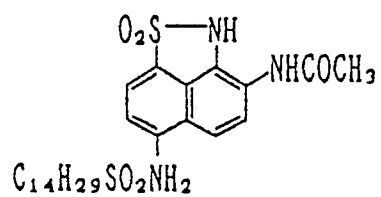
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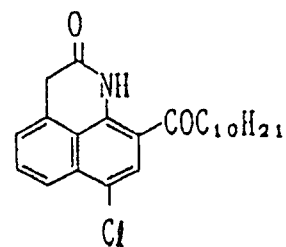
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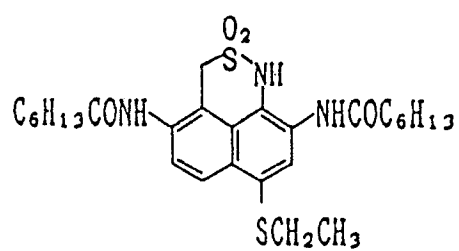
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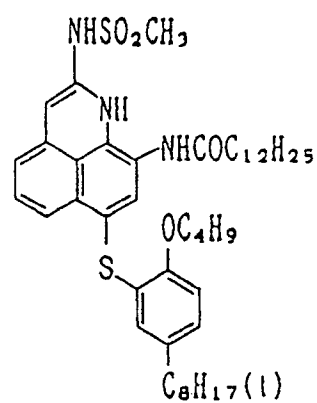
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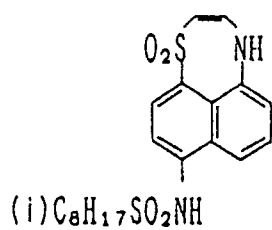
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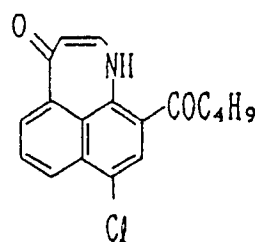
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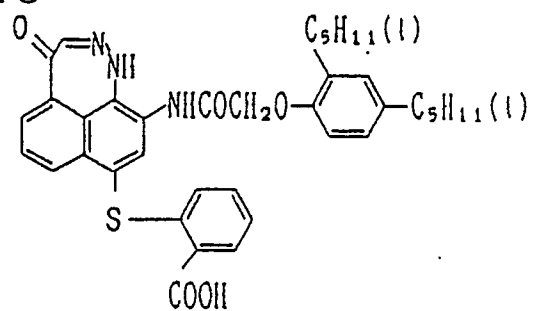
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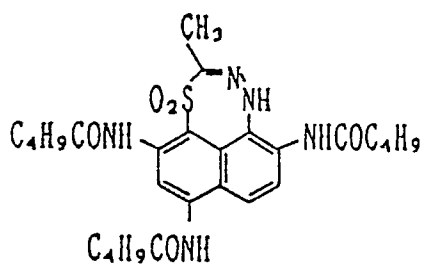
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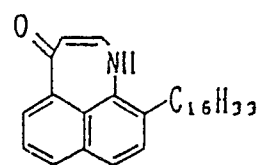
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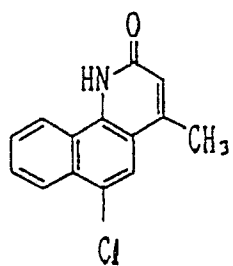
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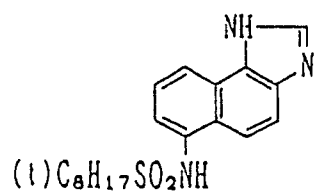
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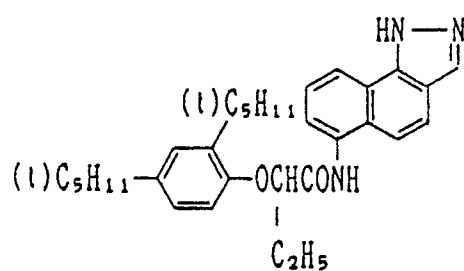
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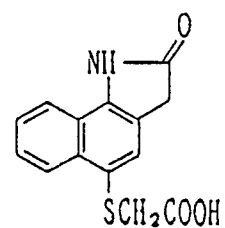
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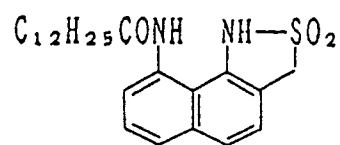
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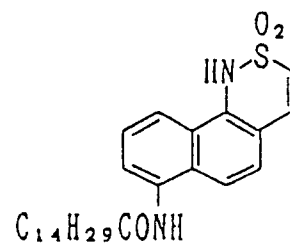
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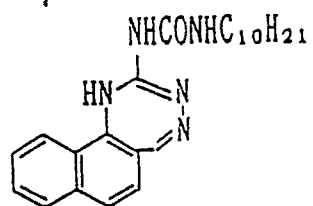
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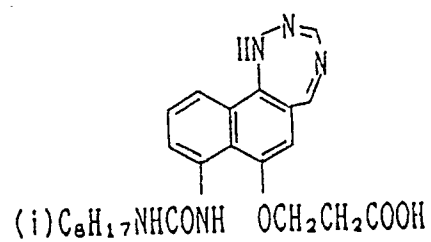
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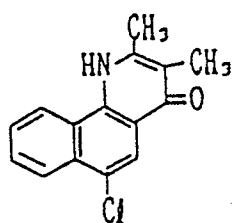
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IV-8



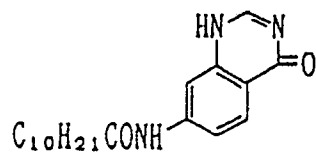
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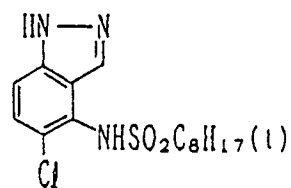
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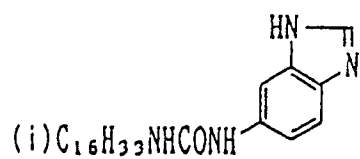
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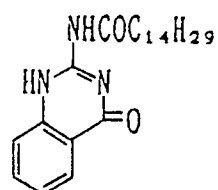
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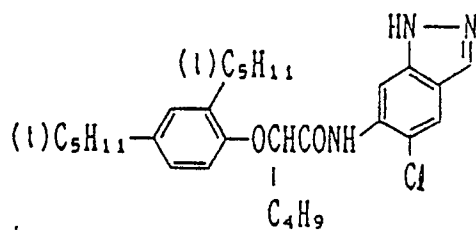
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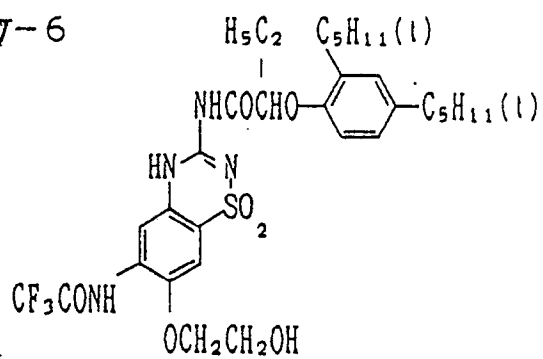
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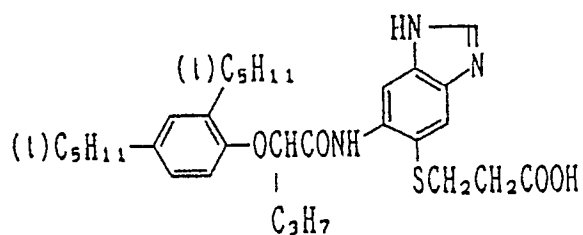
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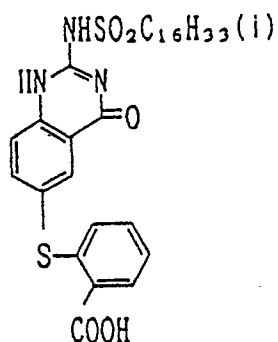
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V-7



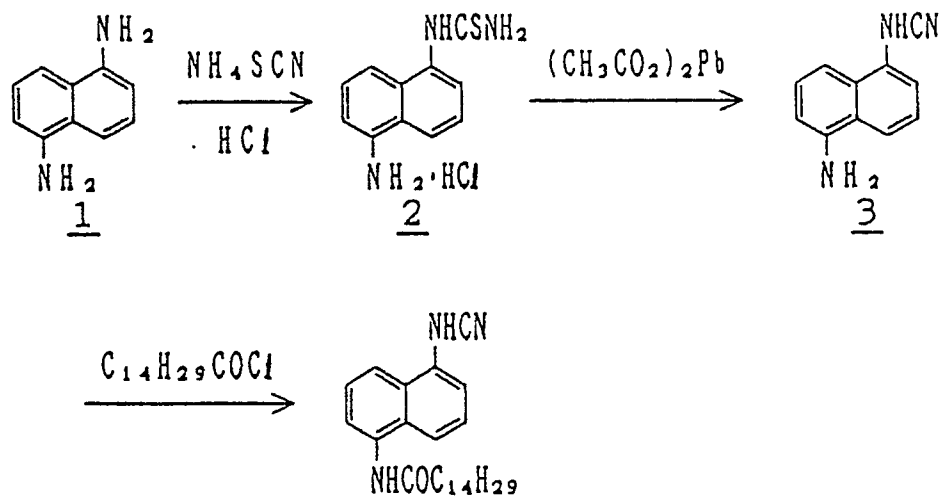
V-8



Syntheses of these couplers of the invention can be carried out in accordance with the methods described in the Organic Syntheses collective, Vol.4, pp.180 and 172.

Syntheses of some of the couplers of the invention are detailed below:

Synthesis of Compound II-2:



(Compound II-2)

Synthesis of intermediate 2:

There were suspended 47.5g of 1,5-diaminonaphthalene in 300 ml of water and dissolved by adding 55 ml of 12N hydrochloric acid thereto. The solution, to which 25g of ammonium thiocyanate were added, was heated at 80 to 90 °C with stirring for one hour. The reaction liquid was slowly concentrated to precipitate the solid, which was brayed finely in a mortar and then heated at 150 to 200 °C for 5 hours. The solid
5 suspended in 300 ml of water was heated to 70 °C to dissolve it, and then cooled to room temperature. The precipitated solid was filtered, dried, and recrystallized in a toluene-ethanol mixture solvent, whereby 23.7g of a white crystalline intermediate 2 were obtained, which was identified by ¹HNMR, FD mass spectrum and IR.

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Synthesis of intermediate 3:

To a suspension of 22.9g of the intermediate 2 in 100 ml of boiled water were added a heated solution of 49.5g of potassium hydroxide dissolved in 60 ml of water; there was added immediately a heated
15 saturated aqueous solution of 37.7g of lead diacetate trihydrate, and the liquid was boiled for 10 minutes. The black insoluble matter was filtered off while heating, and the filtrate was cooled to room temperature, whereby white crystals were precipitated. The crystals were filtered, washed and dried, whereby 14.3g of an intermediate 3 were obtained, which was identified by ¹HNMR, FD mass spectrum and IR.

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Synthesis of Compound II-2:

To a suspension of 14.0g of the intermediate 3 in 300 ml of ethyl acetate was added a solution of 7.5g of sodium acetate dissolved in 50 ml of water, and it was cooled to 5 °C. This mixture liquid, after adding
25 dropwise thereto in about 30 minutes an ethyl acetate solution of 21.9g of pentadecanoic acid chloride. was stirred at 5 °C for 4 hours. The reaction liquid was separated, washed three times with 200 ml of water and dried with magnesium sulfate. The solvent was distilled off under reduced pressure to obtain the solid, which was re-crystallized with acetonitrile. whereby 22.1g of white crystal, a compound II-2, was obtained, which was identified by ¹HNMR, FD mass spectrum and IR.

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Synthesis of Compound III-3:

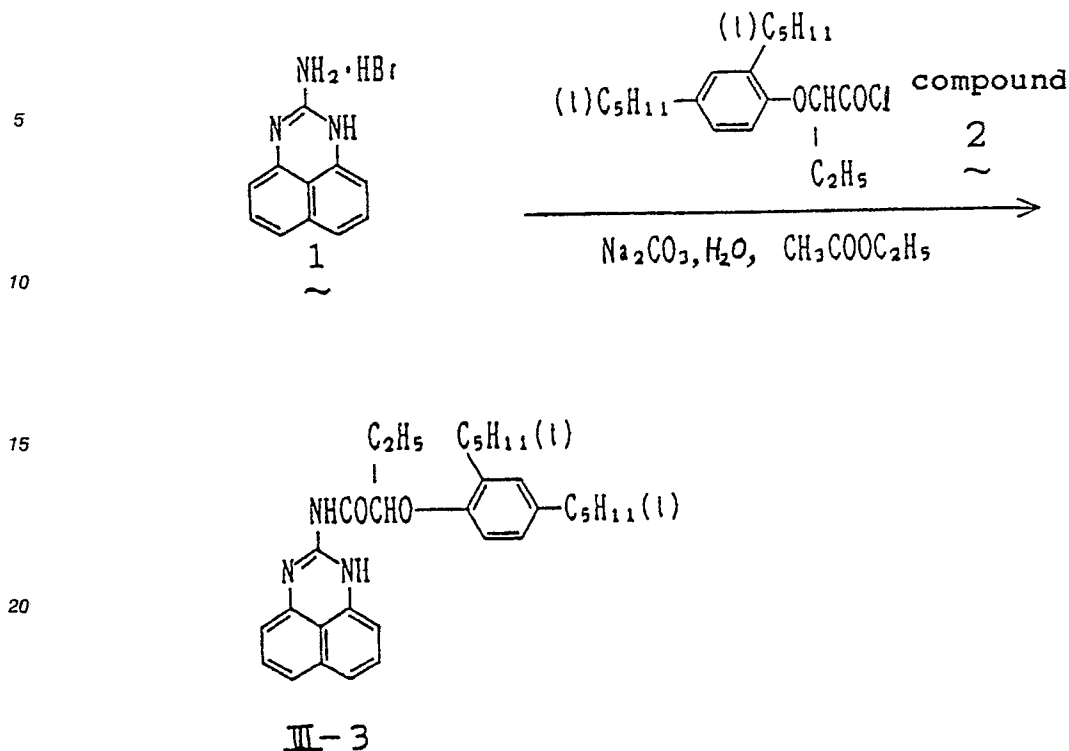
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To a 500ml aqueous solution of 20g sodium carbonate were added 700 ml of ethyl acetate and 26.4g of 2-aminoperimidine hydrobromide to prepare a suspension. The suspension, after adding dropwise thereto in about 30 minutes a solution of 37.3g of a compound 2 dissolved in ethyl acetate, was stirred at room temperature for 2 hours. The reaction liquid was separated, washed three times with 500 ml of water and dried with magnesium sulfate. The solvent was distilled off under reduced pressure, and the residual yellow oily product was refined by silica gel column chromatography, whereby 29.5g of light yellow powder III-3 were obtained, which was identified by ¹HNMR, FD mass spectrum and IR spectrum.

The coupler of the invention is used normally in an amount of 1×10^{-3} mole to 1 mole, and preferably 1×10^{-2} mole to 8×10^{-1} mole per mole of silver halide.

The coupler of the invention may be used in combination with different other cyan couplers.

The coupler of the invention may be used as a color photographic component material in any color-forming processes - a coupler-in-developer process and a coupler-in-emulsion process. In the coupler-in-developer process, the coupler of the invention dissolved in an alkaline aqueous solution or an organic solvent such as an alcohol, is added to a developer.

In the coupler-in-emulsion process, the coupler of the invention is incorporated into a photographic light-sensitive material.

In a typical manner, the coupler of the invention is incorporated into a silver halide emulsion, and the emulsion is coated on a support to form a color light-sensitive material. The coupler of the invention may be applied to any photographic light-sensitive materials such as color negative and positive films and a color photographic paper.

The light-sensitive materials in which the coupler of the invention is used may be of either monochrome or multicolor. In a multicolor light-sensitive material, the coupler of the invention is normally incorporated into a red-sensitive silver halide emulsion layer. The multicolor light-sensitive material comprises the dye image forming component layers spectrally sensitive to three primary color regions of the spectrum. Further, each light-sensitive layer comprises a single emulsion layer or a plurality of emulsion layers sensitive to the prescribed regions of the spectrum. The overall photographic component layers including the image-forming layers may be arranged in various orders. A typical multicolor light-sensitive material comprises a support having thereon a red-sensitive silver halide emulsion layer containing a cyan coupler, a green-sensitive silver halide emulsion layer containing a magenta coupler and a blue-sensitive silver halide emulsion layer containing a yellow coupler.

The light-sensitive material may also have other layers such as a filter layer, an intermediate layer, a protective layer and a subbing layer. The coupler of the invention is incorporated in accordance with known

methods. For example, the couplers of the invention dissolved in high or low-boiling organic solvents are mixed with a gelatin aqueous solution containing a surface active agent, and after emulsifying by a high-speed rotary mixer or a colloid mill, silver halide was added, whereby the silver halide emulsion used in the invention is prepared.

5 The silver halides suitably usable for the light-sensitive material containing the coupler of the invention are silver chloride, silver chlorobromide and silver chloriodobromide. A mixture of silver halides such as silver chloride plus silver bromide is also preferable. A silver halide emulsion used for a color photographic paper for which a particularly high-speed developability is required comprises preferably silver chloride, and more preferably silver chlorobromide or silver chloriodobromide each containing at least 1% silver
10 chloride.

The silver halide emulsion is chemically sensitized in usual manner, and also spectrally sensitized to a desired wavelength region.

The light-sensitive material containing the coupler of the invention may contain conventional additives such as an antistain agent, an antifoggant, a dye image stabilizer, a UV absorber, an antistatic agent, a
15 matting agent and a surface active agent.

The photographic light-sensitive material comprising the coupler of the invention is subjected to color developing, bleaching and fixing. The bleaching and fixing may be performed simultaneously in a single bath.

After fixing, the light-sensitive material is normally subjected to washing. The washing may be replaced
20 by stabilization or performed in combination therewith.

EXAMPLES

25 The invention is illustrated in detail by the following examples.

EXAMPLE 1

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The following layers were coated in sequence on a polyethylene-laminated paper support, whereby the red-sensitive color light-sensitive material Sample I was prepared. The compounds used are indicated in amounts per m² unless otherwise stated, and silver halide is in silver equivalent.

35 Layer 1: Emulsion layer

A red-sensitive layer containing 1.2g of gelatin. 0.30g of a red-sensitive silver chlorobromide emulsion containing 96 mole% silver chloride, and 9.1×10^{-4} mole of a comparative cyan coupler A dissolved in 1.35g of dioctyl phosphate.

Layer 2: Protective layer

40 A protective layer containing 0.50g of gelatin and sodium 2,4-dichloro-6-hydroxy-s-triazine as a hardening agent in an amount of 0.017g per gram of the gelatin.

Next, Samples 2 to 15 of the invention and 16 for comparison were prepared in the same manner as in Sample 1 except that the comparative coupler A was replaced by the couplers given in Table 1 without changing the addition amount.

45 Each of Samples 1 to 16 was exposed through a wedge in the usual manner, and then processed in the following steps:

Processing steps		
Color developing	38 ° C	3 min. 30 sec.
Bleach-fixing	38 ° C	1 min. 30 sec.
Stabilizing	25 ° C to 30 ° C	3 min.
Drying	75 ° C to 80 ° C	2 min.

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The compositions of the processing solutions used in the above steps are as follows:

Developer	
Benzyl alcohol	15 ml
Ethylene glycol	15 ml
Potassium sulfite	2.0 g
Potassium bromide	0.7 g
Sodium chloride	0.2 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	3.0 g
Polyphosphoric acid (TPPS)	2.5 g
3-Methyl-4-amino-N-ethyl-N-(β -methanesulfonamidoethyl)-aniline sulfate	5.5 g
Brightening agent, 4,4'-diaminostilbenedisulfonic acid derivative	1.0 g
Potassium hydroxide	2.0 g
Water to make 1 liter. Adjust pH to 10.20.	

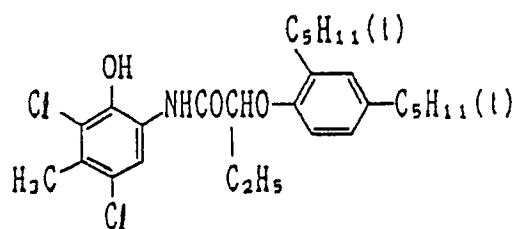
Bleach-fixer	
Ferric-ammonium ethylenediaminetetraacetate dihydrate	60 g
Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70% solution)	100 ml
Ammonium sulfite (40% solution)	27.5 ml
Adjust pH to 7.1 with potassium carbonate or glacial acetic acid, and add water to make 1 liter.	

Stabilizer	
5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	10 g
Water to make 1 liter.	

Each of the processed Samples 1 to 16 was subjected to measurement of an initial density with a densitometer, and then allowed to stand over a period of 14 days under a high temperature/humidity condition (60°C/80%RH) for examination of the dye image's resistance to heat and moisture.

Each processed sample was exposed for days to the light of a xenon fadeometer to measure light resistance. The results are given in Table 1. The heat/moisture resistance and the light resistance of the dye image are expressed in residual rates (%) of the dye after the resistance tests to the initial density of 1.0.

Comparative coupler A



Comparative coupler B

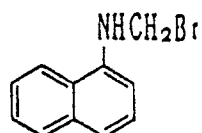
 σ_p value: 0.12

Table 1

Sample No.	Cyan coupler	Dye residual rate(%)	
		Heat/moisture resistance	Light resistance
1	Comparative A	59	81
2	Invention I-2	89	84
3	" I-6	91	87
4	" I-11	87	80
5	" I-13	85	82
6	" II-2	93	81
7	" II-11	90	79
8	" II-23	89	79
9	" III-3	84	84
10	" III-5	86	85
11	" III-7	85	84
12	" III-8	89	87
13	" IV-3	88	86
14	" IV-6	88	87
15	" V-3	84	80
16	Comparative B	No color development	

As is apparent from Table 1, the samples of the invention which contain the couplers of the invention have higher dye residual rates and more excellent resistance to heat, moisture and light than the sample containing the comparative coupler. Sample 16 containing comparative coupler B in which $-\text{CH}_2\text{Br}$ corresponding Y in formula II has the σ_p value of 0.12 developed no color.

EXAMPLE 2

The following layers were coated in order on a subbed triacetate film base, whereby a red-sensitive color light-sensitive material Sample 17 was prepared. The compounds used are indicated in amounts per m², and silver halide is in silver equivalent.

Layer 1: Emulsion layer

A red-sensitive emulsion layer containing 1.4g of gelatin, 1.5g of a red-sensitive silver iodobromide emulsion containing 4 mole% silver iodide, and 8.0×10^{-4} mole of a comparative cyan coupler C dissolved in 1.5g of tricresyl phosphate.

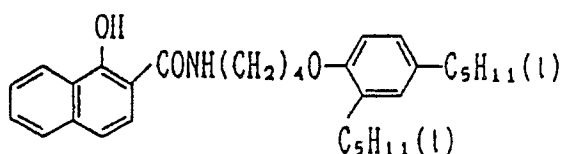
Layer 2: Protective layer

A protective layer containing 1.5g of gelatin and sodium 2,4-dichloro-6-hydroxy-s-triazine as a hardening agent in an amount of 0.017g per gram of the gelatin.

Samples 18 to 31 of the invention were prepared in the same manner as Sample 17 except that the comparative coupler C was replaced by the couplers given in Table 2 without changing the addition amount.

Each of Samples 17 to 31 was exposed through a wedge in the usual manner, and then processed in the following steps.

Comparative coupler C



Processing steps		
Color developing	38° C	3 min. 15 sec.
Bleaching	38° C	6 min. 30 sec.
Washing	25 to 30° C	3 min. 15 sec.
Fixing	38° C	6 min. 30 sec.
Washing	25 to 30° C	3 min. 15 sec.
Stabilizing	25 to 30° C	1 min. 30 sec.
Drying	75 to 80° C	

The compositions of the processing solutions used in the above steps are as follows:

Color developer :	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate monohydrate	2.5 g
Potassium hydroxide	1.0 g
Water to make 1 liter.	
Adjust pH to 10.6 with sodium hydroxide.	

Bleacher :	
Ferric-ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
Water to make 1 liter.	
Adjust pH to 6.0 with ammonia water.	

Fixer :	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.6 g
Sodium metarsulfite	2.3 g
Water to make 1 liter.	
Adjust pH to 6.0 with acetic acid.	

Stabilizer :	
Formalin (37% by weight)	1.5 ml
Koniducks (product of KONICA Corporation)	7.5 ml
Water to make 1 liter.	

Each of the processed Samples 17 to 31 was subjected to the resistance tests in the same manner as in Example 1. The results are shown in Table 2.

Table 2

Sample No.	Cyan coupler	Dye residual rate(%)	
		Heat/moisture resistance	Light resistance
17	Comparative C	74	81
18	Invention I-4	86	84
19	" I-12	91	87
20	" II-3	90	82
21	" II-8	84	81
22	" II-11	88	84
23	" II-16	92	85
24	" II-28	89	83
25	" III-4	89	85
26	" III-10	80	83
27	" III-15	83	82
28	" IV-5	85	82
29	" IV-9	84	84
30	" IV-10	84	83
31	" V-6	88	85

As is apparent from Table 2, the samples of the invention which contain the couplers of the invention have higher dye residual rates and more excellent resistance to heat, moisture and light than the sample containing the comparative coupler.

5

EXAMPLE 3

The following layers were coated in order on a triacetyl cellulose film support, whereby red-sensitive color reversal photographic light-sensitive material Samples 32 to 42 were prepared.

Layer 1: Emulsion layer

A red-sensitive emulsion layer containing 1.4g of gelatin, 0.5g of a red-sensitive silver chlorobromide emulsion containing 96 mole% silver chloride, and 9.1×10^{-4} mole of a coupler given in Table 3 dissolved in 1.5g of dibutyl phthalate.

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Layer 2: Protective layer

A protective layer containing 0.5g of gelatin and sodium 2,4-dichloro-6-hydroxy-s-triazine as a hardening agent in an amount of 0.017g per gram of the gelatin

20

Reversal processing step	Time	Temperature
First developing	6 minutes	38 °C
Washing	2 minutes	38 °C
Reversal	2 minutes	38 °C
Color developing	6 minutes	38 °C
Compensating	2 minutes	38 °C
Bleaching	6 minutes	38 °C
Fixing	4 minutes	38 °C
Washing	4 minutes	38 °C
Stabilizing	1 minute	38 °C
Drying		Room temperature

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The compositions of the processing solutions used are as follows:

First developer	
Sodium tetrapolyphosphate	2 g
Sodium sulfite	20 g
Hydroquinone monosulfonate	30 g
Sodium carbonate monohydrate	30 g
1-Phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2 g
Potassium bromide	2.5 g
Potassium thiocyanate	1.2 g
Potassium iodide (0.1% solution)	2 ml
Water to make	1000 ml

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Reversal Solution	
Hexasodium nitrilotrimethylenephosphonate	3 g
Stannous chloride dihydrate	1 g
p-Aminophenol	0.1 g
Sodium hydroxide	5 g
Glacial acetic acid	15 ml
Water to make	1000 ml

Color developer	
Sodium tetrapolyphosphate	2 g
Sodium sulfite	7 g
Sodium tertiary phosphate dodecahydrate	36 g
Potassium bromide	1 g
Potassium iodide (0.1% solution)	90 ml
Sodium hydroxide	3 g
Citrazine acid	1.5 g
N-ethyl-N-(β -methanesulfonamidoethyl)-3-methyl-4-aminoaniline sulfate	11 g
Ethylenediamine	3 g
Water to make	1000 ml

Compensating Solution	
Sodium sulfite	12 g
Sodium ethylenediaminetetraacetate dihydrate	8 g
Thioglycerol	0.4 ml
Glacial acetic acid	3 ml
Water to make	1000 ml

Bleacher	
Sodium ethylenediaminetetraacetate dihydrate	2.0 g
Ferric-ammonium ethylenediaminetetraacetate dihydrate	120.0 g
Potassium bromide	100.0 g
Water to make	1000 ml

Fixer	
Ammonium thiosulfate	80.0 g
Sodium sulfite	5.0 g
Sodium hydrogensulfite	5.0 g
Water to make	1000 ml

Stabilizer	
Formalin (37% by weight)	5.0 ml
Koniducks (product of KONICA Corporation)	5.0 ml
Water to make	1000 ml

Each processed sample was subjected to tests of heat/moisture and light resistance in the same manner as in Example 2. The results are shown in Table 3.

Table 3

Sample No.	Cyan coupler	Dye residual rate(%)	
		Heat/moisture resistance	Light resistance
32	Comparative A	63	83
33	Invention I-5	90	83
34	" I-10	90	84
35	" II-2	87	82
36	" II-9	91	83
37	" II-22	85	87
38	" III-3	84	84
39	" III-8	89	84
40	" III-20	84	83
41	" IV-7	80	83
42	" V-3	82	85

As is apparent from Table 3, the samples of the invention which contain the couplers of the invention have higher dye residual rates and more excellent resistance to heat, moisture and light than the sample containing the comparative coupler.

EXAMPLE 4

A multicolor film Sample 43 was prepared by coating the following component layers on a support having an antihalation layer.

Component layers.... Pro layer, BH layer, BL layer, YF layer, GH layer, GL layer, IL layer, RH layer, RL layer, and support.

The above layers are explained.

RL layer: Low-speed red-sensitive silver halide emulsion layer containing 1.0g of a red-sensitive AgBrI emulsion comprising Emulsion I having an average grain size ($\bar{r}$) of $0.47\mu\text{m}$, variation coefficient ($s/\bar{r}$) of 0.12 and an average AgI content of 8 mole%; 1.0g of an AgBrI emulsion (Emulsion II) having an average grain size of $0.31\mu\text{m}$, a variation coefficient of 0.10 and an average AgI content of 8 mole%; and a dispersion prepared by dispersing in an aqueous solution of 2.4g gelatin a solution of 0.07g of disodium 1-hydroxy-4-[4-(1-hydroxy-8-acetamido-3,6-disulfo-2-naphthylazo)-phenoxy]-N-[δ -(2,4-di-t-amylphenoxy)butyl]-2-napthoamide (CC-A). 0.4g of 1-hydroxy-2-[δ -(2,4-di-t-a mylphenoxy)-n-butyl]napthoamide (C-A) and 0.06g of DIR compound D-1 each dissolved in 1.0g of tricresyl phosphate (TCP).

RH layer: High-speed red-sensitive silver halide emulsion layer containing 2.0g of a red-sensitive AgBrI emulsion comprising Emulsion III having an average grain size of $0.7\mu\text{m}$, a variation coefficient of 0.12 and an average AgI content of 6 mole%; and a dispersion prepared by dispersing in an aqueous solution of 1.2g gelatin a solution of 0.20g of a cyan coupler (C-A) and 0.03g of a colored cyan coupler (CC-A) each dissolved in 0.23g of TCP.

GL layer: Low-speed green-sensitive silver halide emulsion layer containing 1.5g of green-sensitive

Emulsion I; 1.5g of green-sensitive Emulsion II; and a dispersion prepared by dispersing in an aqueous solution of 2.4g gelatin a solution of 0.35g of 1-(2,4,6-trichlorophenyl)-3-[3-(p-dodecyloxybenzenesulfonylamido)benzamido]-5-pyrazolone (M-A), 0.10g of 1-(2,4,6-trichlorophenyl)-4-(1-naphthylazo)-3-(2-chloro-5-octadecenylsuccinimidoanilino)-5-pyrazolone (CM-A) and 0.04g of DIR compound D-1 each dissolved in 0.68g of TCP.

5 GH layer: High-speed green-sensitive silver halide emulsion layer containing 2.0g of green-sensitive Emulsion III; and a dispersion prepared by dispersing in an aqueous solution of 2.4g gelatin a solution of 0.14g of magenta coupler M-A and 0.045g of colored magenta coupler CM-A each dissolved in 0.27g of TCP.

10 BL layer: Low-speed blue-sensitive silver halide emulsion layer containing 0.5g of blue-sensitive Emulsion I; 0.5g of blue-sensitive Emulsion II; and a dispersion prepared by dispersing in an aqueous solution of 1.8g gelatin a solution of 0.7g of α -pivaloyl- α -(1-benzyl-2-phenyl-3,5-dioxyimidazolidine-4-yl)-2-chloro-5-[α -dodecyloxycarbonyl]-ethoxycarbonyl]acetanilide (Y-A) and 0.02g of DIR compound D-1 each dissolved in 0.68g of TCP.

15 BH layer: High-speed blue-sensitive silver halide emulsion containing 0.9g of a blue-sensitive AgBrI emulsion having an average grain size of 0.80 μ m, a variation coefficient of 0.14 and an average AgI content of 6 mole%, and a dispersion prepared by dispersing in an aqueous solution of 2.0g gelatin a solution of 0.25g of yellow coupler Y-A dissolved in 0.25g of TCP.

20 IL layer: Intermediate layer containing a solution of 0.07g of 2,5-di-t-octylhydroquinone (HQ-1) dissolved in 0.07g of dibutyl phthalate (DBP).

YF layer: Yellow filter layer containing 0.15g of yellow colloidal silver; 0.2g of HQ-1 (antistain agent) dissolved into 0.11g of DBP; and 1.0g of gelatin.

Pro layer: Protective layer containing 2.3g of gelatin.

25 Samples 44 to 63 were prepared in the same manner as in Sample 43 except that C-A contained in the low-speed and high-speed red-sensitive silver halide emulsion layers of Sample 43 was replaced by the same molar amount of the couplers of the invention as shown in Table 4.

Each of Samples 43 to 63 was exposed through a wedge to a white light, and then processed in the same manner as in Example 2. The color density of each sample was measured through a red filter. The results are shown in Table 4.

30 DIR compound D-1

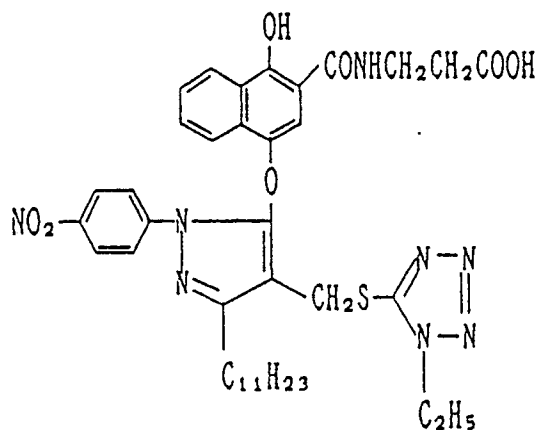


Table 4

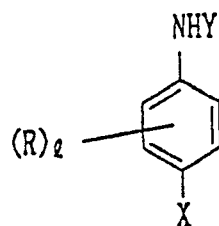
Sample No.	Cyan coupler	Fog (D min)	Relative sensitivity
43	C-A (Comparative)	0.10	100
44	I-2 (Invention)	0.09	121
45	I-7 (")	0.10	119
46	I-4 (")	0.11	130
47	II-4 (")	0.08	128
48	II-8 (")	0.09	124
49	II-12 (")	0.09	125
50	II-14 (")	0.10	122
51	II-16 (")	0.08	121
52	II-23 (")	0.11	126
53	II-27 (")	0.08	125
54	III-3 (")	0.12	110
55	III-4 (")	0.09	129
56	III-6 (")	0.11	115
57	III-7 (")	0.10	122
58	III-8 (")	0.12	133
59	III-9 (")	0.09	136
60	IV-3 (")	0.09	121
61	IV-8 (")	0.11	130
62	V-2 (")	0.09	122
63	V-8 (")	0.08	124

As is apparent from Table 4, Samples 44 to 63 containing the couplers of the invention show much higher relative sensitivities than that of Sample 43 containing the conventional cyan coupler, while they have almost equal fog.

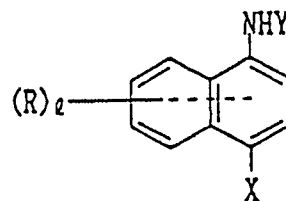
Claims

1. A silver halide photographic light-sensitive material comprising a support and provided thereon photographic component layers including a silver halide emulsion layer containing at least one of the compounds represented by the following Formulas I to V:

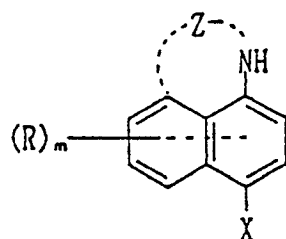
Formula I



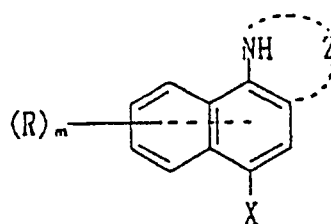
Formula II



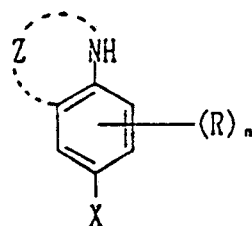
Formula III



Formula IV



Formula V



wherein R represents a substituent; Y represents a substituent having a Hammett's substituent constant σ_p of not less than 0.3 and not more than 1.5; Z represents the group of atoms necessary to form a 5 to 7-membered nitrogen containing heterocyclic ring; l represents an integer of 0 to 4; m represents an integer of 0 to 5; n represents an integer of 0 to 3, provided that when l , m or n is 2 or more, R's may be the same or different; and X represents a hydrogen atom or a substituent capable of splitting off upon a reaction with an oxidation product of a developing agent.

2. The light-sensitive material of claim 1, wherein R represents an alkyl group, an aryl group, a carboxyl group, an oxycarboxyl group, a cyano group, a hydroxy group, an alkoxy group, an aryloxy group, an amino group, an amide group, a sulfonamide group, or a halogen atom.

3. The light-sensitive material of claim 1, wherein R's are allowed to combine each other to form a 5 to 8-membered heterocyclic ring when l , m or n is 2 or more.

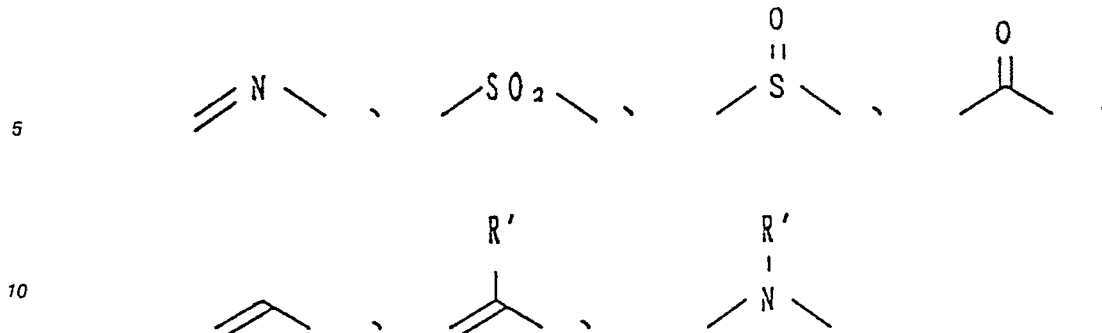
4. The light-sensitive material of claim 3, wherein said ring is a pyridine or quinoline ring.

5. The light-sensitive material of claim 1, wherein Y represents a cyano group, a nitro group, a sulfonyl group, a β -carboxyvinyl group, a sulfinyl group, a β,β -dicyanovinyl group, a halogenated alkyl group, a formyl group, a carboxyl group, a carbonyl group, an alkoxycarbonyl group, an aryloxy carbonyl group, a 1-terazolyl group, a 5-chloro-1-terazolyl group, a carbamoyl group, or a sulfamoyl group.

6. The light-sensitive material of claim 5, wherein Y is a cyano group, a sulfonyl group or a sulfamoyl group.

7. The light-sensitive material of claim 1, wherein Z represents the group of non-metallic atoms.

8. The light-sensitive material of claim 7, wherein said group comprises the following units:



wherein R' and R'' each represent the same groups as those defined for R in Formulas I to V; provided that the group may contain two or more units.

9. The light-sensitive material of claim 1, containing said compound in an amount of 1×10^{-3} to 1 mol per mol of silver halide.

10. The light-sensitive material of claim 10, wherein said amount is 1×10^{-2} to 8×10^{-1} mol per mol of silver halide.

11. The light-sensitive material of claim 1, wherein said silver halide emulsion comprises at least one of silver chloride, silver chlorobromide and silver chlorobromiodide.



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)
Y	US-A-3 245 795 (B. GASPAR) * whole document * ---	1-8	G 03 C 7/32 C 09 B 55/00
Y	US-A-2 486 440 (W. SCHMIDT) * column 15, color formers 7,9 * ---	1-8	
Y	FR-A-2 371 711 (AGFA) * claim 2; page 12, compounds 1,3 * ---	1-8	
A	* page 13, compounds 4-7 * ---	1	
Y	EP-A-0 093 556 (EASTMAN KODAK) * claims 4-11 * ---	1-8	
A	GB-A-1 311 597 (L'OREAL) * whole document * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G 03 C 7/00 G 03 C 8/00 C 09 B 53/00 C 09 B 55/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 18-05-1990	Examiner STOCK H
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 L : document cited for other reasons ----- & : member of the same patent family, corresponding document	