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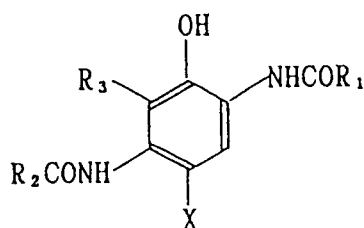
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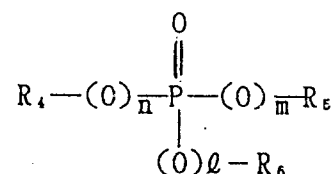
⑤④ **Silver halide photographic light-sensitive material offering excellent color reproduction.**

⑤⑦ A silver halide color photographic light-sensitive material which is excellent in color reproduction and image preservability comprises a support having thereon a silver halide emulsion layer, wherein said silver halide emulsion layer contains a cyan-dye forming coupler represented by the formula [C-I] and a compound represented by the formula [I] :

formula [C-I]



formula [I]



BACKGROUND OF THE INVENTION

The present invention relates to a silver halide color photographic light-sensitive material which is excellent in color reproduction and image preservability.

When a silver halide photographic light-sensitive material is subjected to exposure and then to a color processing, the oxidized aromatic primary amine color developing agent reacts with a dye forming coupler, and a dye is formed to produce a dye image.

Generally, this photographic process is based on the subtractive color process for color reproduction, wherein yellow, magenta and cyan images are formed.

Traditionally, phenols or naphthols have been commonly used as cyan dye forming couplers.

However, the cyan dyes obtained from conventional phenols or naphthols have a major problem in color reproduction, namely the presence of unwanted absorption in the green band and unsharp absorption edge in shorter wavelength-side. This necessitates correction of the unwanted absorption using masking or other means for negative films. In the case of photographic paper, there is no means of correction, which hampers the obtainment of good color reproduction to significant extent.

The dye images obtained from conventional phenols or naphthols also pose some problems in preservability. For example, the dye images obtained with the 2-acylaminophenol cyan coupler described in US Patent Nos. 2,367,531 and 2,423,730 are generally poor in color fastness to heat; the dye images obtained with the 2,5-diacylaminophenol cyan coupler described in US Patent Nos. 2,369,929 and 2,772,162 are generally poor in color fastness to light; and the dye images obtained with 1-hydroxy-2-naphthamide cyan coupler are generally unsatisfactory in both color fastness to light and color fastness to heat.

The 2,5-diacylaminophenol cyan coupler described in US Patent No. 4,122,369 and Japanese Patent O.P.I. Publication Nos. 155538/1982 and 1574246/1982, and the 2,5-diacylaminophenol cyan coupler having an hydroxy group in the ballast moiety described in US Patent No. 3,880,661 do not offer sufficient levels of color fastness to light or heat in long-term storage.

On the other hand, in the field of printing plate-making, the so-called color proof system has recently been available, which uses a silver halide color photographic light-sensitive material (hereinafter referred to as color light-sensitive material), from the viewpoint of simple handling, cost reduction, time saving and other advantages.

When using a color light-sensitive material (color paper) as a color proof, it is difficult to exactly reproduce the color of printing ink because the single color formed from yellow, magenta or cyan coupler differs from the yellow, magenta or cyan color of printing ink in tone. Object of the invention

It is an object of the present invention to provide a silver halide color photographic light-sensitive material which offers excellent color reproduction wherein the spectral absorption of the cyan dye image is sharp and is accompanied by little unwanted absorption.

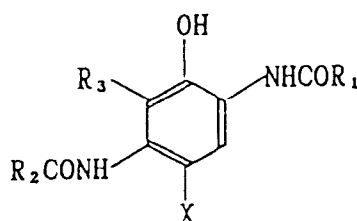
It is another object of the present invention to provide a silver halide color photographic light-sensitive material which offers cyan dye images with excellent color fastness to light.

It is still another object of the present invention to provide a color light-sensitive material which offers color reproduction similar to that of printing ink and improved fastness to light.

Constituents of the invention

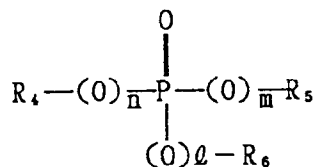
The objects of the present invention described above can be accomplished by a silver halide photographic light-sensitive material having at least one silver halide emulsion layer on the support, wherein at least one or more of said silver halide emulsion layer(s) contains at least one of the cyan coupler represented by the Formula [C-I] given below and at least one of the compound represented by the Formula [I] given below.

Formula [C-I]



wherein R_1 and R_2 independently represent an alkyl group, cycloalkyl group, alkenyl group, aryl group or heterocyclic group. R_3 represents a hydrogen atom, halogen atom, alkyl group or alkoxy group. R_2 and R_3 may be combined to form a ring. X represents a hydrogen atom or a group which is capable of splitting off on reaction with the oxidation product of a color developing agent.

Formula [I]



wherein R_4 , R_5 and R_6 independently represent an aliphatic group or aromatic group; ℓ , m and n independently represent 0 or 1; not all of ℓ , m and n are 1.

The present invention is hereinafter described in more detail.

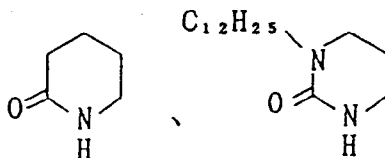
With respect to the cyan coupler represented by the Formula [C-I] above according to the present invention (hereinafter referred to as the cyan coupler of the present invention), the group represented by R_1 or R_2 has a carbon number of 1 to 32 for an alkyl group, 2 to 32 for an alkenyl group and 3 to 12 for a cycloalkyl group, and these alkyl, alkenyl and cycloalkyl groups may have a substituent.

The aryl group represented by R_1 or R_2 is preferably a phenyl group, which may have a substituent

The heterocyclic group represented by R_1 or R_2 is preferably a 5- to 7-membered ring, which may be substituted or condensed.

R_3 represents a hydrogen atom, halogen atom, alkyl group or alkoxy group, with preference given to a hydrogen atom.

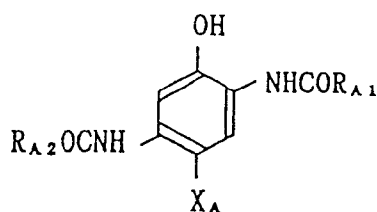
The ring formed by R_2 and R_3 in cooperation is preferably a 5- or 6-membered rings. Examples of the 5- or 6-membered ring formed include the following:



Examples of the group capable of splitting off by reaction with the oxidation product of a color developing agent, represented by X in the Formula [C-I], include a halogen atom, alkoxy group, aryloxy group, acyloxy group, sulfonyloxy group, acylamino group, sulfonylamino group, alkoxycarbonyloxy group, aryloxycarbonyloxy group and imide group, with preference given to a halogen atom, aryloxy group and alkoxy group.

A particularly preferred cyan coupler of the present invention is represented by the Formula [C-II] given below.

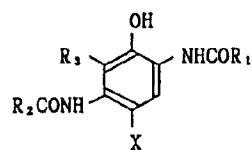
Formula [C-II]



wherein R_{A1} represents an alkyl group, alkenyl group, cycloalkyl group or phenyl group substituted with at least one halogen atom, which alkyl group, alkenyl group, cycloalkyl group or phenyl group may have a substituent other than the halogen atom. R_{A2} has the same definition as of R_2 in the Formula [C-I]. X_A represents an aryloxy group or alkoxy group.

Examples of the cyan coupler represented by the Formula [C-I] are given below.

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Exemplified compound No.	R ₁	R ₂	R ₃	X
C - 1	-(CF ₂) ₄ H		H	Cl
C - 2			H	-Cl
C - 3			H	-Cl
C - 4		C ₁₂ H ₂₅ -	-Cl	-Cl
C - 5			H	-O-C ₆ H ₄ -C ₆ H ₁₇ (t)
C - 6			H	H
C - 7			H	-Cl
C - 8			H	-Cl
C - 9			H	-O-C ₆ H ₄ -OCH ₃

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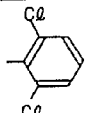
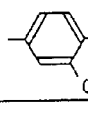

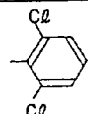
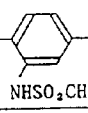
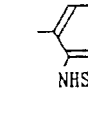
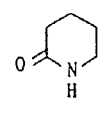
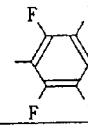
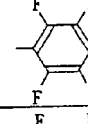
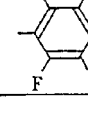
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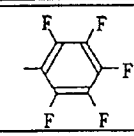
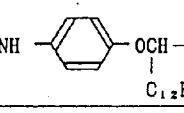
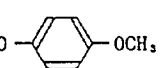
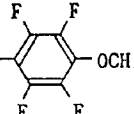
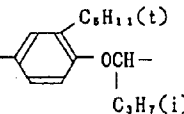
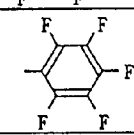
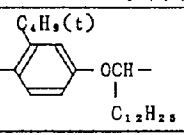
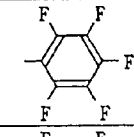
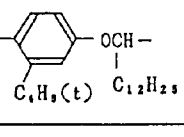
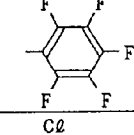
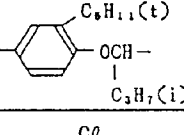
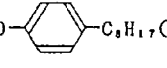
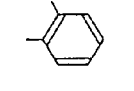
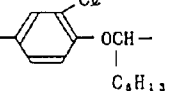
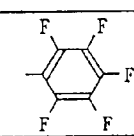
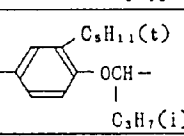
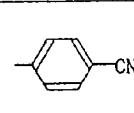
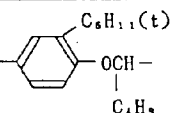
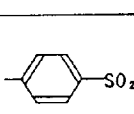
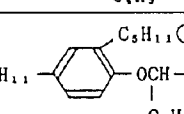
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Exemplified compound No.	R ₁	R ₂	R ₃	X
C - 10		$(\text{CH}_3)_2\text{NSO}_2\text{NH}-\text{C}_6\text{H}_4-\text{OCH}-\text{C}_6\text{H}_5$	H	-Cl
C - 11		$\text{C}_{12}\text{H}_{25}-\text{C}_6\text{H}_4-\text{SO}_2\text{NH}-\text{C}_6\text{H}_5$	H	-Cl
C - 12		$\text{Cl}-\text{C}_6\text{H}_3(\text{Cl})_2-\text{OCH}-\text{C}_{10}\text{H}_{21}$	H	$-\text{OCH}_2\text{CONHC}_3\text{H}_7$
C - 13		$\text{C}_6\text{H}_5\text{O}-\text{C}_6\text{H}_3(\text{t})_2-\text{OCH}-\text{C}_{12}\text{H}_{25}$	H	-Cl
C - 14		$\text{HO}-\text{C}_6\text{H}_3(\text{t})_2-\text{OCH}-\text{C}_{12}\text{H}_{25}$	H	-Cl
C - 15		$\text{C}_5\text{H}_{11}(\text{t})-\text{C}_6\text{H}_3(\text{t})_2-\text{C}_5\text{H}_{11}(\text{t})$		-Cl
C - 16		$\text{C}_{12}\text{H}_{25}-\text{N}(\text{C}_6\text{H}_5)_2$		-Cl
C - 17		$(\text{CH}_3)_2\text{NSO}_2\text{NH}-\text{C}_6\text{H}_4-\text{OCH}-\text{C}_{12}\text{H}_{25}$	H	-Cl
C - 18		$(\text{C}_2\text{H}_5)_2\text{NSO}_2\text{NH}-\text{C}_6\text{H}_4-\text{OCH}-\text{C}_{12}\text{H}_{25}$	H	-Cl

Exemplified compound No.	R ₁	R ₂	R ₃	X
C - 19		$(C_2H_5)_2NSO_2NH$ -  $OCH - C_{12}H_{25}$	H	- O -  OCH_3
C - 20		$(t)C_8H_{11}$ -  $OCH - C_3H_7(i)$	H	- Cl
C - 21		HO -  $OCH - C_{12}H_{25}$	H	- Cl
C - 22		CH_3COO -  $OCH - C_{12}H_{25}$	H	- Cl
C - 23		$(t)C_8H_{11}$ -  $OCH - C_3H_7(i)$	H	- O - 
C - 24		$(t)C_8H_{11}$ -  $OCH - C_8H_{13}$	H	- Cl
C - 25		$(t)C_8H_{11}$ -  $OCH - C_3H_7(i)$	H	$OCH_2CONHCH_2CH_2OCH_3$
C - 26		$(t)C_8H_{11}$ -  $OCH - C_4H_9$	H	H
C - 27		$(t)C_8H_{11}$ -  $OCH - C_2H_5$	H	H

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Exemplified compound No.	R ₁	R ₂	R ₃	X
C-28			H	H
C-29			H	-Cl
C-30			H	
C-31			H	
C-32			H	H
C-33	-C3F7		H	H
C-34	-(CF2)4H		H	H
C-35			H	H
C-36			H	-OCH2COOCH3
C-37	-C3F7		H	-Cl

Exemplified compound No.	R ₁	R ₂	R ₃	X
C-38	-C ₃ F ₇		H	-O--OCH ₃
C-39	-C ₃ F ₇		H	-O--C ₈ H ₁₇ (t)
C-40	-C ₃ F ₇		H	-OCH ₂ COOCH ₃
C-41	-(CF ₂) ₄ H		H	-OCH ₂ COOCH ₃
C-42	-(CF ₂) ₄ H		H	-O--C ₈ H ₁₇ (t)
C-43	-C ₃ F ₇		H	C2
C-44	-C ₃ F ₇		H	-OCH ₂ COOCH ₃
C-45	-C ₃ F ₇		H	-O--OCH ₃
C-46	-C ₃ F ₇		H	-OCH ₂ COOCH ₃
C-47	-(CF ₂) ₄ H		H	-O--C ₈ H ₁₇

The cyan coupler of the present invention includes the 2,5-diacylamino cyan couplers described in the specification for Japanese Patent Application No. 21843/1986, pp. 26-35, the official gazette for Japanese Patent O.P.I. Publication No. 225155/1985, lower left column, p. 7 through lower right column, p. 10, the official gazette for Japanese Patent O.P.I. Publication No. 22853/1985, upper left column, p. 6 through lower right column, p. 8, and the official gazette for Japanese Patent O.P.I. Publication No. 185335/1984, lower left column,

p. 6 through upper left column, p. 9, and can be synthesized in accordance with the methods described in these specification and official gazettes. The cyan coupler of the present invention is used normally in a silver halide emulsion layer, particularly in a red-sensitive emulsion layer. Its addition amount is normally 2×10^{-3} to 8×10^{-1} mol, preferably 1×10^{-2} to 5×10^{-1} mol per mol silver halide.

5 The compound represented by the Formula [I] (hereinafter referred to as the compound of the present invention) is described below.

Examples of the aliphatic group represented by R_4 , R_5 or R_6 include an alkyl group having a carbon number of 1 to 32, alkenyl group, alkynyl group, cycloalkyl group and cycloalkenyl group. The alkyl group, alkenyl group and alkynyl group may be linear or branched. These aliphatic groups may have a substituent.

10 Examples of the aromatic group represented by R_4 , R_5 or R_6 include an aryl group such as a phenyl group and an aromatic heterocyclic group such as a pyridyl group or furyl group. These aromatic groups may have a substituent.

Preferably, R_4 , R_5 and R_6 are independently an alkyl group or aryl group, and they may be identical or not. The total carbon number of R_4 , R_5 and R_6 is preferably 6 to 50.

15 There is no limitation on the substituent for the aliphatic group or aromatic group represented by R_4 , R_5 or R_6 , but with preference given to an alkoxy group, aryloxy group, acyl group, acyloxy group, alkoxycarbonyl group, aryloxycarbonyl group, carbamoyl group, sulfamoyl group, acylamino group and amino group.

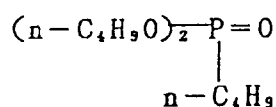
ℓ , m and n independently represent 0 or 1, but not all of ℓ , m and n are 1, i.e., at least one of the aliphatic groups or aromatic groups represented by R_4 , R_5 and R_6 is in direct bond with a phosphorus atom.

20 It is preferable that all of ℓ , m and n are 0.

Examples of the compound of the present invention are given below, but the invention is not to be interpreted as limited by them.

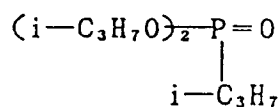
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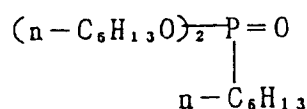


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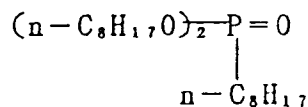


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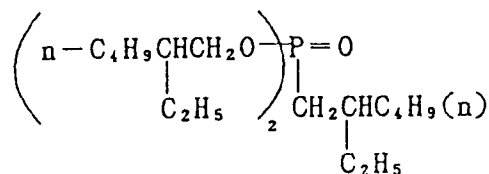
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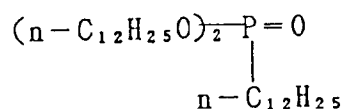
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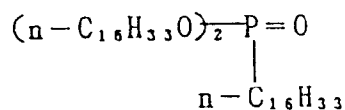
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I — 7

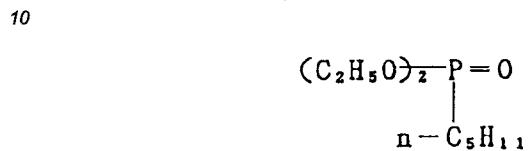


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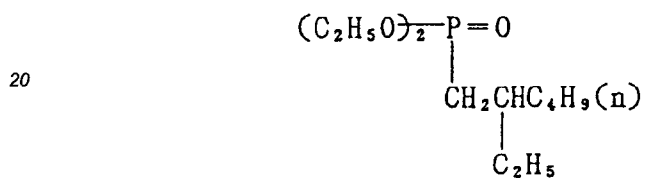
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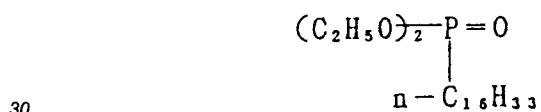
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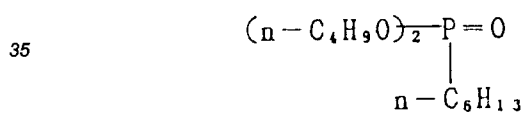
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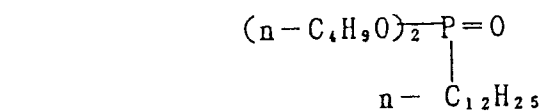
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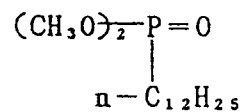
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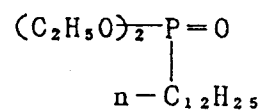
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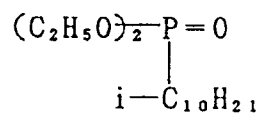
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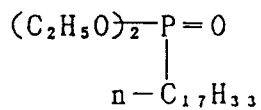
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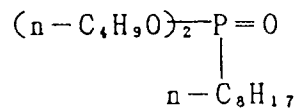
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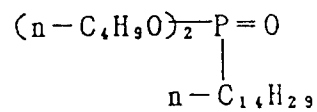
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I — 17

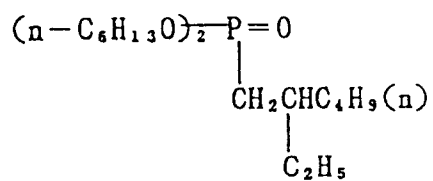
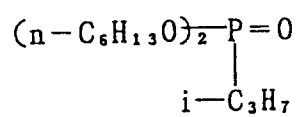


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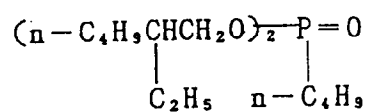


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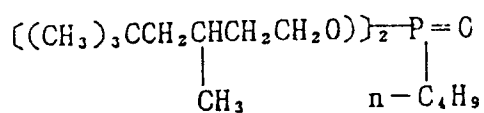
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I - 22

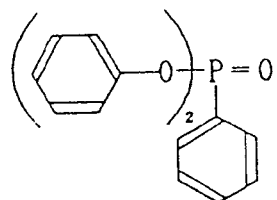
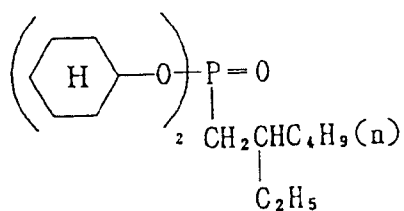


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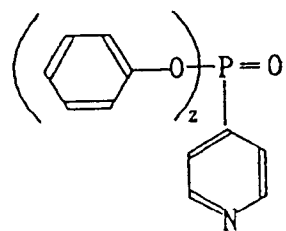


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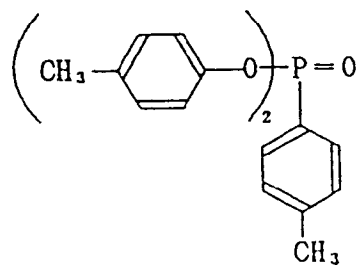
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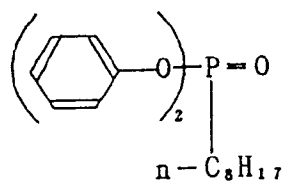
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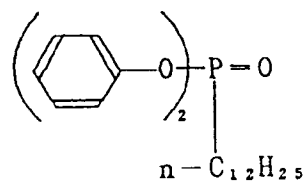
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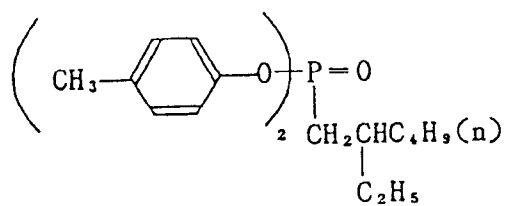
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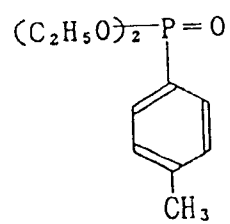
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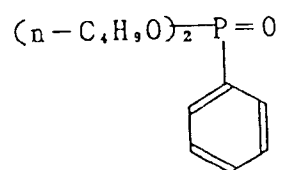
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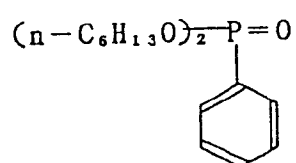
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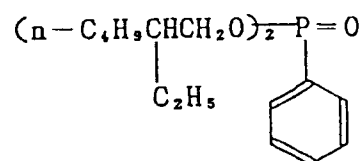
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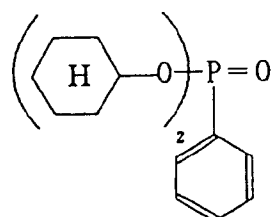
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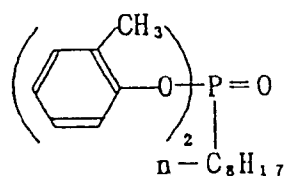
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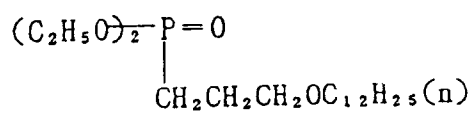
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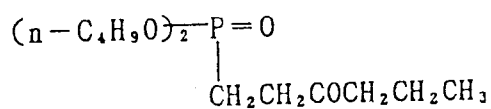
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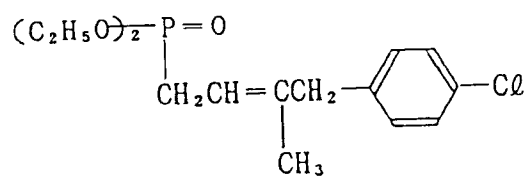
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I - 38

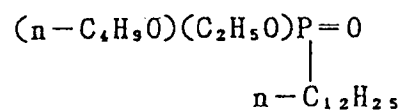


I - 39



I — 40

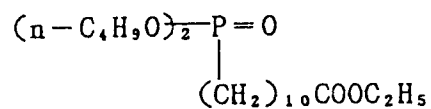
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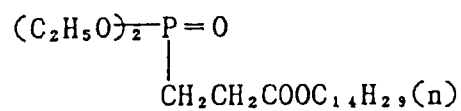
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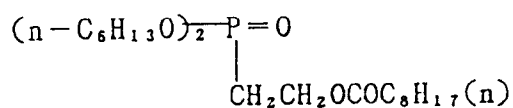
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I — 43

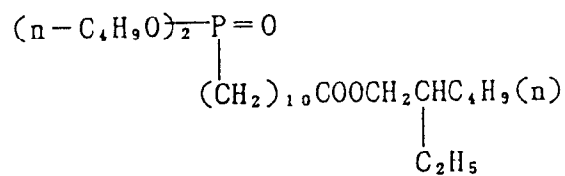
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I — 44

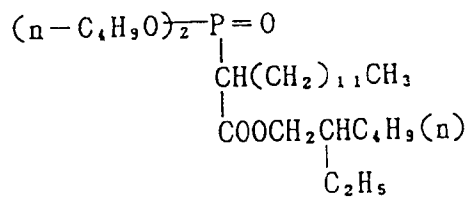
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I — 45

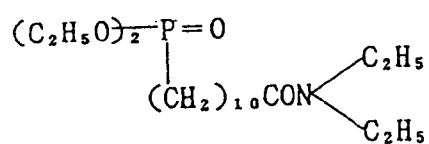
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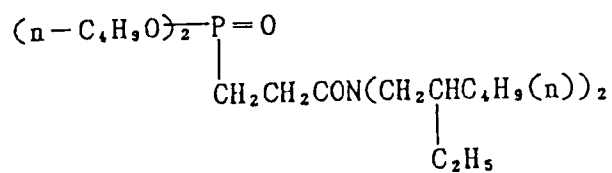
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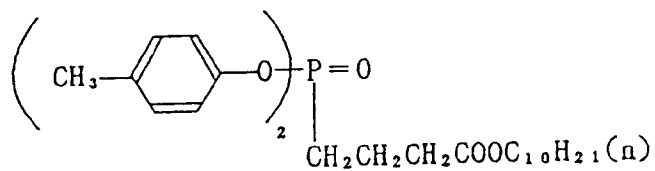
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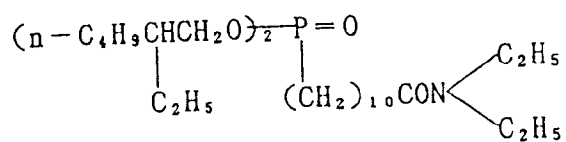
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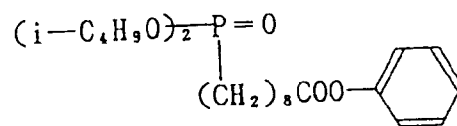
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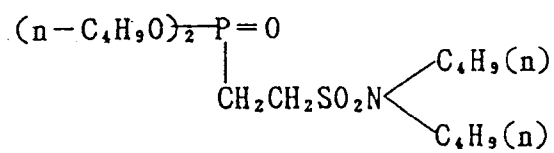
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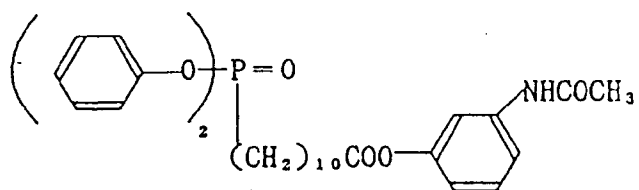
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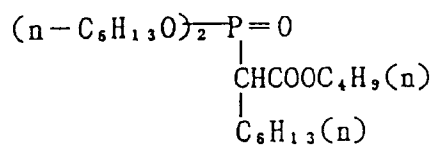
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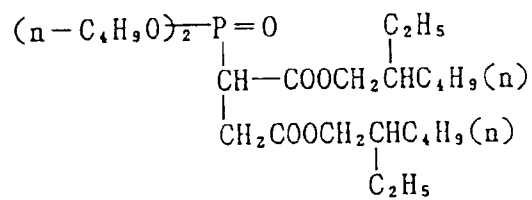
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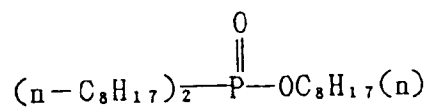
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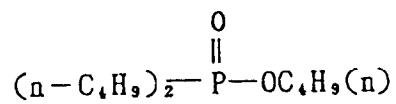
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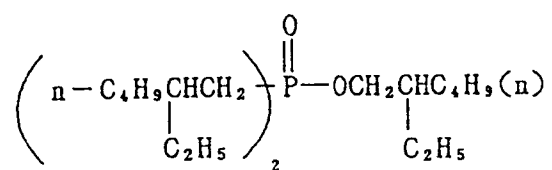
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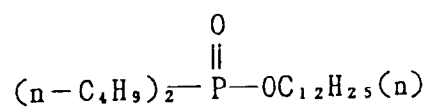
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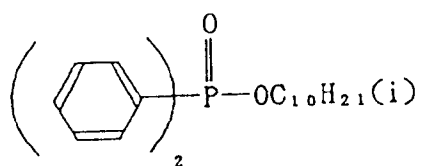
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I - 58

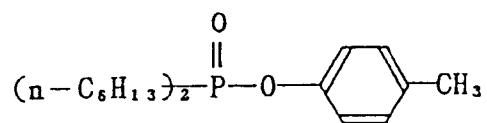


I - 59



I — 60

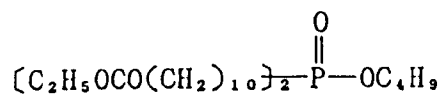
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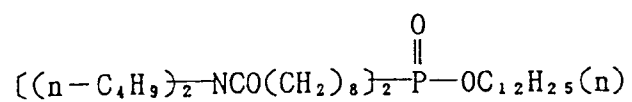
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I — 62

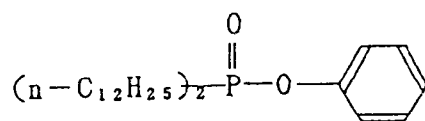
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I — 63

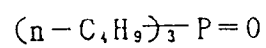
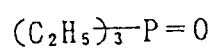
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I — 64

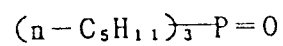
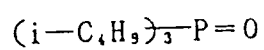
I — 65



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I — 66

I — 67



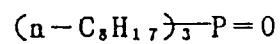
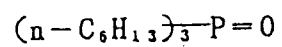
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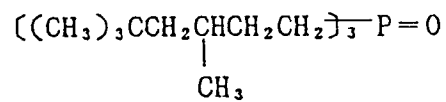
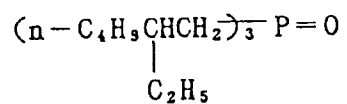
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I — 69



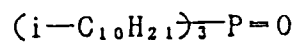
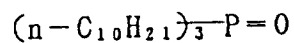
I — 70

I — 71



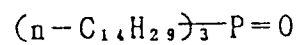
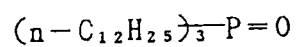
I — 72

I — 73



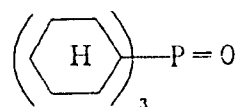
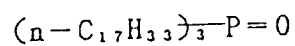
I — 74

I — 75



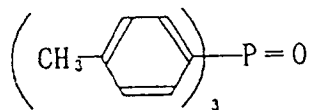
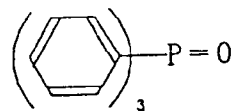
I — 76

I — 77



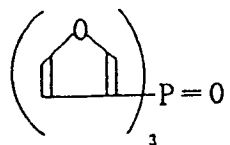
I — 78

I — 79



I - 80

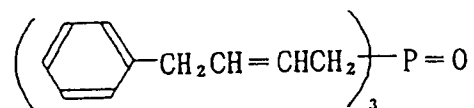
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I - 81

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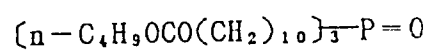
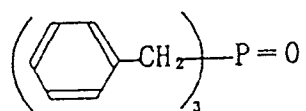


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I - 82

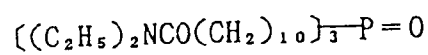
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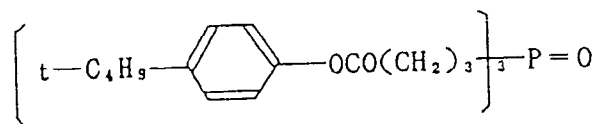
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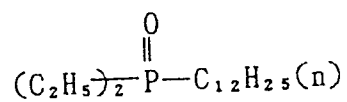
I - 85



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I - 86

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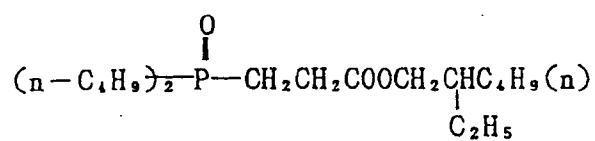


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I - 87

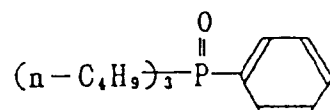
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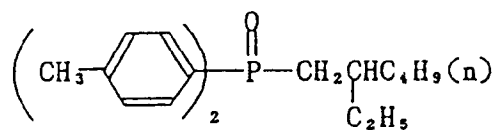
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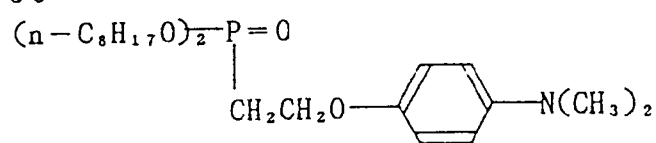
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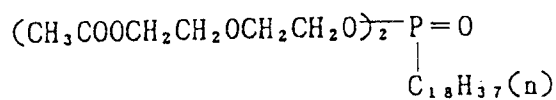
I - 90



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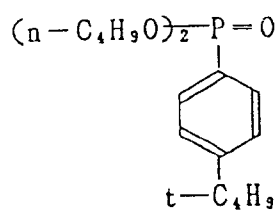
I - 91

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I - 92

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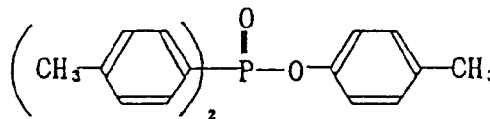
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I - 93

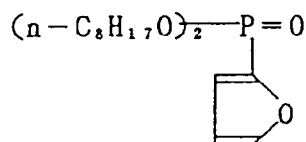
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I - 94

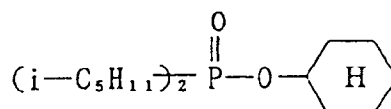
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I - 95

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The compound of the present invention includes the compound described in the specification for Japanese Patent O.P.I. Publication No. 19049/1981, pp. 4-5.

30 The compound of the present invention is commercially available, but can also be synthesized in accordance with the methods described in Japanese Patent O.P.I. Publication No. 19049/1981, British Patent No. 694,772, the Journal of the American Chemical Society, 79, 6524 (1957), the Journal of Organic Chemistry, 25, 1000 (1960) and Organic Synthesis, 31, 33 (1951).

The addition ratio of the compound of the present invention is preferably 5 to 500 mol%, more preferably 10 to 300 mol% to the cyan coupler of the present invention.

35 The compound of the present invention may be used singly or in combination of two or more kinds.

It is preferable to use the cyan coupler of the present invention and the compound of the present invention in the same layer. Ideally, they are present in the same hydrophobic organic phase such as an oil phase in the same layer. Specifically, it is preferable to add the cyan coupler of the present invention and the compound of the present invention to the desired hydrophilic colloidal layer after being dissolved at the same time in a high boiling organic solvent used as needed, and a low boiling and/or water-soluble organic solvent used as needed and being emulsion dispersed in a hydrophilic binder such as an aqueous solution of gelatin in the presence of a surfactant.

In this case, the compound of the present invention itself may be used as the high boiling organic solvent.

45 The high boiling organic solvent used as needed is preferably an organic solvent having a boiling point above 150°C such as a phenol derivative, phthalate, phosphate, citrate, benzoate, alkylamide, fatty acid ester or trimesate which does not react with the oxidation product of the color developing agent.

Examples of the low boiling organic solvent used as needed include ethyl acetate, cyclohexanol and methyl ethyl ketone.

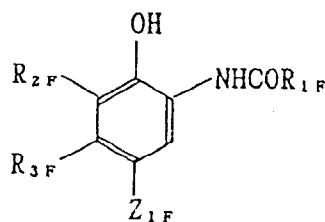
50 In the present invention, the yellow coupler is preferably an acylacetanilide coupler, with further preference given to a benzoylacetanilide and pivaloylacetanilide for more advantage.

In the present invention, the magenta coupler is preferably a known 5-pyrazolone coupler, pyrazolotriazole coupler or another pyrazoloazole coupler.

The cyan coupler of the present invention may be used in combination with a conventional cyan coupler, as long as the object of the present invention is not interfered with.

55 Examples of the preferred cyan coupler include the coupler represented by the Formula [F] below.

Formula [F]



wherein R_{1F} represents a ballast group. R_{2F} represents a hydrogen atom, halogen atom or alkyl group. R_{3F} represents an alkyl group having a carbon number of 1 to 6.

Z_{1F} represents a hydrogen atom or a group capable of splitting off by reaction with the oxidation product of an aromatic primary amine color developing agent.

Examples of these cyan couplers are given in Japanese Patent O.P.I. Publication Nos. 37425/1972, 10135/1975, 25228/1975, 112038/1975, 117422/1975 and 130441/1975, US Patent Nos. 2,369,929, 2,423,730, 2,434,272, 2,474,293, 2,698,794 and 2,895,826, Japanese Patent O.P.I. Publication Nos. 112038/1975, 109630/1978 and 163537/1980 and US Patent Nos. 3,772,002 and 4,443,536.

The silver halide for the present invention includes any silver halides such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide and silver chloriodide.

However, grains of silver halide having a silver chloride content above 90 mol% is preferred for use in a silver halide photographic light-sensitive material requiring fast development, such as color photographic paper.

In this case, the silver halide grains preferably have a silver chloride content above 90 mol%, a silver bromide content below 10 mol% and silver iodide content below 0.5 mol%. Further preference is given to a silver chlorobromide having a silver bromide content of 0.1 to 5 mol%.

The silver halide for the present invention may be a polydispersed emulsion wherein the average grain size distribution is broad, but preference is given to a monodispersed emulsion.

These silver halide emulsions may be chemically sensitized with active gelatin, sulfur sensitizer, selenium sensitizer, reduction sensitizer, noble metal sensitizer or another chemical sensitizer.

The silver halide for the present invention may be optically sensitized by adding an appropriate sensitizing dye for the purpose of providing light sensitivity in the desired wavelength band.

The silver halide photographic light-sensitive material of the present invention may incorporate an anti-fogging agent, image stabilizer, hardener, plasticizer, polymer latex, ultraviolet absorbent, formalin scavenger, mordant, development promoter, development retarder, fluorescent brightening agent, matting agent, lubricant, antistatic agent, surfactant and other additives.

The silver halide photographic light-sensitive material of the present invention can be developed by various color developing processes.

The silver halide photographic light-sensitive material of the present invention is applicable to color negative and positive films, and negative-positive and positive-positive color photographic paper.

EXAMPLES

The present invention is hereinafter described in more detail by means of the following working examples, but the mode of embodiment of the invention is not limited by these examples.

Example 1

Preparation of silver halide emulsions

The six kinds of silver halide emulsion listed in Table 1 were prepared by the neutralization method or double-jet precipitation method.

Table 1

Emulsion number.	AgCl content (mol%)	AgBr content (mol%)	Average grain size (μ)	Chemical sensitizer	Spectral sensitizing dye
Em-1	99.5	0.5	0.67	Sodium thiosulfate*1, chloroauric acid*2	SD-1*3
Em-2	99.5	0.5	0.46		SD-2*4
Em-3	99.5	0.5	0.43		SD-3*5
Em-4	10	90	0.67	Sodium thiosulfate*1	SD-1*3
Em-5	30	70	0.46		SD-2*4
Em-6	30	70	0.43		SD-3*5

*1: Added in 2 mg per mol silver halide.

*2: Added in 2×10^{-5} mol per mol silver halide

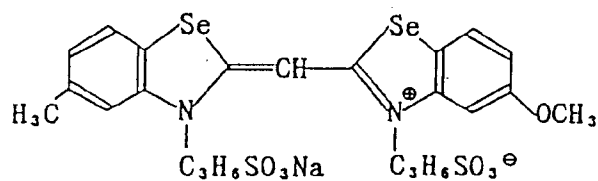
*3: Added in 0.9 mmol per mol silver halide.

*4: Added in 0.7 mmol per mol silver halide.

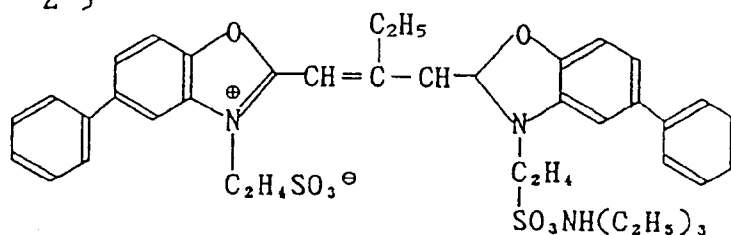
*5: Added in 0.2 mmol per mol silver halide.

To each silver halide emulsion was added the following STB-1 as an emulsion stabilizer in a ratio of 5×10^{-3} mol per mol silver halide after completion of chemical sensitization.

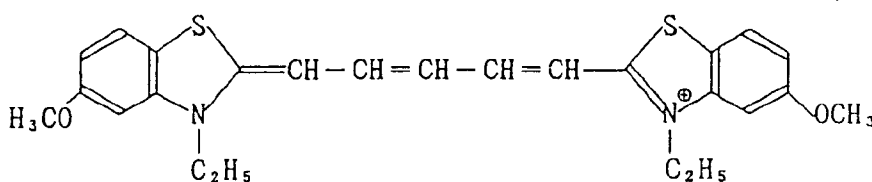
[S D — 1]



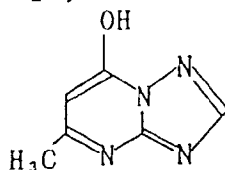
[S D - 2]



[S D - 3]



[S T D - 1]



Preparation of silver halide color photographic light-sensitive material samples

Next, the following layers 1 through 7 were coated (simultaneous coating) in this order on a paper support coated with polyethylene on both faces to prepare silver halide color photographic light-sensitive material sample Nos. 1 through 22. In the examples given below, the addition amounts are shown in amount per m^2 light-sensitive material.

Layer 1: A layer containing 1.2 g of gelatin, 0.29 g (as silver, the same applies below) of a blue-sensitive silver halide emulsion Em-1 and a solution of 0.75 g of a yellow coupler Y-1, 0.3 g of a light stabilizer ST-1 and 0.015 g of 2,5-diethylhydroquinone HQ-1 in 0.3 g of dinonyl phthalate DNP.

Layer 2: A layer containing 0.9 g of gelatin and a solution of 0.04 g of HQ-1 in 0.2 g of dioctyl phthalate DOP.

Layer 3: A layer containing 1.4 g of gelatin, 0.2 g of a green-sensitive silver halide emulsion Em-2, a solution of 0.50 g of a magenta coupler M-1, 0.25 g of a light stabilizer ST-2 and 0.01 g of HQ-1 in 0.3 g of DOP, and 0.3 g of the following filter dye Al-1.

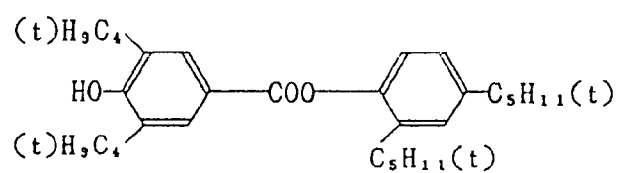
Layer 4: A layer containing 1.2 g of gelatin, 0.6 g of the following ultraviolet absorbent UV-1 and a solution of 0.05 g of HQ-1 in 0.3 g of DNP.

Layer 5: A layer containing 1.4 g of gelatin, 0.20 g of a red-sensitive silver halide emulsion Em-3, a cyan coupler listed in table 2, the compound and high boiling organic solvent of the present invention, 0.3 g of ST-1 and 0.01 g of HQ-1.

Layer 6: A layer containing 1.1 g of gelatin, a solution of 0.2 g of UV-1 in 0.2 g of DOP, and 5 mg of the following filter dye Al-2.

Layer 7: A layer containing 1.0 g of gelatin and 0.05 g of 2,4-dichloro-6-hydroxytriazine sodium.

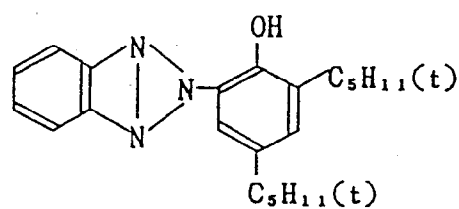
S T - 1



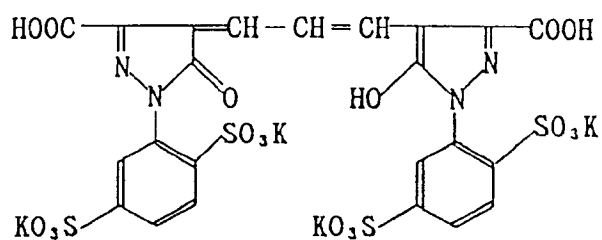
S T - 2



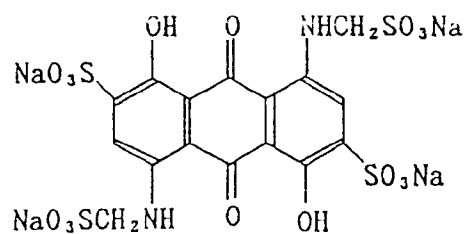
U V - 1



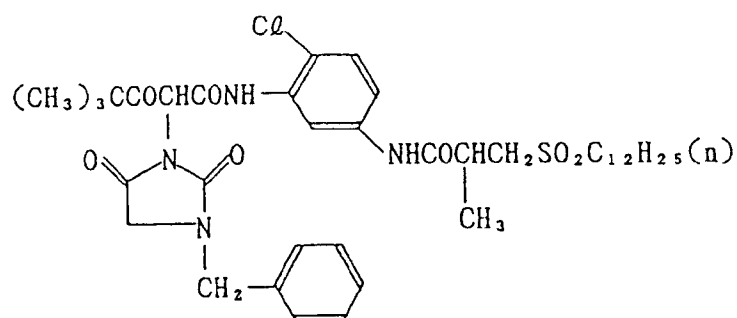
A I - 1



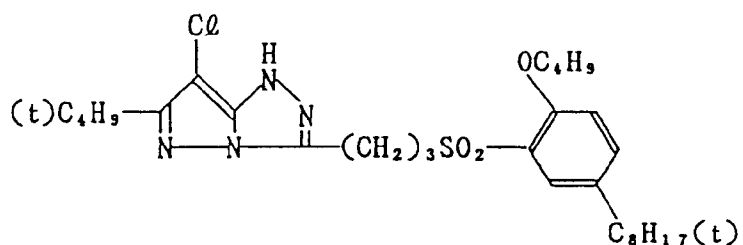
A I - 2



Y - 1



M - 1



The samples thus obtained were subjected to exposure through an optical wedge and then processed in the following procedures.

Processing procedures	Temperature	Time
Color development	34.7 \pm 0.3°C	45 seconds
Bleach-fixation	34.7 \pm 0.5°C	50 seconds
Stabilization	30 to 34°C	90 seconds
Drying	60 to 80°C	60 seconds

The processing solutions used had the following compositions.

Color developer

Water	800 ml
Triethanolamine	8 g
N,N-diethylhydroxylamine	5 g
Potassium chloride	2 g
N-ethyl-N- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	5 g
Sodium tetrapolyphosphate	2 g

Potassium carbonate	30 g
Potassium sulfite	0.2 g
5 Fluorescent brightening agent	
(4,4'-diaminostilbene disulfonic	
10 acid derivative)	1 g

Water was added to make a total quantity of 1ℓ, and the solution was adjusted to a pH of 10.2.

Bleach-fixer

15 Ferric ammonium ethylenediaminetetraacetate	
dihydrate	60 g
20 Ethylenediaminetetraacetic acid	3 g
Ammonium thiosulfate (70% solution)	100 ml
Ammonium sulfite (40% solution)	27.5 ml

25 Potassium carbonate or glacial acetic acid was added to obtain a pH of 5.7, and water was added to make a total quantity of 1ℓ.

30 Stabilizer

5-chloro-2-methyl-4-isothiazolin-3-one	1 g
1-hydroxyethylidene-1,1-diphosphonic acid	2 g

35 Water was added to make a total quantity of 1ℓ, and sulfuric acid or potassium hydroxide was added to obtain a pH of 7.0.

With respect to sample Nos. 1 through 22 thus processed, the maximum absorption wavelength λ_{\max} at a cyan dye image density of 1.0 and the densities at 420 nm and 550 nm (D_B and D_G) were determined using a recording spectrophotometer Model 320, produced by Hitachi Ltd.

40 As the values for D_B and D_G decrease, unwanted absorption respectively in the blue and green bands decreases and the color reproducibility increases. The processed samples were irradiated with a xenon fade-0-meter for 14 days to examine the fastness to light of cyan dye images. Separately, each sample was kept in a hot humid atmosphere at 60°C temperature and 80% relative humidity for 14 days to examine the tropical heat stability of cyan dye images. The results obtained are given in Table 2. The fastness to light and tropical heat stability of the dye images are expressed in residual dye density percent ratio to an initial density of 1.0 after the light fastness and incubation tests.

Table 2

Sample number	Cyan compier (0.9 mmol/m ²)	Compound (g/m ²)	High boiling organic solvent (g/m ²)	λ_{max} (nm)	D _B	D _G	Light fastness (% residue)	Tropical heat stability (% residue)	Remark
1	CC-1	-	DOP (0.2)	650	0.405	0.440	95	66	Comparative
2	CC-1	I-69 (0.25)	-	649	0.398	0.445	93	67	Comparative
3	CC-2	I-69 (0.20)	DOP (0.15)	649	0.401	0.442	93	67	Comparative
4	C-1	-	DOP (0.2)	650	0.305	0.445	75	95	Comparative
5	C-1	I-69 (0.25)	-	655	0.282	0.395	90	98	Comparative
6	C-2	-	-	649	0.308	0.460	79	97	Comparative
7	C-2	I-5 (0.25)	-	648	0.285	0.405	90	98	Inventive
8	C-2	I-25 (0.3)	-	649	0.285	0.404	91	98	Inventive
9	C-2	I-69 (0.25)	-	650	0.280	0.398	92	98	Inventive
10	C-18	I-70 (0.25)	-	650	0.281	0.397	92	98	Inventive
11	C-23	I-23 (0.20)	DOP (0.15)	649	0.275	0.380	91	97	Inventive
12	C-23	I-74 (0.20)	DOP (0.15)	655	0.265	0.372	91	97	Inventive
13	C-24	-	TCP (0.2)	649	0.310	0.462	77	95	Comparative
14	C-24	I-69 (0.25)	-	650	0.285	0.393	92	98	Inventive
15	C-40	-	TCP (0.2)	650	0.308	0.455	75	94	Comparative
16	C-40	I-21 (0.25)	-	650	0.277	0.390	90	96	Inventive
17	C-40	I-27 (0.25)	-	649	0.276	0.385	90	98	Inventive
18	C-40	I-69 (0.25)	-	652	0.265	0.371	92	97	Inventive
19	C-40	I-69 (0.20)	TCP (0.15)	649	0.262	0.370	92	98	Inventive
20	C-40	I-70 (0.25)	-	653	0.262	0.373	90	96	Inventive
21	C-42	I-69 (0.20)	DOP (0.15)	650	0.264	0.373	91	97	Inventive
22	C-44	I-70 (0.25)	-	650	0.258	0.370	94	98	Inventive

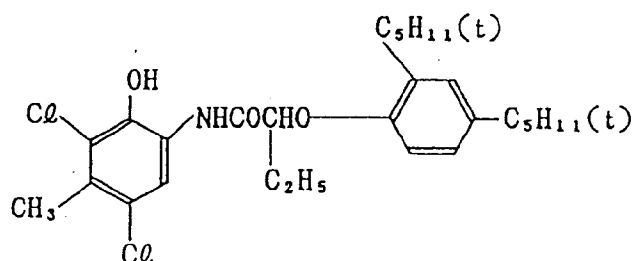
Figures in parentheses are addition amounts.

DOP: Dioctyl phthalate

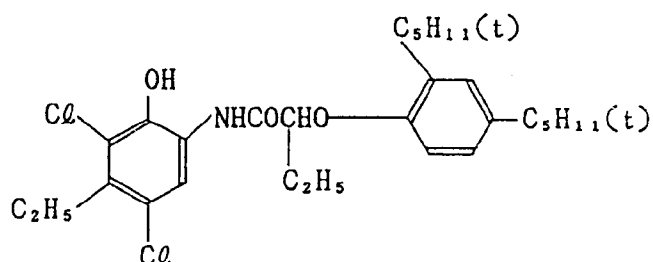
TCP: Tricresyl phthalate

TOP: Tri-2-ethylhexyl phthalate

C C - 1



C C - 2



As is evident from Table 2, the samples according to the present invention were found to be excellent in color reproduction due to decreased values of D_B and D_G and to have improved light fastness and tropical heat stability.

Among them, the sample prepared with a more preferred cyan coupler of the present invention represented by the Formula [C-II] and a compound of the present invention was found to have an excellent improving effect due to great reduction in D_B and D_G .

Example 2

Silver halide color photographic light-sensitive material sample Nos. 23 through 44 were prepared in the same manner as in Example 1 except that the blue-sensitive silver halide emulsion in Layer 1 was replaced with Em-4 in Table 1, the green-sensitive silver halide emulsion in Layer 3 was replaced with Em-5 in Table 1 and the red-sensitive silver halide emulsion in layer 5 replaced with Em-6 in table 1, and Layer 5 incorporates a cyan coupler listed in Table 3, a compound and high boiling organic solvent of the present invention.

The samples thus obtained were subjected to exposure through an optical wedge in the same manner as in Example 1 and then processes in the following processing procedures, and subjected to measurements similar to those in Example 1.

The results are given in Table 3.

Processing procedures

Color development	3 minutes 30 seconds	33°C
Bleach-fixation	1 minute 30 seconds	33°C
Washing	3 minutes	33°C

The processing solutions had the following compositions.

Color developer

	N-ethyl-N- β -methanesulfonamidoethyl-3-methyl-	
5	4-aminoaniline sulfate	4.9 g
	Hydroxylamine sulfate	2.0 g
	Potassium carbonate	25.0 g
10	Sodium bromide	0.6 g
	Anhydrous sodium sulfite	2.0 g
15	Benzyl alcohol	13 ml
	Polyethylene glycol	
20	(average degree of polymerization 400)	3.0 ml

Water was added to make a total quantity of 1ℓ, and sodium hydroxide was added to obtain a pH of 10.0.

25 Bleach-fixer

	Iron sodium ethylenediaminetetraacetate	6.0 g
	Ammonium thiosulfate	100 g
30	Sodium bisulfite	10 g
	Sodium metabisulfite	3 g
35	Water was added to make a total quantity of 1ℓ, and	
	aqueous ammonia was added to obtain a pH of	7.0.

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Table 3

Sample number	Cyan coupler (0.9 mmol/m ²)	Compound (g/m ²)	High boiling organic solvent (g/m ²)	λ_{\max} (nm)	D _B	D _G	Light fastness (% residue)	Tropical heat stability (% residue)	Remark
23	CC-1	-	DOP	648	0.410	0.445	96	67	Comparative
24	CC-1	I-69	-	648	0.404	0.445	95	67	Comparative
25	C-1	-	DOP	647	0.315	0.450	72	96	Comparative
26	C-1	I-70	-	650	0.279	0.395	91	95	Inventive
27	C-2	-	DOP	647	0.313	0.455	91	95	Comparative
28	C-2	I-5 (0.3)	-	648	0.285	0.399	93	94	Inventive
29	C-2	I-70 (0.3)	-	648	0.278	0.385	93	95	Inventive
30	C-40	-	DOP	649	0.310	0.450	93	98	Comparative
31	C-40	I-4 (0.3)	-	650	0.275	0.380	92	97	Inventive
32	C-40	I-69 (0.3)	-	651	0.265	0.372	92	97	Inventive
33	C-40	I-79 (0.3)	-	651	0.267	0.373	92	97	Inventive

As is evident from Table 3, the samples according to the present invention were found to be excellent in color reproduction for green and blue colors due to decreased values of D_B and D_G and to have improved image preservability.

5 Example 3

A paper support of 135 μm in thickness coated with polyethylene containing titanium oxide on the top face and polyethylene on the back face was coated with the following layers 1 through 7 on the top face and with a backing layer on the back face to yield a color light-sensitive material.

10 In the table, the amount of addition is expressed in gram per m^2 , unless otherwise specified. Also, the amount of silver halide emulsion is expressed on the basis of the amount of silver.

	Layer 7: Protective layer	Addition amount
15	Gelatin	1.0
	Silicon dioxide powder	
20	(average grain size 3 μm)	0.03
	Layer 6: Ultraviolet absorbing layer	
25	Gelatin	0.6
	UV absorbent UV-1	0.2
	UV absorbent UV-2	0.2
30	Antistaining agent HQ-1	0.01
	DNP	0.2
35	PVP	0.03
	Anti-irradiation dye AI-2	0.065
40	Layer 5: Red-sensitive layer	
	Gelatin	1.40
45	Red-sensitive silver halide emulsion spectrally sensitized with sensitizing dye D-3	0.24
50	Cyan coupler C-a	0.40
	Antistaining agent HQ-1	0.01
55	DOP	0.30

Layer 4: Ultraviolet absorbing layer

	Gelatin	1.30
5	UV absorbent UV-1	0.40
	UV absorbent UV-2	0.40
10	Antistaining agent HQ-1	0.03
	DNP	0.40

15 Layer 3: Green-sensitive layer

	Gelatin	1.40
20	Green-sensitive silver halide emulsion spectrally sensitized with sensitizing dye D-2	0.27
25	Magenta coupler M-b	0.35
	Yellow coupler Y-c	0.12
	Dye image stabilizer ST-3	0.20
30	Dye image stabilizer ST-4	0.10
	Antistaining agent HQ-1	0.01
35	HB-2	0.30
	Anti-irradiation dye AI-1	0.01

40 Layer 2: Interlayer

	Gelatin	1.20
45	Antistaining agent HQ-1	0.12
	DIDP	0.15

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Layer 1: Blue-sensitive layer

	Gelatin	1.30
5	Blue-sensitive silver halide emulsion	
	spectrally sensitized with sensitizing	
10	dye D-1	0.30
	Yellow coupler Y-b	0.80
	Dye image stabilizer ST-1	0.30
15	Dye image stabilizer ST-2	0.20
	Antistaining agent HQ-1	0.02
	HB-2	0.20
20	Anti-irradiation dye AI-3	0.063

25 Backing layer: Protective layer

	Gelatin	3.00
	Surfactant S-2	0.01
30	Hardener H-1	0.07
	Silica (average grain size 5 μm)	0.3

35 Surfactants ST-1 and S-2 and hardeners H-1 and H-2 were used as coating aids for the emulsion layer side.

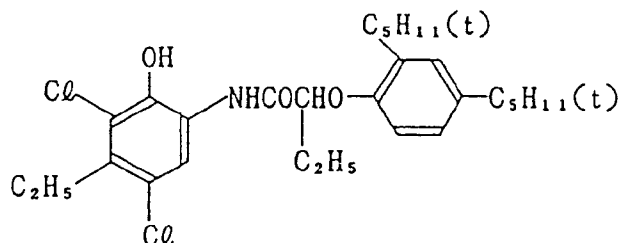
Sample Nos. 34 through 45 were prepared on the basis of the above composition except that the cyan coupler and high boiling organic solvent in Layer 5 were changed as shown in Table 4 and a compound of the present invention was added.

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C-a

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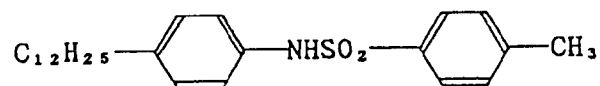


- 55 TOP: Tri-2-ethylhexyl phosphate
DOP: Dioctyl phthalate
DNP: Dinonyl phthalate
DIDP: Diisodecyl phthalate

PVP: Poly(vinyl pyrrolidone)
DOS: Dioctyl sebacate

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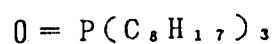
H B - 1



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H B - 2

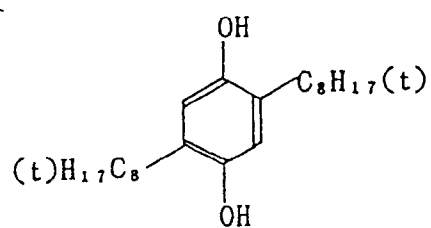
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H Q - 1

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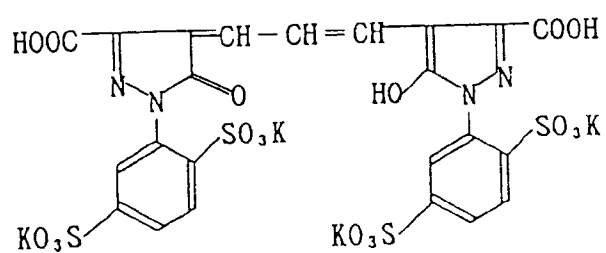


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A I - 1

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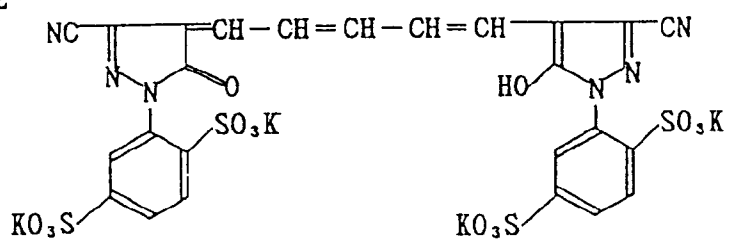


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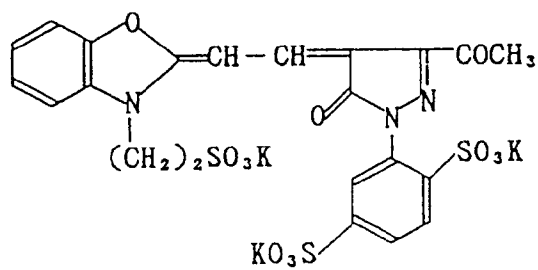
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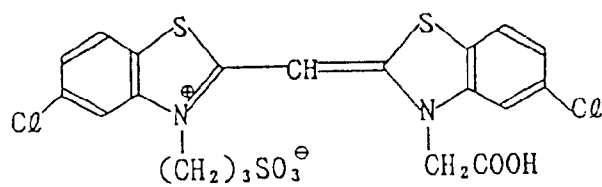
A I - 2



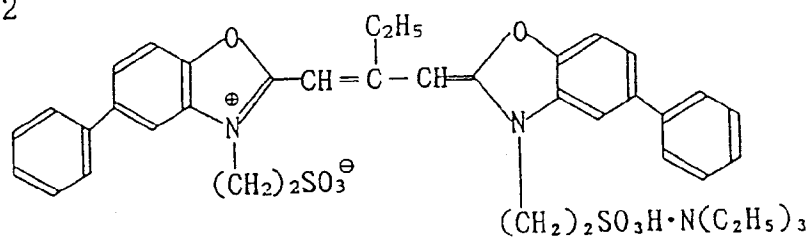
A I - 3



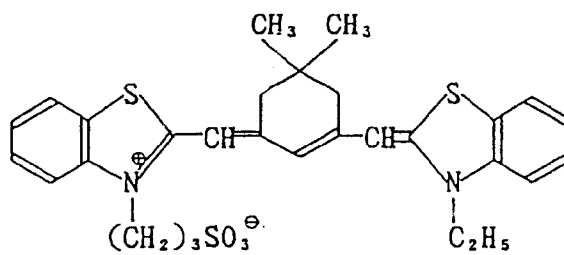
D - 1



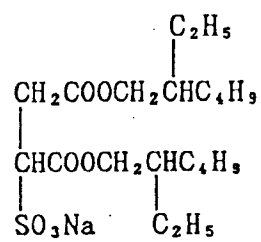
D - 2



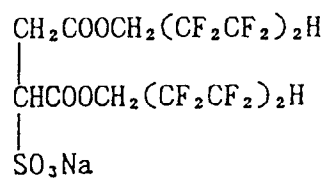
D - 3



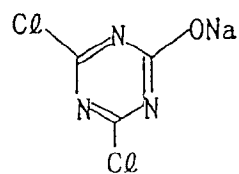
S - 1



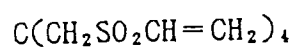
S - 2



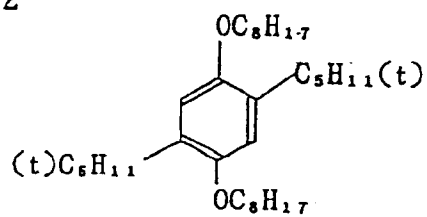
H - 1



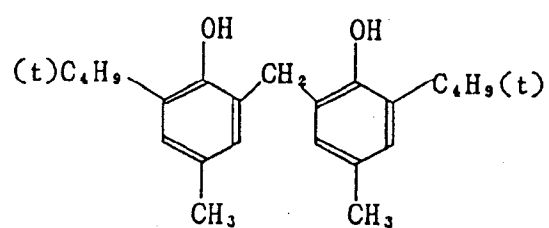
H - 2



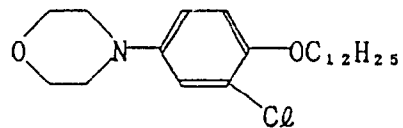
S T - 2



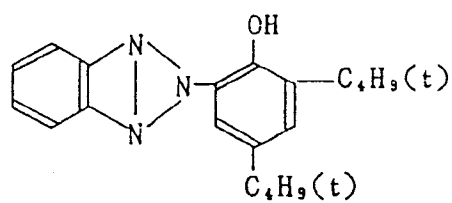
S T - 3



S T - 4



U V - 2



5

Table 4

10	Sample number	Cyan coupler	Inventive compound (g/m ²)	High boiling organic solvent (g/m ²)
	34 (Comparative)	C-a	-	DOP (0.3)
15	35 (Comparative)	C-2	-	DOP (0.3)
	36 (Comparative)	C-24	-	DOS (0.3)
20	37 (Comparative)	C-33	-	TOP (0.3)
	38 (Comparative)	C-40	-	TOP (0.3)
25	39 (Inventive)	C-2	I-70 (0.25)	-
	40 (Inventive)	C-24	I-69 (0.3)	-
30	41 (Inventive)	C-33	I-69 (0.3)	-
	42 (Inventive)	C-40	I-4 (0.3)	-
35	43 (Inventive)	C-40	I-69 (0.3)	-
	44 (Inventive)	C-40	I-69 (0.2)	TOP (0.2)
40	45 (Inventive)	C-44	I-70 (0.3)	-

45

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55 The amount of cyan coupler added to sample Nos. 35 through 45 was the same on a molar basis as the amount of cyan coupler C-a in sample No. 34.

The samples described above were subjected to exposure in contact with a black-and-white negative film with the dot point area varied between 0% and 100% at a dot density of 175 lines per inch under evacuated

conditions.

A fluorescent lamp was used as the light source for exposure, and the color separation filters used were Kodak Wratten filter Nos. 47B, 61 and 29 for blue, green and red colors, respectively.

The samples were then processed in the following procedures.

5

Processing procedures	Temperature	Time
Color development	39.8°C	2 minutes
10 Bleach-fixation	33°C	45 seconds
Stabilization	33°C	3 minutes
15 Drying	70°C	1 minute

The processing solutions had the following compositions.

20

Color developer

Hydroxylamine sulfate	2.0 g
Potassium carbonate	25.0 g
25 Sodium chloride	0.1 g
Sodium bromide	0.2 g
30 Anhydrous sodium sulfite	2.0 g
Benzyl alcohol	10.0 ml
N-ethyl-N- β -hydroxyethyl-4-aminoaniline sulfate	4.5 g

35

Water was added to make a total quantity of 1ℓ, and sodium hydroxide was added to obtain a pH of 10.15.

40

Bleach-fixer

Ferric sodium ethylenediaminetetraacetate	60 g
Ammonium thiosulfate	100 g
45 Sodium bisulfite	20 g

Water was added to make a total quantity of 1ℓ, and sulfuric acid was added to obtain a pH of 7.0.

50

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Stabilizer

5	5-chloro-2-methyl-4-isothiazolin-3-one	1.0 g
	Ethylene glycol	1.0 g
	1-hydroxyethylidene-1,1-diphosphonic acid	2.0 g
10	Ethylenediaminetetraacetic acid	1.0 g
	Ammonium hydroxide (70% solution)	3.0 g
	Ammonium sulfite	3.0 g
15	Fluorescent brightening agent	
	(4,4'-diaminostilbene disulfonic	
20	acid derivative)	1.5 g

Water was added to make a total quantity of 1ℓ, and sulfuric acid or potassium hydroxide was added to obtain a pH of 7.0.

The processed samples thus obtained were subjected to evaluation of the color tone of cyan color forming dye as directed below.

Evaluation of cyan color tone

The samples were visually evaluated with respect to color tone in the single cyan coloring portion on the finished dot image in comparison with a printing ink color sample, expressed in the following ten grades.

Grade	Color tone
35	1
	2
	3
40	4
	5
	6
45	7
	8
50	9
	10

The processed samples described above were irradiated with a xenon fade-0-meter at 7000 lux for 24 hours and then examined for fastness to light of cyan dye image.

The results obtained are given in Table 5.

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Table 5

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Sample number	Color tone grade	Color fastness to light (% residue)
34 (Comparative)	4	92
35 (Comparative)	4	55
36 (Comparative)	4	58
37 (Comparative)	5	40
38 (Comparative)	54	50
39 (Inventive)	8	90
40 (Inventive)	8	91
41 (Inventive)	8	89
42 (Inventive)	9	90
43 (Inventive)	9	90
44 (Inventive)	9	91
45 (Inventive)	9	92

45

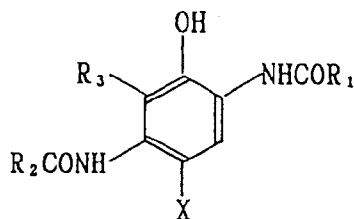
50 As is evident from Table 5, the samples prepared in accordance with the present invention were found to offer a good color tone nearly equivalent to that obtained with the printing cyan ink and to permit accomplishment of a practically acceptable level of color fastness to light.

55 Among them, sample Nos. 42 through 45, incorporating a more preferred cyan coupler of the present invention represented by the Formula C-II and a compound of the present invention, were found to show an excellent improving effect and offer a good color tone nearly equivalent to that obtained with cyan ink.

Claims

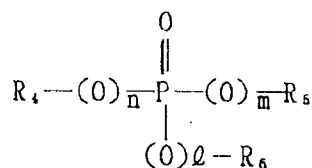
1. A silver halide photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer, wherein said silver halide emulsion layer contains a cyan-dye forming coupler represented by the formula [C-I] and a compound represented by the formula [I]:

formula [C-I]



wherein R_1 and R_2 independently represent an alkyl group, cycloalkyl group, alkenyl group, aryl group or heterocyclic group; R_3 represents a hydrogen atom, halogen atom, alkyl group or alkoxy group; and X represents a hydrogen atom or a group capable of splitting off by reaction with the oxidation product of a color developing agent;

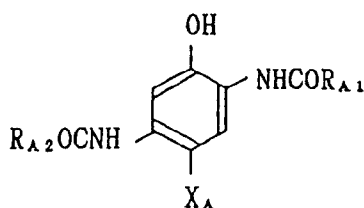
formula [I]



wherein R_4 , R_5 and R_6 independently represent an aliphatic group or aromatic group; l , m and n independently represent 0 or 1, with the proviso that all of l , m and n are not 1 at the same time.

2. A silver halide photographic material of claim 1, wherein said cyan coupler is represented by the following formula [C-II]:

formula [C-II]

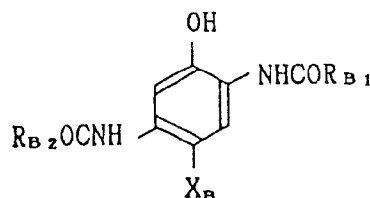


wherein R_{A1} represents an alkyl group, alkenyl group, cycloalkyl group or phenyl group, each of which is substituted with at least one halogen atom and may have a substituent other than the halogen atom; R_{A2} has the same definition as R_2 in the formula [C-I] of claim 1; and X_A represents an aryloxy group or alkoxy group.

3. A silver halide photographic material of claim 1 or 2, wherein said cyan coupler is contained in a red-sensitive silver halide emulsion layer in amount of 1×10^{-2} to 5×10^{-1} mol per mol silver halide.
4. A silver halide photographic material of claim 1, wherein R_4 , R_5 and R_6 in the formula [I] independently represent an alkyl group having a carbon number of 1 to 32, alkenyl group, alkynyl group, cycloalkyl group or cycloalkenyl group, aryl group or heterocyclic group.

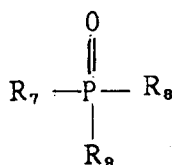
5. A silver halide photographic material of claim 4, wherein said R_4 , R_5 and R_6 are independently an alkyl group or aryl group and the total carbon number of R_4 , R_5 and R_6 is within the range of 6 to 50.
6. A silver halide photographic material of claim 1, wherein all of ℓ , m and n in the formula [I] are 0.
7. A silver halide photographic material of claim 1, wherein said compound of the formula [I] is contained in an amount of 10 to 300 mol% to said cyan coupler.
8. A silver halide photographic material of claim 1, wherein said cyan coupler and said compound of the formula [I] are present in the same hydrophobic organic phase.
9. A silver halide photographic material of claim 1, wherein said silver halide emulsion contains silver halide grains having silver chloride content of not less than 90 mol%.
10. A silver halide photographic light-sensitive material comprising a support having thereon a silver halide emulsion layer, wherein said silver halide emulsion layer contains a cyan-dye forming coupler represented by the formula [C-III] and a compound represented by the formula [II]:

formula [C-III]



wherein R_{B1} represents an substituted aryl group; R_{B2} represents an alkyl group, cycloalkyl group, alkenyl group, aryl group or heterocyclic group; and X_B represents a hydrogen atom or a group capable of splitting off on reaction with the oxidation product of a color developing agent;

formula [II]



wherein R_7 , R_8 and R_9 independently represent an alkyl group.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 4739

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	EP-A-0280238 (FUJI) * page 6, lines 13 - 33 * * page 16, lines 49 - 51 * * page 22, lines 1 - 18 * * page 77, lines 9 - 15 * * page 83, lines 9 - 11; claim 1 * ---	1-10	G03C7/30 G03C7/34 G03C7/388 G03C7/392
Y	EP-A-0286431 (KONICA) * page 3, lines 1 - 10 * * page 21, line 64 - page 34, line 30 * * page 48, lines 15 - 30 * -----	1-10	
			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 17 SEPTEMBER 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 L : document cited for other reasons & : member of the same patent family, corresponding document			

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