(9)	Europäisches Patentamt European Patent Office Office européen des brevets	Publication number: 0 286 331 A2	
(12)	EUROPEAN PATE	ENT APPLICATION	
(2) (2)	Application number: 88302950.6 Date of filing: 31.03.88	 Int. Cl.⁴: G03C 1/84 , G03C 1/12 , G03C 1/92 , G03C 1/02 , G03C 1/30 , G03C 7/26 	
(B) (B) (C) (C) (C) (C) (C) (C) (C) (C) (C) (C	Priority: 04.04.87 JP 83521/87 24.12.87 JP 327694/87 Date of publication of application: 12.10.88 Bulletin 88/41 Designated Contracting States: DE FR GB IT NL	 7 Applicant: KONICA CORPORATION No. 26-2, Nishi-Shinjuku 1-chome Shinjuku-ku Tokyo 106(JP) 7 Inventor: Sasaki, Masao Konica Corporation 28 Horinouchi Odawara-shi Kanagawa-ken(JP) Inventor: Onodera, Kaoru Konica Corporation 28 Horinouchi Odawara-shi Kanagawa-ken(JP) 7 Representative: Ellis-Jones, Patrick George Armine et al J.A. KEMP & CO. 14 South Square Gray's Inn London WC1R 5EU(GB) 	

Rapidly processable silver halide photographic light-sensitive element and processing method therefore.

(c) A silver halide photographic light-sensitive element and a processing method therefor are disclosed. The photographic element comprises a support having thereon photographic component layers including at least one silver halide emulsion layer which contains silver halide grains comprising not less than 90 mol% of silver chloride, and at least one layer among said photographic component layers contains a compound presented by the followinf formula [I] and a capturing agent for fluorecent whitening agent:

$$R_{1} - C - C = L_{1} - (L_{2} = L_{3})_{m} + (L_{4} = L_{5})_{n} + C - R_{2}$$

$$N_{N} - C = O \qquad HO - C_{N} + N$$

$$|_{R_{3}}$$

The photographic element is preferably developed with a developer containing a primary aromatic amine color developing agent and not containing benzyl alcohol for 20 to 60 seconds. The photographic element is improved in sharpness of the dye images formed on it.

÷

RAPIDLY PROCESSABLE SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE ELEMENT AND PROCESS-ING METHOD THEREFORE

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive element which enables rapid processing and is characterized by sharpness of the dye images produced.

BACKGROUND OF THE INVENTION

- 10 In recent years, there are mounting needs, in the photographic art, for the rapidly processable silver halide light-sensitive elements being capable of providing high-quality images.
 - Nowadays, the development of silver halide photographic light-sensitive elements is carried out ordinarily by a running process with an automatic developing machine installed each developing service station. The order for this developing service is now required to be processed and finished within the same
- 15 day as part of the improvement in the service rendered to the customers, but the request is now mounting for the order to be finished and handed over to the customer within a matter of a few hours, the situation thus intensifying the need for a more rapid process in the development service. The development of a more rapid process is also being urged from the viewpoint of the productivity because a reduction in cost can be achieved by reducing the time for the development.
- An approach to a more rapid process is being attempted in two ways, with respect to the light-sensitive element as well as the processing solutions. With respect to the color developing, it has been attempted, for example, to use a high temperature, higher pH level, and high-concentration color developing agent. It is also attempted to use some additives as development accelerator. Some examples of such development accelerators are 1-phenyl-3-pyrazolidone disclosed in British Patent No. 811,185, N-methyl-p-aminophenol
- in U.S. Patent No. 2,417,514, and N. N. N', N'-tetramethyl-p-phenylenediamine in Japanese Patent Publication Open to Public Inspection, hereinafter referred to as Japanese Patent O.P.I. Publication, No. 15554/1975. Such accelerators, however, have been unable to achieve satisfactory results in speeding up the process and their use often incurs degradation in performance, such as fogging.
- On the other hand, it is known that the developing speed etc. is greatly influenced by the configuration, size, and composition of the silver halide grains which constitute the emulsion of a photographic lightsensitive element. Especially, the halogen composition has a significant influence and the use of a silver halide with a high content of chloride is known to show remarkable increasing in the developing speed.

For the purpose of preventing halation and irradiation, or providing filtering, or adjusting the sensitivity of emulsions, it is attempted to dye a hydrophilic colloidal layer with a dye so as to make it absorb light of specific wavelength.

Prevention of halation or irradiation, or the like, is often practiced for the purpose of improving the sharpness of resulting images.

The dyes used for such purposes must satisfy various requirements, for example: the dye is required to have a satisfactory spectral absorption characteristic according to the intended purpose; the dye must be completely decolorized in the processing bath, readily eludes out of the photographic element so that no residual staining by the dye occurs after the developing process; the dye should not cause the emulsions to undergo fogging, desensitization, or the like adverse influences; the dye is required to have good shelf life while it is in solution as well as when it is in the photographic element, and does not undergo fading or discoloration.

- There has hitherto been expended much effort toward discovery of dyes which satisfy such requirements, and, as a result, a large number of dyes have been proposed for use. Some of such dyes are, for example, oxonol dyes disclosed in U.S. Patent Nos. 506.385 and 3,247,127. Japanese Patent Examined Publication Nos. 22069/1964 and 13168/1978; styryl dyes disclosed, for example, in U.S. Patent No. 1,845,404; merocyanine dyes disclosed, for example, in U.S. Patent Nos. 2,493,747, 3,148,187 and 3,282,699; cyanine dyes etc. disclosed, for example, in U.S. Patent No. 2,843,486; and anthraquinone dyes
 - disclosed, for example, in U.S. Patent No. 2,865,725.

The inventors, through their studies on dyes especially in pursuit of their satisfactory decolorization property even in rapid processing, discovered that dyes of some specific structure satisfy the requirements when used in combination with a silver halide with a high content of chloride which, as mentioned before,

has a high developing speed and suits rapid processing.

However, the above-mentioned dyes, which were intended to improve the sharpness of photographic images, were found to be unable to achieve the expected results in sharpness because of some problems such as one relating to spectral absorption characteristic that a gelatin coating incorporating such a dye with an especially satisfactory decolorization property incurs the problem being that the maximum absorption

wavelength was on the short wave side and the form of the absorption wave was broad. Through further studies focussed on the solution of the problems relating to the spectral absorption characteristic of the gelatin coating, that is, on control of the maximum absorption wavelength and on sharpening of the absorption wave form, the inventors in their commitment to improvement of the sharpness

- 10 of finished picture images have eventually discovered that by additionally incorporating a specific compound into the system of a silver halide with a high content of chloride combined with a specific dye having a good decolorization property, a distinct improvement in sharpness of a finished picture image is attainable without impairing the adaptability to rapid processing or the decolorization property of the dye, and have brought their studies to formulation of the present invention.
- 15 .

SUMMARY OF THE INVENTION

The object of the present invention is to provide a silver halide photographic light-sensitive element which is excellent in adaptability to rapid processing and in decolorization property of the dye and finally produces a picture image with a distinct improvement in sharpness.

The object of the present invention can be accomplished by a silver halide photographic light-sensitive element comprising a support having thereon photographic component layers including at least one silver halide emulsion layer which contains silver halide grains comprising not less than 90 mol% of silver chloride, and at least one layer among said photographic component layers contains a compound presented by the following formula [I] and a capturing material for fluorescent whitening agent:

Formula [I]

$$R_{1} - C - C = L_{1} - (L_{2} = L_{3})_{in} - (L_{4} = L_{5})_{in} - C - R_{2}$$

$$H_{0} - C - R_{1}$$

$$H_{0} - C - R_{1}$$

wherein R₁ and R₂ independently represent a -CN group, a -CFR₅R₆ group, a -COR₇ group, a -COOR₇ group or a -CONHR₅ group, in which R₅ and R₆ represent a hydrogen atom, a fluorinated alkyl group having one to four carbon atoms, respectively, and R₇ represents an alkyl group or an aryl group which may have a substituent: R₃ and R₄ independently represent a hydrogen atom, an aliphatic group, an alicyclic group, an automatic group or a heterocyclic group, which may have a substituent; L₁, L₂, L₃, L₄, and L₅ independently represent a methine group which may have a substituent; and m and n represent an integer of 0 or 1, respectively.

45

50

55

30

35

40

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, at least one of the silver halide emulsion layers contain silver halide grains comprising not less than 90 mol% of silver chloride grains.

The silver halide grains according to the invention comprise not less than 90 mol[%], preferably, not less than 95 mol[%] of silver chloride grains. The content of silver bromide grains is preferably 5 mol[%] or less and that of silver iodide is preferably 0.5 mol[%] or less.

The silver halide grains prepared according to this invention can be used alone or in a mixture with another type of silver halide grains having a different composition. The silver halide grains according to the invention may be used also by mixing with another type of silver halide grains comprising a silver chloride content of less than 10 mol%.

In the silver halide emulsion layer according to the invention wherein the silver halide grains comprising

not less than 90 mol% of silver chloride grains, the proportion of the silver halide grains comprising not less than 90 mol% of silver chloride grains per total silver halide grains in said emulsion layer is not less than 60 wt%, or, preferably, not less than 80 wt%.

The composition of the individual silver halide grains according to the present invention may be uniform 5 from the inside to the surface, or different between the inner portion and the surface. Where the composition differs between the inner and outer portions, the composition may vary in some sequential order or in no sequence.

This invention does not restrict the grain size of the silver halide grains to any particular range. But, the preferred grain size is within the range from 0.2 to 1.6 μ m, or in particular, within the range from 0.25 to 1.2

Ł

ŝ

- μm, with the adaptability to rapid processing, sensitivity, and other photographic properties taken into consideration. The grain size can be measured by an ordinary method in general use in the technical fields concerned. Methods most generally applicable are described in "Grain Size Analysis" by Labrand (A.S.T.M. Symposium on light Microscopy, 1955, pp. 94-122) and "Theory of Photographic Process" by Meas & James (3rd Ed. Mcmillan, 1966, Chapter 2).
 - The grain size can be measured by using the projected area of the grain or by using an approximate value of the diameter. When the grains are virtually uniform in shape, the grain size distribution can be determined fairly accurately in terms of diameter or projected area.

The grain size distribution of the silver halide grains according to this invention may assume a multidispersed system or a monodispersed system. It is preferable for the silver halide grains to be a monodispersed system with a variation coefficient of 0.22 or less, or more favorably 0.15 or less, in the grain size distribution of silver halide grains. This variation coefficient is a coefficient which indicates the extent of the grain size distribution, and can be defined by the following formulas:

²⁵ Variation coefficient $(S/\bar{r}) = \frac{\text{Standard deviation of}}{\text{Average grain size}}$ ³⁰ Standard deviation of grain size distribution $(S) = \sqrt{\frac{\Sigma(\bar{r} - ri)^2 ni}{\Sigma ni}}$ ³⁵ Average grain size $(\bar{r}) = \frac{\Sigma niri}{\Sigma ni}$

wherein ri represents the grain size of the individual grains and ni their quantity. The term "grain size"
herein used means the diameter when the silver halide grains are spherical; when the grains are cubic or of a shape other than spherical, the term means the diameter obtained by converting the projected image into a corresponding circular area.

Σni

The present invention permits the silver halide grains to be formed in any desired configurations. One preferable configuration is a cube having {100} face as crystalline faces. It is also possible to produce the grains having octahedral, tetradecahedral or dodecahedral configuration or the like by a method described, for example, in U.S. Patent Nos. 4,183,756 and 4,225,666, and Japanese Patent O.P.I. Publication No. 26589,1980 and Japanese Patent Examined Publication No. 42737,1980 and in the literature such as The Journal of Photographic Science <u>21</u>, 39 (1973).

During the formation and or growth in the production of silver halide grains for the emulsion according to the present invention, a metal ion can be added and incorporated into the interior and or the surface of the grains by using a cadmium salt, zinc salt, lead salt, thallium salt, iridium salt or iridium complex salt, rhodium salt or rhodium complex salt, and iron salt or iron complex salt, and then by palcing the grains in a suitable reducing environment, reduction-sensitizing nuclei can be imparted to the grain at the interior and/or the surface.

⁵⁵ The silver halide grains used for the emulsion according to this invention are preferably to be grains wherein a latent image is primarily formed on the grains surfaces.

The emulsion according to the invention is chemically sensitized by a conventional method. Some of such methods are sulfur-sensitizing method using a sulfur compound reactive with silver ion or using active

gelatin; selenium-sensitizing method using a selenium compound; reduction-sensitizing method using a reducing substance; and noble metal-sensitizing method using a noble metal compound such as of gold. Such methods can be used singly or in combination.

Chalcogen sensitizers, for example, are useful for chemical sensitization in the practice of this invention. 5 Among chalcogen sensitizers, sulfur sensitizers and selenium sensitizers are advantageous. The sulfur sensitizers useful for this purpose are, for example, thiosulfate, alkyl thiocarbazide, thiourea, aryl isothiocyanate, cystine, p-toluene thiosulfonate, and rhodanine. Sulfur sensitizers useful for this purpose are also found in the specifications of U.S. Patent Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668 3,501,131, and 3,656,955, West German OLS Patent No. 1,422,869, and Japanese Patent O.P.I. Publication Nos.

10 24937/1981 and 45016/1980. The quantity of the sulfur sensitizer added varies widely depending on various conditions such as pH, temperature, and size of the silver halide grains. Roughly, sulfur sensitizer is used in a quantity in a range of 10⁻⁷ mol to 10⁻¹ mol per mol silver halide.

The selenium sensitizers useful for the purpose are selenides such as aliphatic isoselenocyanates such as alkyl isoselenocyanate; selenoureas, selenoketones, selenoamides, selenocarboxylates and esters; selenophosphates; selenides such as diethylselenide, and diethyldiselenide. Examples of such sensitizers are described in U.S. Patent Nos. 1,574,944, 1,602,592, and 1,623,499.

Reduction sensitization can be used in combination with other sensitizing processes. The reducing agents useful for this purpose are stannous chloride, thiourea dioxide, hydrazine, polyamide, and the like.

Noble metal compounds other than gold, such as palladium compound, can also be used in combination.

It is preferable for the silver halide grains embodying this invention to contain a gold compound. A gold compound suitable for the use in the practice of the present invention may have a gold oxidation number of +1 or +3, whereby a wide variety of gold compounds are applicable. Some examples of such gold compounds are chloraurate, potassium chloraurate, auric trichloride, potassium auric thiocyanate, potassium iodine aurate, tetracyanoauric azide, ammonium aurothiocyanate, pyridyl trichlorogold, gold sulfide, and

gold selenide.

20

25

A gold compound can be used either in such a way as to sensitize the silver halide grains or in such a way not to contribute to sensitization virtually.

The quantity of a gold compound used varies depending on various conditions. Roughly, a gold compound is used in a quantity of a range of 10⁻⁸ mol to 10⁻¹⁰ mol, or, preferably, 10⁻⁷ mol to 10⁻² mol per mol silver halide. Such a gold compound can be added at any of the stages of formation of the silver halide grains, physical ripening, chemical ripening, and after the chemical ripening.

The emulsion produced according to the present invention can be spectrally sensitized at a desired wavelength range by using a sensitizing dye. The sensitizing dyes can be used singly or in combination of two or more kinds.

In combination with a sensitizing dye in the emulsion can be used a supersensitizing dye which is a dye or compound not having the spectral sensitization function or not actually absorbing visible light, though such a dye or compound is capable of enhancing the sensitizing action of the sensitizing dye.

No specific restriction applies to the silver halide grains used for an emulsion layer other than that of the present invention. But, it is preferable for such silver halide grains to comprise not less than 90 mol% of silver chloride grains, that is. such silver halide grains should, like those of the invention, comprise not less than 90 mol% of silver chloride grains.

The photographic light-sensitive element according to the present invention has a compound expressed by formula [I] and a capturing material for fluorescent whitening agent in at least one layer selected from 45 among the photographic structural light-sensitive layers, that is, the silver halide emulsion layers according to the invention, and other silver halide emulsion layers, or among the non-light-sensitive layers, that is, intermediate layer, protective layer, filter layer, anti-halation layer and the like.

A description will now be provided hereunder with respect to the compounds defined by formula [I] which are in use in the present invention. said such compound(s) will hereinafter be referred to as "the dye-(s) of the invention".

In formula [I], R: and R₂ individually represent -CN, -CFR₅R₆, -COR₇, or -CONHR₅, wherein the fluorinated alkyl groups with 1 to 4 carbon atoms represented by R₅ or R₆ -CFR₅R₆ and -CONHR₅ above are, for example, difluoromethyl group, trifluoromethyl group, 1,1,2,2,3,3,4,4-octafluorobutyl group, and 1,1,2,2,3,3-hexafluoropropyl group.

R₇ in -COR₇ or -COOR₇ represented by R₁ or R₂ represents an alkyl group or aryl group, wherein such an alkyl group or aryl group may have a substituent group.

R₃ and R₄ individually represent a hydrogen atom, aliphatic group, alicyclic group, aromatic group, or heterocyclic group, of which the aliphatic group is, for example, an alkyl group or alkenyl group; the

55

alicyclic group is, for example, a cycloalkyl group; the alicyclic group is, for example, a cycloalkyl group; the aromatic group is, for example, an aryl group such as phenyl group or naphthyl group; the heterocyclic group is, for example, benzothiazolyl group or benzoxazolyl group.

R₃ and R₄ represent, as above, an aliphatic group, alicyclic group, aromatic group or heterocyclic group, including those having a substituent.

The methine group represented by each of L_1 , L_2 , L_3 , L_4 , and L_5 may be a group substituted by an alkyl or aryl group with 1 to 4 carbon atoms.

It is preferable for said R_1 and R_2 to be -CN group, -CF₃ group, -CONH₂ group, or -COR₇ group, and for R_7 to be an alkyl group. It is preferable for R_3 and R_4 to be an aromatic group, especially preferably to be 4-sulfophenyl group, 2,5-di-sulfophenyl group, or their salts.

With respect to the dyes used according to the invention, it is preferable for such a dye to contain at least one water soluble group (such as sulfo group, carboxyl group, or their salts) in its molecular structure.

Typical examples of dyes according to the invention represented by formula [I] are hereinunder listed on the understanding that these examples in no way restrict the dyes used in the practice of the invention.

15

10

20

25

30

40

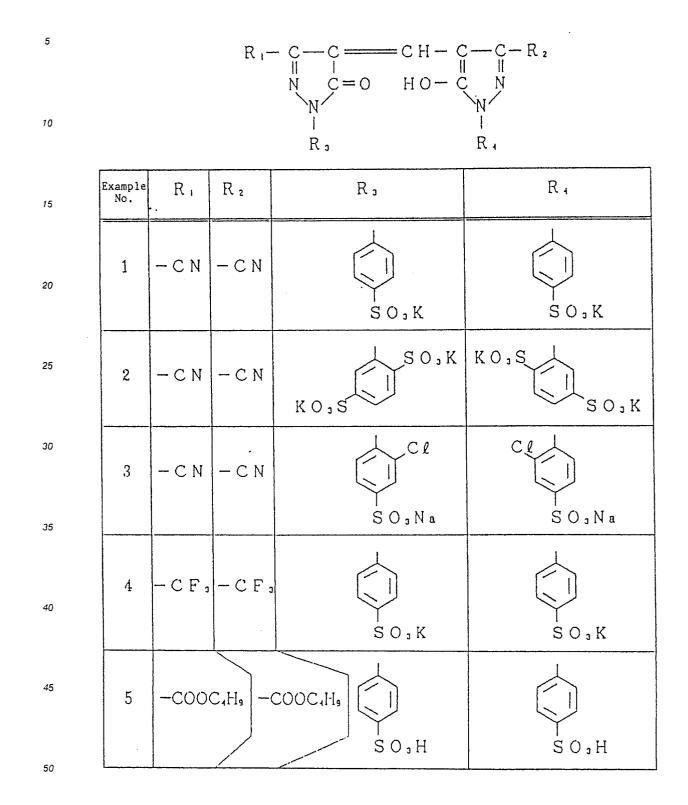
35

45

50

Example dye

.



55

0 286 331

ź

Exam~ ple No. R₁ R 🤉 R 2 R, 5 -COCH₃-COCH₃ 6 ŚO₃K SO₃K 10 SO₃K SO,K -COCH₃ -COCH₃ 7 15 KO₃Ś коъб -CONHCF, -CONHCF, 8 20 SO₃K SO₃K

25

30

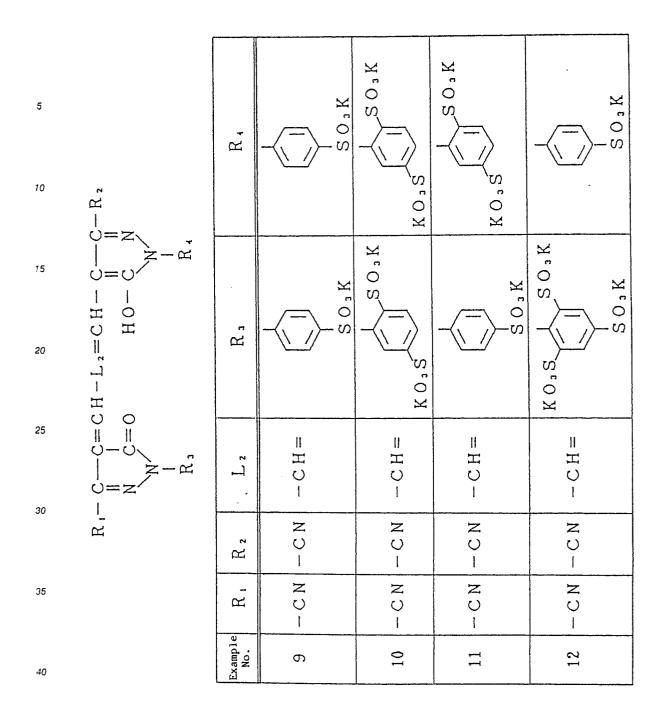
35

40

45

50

55



-

.

5) so,k	S O a K	O H SO ₃ N _a	S 0 3 K
10	R,		K0,S	N aO3 S	
15		S O 3 K	S O s K	SOaNa	
20	R.a.		$-\langle \rangle$		
25			KOs	N aO ₃ S	K O s C
30	L 2		– C H =	– C H =	C 2 H 5 - C =
35	R 2	U U I	U C I	C N -	U C I
40	R.	– C N	– C N	N C I	– C N
45	Example No.	13	14	15	16

÷

ž

ŝ.

50

5	R ,	N O S N S	S O ₃ K	K O 3 S C 3 K	s0,K
15					
20 25	R 3	K O ^s S	S O s K	K O ₃ S O ₃ K	S O s K
					C H =
30 35	L 2	H C H	= C H = -	– C H =	CONH ₂ – C]
50	2	Z U	ب ب ب		Ϋ́Υ
	Я	l i			
40	R.	– C N	— С F з	– C F ,	-CONH ²
45	Example No.	17	18	19	20

•

×

5 10 15	R ,	K O 3 K	K O s K C s c O K	K O ª S O ª K	S O a K	S O a K S O a K
20	R ,	KO,S ^K O,K	S O 3 K	K O a S S O a K	X o 3 K	X E O 3 K S O 3 K
30	Ľ 2	– C H =	- C H =	C H 2 - C =	– C H =	- C H =
35	R 2	CONH2	CONH2	CONH2	CONH2	
40	R.		-CONH2	-CONH2	CONH2	CONH2
45	Example No.	21	22	23	24	25

τ.

÷

50

55

Ο_αΝ_α COOK Š 0.ª K S O 3 N a SOsK Ŋ 5 R, KOOC NªOJS Ю́Н HOOC 10 15 SOJNa COOK COOH Ţ SO₃Na SOaK Q 20 К, N ª O J S K O O C K O ₃ S 25 CH =11 11 -CH =11 L² Ξ C H – C H : ပ 30 ł 1 $-(CF_2)$, $H = -(CF_2)$, H، ب $-(C F_2)_2 H$ н Ц с Г R² \bigcirc 0 | \odot 35 1 1 $-(C F_2)_2 H$ ء بىآ ء بيا ء ب R_ \odot U 1 \bigcirc 40 ł Ł Example No. 26 27 28 29 30 45

50

.

.

55

0 286 331

_					1
5	R ,	S O 3 K	S O a K	S O s K	S O S K
10	R		H, C		
15			ĊCH = s K	~	×
20	R,	S O 3 K	C H S O 3 K	No. No. No. No.	S O 3K
25	L 2	н н г С Н г	– C H =	= C H -	H C H
30	2	- C F 2 H -	- COOC2H5 -	- COOC2H5	COCH3
35	R	U I	[
40	e R.	- C F 2 H	-COOC2H5	-COOC2H5	- C O C H 3
-45	Example No.	31	32	33	34

55

۶

÷

-

0 286 331

5	R.	K 0 s K S 0 s K	S O 3 K	K 0 a S S O a K	K0,S K
20	R.	S 0 3 K	S O a K	S O 3 K	K O s K
25		KOsS			K 0 s
30	L 2	= C H = - C H	C 2 H 5 - C =	= H D	– C H =
35	R 2	cocµ3	-cocH	COCH	-coc ₂ H ₅
40	R.	-cocH,	-cocH	-cocH,	-COC ₂ H5
45	Example No.	35	36	37	38

50

•

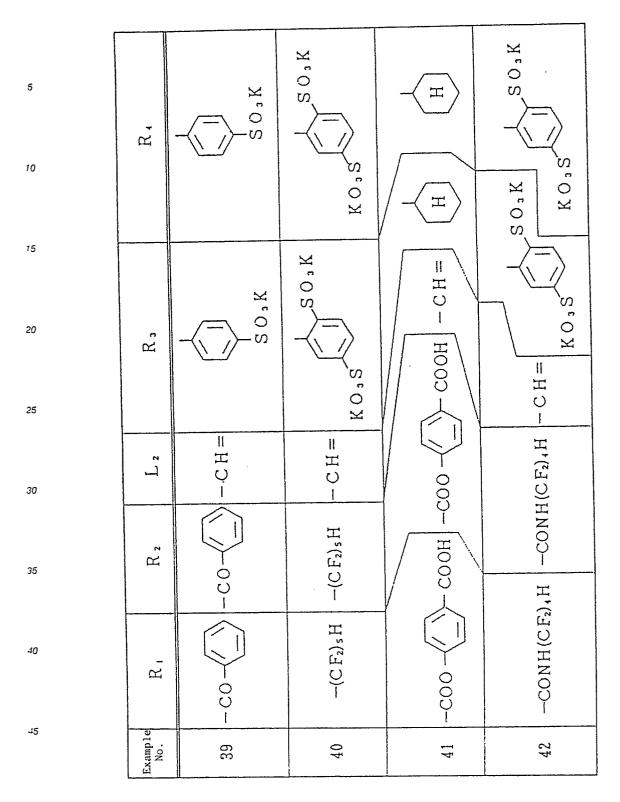
-

-

*

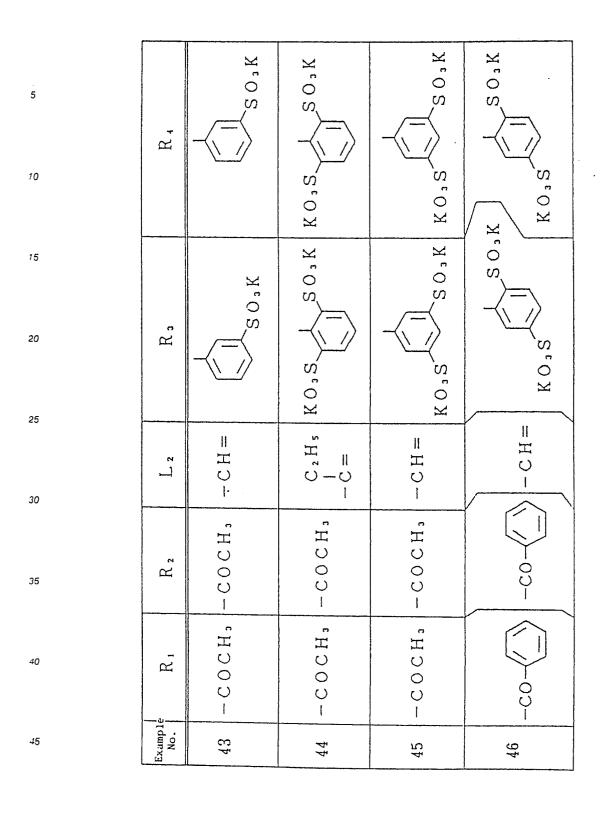
55

÷



50

0 286 331



50

.

55

$ \begin{array}{c} $	R.	S O a K	K 0 a S S O a K	KO ₃ S ^K SO ₃ K
- 0 H H О = H О - H О - H О -		so, K	S O J K	S 0 s K
$\begin{array}{c} -H \\ H \\ D \\ H \\ D \\ H \\ D \\ H \\ D \\ - \varepsilon \\ T \\ H \\ D \\ H \\ D \\ H \\ D \\ - \varepsilon \\ T \\ H \\ D \\ H \\ D \\ - \varepsilon \\ T \\ = H \\ T \\$	R,	~v	K O ³ S ² O X	KO,S
N C C H N C	L J	– СН –	= C H -	= C H -
ر ب ع ع	R 2	C N	– C N	U C I
	1e R .	U U U	– C N	C L
40	Example No.	47	48	49

50

55

ŝ

÷

÷

5 10 15	R .	S 0 J K S 0 J K	K 0 3 K	K 0 s S S S S S S S S S S S S S S S S S S	NaO ₃ S SO ₃ Na SO ₃ Na
20 25	R a	S 0 3 K S 0 3 K	S O a K	KO ₃ SO ₃ K SO ₃ K	NaO ₃ S NaO ₃ S NaO ₃ N _a
30 35	L 1		C 2 H 5 = C -	– H – = C H	= C H -
40	R R 2	- C N	- CN	U U U U	- C N - C
45	Example No.	20	21	22	23

•

0 286 331

55

50

÷

Ŧ

ſ				1	
5	R ,	S O a K	COOK	S O a K	C 0 0 K
10				НООС	
15		S O JK	COOK	он Соон	0 K
20 - 25	R 3	S O 3 K	-		C O O K
30		H00	I	K O s S	1
35	ء ل		N = C H	N = C H	U H C H C H C H C H C H C H C H C H C H
55	- R 2		N N	U U U	년 (C 년 년
40	Example R . No.	54 – C N	55 – C N	56 – C N	57 – C I
45	К Р	<u>م</u>	ى م	ۍ ا	വ

0 286 331

.

÷

÷

50

.

5	R.	Н	C ₃ H ₇ C ₃ H ₇	S O a K	K O , S C , K	S O a K
15		, 				× K
20	R ,	$SO_aK = CH -$	COOK = C H -	S O 3 K	X c O S	S 0 3 K
25		- so	C C		K O s S	
30	L 3	-coo		= C H –	= C H -	= C H -
35	R 2	- SO ₃ K	- COOK	۳ لیا ا	ت ب ا	ء C H
40	R,	-coo - (-coo -	-СF,	L C F I	ء ب ا ا
45	Example No.	58	59	60	61	62

.

-

-

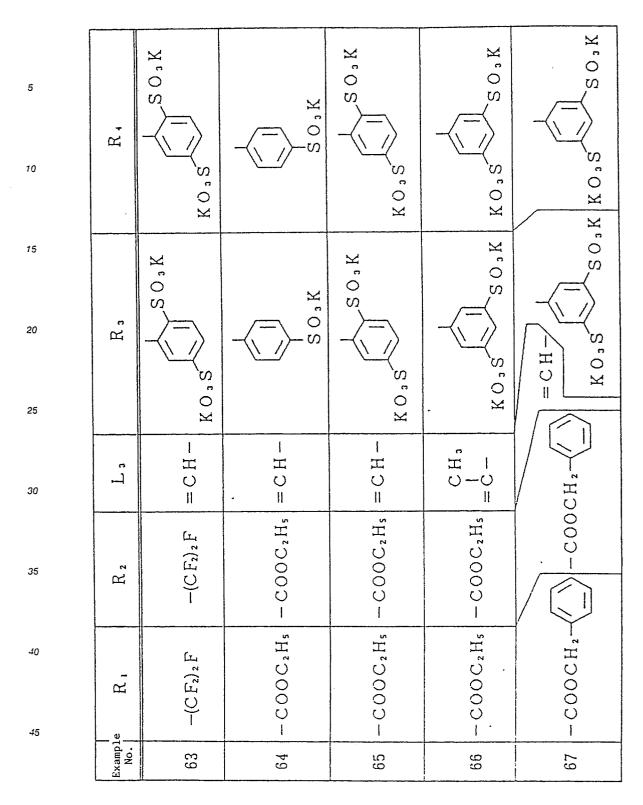
•

.

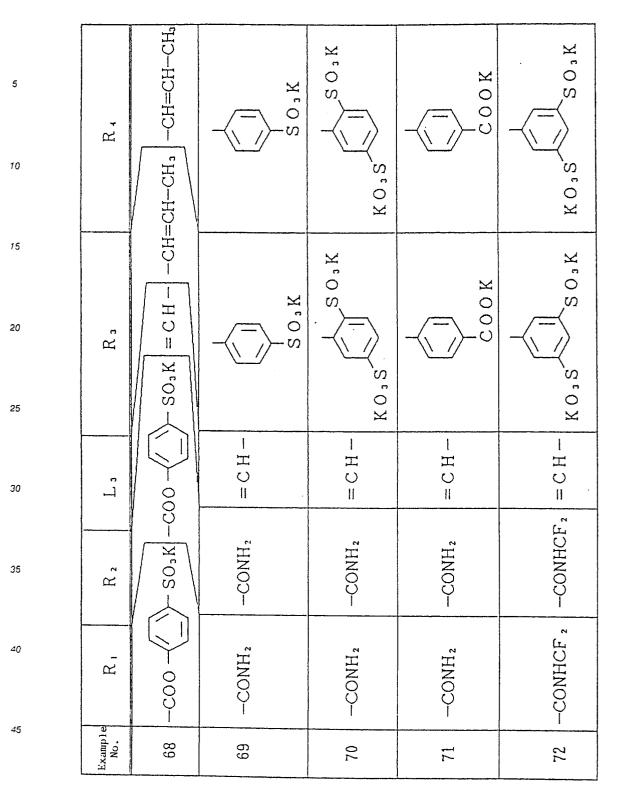
55

50

0 286 331



0 286 331



0 286 331

ŕ

_					1
5	R.	s o s K	S O 3 K	S 0 3 K	SOaK
10			K 0 s		HO, KO.S
15		°°s N	S O ª K	S 0,K	S O a K
20	R,		K O 3 S		H O H
25					
30		- H - = -	= C H	H U U U	н с н
35	R 2	- C O C H 3	- C O C H 3	- C O C H 3	- C O C H 3
-40	R.	- C O C H 3	- C O C H ,	- C O C H ;	- C O C H 1
45	Example No.	73	74	75	76

50

.

0 286 331

.

]			·····		
5 10	R.	K O s K	K0,S,K	COOK	K O 3 S O 3 K
15					×
20 25	R 3	S O 3 K	K0,S S0,K S0,K S0,K	COOK COOK	K O 3 S L S O 3 K
			1	1	
30	L.	= C H	= C H	= C H	= C H
35	R 2	- COCH,	- C O C H ,	-сосн.	– C 0 C ² H s
40	R	- C O C H 3	- C O C H 3	-сосн	- C O C 2 H 5
	Example No.	77	78	62	80
	L <u></u>	<u></u>	l		

50

.

.

•

2

зΚ OJK Ы М K 0, ିତ n 0 0 5 Ы S Ŋ Ŋ S S 0.0 ЧЧ Ŋ 10 ល្អ S n 0 0 Ы Ъ 15 O J K O 3 K O J K O J K O J K S Y Ŋ S S Ŋ 0,0 n 20 Ц S S n Ŋ 0 õ Ы 25 Ы C 3 H 7 (i) ł 1 1 1 Ц H Τ H n し C C C \circ C 30 11 || 11 11 11 Н, n c H Ξ C C \odot 2 35 0 0 0 Ц C \odot \odot 1 1 1 ц, c n 40 I Τ \bigcirc \bigcirc C 0 0 0 Ц 00 S \bigcirc \odot C ł 1 1 45 Example No. 82 83 84 85 81

0 286 331

50

Besides the dyes shown as examples above, dyes applicable effectively to the practice of the present invention are shown in the specification of Japanese Application No. 8796 1986, pp. 179-199, which are Examples (2), (3), (7), (9), (15), (16), (18), (19), (21), (22), (24), (25), (27), (33), (34), (35), (40), (42), (43), (44), (45), (46), (47), (48), (49), (50), (51), (52), (53), (54), (55), (58), (59), (60), and (62).

55

Said dyes according to the present invention can be synthesized by the method described in the above-mentioned specification of Japanese Patent Application No. 8796/1986. The dyes according to the invention expressed by formula [I] can also be used, in a silver halide photographic light-sensitive element embodying the invention, as an anti-irradiation dye by introducing it into a silver halide emulsion layer

according to the invention or other silver halide emulsion layer, or as a filter dye or an anti-halation dye by introducing it into a non-light-sensitive hydrophilic colloidal layer. Where a dye embodying the invention is incorporated into a silver halide emulsion layer, it is preferable for the compound, if m = 0 and n = 0 in the formula [I], to be introduced into a blue-sensitive silver halide emulsion layer; into a green-sensitive silver halide emulsion layer if m = 1 and n = 0; and into a red-sensitive silver halide emulsion layer if m = 1 and n = 1.

5

According to the invention, the preferred compounds are those defined by m = 1 and n = 0; or m = 1 and n = 1. The particularly preferable compounds are those defined by m = 1 and n = 1, wherein one of such compounds is contained at least in a red-sensitive silver halide emulsion layer.

- A dye embodying the invention can be used in combination with another kind or more of the embodiments or in combination with a dye other than the embodiments, depending on the purpose of the use. A dye embodying the invention can be incorporated into a silver halide light-sensitive emulsion or other hydrophilic colloidal layer, usually by dissolving the dye or an organic inorganic alkali salt of the dye in an aqueous solution or an organic solvent, such as alcohol, glycol, cellosolve, dimethylformaldehyde, dibutyl
- phthalate, and tricresylphosphate. dispersing it, if necessary, by emulsifying, adding it to a coating solution, and then by applying to and drying over the support. If the dye is diffusible, the dye can be added to a coating solution for a different layer rather than that of the dye so that the dye, once the solution is applied, is allowed to diffuse and eventually be incorporated, before the solution completely dries, into a layer which contains the capturing material for fluorescent whitening agent.
- It is essential in the practice of the invention that the dye according to the invention is present in the layer containing a capturing material for fluorescent whitening agent. The quantities of the dyes being used vary depending on the purpose of application and are not restricted to any specific amounts. But, generally, it is preferable for the dye applied at a rate of 0.1 1.0 mg/dm², or, preferably, 0.03 0.4 mg/dm².
- As one of the effective means of improving the whiteness of a silver halide photographic light-sensitive element including particularly a photographic print paper, there is a method of adding a water-soluble fluorescent whitening agent into the hydrophilic colloidal layer of a light-sensitive element. The fluorescent whitening agents include, for example, the compounds of a diaminostilbene, a benzidine, an imidazole, a triazole or an imidazolone, each having a hydrophilic group, as described in Japanese Patent O.P.I. No. 71049-1984.
- A fluorescent whitening agent having been added into the hydrophilic colloidal layer of a light-sensitive element is eluted from the hydrophilic colloidal layer into a processing solution in the course of processing the light-sensitive element. On the other hand, there is some kind of compounds capable of capturing a fluorescent whitening agent so as to prevent the fluorescent whitening agent from eluting out of the hydrophilic colloidal layer, so that the compounds have been widely used with the purpose of enhancing the effects of fluorescent whitening agents used in light-sensitive elements, as described in Japanese Patent
- O.P.I. Publication No. 71045-1984.

When a compound having such a fluorescent whitening agent capturing effect as mentioned above coexists, in a light-sensitive element, with a dye represented by the aforegiven Formula [I], the effect of improving the image sharpness of the light-sensitive element may be remarkably displayed.

A substance having such an effect of capturing a fluorescent whitening agent as mentioned above are called a capturing material for fluorescent whitening agents or simply a capturing agent of the invention.

Any compound may be used as a capturing material of the invention. provided that it may be able to capture a fluorescent whitening agent. It is, however, preferred that it is a non-color-developable hydrophilic synthetic macromolecular polymer.

- The typical examples of the hydrophilic polymers include polyvinyl pyrrolidone or copolymers having vinyl pyrrolidone as repeating units, wherein the examples of monomers being capable forming repeating units together with vinyl pyrrolidone include acrylic acid, methacrylate acid, amide compounds of acrylic acid and methacrylic acid, such as acrylamide, methacrylamide, N.N-dimethylacrylamide, N.Ndiethylacrylamide, N-methyloylacrylamide, N-hydroxyethyl acrylamide, N-tert-butylacrylamide, N-cyclohex-
- ylacrylamide, diacetoneacrylamide, N-(1.1-dimethyl-3-hydroxybutyl)acrylamide, N-(β-morpholino)ethylacrylamide, N-benzylacrylamide, N-acryloymorpholine, N-methacryloylmorpholine, N-methyl-N-acryloylpiperazine, N-acryloylpiperazine, N-acryloylpiperidine, N-acryloylpyrrolidine, and N-acryloylhexamethyleneimine); alkyl esters of acrylic acid and methacrylic acid, such as methylmethacrylate, ethylacrylate, hydroxyethylacrylate, propylacrylate, cyclohexylacrylate, 2-ethylhexylacrylate, decylacrylate,
- 55 β-cyanoethylacrylate, β-chloroethylacrylate, 2-ethoxyethylacrylate, and sulfopropylmethacrylate vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl lactate; vinyl ethers, such as methylvinyl ether, butylvinyl ether, and oleylvinyl ether; vinyl ketones, such as methyl vinyl ketone and ethyl vinyl ketone; styrenes such as styrene, methyl styrene, dimethyl styrene, 2,4,6-trimethyl styrene, ethyl styrene,

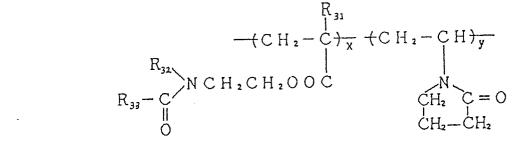
lauryl styrene, chlorostyrene, dichlorostyrene, methoxy styrene, cyanostyrene, dimethylamino styrene, chloromethyl styrene, vinyl benzoate, styrene sulfonate, and α -methyl styrene; vinyl heterocyclic compounds, such as vinyl pyridine, vinyl isooxazoline, and vinyl imidazole; acrylonitrile, vinyl chloride, vinylidene chloride, ethylene, propylene, butadiene, isoprene, chloroprene, maleic anhydride, itaconic anhydride, and vinyl sulfonate; and poly-N-vinyl-5-methyl-2-oxazolidinone described in Japanese Patent Examined Publication No. 31842/1973, polymer of N-vinylamide compound expressed by a formula $CH_2 = CHNR_1COR_2$, in which R¹ represents an alkyl group and R² represents a hydrogen atom or an alkyl group; hydrophilic polymer including a cationic nitrogen-containing active group described in Japanese Patent Examined Publication No. 2522 1969; copolymers of vinyl alcohol and vinyl-pyrrolidone described in Japanese Patent Examined Publication No. 20738 1972; polymers described in Japanese

Patent Examined Publication No. 49028/1972 and represented by the following formula

$$+ CH_2 CH_{\overline{X}} + CH_2 CH_{\overline{Y}}$$

OH OCHNH₂

wherein X + Y = 100 to 500, $\frac{Y}{X+Y}$ = 0.05 to 0.25; and polymers described in Japanese Patent Examined Publication No. 38417 1973 and expressed by the following formula



wherein R_3 represents a hydrogen atom or methyl group; R_{32} and R_{33} individually represent a hydrogen atom and an alkyl group with 1 to 4 carbon atoms: XY = 95.5 to 20.80.

³⁵ It is preferable to employ polyvinyl pyrrolidone or its copolymer as the capturing material of the invention.

It is preferable for said hydrophilic polymers to have a molecular weight of not less than 1,000. in particular, a molecular weight of not less than 10.000, in terms of weight-average molecular weight in the practice of the invention. Still more advantageous is a molecular weight in the range of 50,000-1,000,000.

⁴⁰ The capturing material of the invention can be incorporated into any desirable layer in the photographic structural layers, that is, in a light-sensitive layer including the silver halide emulsion layer according to the invention as well as in a non-light-sensitive layer. It is preferable for the capturing material of the invention to be contained in a non-light-sensitive layer.

It is preferable for the capturing material of the invention to be used ordinarily at a rate of 0.05 to 3.0 mg.dm², more preferably 0.1 to 20 mg.dm². It is also preferable for the capturing material of the invention to be used at a rate of 0.1 to 50 wt%, or, more favorably, at a rate of 1 to 30 wt% per amount of gelatin which is used as a binder in the photographic structural layer where the capturing material is contained.

It is preferable for a sensitizing dye used in the green-sensitive silver halide emulsion layer according to the invention to be one expressed by the following formula [B]:

50

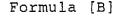
5

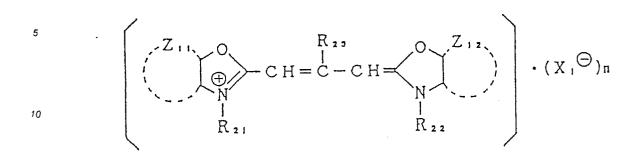
10

15

25

30

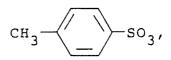




- wherein Z₁₁ and Z₁₂ individually represent a group of atoms required to form a benzene ring or naphthalene ring condensed into an oxazole. The rings formed include those having substituents and the preferable substituents are halogen atoms, aryl group, alkyl group, or alkoxy group. Halogen atoms, phenyl group, and methoxy group are more advantageous as substituents, and phenyl group is most favorable as a substituent.
- According to the preferred embodiments of the invention, both Z₁₁ and Z₁₂ represent a benzene ring condensed into an oxazole ring, wherein at least one of these benzene rings has a substituent phenyl group in the 5-position, or one of these benzene ring has a substituent phenyl group in the 5-position, and the other benzene ring has in the 5-position a halogen atom as a substituent group.
- R₂₁ hand R₂₂ individually represent an alkyl group, alkenyl group, or aryl group, preferably an alkyl group. It is more advantageous for R₂₁ and R₂₂ individually to be an alkyl group having a carboxyl or sulfo group as a substituent group. The more favorable example of R₂₁ and R₂₂ is a sulfoalkyl group having 1 to 4 carbon atoms, where the most favorable is a sulfoethyl group.

 R_{23} represents a hydrogen atom, or an alkyl group having 1 to 3 carbon atoms, or, preferably, a hydrogen atom or ethyl group.

30 X: e represents an anion, such as a halogen ion of chloride, bromine, or iodine, or an anion such as



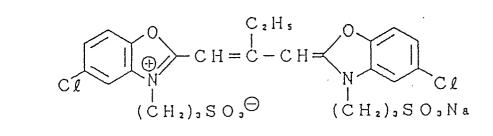
CH₃SO₄, or C₂H₅SO₄. n represents 1 or 0. When a compound forms an inner salt, however, n represents 0.
 Examples of sensitizing dyes preferable in the practice of the present invention, expressed by the formula [B], will now be shown hereunder.

45

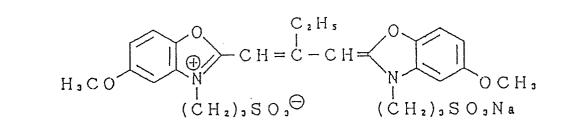
35

50

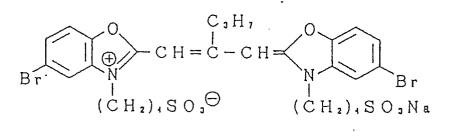
B - 1



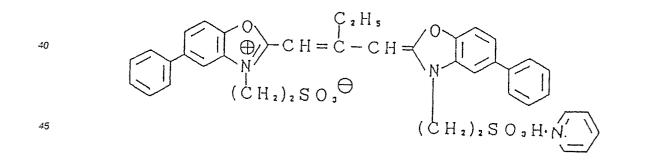
B - 2

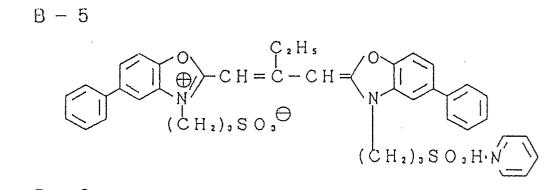


В — З



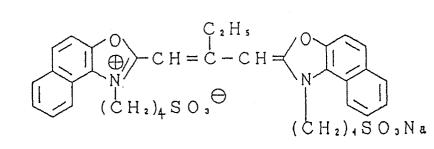
₃₅ B - 4

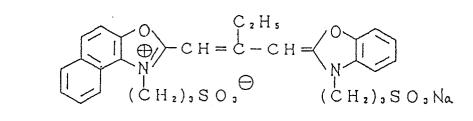




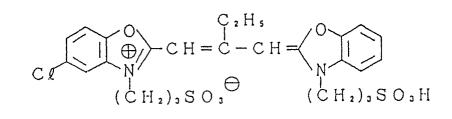
B - 6

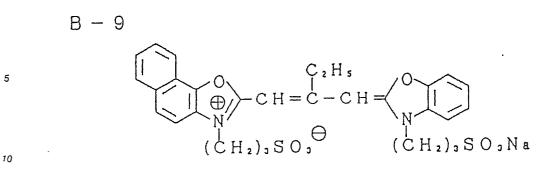
B - 7



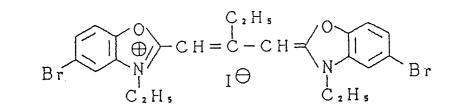


³⁵ B - 8

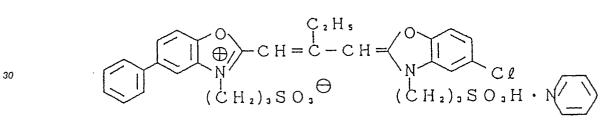




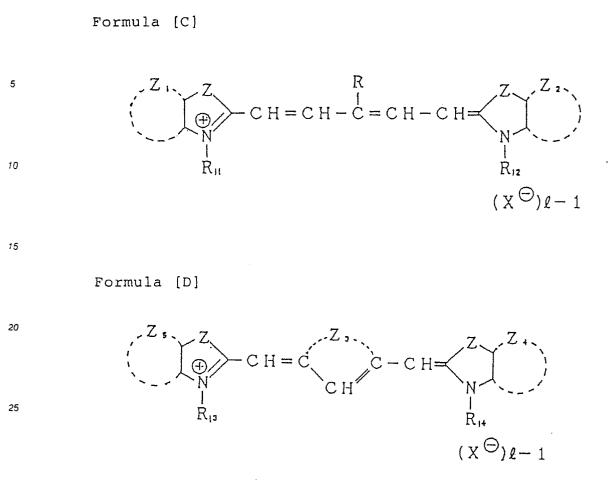
B - 1 0



B - 1 1



It is preferable for a sensitizing dye incorporated into the red-sensitive silver halide emulsion layer according to the invention to be one expressed by the following formula [C] or another expressed by the following formula [D].



40

45

wherein R represents a hydrogen atom, or an alkyl group: R_{1+} through R_{1+} individually represent an alkyl group or aryl group: Z_1 , Z_2 , Z_4 , and Z_5 individually represent a group of atoms required to form a benzene or naphthalene ring condensed into a thiazole or selenazole ring; Z_3 represents a group hydrocarbon atoms required to form a six-membered ring; t represents 1 or 2; Z represents a sulfur atom or selenium atom:

35 Xe represents an anion.

R in the formulas above represents preferably an hydrogen atom, methyl group or ethyl group. It is especially preferable from R to be a hydrogen atom or ethyl group.

R11, R12, R13, and R14 individually represent a straight-chained or branched alkyl or aryl group, wherein an alkyl group or aryl group may have a substituent.

The rings formed by Z₁, Z₂, Z₁, and Z₃ include those having substituents, wherein preferred substituents are halogen atoms. aryl group, alkyl group, and alkoxy group. Particularly preferred substituents are halogen atoms such as chlorine atoms, ohenyl group, and methoxy group.

The ring formed by Z_3 may have a substituent such as alkyl group.

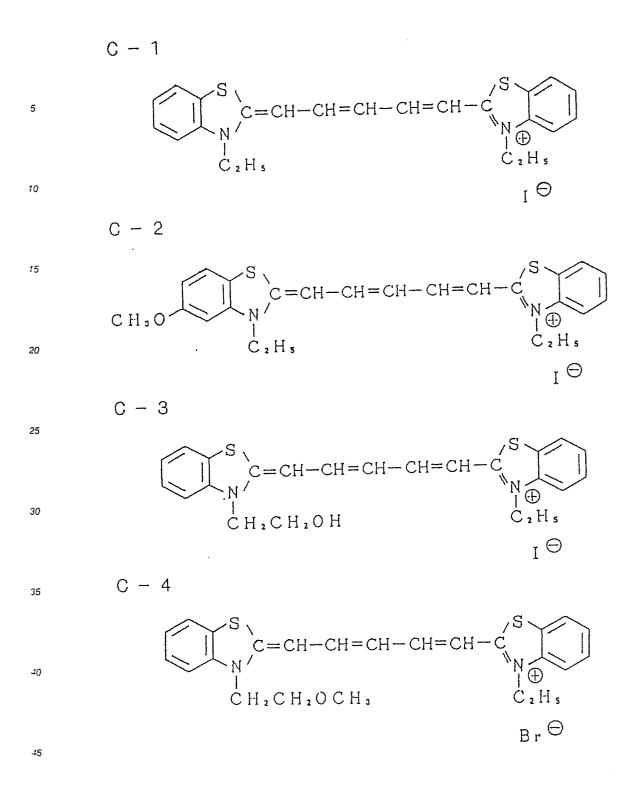
X represents an anion (such as Ct. Br, I,

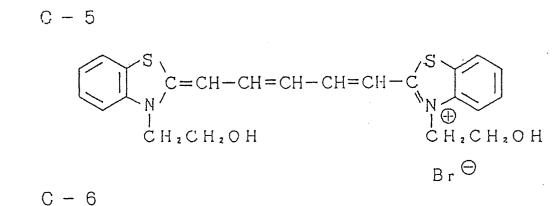
50

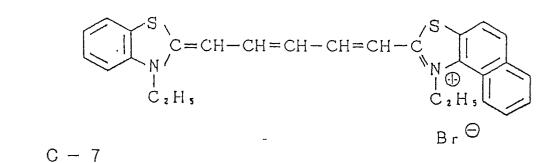
 $CH_3SO_4,$ and $C_2H_5SO_4);$ and $\mathfrak t$ represents 1 or 2.

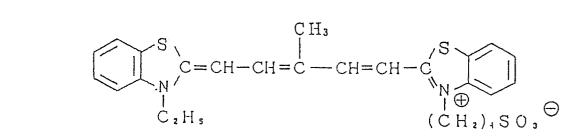
When a compound forms an inner salt, however, it represents 1.

Typical examples of sensitizing dyes preferable in the practice of the present invention, expressed by the formulas [C] and [D], will now be shown hereunder.

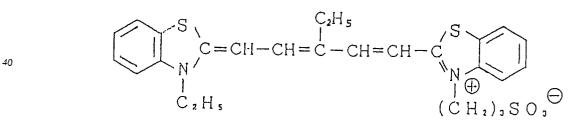


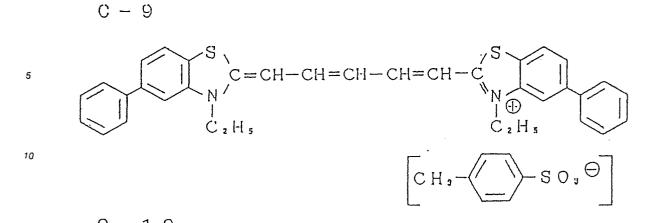


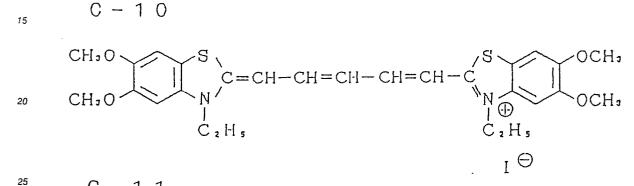




C - 8



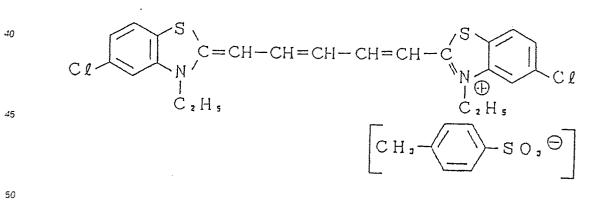




²⁵ C - 1 1²⁶ CH_3 CH_3 C=CH-CH=CH-C S CH_3 ³⁰ CH_3 C=CH-CH=CH-C $N \oplus CH_3$ CH_3 CH_3 CH_3 C=CH-CH=CH-C CH=CH-C CH_3 CH_3

35

C - 1 2



C - 1 3 $\begin{bmatrix}
S \\
C = CH - CH = CH - CH = CH - C
\end{bmatrix}$ $\begin{bmatrix}
Se \\
N \\
I \\
C \\
2 \\
H \\
Se
\end{bmatrix}$ $\begin{bmatrix}
Se \\
N \\
I \\
C \\
2 \\
H \\
Se
\end{bmatrix}$ 5 10 Θ C - 1 415 Se = CH - CH = CH - CH = CH - C = CH20 сн, — _ _ _ _ _ _ Ө 25 30 35 .

55

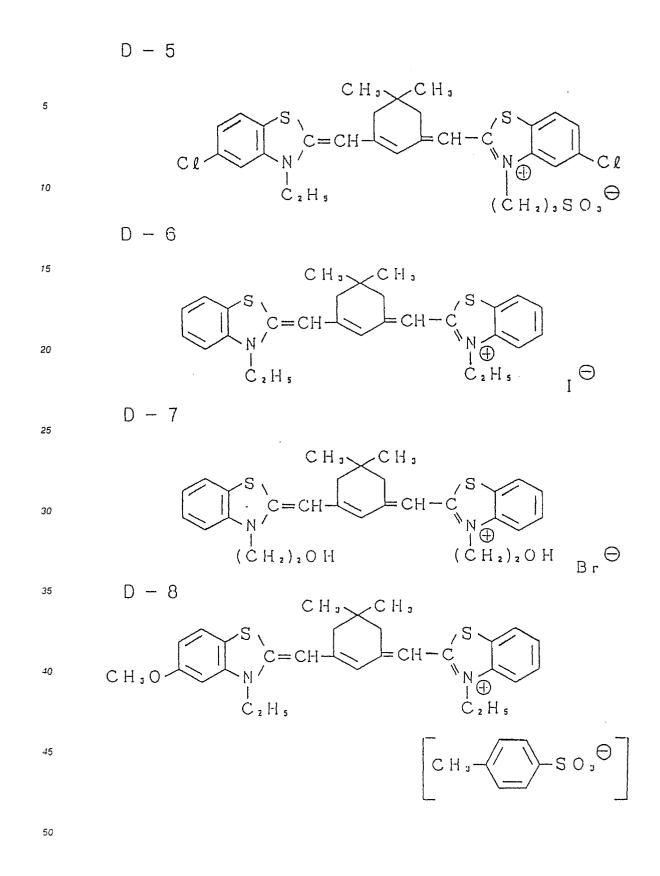
40

45

50

D - 1 СН л СН л /S · 5 Ć N⊕ (CH₂),SO,⊖ СН-·N [/] ∣ C₂H₅ 10 D - 2 CH , CH, 15 CH-C C=CH-N CH₂CH₂OH Ð (CH₂)₃SO₃⊖ 20 D - 3 25 CH , CH, = CH-C N (CH₂), SO, O CHJO $\begin{bmatrix} C \\ C \\ N \\ I \\ C \\ 2 \\ H \\ S \end{bmatrix}$ C=CH-CHJO 30 D - 4 35 CH 3 CH 3 = CH - C $N \oplus$ $(CH_2), SO_3 \oplus$ CH₀O. $\int_{C_2}^{C} C = CH$ 40 CH_JO 45

50



•

•

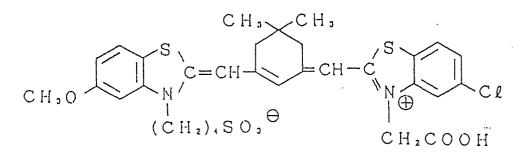
D - 9 ∠CH₁ CHa S 5 CH :CH Μ CH₃O Ð (CH,),SO,⊖ Î CH₂COOH 10 D - 10 CH J CHJ 15 S осн. N/ I CH2CH2OH Ð (CH₂)₃SO;⊖ 20 D - 11 25 CH3 CH3 , S CH CH N [/] | C H ₂ C O O H CH,C 30 \oplus (ĊH₂),SO,⊖ D - 12 35 CH3_CH3 CH_JO СН 40 CH₀O Θ (CH₂)₃SO₃ 45 $(CH_2)_3 SO_3 H \cdot N(C_2H_5)_3$

50

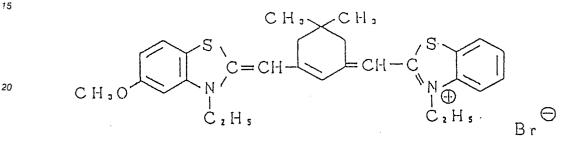
D - 13



10



D - 14



25

30

Any of methods well known in the art may be used as a method for adding the sensitizing dyes.

For example, any of these sensitizing dyes is dissolved in water soluble solvent such as pyridine, methyl alcohol ethyl alcohol, methyl Cellosolve and acetone (or the mixture of any of these solvents), whereby the solution is diluted with water to form a solution being added into a coating solution, or. otherwise, any of these sensitizing dyes is dissolved in water to prepare a solution being added into a coating added into a coating solution.

The amount of sensitizing dye being added is not specifically limited. A preferred range of addition is 2 \times 10⁻⁶ to 1 \times 10⁻³ mol, in particular, 5 \times 10⁻⁶ to 5 \times 10⁻⁴ mol per mol silver halide.

The silver halide photographic light-sensitive element of the invention having the constitution described above may be, for example, a color negative film, color positive film, or color photographic paper. The effect of the invention is best demonstrated when the material takes the form of a color photographic paper, which will be directly appreciated by human vision.

The silver halide photographic light-sensitive elements of the invention, typified by the color photographic paper, may be of monochromatic application or multi-color application. To enable subtraction color reproduction, the multi-color silver halide photographic light-sensitive element usually comprises a support having thereon, in an appropriate order and number, silver halide emulsion layers containing as photographic couplers each of magenta, yellow and cyan couplers, as well as non-light-sensitive layers. The order and number of these layers may be deliverately changed in accordance with the target performance and intended application.

If silver halide photographic light-sensitive element used in embodying the invention is the multi-color light-sensitive element, the preferred layer configuration comprises a support provided sequentially thereon in the order of a yellow dye-image forming layer, intermediate layer, magenta dye-image forming layer, intermediate layer, cyan dye-image forming layer, intermediate layer, and protective layer.

Into the silver halide emulsion layers of the silver halide color photographic light-sensitive element according to the invention is incorporated dye-forming couplers.

These dye-forming couplers preferably contains within the molecular structure a group known as a "ballast group" which has not less than 8 carbon atoms and is capable of making the coupler non-diffusible. The preferred yellow dye-forming couplers are acylacetanilide couplers. Among these couplers. benzoylacetanilide compounds and pyvaloylacetanilide compounds are particularly advantageous. The preferred compounds are those represented by the following formula [Y].

55

45

Formula [Y]

5

 $CH_3 - C - C O C H C O N H$

10

15

20

In this formula, Ry1 represents a halogen atom, or alkoxy group. Ry2 represents a hydrogen atom, halogen atom, or alkoxy group. Ry3 represents an acylamino group, alkoxycarbonyl group, alkylsulfamoyl group, arylsulfamoyl group, alkylureide group, arylureide group, succinimide group, alkoxy group or aryloxy group. Z_{y1} represents a group being capable of split off by the reaction with an oxidation product of the color developing agent.

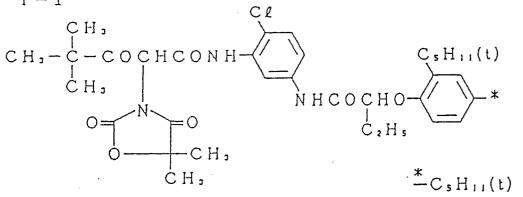
The examples of useful yellow coupler are those described, for example, in British Patent No. 1.077,874, Japanese Patent Examined Publication No. 40757 1970, Japanese Patent O.P.I. Publication Nos. 1031/1972, 26133/1972, 94432/1973, 87650/1975, 3631/1976, 115219/1977, 99433/1979, 133329/1979, and 30127/1981, U.S. Patent Nos. 2,875,057, 3,253,924, 3,265,506, 3,408,194, 3,551,155, 3,551,156, 3,664,841, 3,725,072, 3,730,722, 3,891,445, 3,900,483, 3,929,484, 3,939,500, 3,973,968, 3,990,896, 4,012,259, 4,022,620, 4,029,508, 4,057,432, 4,106,942, 4,133,958, 4,269,936, 4,286,053. 4,304,845, 4,314,023. 4,336,327, 4,356,258, 4,386,155, and 4,401,752.

The typical examples are listed below.

25

30

Y - 1

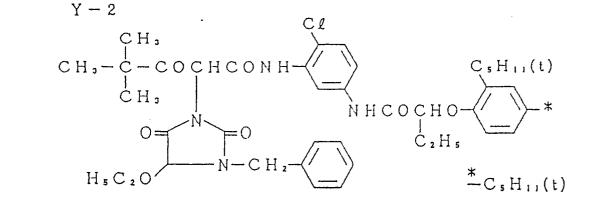


40

45

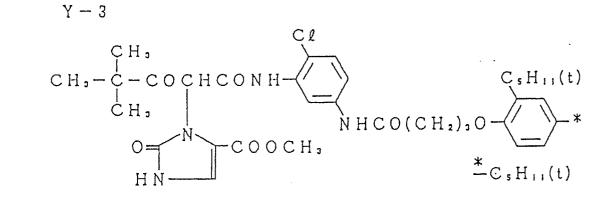
50

35

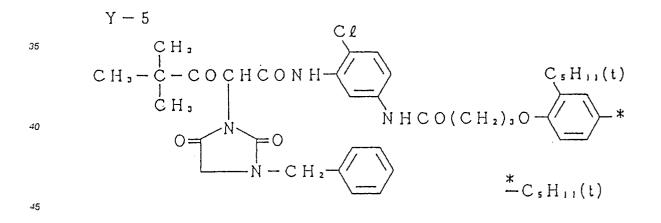


=0

ĊНз

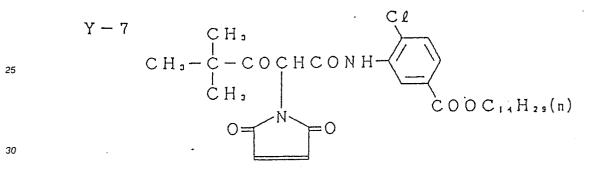


۰.



Y - 6 $CH_{3} - C - COCHCONH - C_{5}H_{11}(t)$ $C_{5}H_{11}(t)$ $C_{7}H_{3} - C_{7}COCHCONH - C_{5}H_{11}(t)$ $H CO(CH_{2})_{3}O - F$ $C_{5}H_{11}(t)$ $C_{7}H_{11}(t)$ $C_{7}H_{11}(t)$ $C_{7}H_{11}(t)$

20



35 Y - 8 $CH_{3} - CH_{2}$ $CH_{3} - CH_{2}$ $CH_{3} - CH_{2}$ $CH_{3} - CH_{2}$ Y – 8 40 $\dot{N} H C O C H C H_2 S O_2 C_{12} H_{25}(\pi)$ ĊHa 45

50

Cl

<u>йнсосно</u>-

Ì C₂H₅ $C_{5}H_{11}(t)$

*

C₅H₁₁(t)

10

5

Y - 9

СН₃ СН₃-С-СОСНСОИН СН₃ 0

CL

Cl

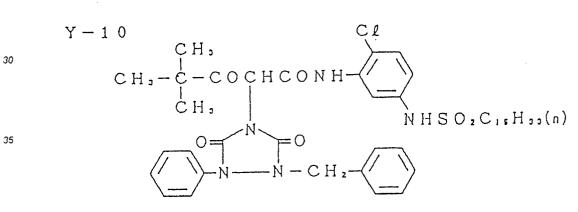
ŚОź

ĠН

15

20

25



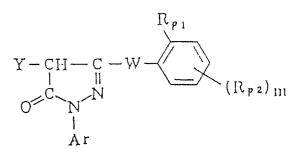
40

45

The preferred magenta dye-forming couplers are 5-pyrazolone couplers and pyrazoloazole couplers. Among these couplers, the particularly preferred couplers are those represented by the following formula [P] or [a].

Formula [P]





0 286 331

In this formula, Ar represents an aryl group, R_{p1} represents a hydrogen atom or a substituent group, R_{p2} represents a substituent group. Y represents a group being capable of split off by the reaction with an oxidation product of the color developing agent. W represents -NH-. -NHCO-(N atom being bonded to a carbon atom on the pyrazolone nuclei), or -NHCONH-. m represents an integer, 1 or 2.

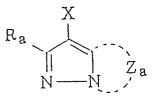
Formula [a]

10

15

20

5



In this formula, Z_a represents a group of non-metal atoms required for forming a nitrogen-heterocycle. The heterocycle formed by this Z_a may have a substituent.

X represents a hydrogen atom, or a group being capable of split off by the reaction with an oxidation product of the color developing agent.

R_a represents a hydrogen atom, or a substituent group.

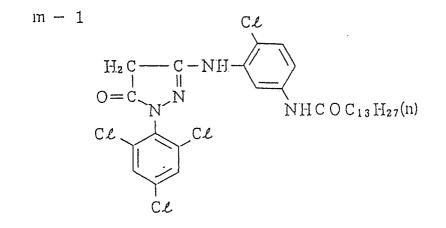
The examples of a substituent group represented by this R_a include a halogen atom, alkyl group, cycloalkyl group, alkenyl group, cycloalkenyl group, alkinyl group, aryl group, heterocyclic group, acyl group, phosphonyl group, carbamoyl group, sulfamoyl group, cyano group, spiro compound residue group, bridged hydrocarbon compound residue group, alkoxy group, aryloxy group, heterocyclic oxy group, siloxy group, acyloxy group, carbamoyloxy group, amino group, acylamino group, sulfonamide group, imide group, ureide group, sulfamoylamino group, alkoxycarbonylamino group, aryloxycarbonylamino group, alkoxycarbonyl group, and heterocyclic thio group.

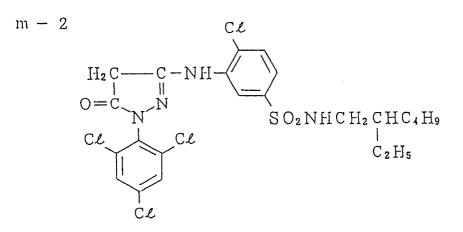
The examples of a magenta coupler are described, for example, in U.S. Patent Nos. 2,600,788, 3,061,432, 3,062,653, 3,127,269, 3,311,476, 3,152,896, 3,419,391, 3,519,429, 3,555,318, 3,684,514, 3,888,680, 3,907,571, 3,928,044 3,930,861, 3,930,866, and 3,933,500, Japanese Patent O.P.I. Publication Nos. 29639/1974, 111631 1974, 129538/1974, 58922/1977, 62454 1980, 118034/1980, 38043/1981, 35858/1982, and 23855/1985, British Patent No. 1,247,493, Belgium Patent Nos. 769,116 and 792,525. West German Patent No. 2,156,111, Japanese Patent Examined Publication No. 60479/1971, Japanese Patent

³⁵ O.P.I. Publication Nos. 125732 1984, 228252 1984, 162548,1984, 171956,1984, 33552 1985, and 43659,1985, West German Patent No. 3,725,067, and U.S. Patent No. 3,725,067. The typical examples are listed below.

40

45

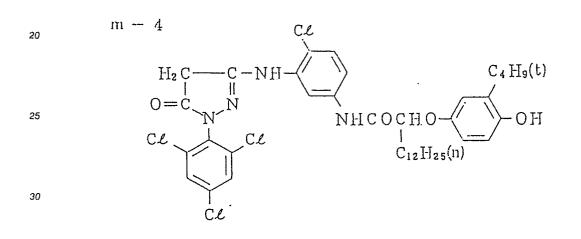


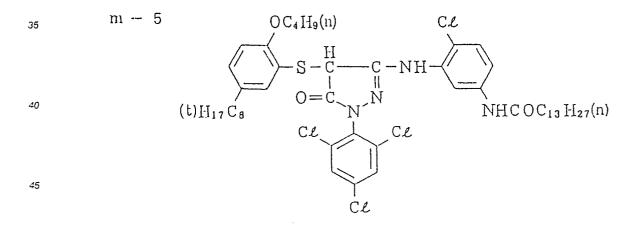


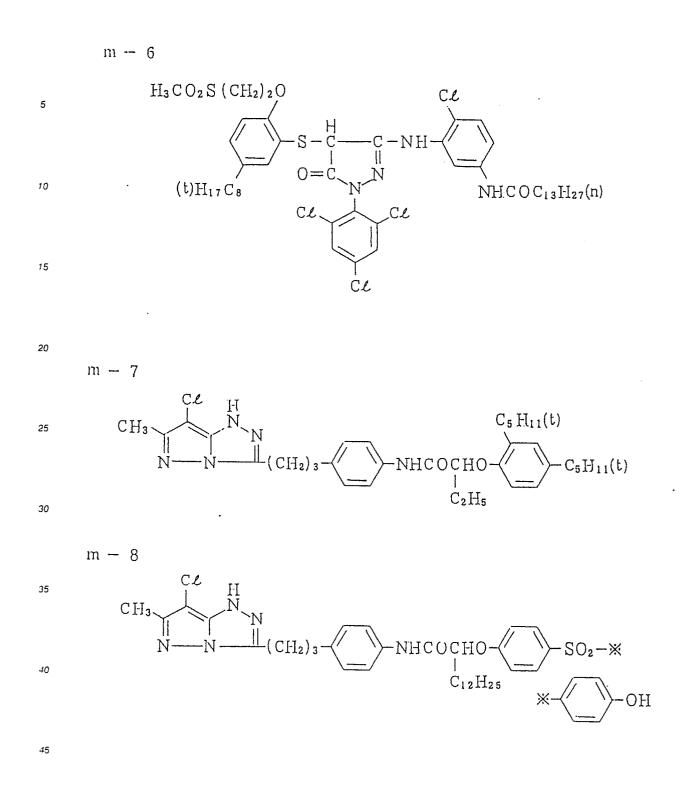
,

•

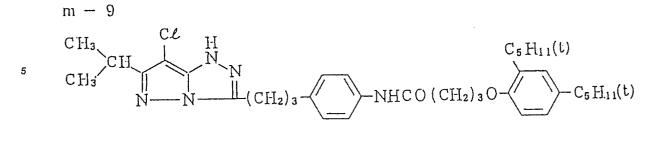
.

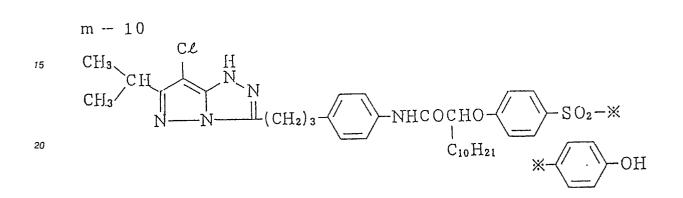


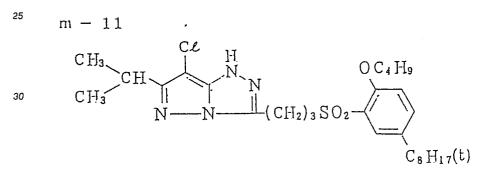




.

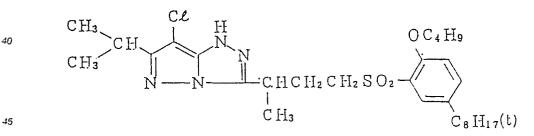


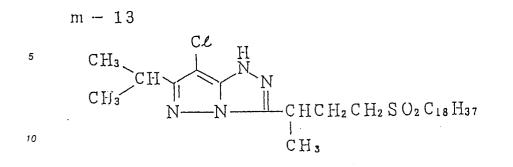


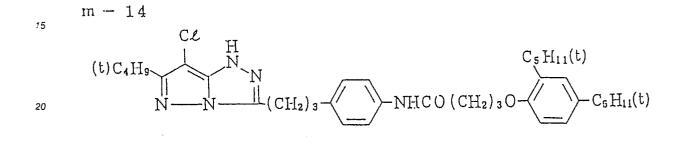


m - 12



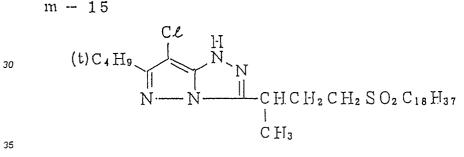






÷





35

40

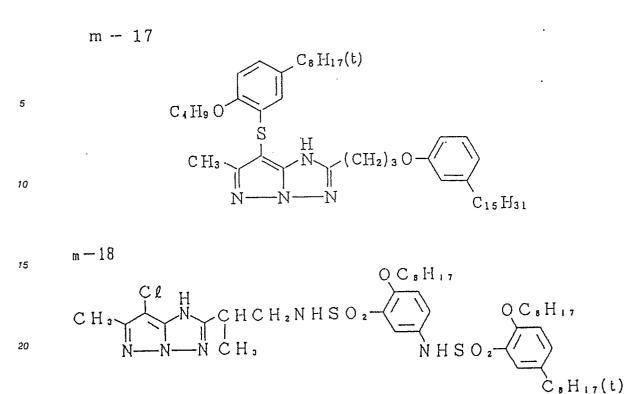
45

50

m -- 16

m - 15

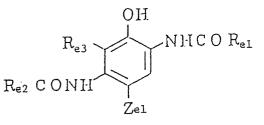
CL ОH



²⁵ The cyan dye-forming couplers used are phenol and naphthol cyan dye forming couplers. Among these couplers, the particularly preferred couplers are those represented by the following formula [E] or [F].

30

35

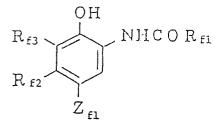


In this formula, R_{e1} represents an alkyl group, cycloalkyl group or heterocyclic group. R_{e2} represents an alkyl group or phenyl group. R_{e3} represents a hydrogen atom, halogen atom, alkyl group or alkoxy group. Z_{e1} represents a hydrogen atom, or a group being capable of split off by the reaction with an oxidation product of the color developing agent.

Re1 through Re3 may have a substituent group.

50

45



55

In this formula, Rf1 represents an alkyl group such as a methyl group, ethyl group, propyl group, butyl

group, and nonyl group. R_{f2} represents an alkyl group such as a methyl group and ethyl group. R_{f3} represents a hydrogen atom, halogen atom such as fluorine, chlorine and bromide, or alkyl group. Z_{f1} represents a hydrogen atom, or a group being capable of split off by the reaction with an oxidation product of the color developing agent.

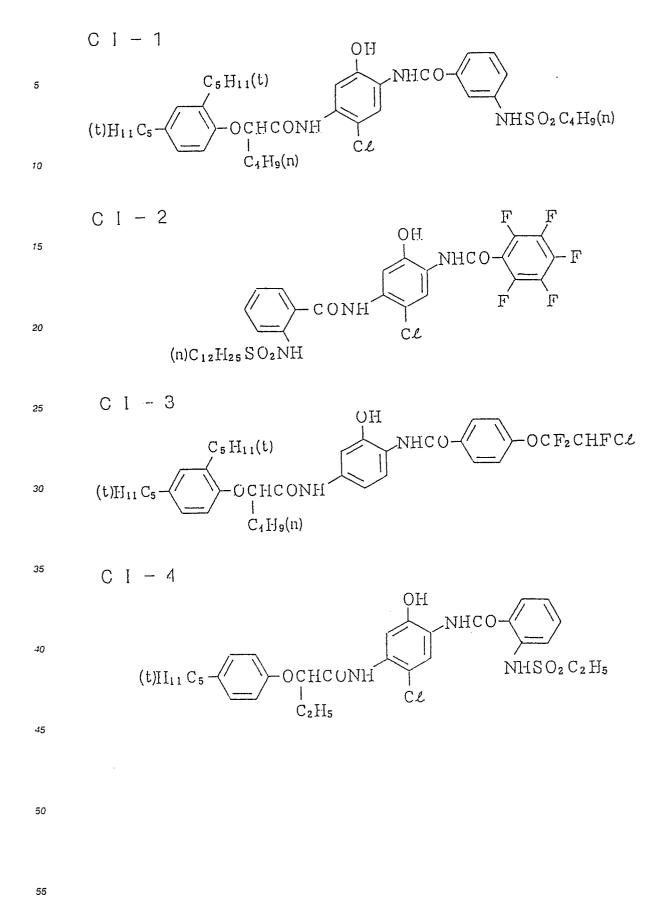
5 R_{f1} through R_{f3} may have a substituent group.

The examples of such a cyan dye-forming coupler are described, for example, in U.S. Patent Nos. 2,306,410, 2,362,598, 2,367,531, 2,369,929, 2,423,730, 2,474,293, 2,476,008, 2,498,466, 2,545,687, 2,728,660, 2,772,162, 2,895,826, 2,976,146, 3,002,836, 3,419,390, 3,446,622, 3,476,563, 3,737,316, 3,758,308, and 3,839,044, British Patent Nos. 478,991, 945,452, 1,084,480, 1,377,233, 1,388,024, and 1,543,040, Japanese Patent O.P.I. Publication Nos. 37425/1972, 10135/1975, 25228/1975, 112038/1975, 117422/1975, 130441/1975, 6551/1976, 37647/1976, 52828/1986, 108841/1976, 109630/1978, 48237/1979, 66129/1979, 131931/1979, 32071/1980, 146050/1984, 31953/1984, and 117249/1985.

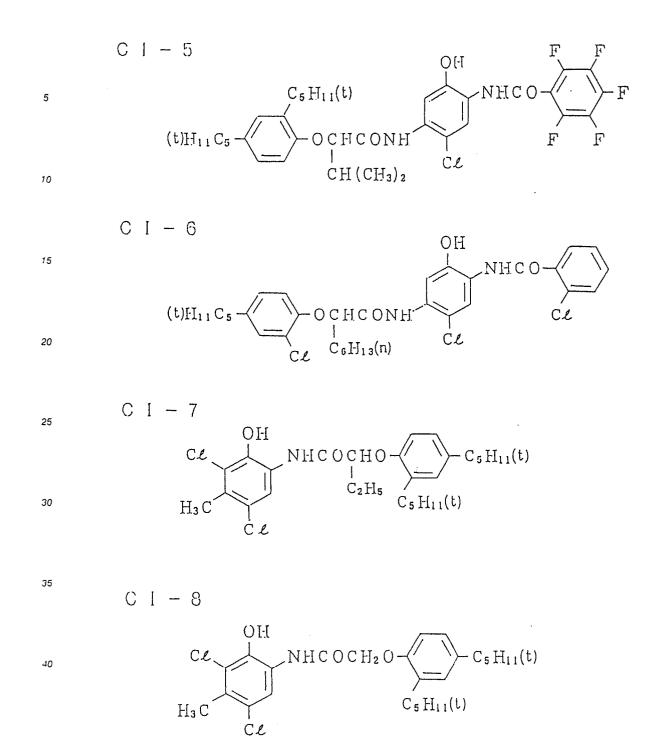
The typical examples are listed below.

÷

0 286 331



.

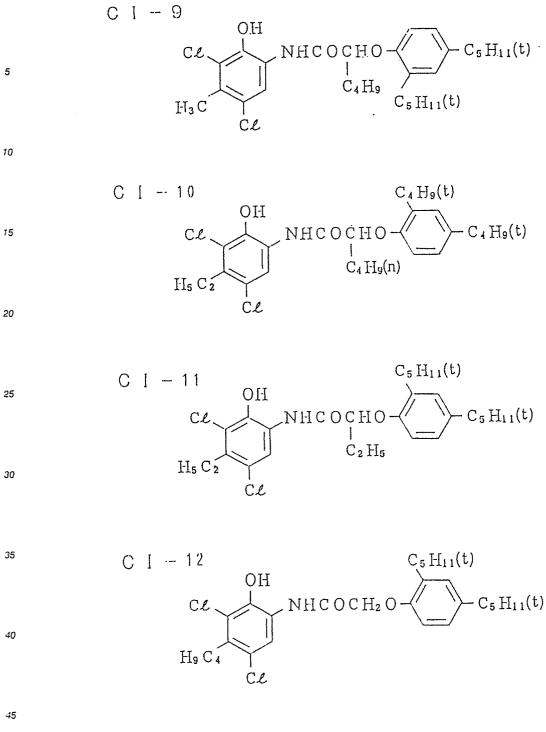


-

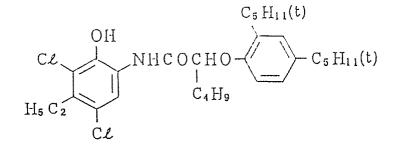
÷

÷

50



C I - 13



.

50

The dye forming coupler used in embodying the invention is incorporated into each silver halide emulsion layer, usually, at a rate of 1×10^{-3} to 1 mol, or, preferably, 1×10^{-2} to 8×10^{-1} mol per mol silver halide.

The advantageous binder, or protective colloid, incorporated into the silver halide photographic lightsensitive element according to the invention is gelatin. Other useful binders include a gelatin derivative, graft polymer of gelatin and another high-molecular compound, protein, sugar derivative, cellulose derivative, and hydrophilic colloid of synthesized high-molecular compound such as monomer or polymer.

The photographic emulsion layers and other hydrophilic colloid layers of the silver halide photographic light-sensitive element of the invention are hardened by singly or combinedly using hardeners which enhance layer strength by bridging between binder, or protective colloid, molecules. The hardeners are preferably incorporated at a rate enough to eliminate hardeners added to processing solutions. However, the hardeners may be added to processing solutions.

According to the invention, a chlorotriazine hardener, represented by the following formula [HDA] or [HDB], is preferably used to harden the silver halide emulsion layers.

 \mathbb{R}_{d^2} \mathbb{N} \mathbb{C}^{ℓ} \mathbb{N} \mathbb{N}

15

5

Formula [HDA]

20

25

In this formula, R_{d1} represents a chlorine atom, hydroxy group, alkyl group, alkoxy group, alkylthio group, -OM group (M represents a monovalent metal atom), -NR'R" group (R' and R" independently represent a hydrogen atom, alkyl group or aryl group), or -NHCOR" group (R" represents an alkyl group or aryl group). R_{d2} is synonymous with R_{d1} above, except for a chlorine atom.

Formula [HDB]

35

40

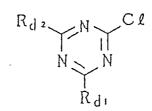
 $\begin{array}{c} R_{d} : \bigvee_{I} N \bigvee_{Q} (Q)_{p} - L - (Q')_{q} \bigvee_{I} N \bigvee_{I} R_{d} \\ N \bigvee_{C \ell} N & N & \\ C \ell & C \ell \end{array}$

In this formula, R_{d3} and R_{d4} independently represent a chlorine atom, hydroxy group, alkyl group, ⁴⁵ alkoxy group, or -OM group in which M represents a monovalent metal atom. Q and Q' independently a connecting group i.e. -O-, -S-or -NH-. L represents an alkylene group or arylene group, p and q independently represent 0 or 1.

The typical examples of the preferred hardeners represented by formula [HDA] or [HDB] above are hereinunder listed.

50

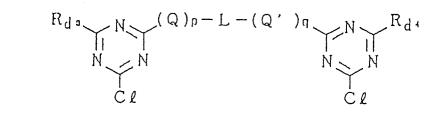
Formula [HDA]



15	Compound No.	R _{d 1}	R _{d 2}
	H D - 1	- 0 H	- 0 N a
	HD-2	- C l	- O N a
20	HD-3	- 0 C H ,	- O N a
	HD-4	- C l	$-OC_{2}H_{5}$
25	H D — 5	- C l	— О К
20	HD-6	- 0 H	- 0 K
	HD-7	- C l	- N H 2
30	H D - 8	– Cl	- N H C O C H a
	H D - 9	- 0 H	— N H C 2 H 5
	HD-10	- C H 3	$-NHC_{6}H_{5}$
35	HD-11	— N H 2	-NHCOC ₆ H ₅
	HD-12	-NHCOCH,	$-C_2H_s$

-45

Formula [HDB]



15	Compound No.	R _d o	R _d ,	Q	ր	୍ଦ '	q	L
20	HD-13	- C £	— C l	0	1	0	1	-
	HD-14	- O N a	— O N a	0	1	0	1	- C H 2 C H 2 -
25	HD-15	-ΟNa	- O N &	_	0		0	- C H 2 C H 2 -
	HD-16	- O C H ,	- 0 С Н,	S	1	S	1	- C H 2 C-H 2 -
30	HD-17	- O N a	-ΟΝα	H - N -	1	- N -	1	- C H 2 C H 2 -
35	HD-18	— O N a	O N a	Н - Х -	1	0	1	- C H 2 C H 2 -
	HD-19	- O H	— O H	0	1	0	1	- C H 2 C H 2 -
	HD-20	- C H 3	- C H 3	0	1	0	1	- C H 2 C H 2 -

40

45

50

55

5

10

The hardener represented by formula either [HDA] or [HDB] can be incorporated into silver halide emulsion layers and other structural layers by dissolving the hardener in water, or a solvent compatible with water such as methanol and ethanol, thereby adding the resultant solution to a coating solution for these structural layers. The method of addition can be either batch process or in-line process. The timing of addition is not specifically limited. However, the preferred timing of addition is immediately before the application of coating solutions.

These hardeners are added at a rate of 0.5 to 100 mg, or, preferably, at a rate of 2.0 to 50 mg per 1 gram gelatin being applied.

To the silver halide photographic light-sensitive element of the invention may be further added various additives such as an anti-stain agent, image-stabilizing agent, ultraviolet absorbent, plasticizer, latex. surface active agent, matting agent, lubricant, and anti-static agent.

The silver halide photographic light-sensitive element according to the invention can form an image by color developing known in the art.

The color developing agents incorporated into the color developers, according to the invention, include aminophenol derivatives and p-phenylenediamine derivatives widely used in various color photographic processes.

To the color developer solution used in processing the silver halide photographic light-sensitive element

of the invention is added, in addition to the primary aromatic amine color developing agent mentioned previously, compounds known as developer components.

The pH value of a color developer solution is normally higher than 7, or, most usually, approx. 10 to 13. The color developing temperature is usually higher than 15°C, or, generally, within a range of 20 to

5 50°C. For rapid developing, the preferred temperature is higher than 30°C. A conventional color developing requires 3 to 4 minutes, while the preferred color developing time intended for rapid processing is usually within a range of 20 to 60 seconds, in particular, 30 to 50 seconds.

Once the color developing is complete, the silver halide photographic light-sensitive element of the invention is subjected to bleaching and fixing. The bleaching and the fixing may be performed simultaneously.

After the fixing, the similar element is usually subjected to rinsing with water. Stabilizing may substitute the rinsing, or these two steps may combinedly used.

As described above, the silver halide photographic light-sensitive element of the invention excels in rapid processability, as well as in decolorization of the dyes, wherein the resultant photographic image provides improves sharpness.

EXAMPLES

20 Example-1

Using double jet precipitation process, the following silver chloro-bromide emulsions and silver chloride emulsions were prepared.

25	

10

	Emulsion No.	Grain size (µm)	Silver chloride content (mol%)	Variation coefficient
30	Em-A (Comparative)	0.5	20	0.12
35	Em-B (Comparative)	0.5	50	0.13
	Em-C (Invention)	0.5	90	0.11
40	Em-D (Invention)	- 0.5	95	0.08
<i>4</i> 5	Em-E (Invention)	0.5	100	0.08

Em-A through Em-E above were, using a conventional method, subjected to sulfur sensitization by adding sodium thiosulfate, and further subjected to optical sensitization using exemplified sensitizing dye No. C-9. Thus, red-sensitive silver halide emulsions Em-R Nos. A through E were prepared.

On a polyethylene-laminated paper support were simultaneously applied and dried the coating solutions for the first and second layers. Thus, mono-color light-sensitive element sample No. 1 was prepared.

The amounts added for each coating solution are indicated by amounts applied per each independent coat formed.

First layer: red-sensitive silver halide emulsion layer

Contains red-sensitive silver halide emulsion listed in Table-1 at a rate, as converted into metal silver, of 3 mg/dm²; example cyan coupler CI-5, at a rate of 2 mg/dm²; example cyan coupler CI-7, at a rate of 2 mg/dm²; dioctylphthalate as a high boiling organic solvent, at a rate of 3 mg/dm²; hydroquinone derivative HQ-1 mentioned later, at rate of 0.15 mg/dm²; gelatin, at a rate of 14 mg/dm²; and HD-2 as a hardener at a rate of 0.05 mg/dm².

10 Second layer: protective layer

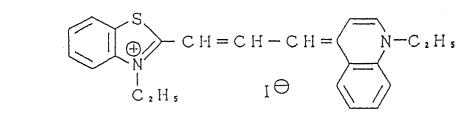
15

Contains respective compound listed in Table-1 at a rate of 0.1 mg/dm² or Comparative-1 as a comparative compound at a rate of 0.2 mg/dm²; polyvinyl pyrrolidone weight average molecular weight. 360,000, as a capturing material for fluorescent whitening agent at a rate of 0.55 mg/dm²; gelatin, at a rate of 20 mg/dm²; and HD-2 as a hardener, at a rate of 0.05 mg/dm².

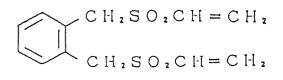
Light-sensitive element sample Nos. 2 through 44 were prepared in manner identical with that of sample No. 1 above, except that the combination of EM, type of compound represented by formula [I], type of fluorescent whitening agent, and coating solution dissolving them, was modified as listed in Table-1, like substances were used in a same weight.

- Additionally, sample No. 45 was prepared in a manner identical with that of sample No. 10, except that the following sensitizing dye A was used instead of exemplified sensitizing dye No. C-9 in Em-E. Sample Nos. 46 and 47 were prepared in a manner identical with sample No. 10, except that polyvinyl pyrrolidone in the second layer of sample No. 10 was replaced for No. 46 with a like weight of polyvinyl alcohol, polymerization degree, approx. 500; saponification degree, 88%, or for No. 47 with a copolymer (1 : 1, by molecular ratio) of polyvinyl alcohol of vinyl pyrrolidone and methacrylic acid. Sample Nos. 48, 49 and 50 were prepared in a manner identical with sample No. 10, except that polyvinyl pyrrolidone added was at a rate of 0.275 mg/dm² (No. 48), 0.11 mg/dm² No. 49), or 0.055 mg/dm² (No. 50). Sample No. 51 was
- prepared in a manner identical with that of sample No. 10, except that a hardener, examplified compound No. HD-2, in the first and second layers was replaced with the same weight of the following hardener H-1.

Sensitizing dye A



Hardener H-1



50

35

40

45

The respective samples prepared above were subjected to the following processes without undergoing exposing, or after undergoing wedge exposing with photographic sensitometer Model KS-7 (Konica Corporation).

[Treatment]

		Temperature	Time
5	Color developing	34.7 ± 0.3°C	50 sec.
	Bleach-fixing	34.7 ± 0.5°C	50 sec.
10	Stabilizing	30 to 34°C	90 sec.
	Drying	60 to 80°C	60 sec.

15

15	
	[Color developer] Pure Water 800 m t
	Ethylene glycol 10 mt
	N,N-diethylhydroxylamine 10 g
	Potassium chloride 2 g
20	Potassium sulfite 0.1 g
	N-ethyl-N- β -methanesulfonamideethyl-3-methyl-4-aminoaniline sulfite 5 g
	Sodium tetrapolyphosphate 2 g
	Potassium carbonate 30 g
	Fluorescent whitening agent (4,4-diaminostylbenzosulfonate derivative 1 g
25	Water was added to the components above to prepare one liter solution, thereby pH level was adjusted to
	10.08.

[Bleach-fixer] Ferric ammonium ethylenediaminetertraacetate dihydrate 60 g
Ethylenediaminetetraacetic acid 3 g
Ammonium thiosulfate (70% aqueous solution) 100 m t
Ammonium sulfite (40% aqueous solution) 27.5 m t
The pH level was adjusted to 7.1 using potassium carbonate or glacial acetic acid, thereby water was added to prepare one liter solution.

35

[Stabilizer] 5-chloro-2-methyl-4-isothiazoline-3-one 1 g
 1-hydroxyethylidene-1,1-diphosphonic acid 2 g
 Water was added to the components above to prepare one liter solution, thereby pH level was adjusted to
 7.0 using sulfuric acid or potassium hydroxide.

Samples treated with the processes above, and sample not treated at all, were tested for performance with the following methods. Table-1 also lists the test results.

45

(1) Sensitometry

After the processes above, exposed samples were subjected to sensitometric measurement using PDA-50 65 (Konica Corporation), whereby the sensitivity and maximum density (Dmax) of each sample was determined. The value of sensitivity is indicated relative to that of light-sensitive element sample No. 1 i.e. 100.

(2) Sharpness

A resolution test chart was printed on each sample using red exposure light, thereby each sample was treated by the previously specified processing, and then, the resultant cyan dye image was measured for density using a microphotometer, wherein the sharpness value was determined by the following expression.

¹⁵ The larger the value is, the more excellent the sharpness is.

(3) Stain

- Each unexposed sample was treated by the previously specified treatment, then using a color analyzer (Model 607, Hitachi, Ltd.), measured for the reflective density at a maximum absorption wavelength described below.
- ²⁵ (4) Maximum absorption wavelength

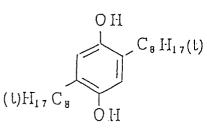
Each non-treated sample was measured for the spectral reflective density using the color analyzer mentioned above, whereby the maximum absorption wavelength was determined.

The structural formulas of hydroquinone derivative HQ-1, and comparative compound, Comparative-1, ³⁰ which employed for comparison with a compound represented by formula [I] are as follows.

Hydroquinone derivative

35

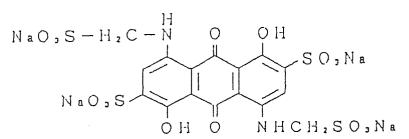
(HQ-1)



40

45

(Comparative-1)



50

5				Comparative	Comparative	Comparative	Comparative	Comparative	Comparative	Comparative	Invention	Invention	Invention	Invention	Comparative	Invention
10		Maximum absorption	wavelength (nm)	675 Cor	675 Cor	675 Coi	675 Coi	666 Co	666 Co	- C 1	676 In	675 In	676 In	675 In	658 Co	667 In
15		Stain ab		0.120	0.118	0.118	0.120	0.092	0.092	0.091	0.093	0.092	0.092	0.093	0.091	0.092
		220ucred	ceand toric	0.45	0.44	0.45	0.46	0.45	0.44	0.29	0.53	0.52	0.53	0.52	0.44	0.53
20			Dmax	2.12	2.14	2.52	2,56	2.55	2.55	2.56	2.55	2.56	2.54	2.55	2.55	2.55
25	E1	Sensitometry	Relative sensitivity	100	103	011	112	113	104	203	115	116	116	115	106	117
30 35	Table	Layer containing capturing material	for fluorescent whitening agent	2nd layer		2nd layer	2nd layer	lst läyer	2nd layer	lst layer		2nd layer				
40		[1]	Layer for coat- for ing solution	2nd layer	2nd layer		2nd layer	2nd layer	lst layer	lst layer	2nd layer	2nd layer				
45		Compound of formulā	Type	Comparative-1	Comparative-1	Comparative-1	Comparative-1	Comparative-1	47		47	47	47	47	69	69
50		no i o l	Em-R No.	A	B	υ	Q	ы	щ	ы	<u>भ</u>	ы	ਸ਼	я	ម	洒
55			sample No.]	2	m	4	5	9	۲	8	6	10	11	12	13

0.44 0.092 0.53 0.093 0.43 0.091 0.43 0.091 0.52 0.092 0.43 0.091 0.52 0.092 0.43 0.091 0.52 0.091 0.53 0.092 0.53 0.092 0.53 0.092 0.53 0.092 0.53 0.092 0.53 0.092
0.53 0.43 0.52 0.43 0.43 0.52 0.44
0.43 0.52 0.43 0.52 0.52 0.44
0.52 0.43 0.52 0.44 0.53
0.43 0.52 0.44 0.53
0.53
0.53
2.12 0.45 0.092
2.55 0.53 0.093
2.53 0.52 0.093
2.54 0.52 0.093
2.54 0.53 0.091

•

•

.

-

			Invention												
	-	c.	Inve	Inve	Jnvé	Inve	Inve	Inve	ivul	Inv	Inv	Inv	Inv	Inv	Inv
	Maximum absorption	wavelength (nm)	677	677	677	677	667	672	672	672	672	672	672	672	672
	Ctatn Ctatn	1	0.093	0.093	0.093	0.092	0.092	0.092	0.092	0.092	0.091	0.092	0.092	0.092	160.0
	55 acr 2 Ch a march 2 C	scand talls	0.53	0.53	0.53	0.52	0.53	0.54	0.53	0.53	0.53	0.53	0.53	0.53	0.54
	try	Dтах	2.55	2.55	2.54	2.54	2.55	2.56	2.55	2.55	2.54	2.55	2.55	2.55	2.56
inued 2)	Sensitometry	Relative sensitivity	116	116	116	116	117	117	116	117	115	116	116	117	117
Table 1 (continued	Layer containing capturing material	for fluorescent whitening agent	2nd layer												
<u> </u>	f formula [I]	Layer for coat- ing solution	2nd layer												
	Compound of formula	Type	60	61	62	72	70	73	85	75	81	82	76	17	74
	Emitletion	Em-R No.	ы	મ	ы	ш	<u></u> ы	£4	(±1	ы	EL	ы	ન	£	ы
		-on	27	28	29	30	31	32	33	34	35	36	37	38	39

0 286 331

-. - ---

1	5	

•

-

.

•

(continued	
Table l	
H	

Э) Э

Sample	Emulsion	Compound of formul	of formula [I]	Layer containing capturing material	Sensitometry	ry	Sharpness	Stain	Maximum absorption		
No.	Em-R No.	Type	Layer for coat- ing solution	for fluorescent whitening agent	Relative sensitivity	Dmax			wavelength (nm)		
40	ы	78	2nd layer	2nd layer	116'	2.55	0.53	0-090	672	Invention	
41		62	2nd layer	2nd layer	116	2.56	0.54	0.093	672	Invention	
42	£	BO	2nd layer	2nd layer	116	2.55	0.53	0.092	670	Invention	
43	ш	83	2nd layer	2nd layer	115	2.55	0.53	0.093	671	Invention	
44	ы	84	2nd layer	2nd layer	115	2.55	0.53	0.092	671	Invention	
45	<u>ы</u>	47	lst layer	2nd layer	110	2.54	0.53	0.092	676	Invention	
46	ы	47	lst layer	2nd layer	116	2.53	0.52	0.093	672	Invention	
47	e	47	lst layer	2nd layer	116	2.54	0.52	0,093	673	Invention	
48	ш	47	lst layer	2nd layer	116	2.54	0.53	0.092	675	Invention	
49	ш	47	lst layer	2nd layer	116	2.55	0.52	160.0	674	Invention	
50	ដា	47	lst layer	2nd layer	116	2.55	0.52	0.092	672	Invention	
51	24	47	lst layer	2nd layer	116	2.55	0.52	0.092	675	Invention	

0 286 331

As apparent from the results in Table-1, sample Nos. 1 and 2, which used an emulsion, not in compliance with the invention, of a lower silver chloride content and containing comparative dye and a capturing material of the invention for fluorescent whitening agent, respectively showed insufficient sensitiv-5 ity and maximum density, and, especially, greater stain, and also failed to attain satisfactory level of sharpness. Sample Nos. 3 through 5, having an emulsion of the invention of a higher silver chloride content

- unlike sample Nos. 1 and 2, showed still insufficient improvement in stain and sharpness. in spite of improved sensitivity and maximum density. Sample No. 6 and sample Nos. 8 through 51 respectively incorporating a dye represented by formula [I] according to the invention respectively showed improvement to nearly satisfactory level in terms of stain. However, as in the case of sample Nos. 6, 12, 14, 16, 18 and
- 20, a sample not containing the capturing material of the invention did not show significant improvement in sharpness, and, further, incurs greater loss in sensitivity, thus posing disadvantage. Sample No. 7, which did not contain a compound represented by formula [I], though containing a compound for capturing fluorescent whitening agent, showed extremely poor sharpness in spite of excellent sensitometric result; this
- 15 sample is not employable in practical operation. In contrast, samples according to the invention Nos. 8 through 11, 13, 15, 17, 19, 21, and 45 through 51, respectively containing both a dye represented by formula [I] of the invention and a compound according to the invention for capturing fluorescent whitening agent, showed satisfactorily high sensitivity and high maximum density even by the rapid processing, and smaller stains, having the maximum absorption wavelength shifted to the longer wave side when compared the sensitivity of the approximate the sensitivity and high maximum density even by the rapid processing, and smaller stains, having the maximum absorption wavelength shifted to the longer wave side when compared the sensitivity.
- to samples not containing a compound for capturing fluorescent whitening agent, and indicated excellent sharpness due to improved spectral absorption property.

As can be understood from the results for sample Nos. 8 through 11, the effects of the invention were attained unchangingly even by using a variously changed combination of a dye represented by formula [I] and a coating solution where a compound or capturing fluorescent whitening agent was incorporate.

Additionally, with dye Nos. 51, 53, 54, 55, 56, 58, 59, 63, 65, 66, 67, 68 and 71, respectively of the invention, the effects above were achieved.

Also, the use of HD-5, HD-13, or HD-15, instead of HD-2, achieved the same effects above.

The use of an emulsion similar to Em-D, except for the variation coefficient of 0.25, also showed the effects of the invention.

Furthermore, the effects of the invention were achieved by a sample prepared by simultaneously applying and drying not only a coating solution for the first layer, which was a coating solution, unlike the original coating solution, prepared by incorporating dye of the invention No. 2, 4, 6 or 7 into the coating solution for the first layer on Example-3, but a coating solution for the second layer, protective layer, containing polyvinyl pyrrolidone, weight average molecular weight, 360.000, at a rate of 0.55 mg dm².

Example-2

45

55

To Em-A through Em-E was added sodium thiosulfate by a conventional method, whereby each emulsion was subjected to sulfur sensitization, and then, to spectral sensitization using sensitizing dye, exemplified compound No. B-11. Thus, green-sensitive silver halide emulsions Em-G Nos. A through E were prepared.

On a polyethylene-laminated paper support were simultaneously applied and dried the coating solutions for the first and second layers. Thus, mono-color light-sensitive element sample No. 2-1 was prepared.

The amounts added for each coating solution are indicated by amounts applied per each independent coat formed.

50 First layer: green-sensitive silver halide emulsion layer

Contains green-sensitive silver halide emulsion, listed in Table-2, at a rate, as converted into metal silver, of 4 mg/dm²: example magenta coupler m-3 at a rate of 4 mg/dm²: dioctylphthalate as a high boiling organic solvent, at a rate of 3 mg/dm²; hydroquinone derivative HQ-1 at a rate of 0.15 mg/dm²; gelatin, at a rate of 14 mg/dm²; and HD-2 as a hardener at a rate of 0.05 mg/dm².

Second layer: protective layer

Contains compound represented formula [I] listed in Table-2, at a rate of 0.1 mg/dm² or comparative-2 specified below as a comparative compound at a rate of 0.1 mg/dm²; polyvinyl pyrrolidone as a capturing material for fluorescent whitening agent at a rate of 0.55 mg/dm²; gelatin, at a rate of 20 mg/dm²; and HD-2 as a hardener, at a rate of 0.05 mg/dm².

Light-sensitive element sample Nos. 2-2 through 2-17 were prepared in a manner identical with that of sample No. 2 above, except that the combination of type of compound represented by formula [I], and coating solution dissolving it, was modified as listed in Table-2, like substances were used in a same weight.

Each of the samples prepared above was evaluated for sharpness in a manner identical with example-1 except that a resolution test chart was printed on each sample using green exposure light in order to form a magenta dye image. The results are listed in Table-2.

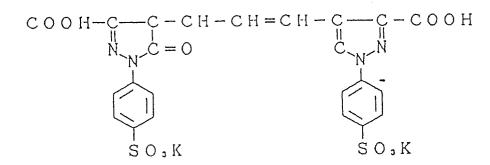
The structural formula of comparative compound, comparative-2, employed as comparison with a compound represented by formula [I] is as follows.

Comparative-2

20

25

10



30

35

40

45

55

5				Comparative	Comparative	Comparative	Comparative	Comparative	Invention							
10		5 1 2 1 2		0.115	0.115	0.117	0.116	0.118	0.098	0.097	960.0	0.098	860.0	0.097	0.098	0.098
15		3390001 E 40		0.58	0.59	0.58	0.60	0.60	0.71	0.71	0.72	0.71	0-70	0.70	0.72	0.71
20		try	Dтах	2.26	2.29	2.37	2.39	2.40	2.43	2.44	2.44	2.44	2.45	2.44	2.45	2.43
25	2	Sensitometry	Relative sensitivity	100	102	105	107	108	113	113	113	112	114	114	114	113
30 35	Table	Layer containing capturing material for fluorescent whitening agent		2nd layer	2nd layer	2nd layer	2nd layer	2nd layer	2nd layer	2nd layer	2nd layer	2nd layer				
40		formula [I]	Layer for coat-	lst layer	lst layer	lst layer	lst layer	lst layer	lst layer	lst layer	lst layer	lst layer				
45		Compound of	Type	Comparative-2	Comparative-2	Comparative-2	Compatative-2	Comparative-2	6	14	10	11	18	19	20	24
50		Emit] et on	Em-G No.	V	ł	C	G	щ	<u>ы</u>	μ	£4	<u>ы</u>	ы —	ы ы	ы	Э
55			No.	2-1	2-2	2-3	-2-4	2-5	2-6	2-7	2-8	2-9	2-10	2-11	2-12	2-13

25

.

Ē

\$

				Table 2 (cor	(continued)				
加山 sion		Compound of formu	of formula [I]	Layer containing capturing material	Sensitometry	try	Sharnness	Stain	
Em-G No.	. –	Type	Layer for coat- ing solution	for fluorescent whitening agent	Relative sensitivity	Datax			
មា	1	25	lst layer	2nd layer	114	2.44	0.71	0.097	Invention
ш		21	lst layer	2nd layer	114	2.45	0.73	0-096	Invention
ш		28	lst layer	2nd layer	113	2.44	0.70	0.097	Invention
ы		34	lst layer	2nd layer	114	2.45	0.72	960*0	Invention
int .		43	lst layer	2nd layer	114	2.43	17.0	0.097	Invention
ш		45	lst layer	2nd layer	114	2.43	0.71	0.096	Invention
<u></u>		35	lst layer	2nd layer	114	2.44	0.73	0.096	Invention
ы		37	lst layer	2nd layer	112	2.44	0.72	960-0	Invention
យ		46	lst layer	2nd layer	113	2.44	0.72	0.098	Invention
ы		21	lst layer	2nd layer	110	2.42	0.63	960-0	Comparative
ы		21	2nd layer	2nd layer	114	2.44	0.73	0.096	Invention

25 ⁻

•

÷

.

.

0 286 331

As apparent from the results in Table-2, when compared to comparative samples, samples according to the invention, incorporating emulsion of the invention having a high silver chloride content which contains both a dye represented by formula [I] of the invention and a capturing material of the invention for fluorescent whitening agent, respectively showed the effects of the invention as demonstrated in Example-1. The use of compound 12, 13, 15, 16, 17, 22, 23, 26, 27, 29, 30, 31, 32, 33, 36, 37, 38, 39, 40, 41, 42, or 44 common showed the effects of the invention.

10 Example-3

The following silver chloro-bromide emulsion was prepared in a manner identical with that of Example-1.

15

5

Emulsion No.	Grain size (µm)	Silver chloride content (mol%)
Em-F	0.8	95

20

Into each of Em-D, Em-E and Em-F prepared in Example-1 and Example-2 was added chloroauric acid at a rate of 5 × 10⁻⁵ mol per mol silver halide, and. further, added sodium thiosulfate at a rate of 2 mg per mol silver halide for chemical sensitization. Next, Em-D sensitized by gold and sulfur as mentioned above was subjected to spectral sensitization using a sensitizing dye, exemplified compound No. D-3, so as to prepare red-sensitive silver halide emulsion Em-R No. D2. Em-E was spectrally sensitized using sensitizing dye, exemplified compound No. B-4, so as to prepare green-sensitive silver halide emulsion Em-G No. E2. Em-F was spectrally sensitized using the following sensitizing dye SD-A, so as to prepare blue-sensitive silver halide emulsion Em-B No. F.

- On a polyethylene-laminated paper support were simultaneously applied and dried the coating solutions prepared based on Em-R No. D2, Em-G No. E2 and Em-B No. F above. Thus, multi-color photographic light-sensitive element was prepared.
- The amounts added for each coating solution are indicated by amounts applied per each independent ³⁵ coat formed.

First layer: blue-sensitive silver halide emulsion layer

- ⁴⁰ Contains yellow coupler Y-5 at a rate of 8 mg dm²; blue-sensitive silver halide emulsion Em-B No. F at a rate, as converted into metal silver, for 3 mg dm²; high boiling organic solvent S-1 at a rate of 3 mg dm²; and gelatin at a rate of 16 mg dm².
- ⁴⁵ Second layer: intermediate layer

Contains hydroquinone derivative HQ-1 at a rate of 0.45 mg/dm²: and gelatin, at a rate of 4 mg/dm².

50 Third layer: green-sensitive silver chloro-bromide emulsion layer

Contains magenta coupler m-3 at a rate of 4 mg dm²; a dye listed in Table-3 at a rate of 0.1 mg dm²; green-sensitive silver chloro-bromide emulsion Em-G No. E2 at a rate, as converted into metal silver, of 3 mg/dm²; high boiling organic solvent S-2 at a rate of 4 mg/dm²; and gelatin at a rate of 16 mg/dm².

Fourth layer: intermediate layer

Contains ultraviolet absorbents, UV-1 at a rate of 3 mg/dm² and UV-2 at a rate of 3 mg/dm²; high boiling organic solvent S-1 at a rate of 4 mg/dm²; hydroquinone derivative HQ-1 at a rate of 0.45 mg/dm²; and gelatin at a rate of 14 mg/dm².

Fifth layer: red-sensitive silver chloride emulsion layer

- Contains cyan couplers, CI-7 at a rate of 2 mg/dm² and CI-5 at a rate of 2 mg/dm²; high boiling organic solvent S-2 at a rate of 2 mg/dm²; red-sensitive silver chloride-bromide emulsion EM-R No. D2 at a rate, as converted into metal silver, of 2 mg/dm²; a dye listed in Table-3, amount of addition also listed in Table-3; and gelatin at a rate of 14 mg/dm².
- 15

5

Sixth layer: intermediate layer

Contains ultraviolet absorbents. UV-1 at a rate of 2 mg/dm² and UV-2 at a rate of mg/dm²; capturing material listed in Table-3 for fluorescent whitening agent, amount of addition also listed in Table-3; high boiling organic solvent S-1 at a rate of 2 mg/dm²; and gelatin at a rate of 6 mg/dm².

Seventh layer: protective layer

25 Contains gelatin at a rate of 9 mg/dm².

Sample Nos. 3-1 through 3-26 were prepared by variously changing type and amount added of a compound represented by formula [I] and being added into the third and fifth layers, and also by changing type and amount added by a compound as a capturing material of the invention being added into the sixth layer. Additionally, sample Nos. 3-27 through 3-32 were prepared by incorporating a dye of the invention into a coating solution for the second, fourth, sixth or seventh layer.

Those dyes added into the third and fifth layers as listed in Table-3 were as follows: comparative dye No. 1 was same as that in example-1, comparative dye No. 2 was same as that in example-2. The structural formulas of high boiling organic solvents S-1 and S-2, ultraviolet absorbents UV-1 and UV-2, and sensitizing dye SD-A are as follows.

35

30

40

45

50

0 286 331

÷

ž,

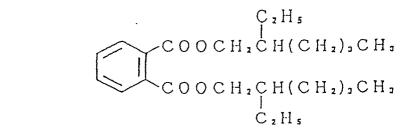
Ģ

(S-1) $CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$ $CH_{3}CH_{3$

15

20

(S-2)



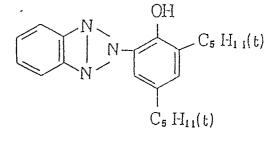
25

30

35

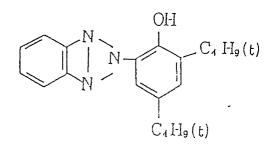
40

45



(UV-2)

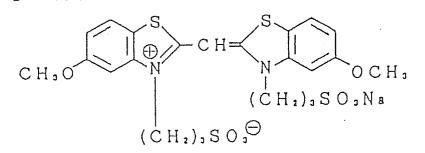
(UV - 1)



50



(SD - A)



The respective samples prepared above were subjected to the following processes without undergoing exposing, or after undergoing exposing through an optical wedge with photographic sensitometer Model KS-15 7 manufactured by Konica Corporation.

[Treatment]

20		Temperature	Time
	Color developing	34.7 ± 0.3°C	45 sec.
	Bleach-fixing	34.7 ± 0.3°C	45 sec.
25	Stabilizing	30 to 34°C	2 min.
	Drying	60 to 80°C	2 min.

30

800 m t [Color developer] Pure water Diethylene glycol 12 m l N.N-diethylhydroxylamine 12 m t 35 Potassium chloride 2.2 g Potassium sulfite 0.2 g N-ethyl-N-ß-methanesulfonamideethyl-3-methyl-4-aminaniline sulfate 5.0 g Diaminostylbene water soluble fluorescent whitening agent 2.0 g Water was added to the components above to prepare one liter solution, thereby pH level was adjusted to 40 10.1.

600 m t [Bleach-fixer] Pure water Ferric ammonium ethylenediamineteraacetate dihydrate 60 g 45 Ethylenediaminetetraacetic acid 3 g Ammonium thiosulfate (70% aqueous solution) 100 m i Ammonium sulfite (40% aqueous solution) 27.5 m t Water was added to the components above to prepare one liter solution, thereby pH level was adjusted to 5.5.

50

Samples treated or not treated were subjected to performance test as specified in (1) through (3) of Example-1.

Table-3 lists the test results.

	Statn ntatn		060-0	060.0	160.0	0.091	0.092	060-0	0.090	0.097	060.0	060.0	060.0
	Shanthess		0.37	0.39	0.47	0.51	0.52	0.50	0.53	0.52	0.49	0.51	0.52
	l tivity	¢	100	66	104	104	103	104	101	102	105	104	105
	Relative sensitivity	U	100	100	102	102	100	100	101	100	102	103	103
	Relativ	В	100	100	100	100	100	100	100	100	101	101	101
	Capturing material in	6th layer (mg/dm ²)	1		P-1 (0.2)	P-1 (0.5)	P-1 (1.0)	P-1 (0.2)	P-1 (0.2)	p-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)
e S	6th,	Coating solution	1										
Table	Dye in 2nd, 4th, or 7th layer	Example compound formula [I] (mg/dm ²)	•										
	م و تر م و تر		Comparative-1 (0.1)	(0.1)	(0.1)	(1.0)	(1.0)	(0.1)	(0.1)	(0.1) (0.1)	(0.1)	(0.1)	(1.0)
	Line in 5th 1	Dye in 5th la (mg/dm ²)		47	47	47	47	47	47	47 Comparative-	48	48	60
		Dye in 3rd layer (mg/dm²)		Comparative-2 (0.1)	Comparative-2 (0.1)	Comparative-2 (0.1)	Comparative-2 (0.1)	([-0]) ((0.1)	(0.1)	Comparative-2 (0.1)	0 (0.1)	6 (0.1)
	i		Comparative-2 (0.1)	Compara	Compara	Compara	Compará	10	21	21	Comparé	10	18
		samp.le No.	3-1	3-2	3-3	3-4	3-5	3-6	3-7	3-8	3-9	3-10	3-11

•

.

ş

	Stain		060.0	0.096	060.0	060-0	060-0	060-0	0.091	160.0	060.0	060.0	060.0
	Shanrness		0.51	0.53	0.53	0.56	0.51	0.51	0.51	0.52	0.49	0.53	0.51
	itivity	ж	104	100	105	85	105	105	104	106	105	105	88
	Relative sensitivity	υ	104	100	104	9 4	104	104	102	102	100	101	67
	Relati	щ	101	100	101	95	102	102	101	101	100	100	86
1)	Capturing material in	6th layer (mg/dm ²)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-2 (0.5)	P-2 (0.5)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)
(continued	6th,	Coating solution				1]						
Table 3 (cont	Dye in 2nd, 4th, or 7th layer	Example compound formula [1] (mg/dm ²)							2				
ц	Dye in 5th layer (mg/dm²)		(0.1)	(0.1) (0.1) (0.1)	(0.1)	([.0)	(0.1)	(1.0)	(1.0)	(0.1)	(["0)	(0.1)	(0.1)
			48	47 Comparative-1	48	48	48	48	60	74	74	74	47
	3rd läver	Dye in 3rd layer (mg/dm ²)		(0.1)	(0.1)	(0.1)	(1.0)	(0.1)	(0.1)	(1.0)	Comparative-2 (0.1)	(0.1)	(0.1)
	1		20	.20	21	21	34	39	33	33	Comparat	10	6
	Sample	No.	3-12	3-13	3-14	3~15	3-16	3-17	3-18	3-19	3-20	3-21	3-22

. .

ż

-

÷

	-			r									
5		statn Statn		060-0	0.090	160.0	0.092	060-0	060*0	0.091	060-0	060.0	060.0
10		Shanrness		0.51	0.52	0.56	0.59	0.52	0.52	0.52	0.53	0.52	0.52
		tivity	æ	105	105	86	79	105	105	105	105	105	105
15		Relative sensitivity	ю	102	102	4 6	88	104	103	τοι	102	102	102
20		Relati	ß	100	101	8	63	101	101	101	101	101	101
20	2)	Capturing material in	6th layer (mg/dm ²)	р-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)	P-1 (0.2)
25	(continued	6th,	Coating solution					2nd layer	4th layer	2nd layer	4th layer	6th layer	7th layer
30 35	Table 3 (co	Dye in 2nd, 4th, or 7th layer	Example compound formula [I] (mg/dm ²)					21 (0.1)	21 (0.1)	74 (0.1)	74 (0.1)	74 (0.1)	74 (0.1)
40	H	Dye in 5th layer (mg/dm ²)		74 (0.1)	74 (0.1)	74 (0.2)	74 (0.3)	74 (0.1)	74 (0.1)				
4 5		3rd laver	(zmb/gm)	(0.1)	([.0)	(0.1)	(1.0)			(0.1)	(0.1)	(1.0)	(0.1)
50				34	21	21	21			21	21	21	21
55		o l cmeo	No.	3-23	3-24	3-25	3-26	3-27	3-28	3-29	3-30	3-31	3-32

ŝ,

ŧ

Ē

* P-1: Pulyvinyl pyrrolidone, weight average molecular weight, 360,000

Vinylpyrrolidone-vinyl acetate (7 : 3) copolymer

P-2:

As apparent from the results in Table-3, when compared to comparative sample Nos. 3-1 through 3-32 according to the invention show significantly improved sensitivity-sharpness correlation in the case of the multi-layered samples. Additionally, it is also apparent that increased addition of capturing material for fluorescent whitening agent in the sixth layer remarkably improved the sharpness.

It is also apparent the effects of the invention are attained regardless of to which coating solution the dye of the invention is added; a coating solution for any of the second, fourth, sixth and seventh layers.

The effects of the invention were attained even by replacing sensitizing dye D-3 in Em-R No. D2 with D-13, or by replacing sensitizing dye B-4 in Em-G No. E2 with B-7.

10

5

Example-4

Sample Nos. 4-1 through 4-16 were prepared in a manner identical with sample No. 3-25 in Example-3, except that the combination of a yellow coupler in the first layer, a magenta coupler in the third layer, and a cyan coupler in the fifth layer was changed, while maintaining same mol ratios, as listed in Table-4 below.

- 20
- 25
- 30
- 35
- 40

45

50

Tabl	e-	4
------	----	---

÷

â

₹

5	L					
	Sample No.	Yellow coupler in 1st layer	Magenta coupler in 3rd layer	Cyan coupler in 5th layer	Sharpness	Stain
10	4-1	¥-2	m-1	CI-6/CI-7	0.56	0.091
	4-2	· Y-2	m-3	CI-6/CI-7	0.56	0.092
:	4-3	¥-2	m-5	CI-6/CI-7	0.56	0.091
15	4-4	¥-2	m-12	CI-6/CI-7	0.56	0.091
	4-5	¥-2	m-14	CI-6/CI-7	0.56	0.092
20	4-6	Y-2	m-18	CI-6/CI-7	0.56	0.092
	4-7	Y-4	m-1	CI-5/CI-7	0.56	0.092
25	4-8	Y-4	m-1	CI-5/CI-7	0.56	0.092
	4-9	¥-4	m-1	CI-10	0.56	0.092
	4-10	¥-4	m-5	CI-10	0.56	0.091
30	4-11	¥-б	m-3	CI-11	0.56	0.092
	4-12	¥-б	m-4	CI-11	· 0.56	0.091
35	4-13	Ү -б	m-4	CI-11	0.56	0.091
	4-14	¥-8	m-3	CI-5/CI-7	0.56	0.092
40	4-15	Y-8	m-12	CI-5/CI-7	0.56	0.091

* Mixing ratio of CI-5/CI-7 is 1 : 1, in terms of molar ratio.

45

Sample Nos. 4-1 through 4-16 mentioned above were tested in a manner identical with that of Example-3, whereby it was confirmed that like effects of the invention were achieved even by changing couplers in the respective dyes while the dyes of the invention were maintained.

50

Claims

 A silver halide photographic light-sensitive element comprising a support having thereon photographic component layers including at least one silver halide emulsion layer which contains silver halide grains comprising not less than 90 mol% of silver chloride, and at least one layer among said photographic component layers contains a compound presented by the following formula [I] and a capturing material for fluorescent whitening agent:

Formula [I]

5

$$R_{1} - C - C = L_{1} - (L_{2} = L_{3})_{m} - (L_{4} = L_{5})_{n} - C - R_{2}$$

$$H_{0} - C - R_{1}$$

10

15

wherein R₁ and R₂ independently represent a -CN group, a -CFR₃R₅ group, a -COR₇ group, a -COR₇ group, a -COR₇ group or a -CONHR₅ group, in which R₅ and R₆ independently represent a hydrogen atom, a fluorinated alkyl group having one to four carbon atoms, and R represents a an alkyl group or an aryl group which may have a substituent; R₃ and R₄ independently represent a hydrogen atom, or an aliphatic group, an alicyclic group, an aromatic group or a heterocyclic group, which may have a substituent; L₂, L₂, L₄ and L₆ independently represent a methine group which may have a substituent; and m and n represent an integer of 0 or 1, respectively.

2. The element of claim 1, wherein said capturing material is a polyvinyl pyrrolidone or its copolymer.

3. The element of claim 1, wherein a coating weight of said capturing material is within the range of from 0.05 mg dm² to 3.0 mg/dm².

4. The element of claim 3, wherein a coating weight of said capturing material is within the range of from 0.1 mg/dm² to 2.0 mg/dm².

5. The element of claim 1, wherein an amount of said capturing material is within the range of from 0.1 % to 50 % by weight to the binder contained in the photographic component layer in which said capturing material is contained.

6. The element of claim 5, wherein an amount of said capturing material is within the range of from 1 % to 30 % by weight to the binder contained in the photographic component layer in which said capturing material is contained.

7. The element of claim 1, wherein a coating weight of said compound represented by the formula [I] is within the range of from 0.01 mg/dm² to 1.0 mg/dm².

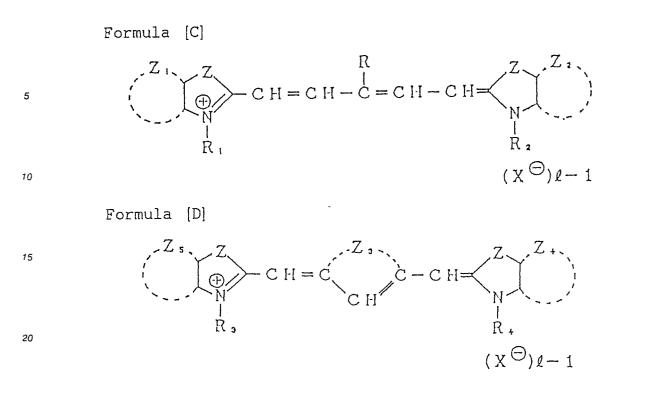
8. The element of claim 7, wherein a coating weight of said compound represented by the formula [I] is within the range of from 0.03 mg/dm² to 0.4 mg dm².

9. The element of claim 1. wherein at least one said silver halide emulsion layer containing silver halide grains comprising not less than 90 mol % of silver chloride is spectrally sensitized with at least one sensitizing dye selected from the compounds represented by the following formula [C] or [D]:

40

45

50



÷

ñ

²⁵ wherein R represents a hydrogen atom or an alkyl group which may have a substituent: R.: through ²⁵ R₁₄ independently represent an alkyl group or an aryl group, which may have a substituent. Z: Z₂, Z₃ and Z₅ independently represent a group of atoms necessary to complete a benzene ring or a naphthalene ring condensed into a thiazole ring or selenazole ring; z₃ represents a hydrocarbon group necessary to complete a six-membered ring; t represents an integer of 1 or 2; Z represents a sulfur atom or a selenium atom; and X represent an anion.

10. The element of claim 1. wherein said photographic component layers are hardened with a hardner selected from the compounds represented by the following formula [HDA] or [HDA]:

 \mathbb{R}_{d^2} \mathbb{N}_{U} \mathbb{N}_{U

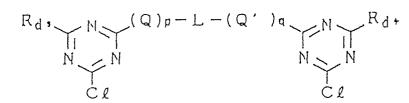
Formula [HDA]

35

40

⁴⁵ wherein Rd+ represents a chlorine atom, a hydroxy group, or an alkyl group, an alkoxy group, an alkylthio group, which may have a substituent, an -OM group, an -NR'R' group or an -NHCOR group, in which M represents a monovalent metal atom; R' and R'' independently represent a hydrogen atom, an alkyl group or an aryl group, which may have a substituent; and R represents an alkyl group or an aryl group, which may have a substituent; and R represents an alkyl group or an aryl group, which may have a substituent; and Rd₂ represents a group, excluding chlorine atom, in the same signification as Rd+:

Formula [HDB]



wherein Rd₃ and Rd₄ independently represent a chlorine atom, a hydroxy group, or an alkyl group,, an alkoxy group, wehich may have a substituent, or an -OM group, in which M represents a monovalent metal atom; Q and Q' independently represents a binding atom or group of -O-, -S-, or -NH-: L represents an alkylene group or an arylene group; and p and q represent an integer of 0 or 1, respectively.

11. A method for processing a silver halide photographic light-sensitive element comprising a step of developing said silver halide photographic light-sensitive element with a color developer containing a primary aromatic amine color developing agent and not containing benzyl alcohol for 20 to 60 seconds, wherein said silver halide photographic light-sensitive element comprising a support having thereon photographic component layers including at least one silver halide emulsion layer which contains silver halide grains comprising not less than 90 mol% of silver chloride, and at least one layer among said photographic component layers contains a compound presented by the followinf formula [I] and a capturing material for a fluorescent whitening agent:

25

30

5

a

à

$$R_{1} - C - C = L_{1} - (L_{2} = L_{3})_{m} (L_{4} = L_{5})_{n} C - R_{2}$$

$$H = C - C - R_{2}$$

$$H = C - C - R_{2}$$

$$H = C - C - R_{2}$$

wherein R- and R₂ independently represent a -CN group. a -CFR₅R₅ group. a -COR₇ group. a -COOR₇
group or a -CONHR₅ group, in which R₅ and R₆ independently represent a hydrogen atom, a fluorinated alkyl group having one to four carbon atoms, and R₇ represents a an alkyl group or an alkyl group, which may have a substituent; R₃ and R₄ independently represent a hydrogen atom, or an aliphatic group, an alicyclic group, an aromatic group or a heterocyclic group, which may have a substituent; L₁, L₂, L₃, L₄ and L₅ independently represent a methine group which may ave a substituent; and m and n represent an integer of 0 or 1, respectively.

45

A

50