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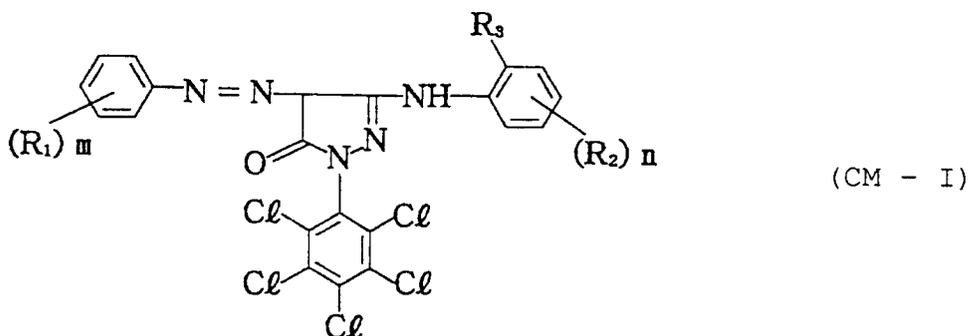
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Light-sensitive silver halide color photographic material.

Disclosed is a light-sensitive silver halide color photographic material having photographic constituent layers including a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer on a support, characterized in that at least one green-sensitive silver halide emulsion layer contains at least one colored magenta coupler represented by the following formula (CM - I), and at least one photographic constituent layer contains at least one vinyl sulfone type hardener,



wherein R_1 represents a substituent; R_2 represents an acylamino group, a sulfonamide group, an imide group, a carbamoyl group, a sulfamoyl group, an alkoxy group, an alkoxy carbonyl group or an alkoxy carbonylamino group; R_3 represents a halogen atom or an alkoxy group; m represents an integer of 0 to 5; and n represents an integer of 0 to 4.

BACKGROUND OF THE INVENTION

This invention relates to a light-sensitive silver halide color photographic material, more specifically to a light-sensitive silver halide color photographic material in which less fog occurs, processing fluctuation is small and also fluctuation between printers is small.

In a light-sensitive color photographic material, the respective yellow, magenta and cyan dyes formed from couplers do not always have ideal absorption characteristics. For example, a magenta dye generally absorbs blue light slightly in addition to green light which should be absorbed thereby, so that distortion of color reproducibility occurs. In order to prevent such distortion of color reproducibility, a coupler colored in yellow or magenta has been used before coupling reaction with an oxidized product of an aromatic primary amine color developing agent. The former coupler is the so-called colored magenta coupler, and the latter is the so-called colored cyan coupler.

Such an automasking method using a colored coupler has been described specifically in, for example, J. Phot. Soc. Am., 13, 94 (1947), J. Opt. Soc. Am., 40, 166 (1950) or J. Am Chem. Soc., 72, 1533 (1950).

As a colored magenta coupler having its main absorption in a blue light region, there have been disclosed 1-phenyl-3-acylamino-4-phenylazo-5-pyrazolone in U.S. Patents No. 2,428,054 and No. 2,449,966; a coupler having a 4-methoxyallylazo group in U.S. Patent No. 2,763,552; 1-phenyl-3-anilino-4-phenylazo-5-pyrazolone in U.S. Patent No. 2,983,608; a coupler having a naphthylazo group in U.S. Patents No. 3,519,429 and No. 3,615,506; a coupler having a water-soluble group in U.S. Patent No. 1,044,778; a coupler having a hydroxyphenylazo group in U.S. Patent No. 3,476,564, and Japanese Provisional Patent Publications No. 123625/1974, No. 131448/1974 and No. 52532/1979; a coupler having an acylaminophenylazo group in Japanese Provisional Patent Publication No. 42121/1977; a coupler having a substituted alkoxyphenylazo group in Japanese Provisional Patent Publication No. 102723/1977; and a coupler having a thiophenylazo group in Japanese Provisional Patent Publication No. 63016/1978, respectively.

However, these colored magenta couplers have various problems that a large amount is required to be added due to small molar absorption coefficient, it is difficult to set their main absorptions to a preferred range, an masking effect is small due to low development activity, development activity is high but fog occurs easily, further, stability relative to light, heat or humidity is low, and a magenta dye formed by reacting with a color developing agent has short wavelength. Thus, these couplers are not satisfactory, and under the present situation, their characteristics are maintained somehow by using several couplers in combination. In recent years, a high sensitivity fine particle silver halide emulsion and a high color forming magenta coupler have been used, so that characteristics required to a colored magenta coupler have been heightened to a great extent.

In recent years, it has been found that particularly when a color paper is printed by using a color negative film, distortion of color hue of finished color prints (hereinafter referred to as "fluctuation between printers") occurs due to difference in kinds of used instruments for printing (hereinafter referred to as "printer"). It has been clarified that one of the reasons is color tone of a color forming dye obtained from a colored magenta coupler used in a color negative film.

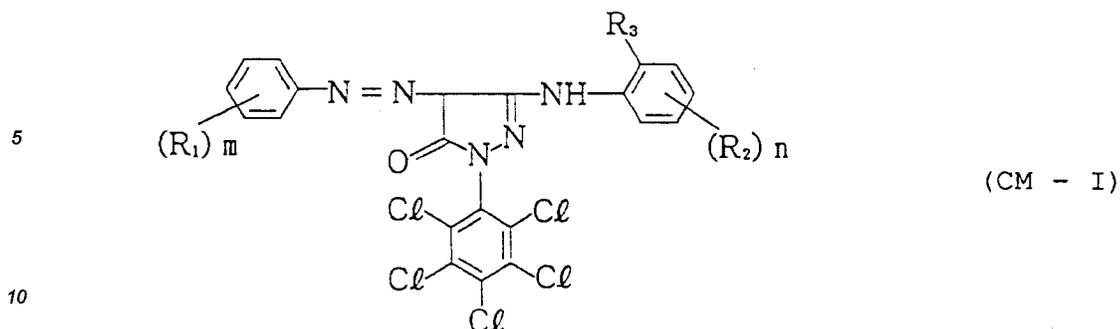
The fluctuation between printers has been greatly improved by using a colored magenta coupler disclosed in Japanese Provisional Patent Publication No. 16939/1992. However, according to investigations by the present inventors, it has been clarified that there are problems that fog is increased when said colored magenta coupler is used, and when a light-sensitive material is subjected to exposure and then color development processing, fluctuation of photographic characteristics (hereinafter referred to as "processing fluctuation") is increased due to change of conditions such as concentration, temperature and pH of a color developing agent in a color developing solution.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive silver halide color photographic material in which less fog occurs, processing fluctuation is small and also fluctuation between printers is small.

The above object of the present invention can be accomplished by the following light-sensitive silver halide color photographic material.

A light-sensitive silver halide color photographic material having photographic constituent layers including a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer on a support, characterized in that at least one green-sensitive silver halide emulsion layer contains at least one colored magenta coupler represented by the following formula (CM - I), and at least one photographic constituent layer contains at least one vinyl sulfone type hardener,



wherein R_1 represents a substituent; R_2 represents an acylamino group, a sulfonamide group, an imide group, a carbamoyl group, a sulfamoyl group, an alkoxy group, an alkoxy carbonyl group or an alkoxy carbonylamino group; R_3 represents a halogen atom or an alkoxy group; m represents an integer of 0 to 5; and n represents an integer of 0 to 4.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 In the following, the present invention is explained in detail.

In the formula (CM-I), as the substituent represented by R_1 , there may be mentioned, for example, an alkyl group, an alkoxy group, an aryl group, an acylamino group, a sulfonamide group, a hydroxyl group, a halogen atom, an alkoxy carbonyl group, an acyl group, a carbamoyl group, a sulfamoyl group and a carboxyl group, and these groups may further have a substituent(s). R_1 is preferably an alkyl group, an alkoxy group, a hydroxyl group or an acylamino group, most preferably an alkoxy group.

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The acylamino group represented by R_2 may include, for example, a 2,4-di-*t*-pentylphenoxyacetamide group and a 4-(2,4-di-*t*-pentylphenoxy)butanamide group; the sulfonamide group, for example, a 4-dodecyloxyphenylsulfonamide group; the imide group, for example, an octadecenylsuccinimide group; the carbamoyl group, for example, a 4-(2,4-di-*t*-pentylphenoxy)butylaminocarbonyl group; the sulfamoyl group, for example, a tetradecanesulfamoyl group; the alkoxy group, for example, a methoxy group, an ethoxy group and an octyloxy group; the alkoxy carbonyl group, for example, a tetradecanoxycarbonyl group; and the alkoxy carbonylamino group, for example, a dodecyloxy carbonylamino group. R_2 is preferably an acylamino group substituted at the para-position relative to R_3 .

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The halogen atom represented by R_3 may include, for example, a chlorine atom, a bromine atom and a fluorine atom, and the alkoxy group may include, for example, a methoxy group and a dodecyloxy group. R_3 is preferably a chlorine atom. m is preferably 1 or 2, and n is preferably 1.

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In the following, specific examples of the compound represented by the above formula (CM - I) according to the present invention are shown, but the present invention is not limited to these.

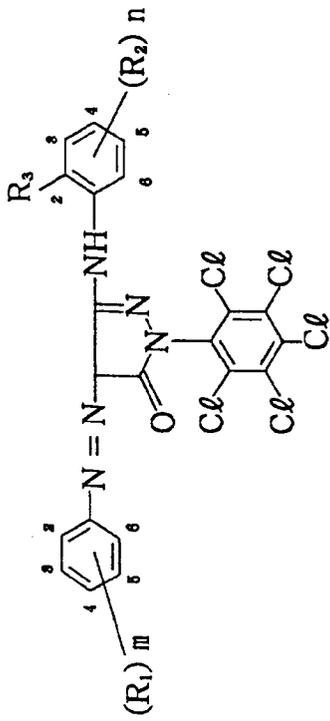
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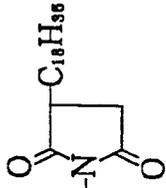
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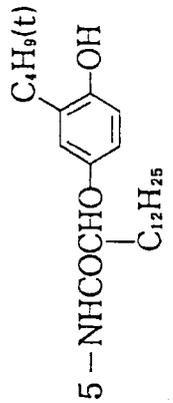
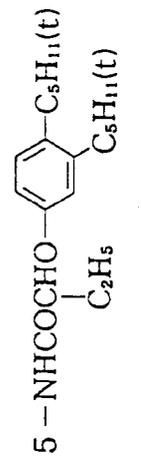
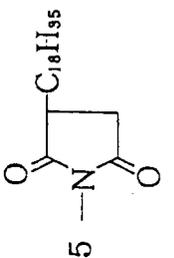
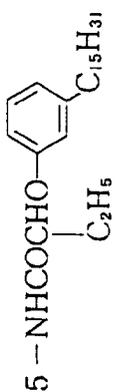
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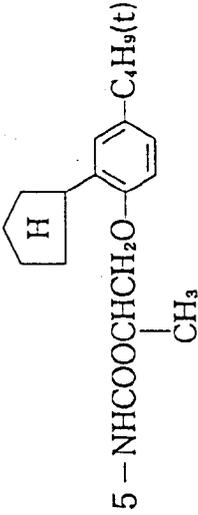
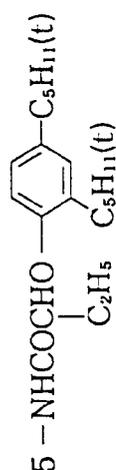
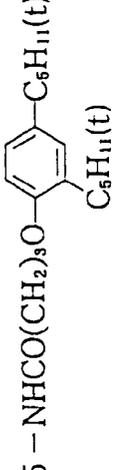
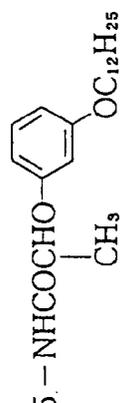


Compound	(R ₁) _m	(R ₂) _n	R ₃
CM - 1	3 - OCH ₃ , 4 - OCH ₃	5 - NHCOCH ₂ O - C ₆ H ₁₁ (t) C ₈ H ₁₁ (t)	-Cl
CM - 2	3 - OCH ₃ , 4 - OCH ₃	5 - NHCOC ₁₈ H ₂₇	-Cl
CM - 3	3 - OCH ₃ , 4 - OCH ₃	4 - NHSO ₂ C ₁₆ H ₃₃	-Cl
CM - 4	3 - OCH ₃ , 4 - OCH ₃	5 - 	-Cl
CM - 5	3 - OCH ₃ , 4 - OCH ₃	5 - NHSO ₂ C ₁₆ H ₃₃	-Cl

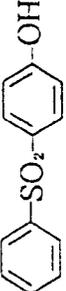
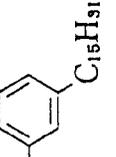
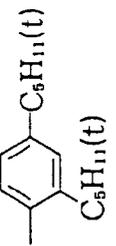
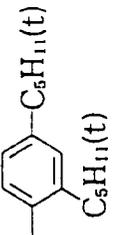
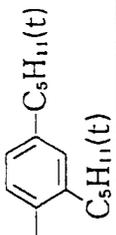
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Compound	$(R_1)_m$	$(R_2)_n$	R_3
CM - 6	3 - OCH ₃ , 4 - OCH ₃	5 - CONHC ₁₄ H ₂₉	- Cl
CM - 7	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	5 - NHCOC ₁₃ H ₂₇	- Cl
CM - 8	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	 <p>5 - NHCOC(12H₂₅)-2-(4-hydroxyphenyl)acetamide</p>	- Cl
CM - 9	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	 <p>5 - NHCOC(2H₅)-2-(4-(1,1-diphenylethyl)phenyl)acetamide</p>	- Cl
CM - 10	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	 <p>5 - NHCOC(18H₃₅)-2-imidazolidinone</p>	- Cl
CM - 11	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	 <p>5 - NHCOC(2H₅)-2-(4-(15H₃₁)phenyl)acetamide</p>	- Cl

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Compound	(R ₁) m	(R ₂) n	R ₃
CM - 12	4 - OCH ₃	 <p>5 - NHCOCHO-CH₂O-C₆H₄-C₄H₉(t) CH₃</p>	-Cl
CM - 13	4 - OCH ₃	 <p>5 - NHCOCHO-CH₂O-C₆H₄-C₅H₁₁(t) CH₃</p>	-Cl
CM - 14	4 - OCH ₃	<p>-(n = 0)</p>	-OC ₁₂ H ₂₅
CM - 15	3 - CH ₃ , 4 - OH	 <p>5 - NHCO(CH₂)₃O-C₆H₄-C₆H₁₁(t) CH₃</p>	-Cl
CM - 16	3 - CH ₃ , 4 - OH	 <p>5 - NHCOCHO-CH₂O-C₆H₄-OC₁₂H₂₅ CH₃</p>	-Cl
CM - 17	4 - OH	<p>5 - NHCOOC₁₆H₃₃</p>	-Cl
CM - 18	4 - OH	<p>4 - OC₈H₁₇, 5 - OC₈H₁₇</p>	-Cl

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Compound	(R ₁) ^m	(R ₂) ⁿ	R ₃
CM - 19	4 - OCH ₂ CH ₂ O- 	5 - NHCOCHO-  -OH C ₁₀ H ₂₁	-OCH ₃
CM - 20	4 - NHCOC ₄ H ₉ (t)	5 - NHCOC ₁₃ H ₂₇	-Cl
CM - 21	4 - NHCOC ₄ H ₉ (t)	5 - NHCOCHO-  -C ₁₅ H ₃₁ C ₂ H ₅	-Cl
CM - 22	3 - C ₃ H ₇ (i), 4 - C ₃ H ₇ (i)	5 - COOC ₁₂ H ₂₅	-Cl
CM - 23	3 - C ₃ H ₇ (i), 4 - C ₃ H ₇ (i)	4 - SO ₂ N(C ₈ H ₁₇) ₂	-F
CM - 24	3 - OCH ₃ , 4 - OCH ₃	5 - NHCOCHO-  -C ₅ H ₁₁ (t) C ₂ H ₅	-Cl
CM - 25	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	5 - NHCOCHO-  -C ₅ H ₁₁ (t) C ₂ H ₅	-Cl
CM - 26	4 - OC ₂ H ₅	5 - NHCOCHO-  -C ₅ H ₁₁ (t) C ₂ H ₅	-Cl

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Compound	(R ₁) ^m	(R ₂) ⁿ	R ₃
CM - 27	4 - OC ₃ H ₇	$5 - \text{NHCOCHO} - \begin{array}{c} \text{C}_5\text{H}_{11}(\text{t}) \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}_5\text{H}_{11}(\text{t}) \end{array}$	- Cl
CM - 28	4 - OC ₄ H ₉	$5 - \text{NHCOCHO} - \begin{array}{c} \text{C}_5\text{H}_{11}(\text{t}) \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}_5\text{H}_{11}(\text{t}) \end{array}$	- Cl
CM - 29	4 - OCH ₃	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \begin{array}{c} \text{C}_5\text{H}_{11}(\text{t}) \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}_6\text{H}_{11}(\text{t}) \end{array}$	- Cl
CM - 30	3 - OCH ₃ , 4 - OCH ₃	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \begin{array}{c} \text{C}_5\text{H}_{11}(\text{t}) \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}_5\text{H}_{11}(\text{t}) \end{array}$	- Cl
CM - 31	3 - OC ₂ H ₅ , 4 - OC ₂ H ₅	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \begin{array}{c} \text{C}_5\text{H}_{11}(\text{t}) \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}_5\text{H}_{11}(\text{t}) \end{array}$	- Cl
CM - 32	4 - OC ₂ H ₅	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \begin{array}{c} \text{C}_5\text{H}_{11}(\text{t}) \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}_5\text{H}_{11}(\text{t}) \end{array}$	- Cl

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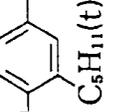
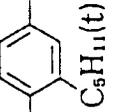
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Compound	(R_1) m	(R_2) n	R_3
CM - 33	4 - OC ₃ H ₇	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \text{C}_6\text{H}_4 - \text{C}_5\text{H}_{11}(t)$ 	-Cl
CM - 34	4 - OC ₄ H ₉	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \text{C}_6\text{H}_4 - \text{C}_5\text{H}_{11}(t)$ 	-Cl
CM - 35	4 - NHCOC ₄ H ₉ (t)	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \text{C}_6\text{H}_4 - \text{C}_5\text{H}_{11}(t)$ 	-Cl
CM - 36	4 - OH	$5 - \text{NHCO}(\text{CH}_2)_3\text{O} - \text{C}_6\text{H}_4 - \text{C}_5\text{H}_{11}(t)$ 	-Cl

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An amount of the colored magenta coupler of the present invention is preferably 0.01 to 1.0 g/m², more preferably 0.03 to 0.3 g/m² based on a light-sensitive material.

The colored magenta coupler represented by the formula (CM - I) of the present invention can be generally synthesized by the so-called diazo coupling reaction which has been conventionally carried out, for example,

a method disclosed in Japanese Patent Publication No. 6540/1971. That is, a desired colored coupler can be obtained by diazotizing an aniline derivative at 0 to - 10 °C in water, hydrated alcohol or hydrated acetone by using 1 to 5-fold moles of conc. hydrochloric acid and 1 to 1.2-fold moles of sodium nitrite, and adding the resulting solution at - 5 to - 10 °C to a pyridine solution of a magenta coupler with an equimolar amount to the

above aniline derivative, which solution is prepared separately, to effect diazo coupling.

Next, specific synthesis examples of the colored magenta coupler represented by the formula (CM - I) of the present invention are described.

Synthesis example 1 (synthesis of CM - 7)

1.4 g of 3,4-diethoxyaniline was dissolved in 3 ml of conc. hydrochloric acid and 18 ml of water by once heating, and then the solution was cooled to - 3 °C. The resulting solution was diazotized by adding 5.3 ml of a 10 % sodium nitrite aqueous solution, and the mixture was stirred at -3 °C for 20 minutes. Subsequently, 0.1 g of urea was added to decompose excessive nitrous acid. Separately, 5.2 g of 1-(2,3,4,5,6-pentachlorophenyl)-3-(2-chloro-5-tetradecanamidoanilino)-5-pyrazolone was dissolved in 100 ml of pyridine, and the solution was cooled to - 5 to - 10 °C and stirred. To the resulting solution was added slowly a solution of the diazonium salt prepared as described above.

After 3 hours, the reaction mixture was poured into 400 ml of ice water containing 100 ml of conc. hydrochloric acid. Crystals were collected by filtration, washed with water, dried and then recrystallized from a mixed solution of ethyl acetate and acetonitrile to obtain 5.5 g of CM - 7.

Synthesis example 2 (synthesis of CM - 13)

1.0 g of 4-methoxyaniline was dissolved in 3 ml of conc. hydrochloric acid and 20 ml of water by once heating, and then the solution was cooled to - 3 °C. The resulting solution was diazotized by adding 5.3 ml of a 10 % sodium nitrite aqueous solution, and the mixture was stirred at - 3 °C for 20 minutes. Subsequently, 0.1 g of urea was added to decompose excessive nitrous acid.

Separately, 5.6 g of 1-(2,3,4,5,6-pentachlorophenyl)-3-{2-chloro-5-[α -(2,4-di-t-amylphenoxy)butanamide]anilino)-5-pyrazolone was dissolved in 100 ml of pyridine, and the solution was cooled to - 5 to - 10 °C and stirred. To the resulting solution was added slowly a solution of the diazonium salt prepared as described above. After 3 hours, the reaction mixture was poured into 400 ml of ice water containing 100 ml of conc. hydrochloric acid. Crystals were collected by filtration, washed with water, dried and then recrystallized from a mixed solution of acetonitrile and ethyl acetate to obtain 5.1 g of CM - 13.

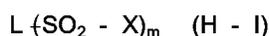
Structures of these compounds were identified by NMR spectra and Mass spectra.

The colored magenta coupler represented by the above formula (CM - I) of the present invention may be used alone or in combination of two or more kinds. In general, based on the principle of automasking, at least one magenta coupler which is substantially colorless is used in combination.

Next, the vinyl sulfone type hardener according to the present invention is described.

The vinyl sulfone type hardener to be used in the present invention includes, for example, aromatic compounds as described in German Patent No. 11 00 942 and U.S. Patent No. 3,490,911; alkyl compounds bonded by hetero atoms as described in Japanese Patent Publications No. 29622/1969, No. 25373/1972 and No. 24259/1972; sulfonamide and ester type compounds as described in Japanese Patent Publication No. 8736/1972; 1,3,5-tris[β -(vinylsulfonyl)-propionyl]hexahydro-s-triazine as described in Japanese Provisional Patent Publication No. 24435/1974; alkyl type compounds as described in Japanese Patent Publication No. 35807/1975 and Japanese Provisional Patent Publication No. 44164/1976; and compounds as described in Japanese Provisional Patent Publication No. 18944/1984.

The vinyl sulfone type hardener preferably used in the present invention is represented by the following formula (H - I)



In the above formula (H - I), L represents an m-valent linking group, which may be substituted; and X represents either -CH=CH₂ or -CH₂CH₂Y where Y represents a group which is substituted by a nucleophilic group or can be eliminated in the form of HY by a base (e.g. a halogen atom, a sulfonyloxy group and monosulfate). X is preferably -CH=CH₂.

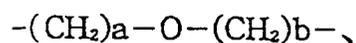
m represents an integer of 2 to 10, more preferably 2 to 6.

The m-valent linking group L may include, for example, an alkylene group, an arylene group or an m-valent group formed by combining these groups with at least one bond represented by -O-, -N(R¹)-, -CO-, -SO-, -SO₂-, -SO₃-, -SO₂N(R¹)-, -COO-, -CON(R¹)-, -N(R¹)CON(R¹)- and -N(-R¹)CO₂-, where R¹ represents a hydrogen atom, an alkyl group or an aralkyl group each having 1 to 15 carbon atoms. When two or more of -N(R¹)-,

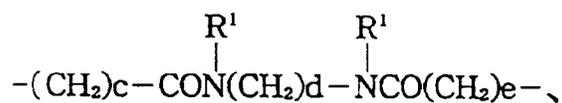
$-\text{SO}_2\text{N}(\text{R}^1)-$, $-\text{CON}(\text{R}^1)-$ and $-\text{N}(\text{R}^1)\text{CO}_2-$ are contained, R^1 's may be bonded to each other to form a ring. Further, L may have a substituent(s), and examples of the substituent include a hydroxy group, an alkoxy group, a carbamoyl group, a sulfamoyl group, an alkyl group and an aryl group. The substituent may be further substituted by at least one group represented by X^3-SO_2- . X^3 has the same meaning as X described above.

5 In the following, representative examples of L are shown. In the examples, a to v each represent an integer of 1 to 6, and only d may be 0. Among these, d, k, l and p are preferably 1 to 3, and a to v except for the above d, k, l and p are preferably 1 or 2. R^1 is preferably hydrogen atom or an alkyl group having 1 to 6 carbon atoms, particularly preferably hydrogen atom, a methyl group and an ethyl group.

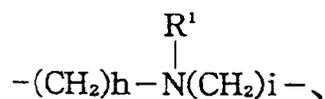
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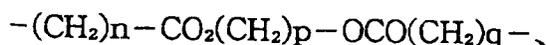
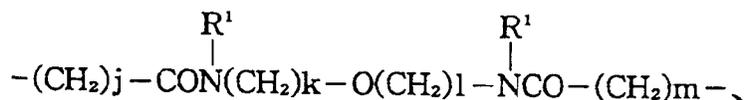
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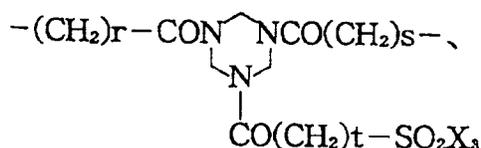
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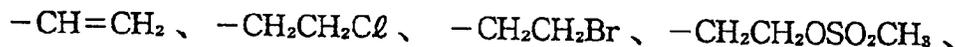


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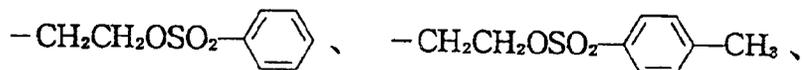


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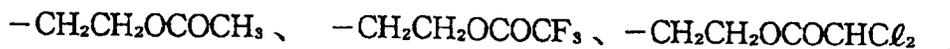
Specific examples of X may include, for example, the following.



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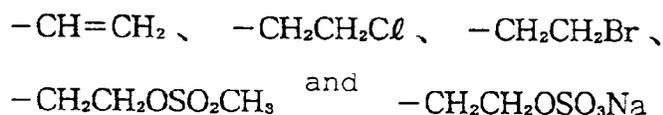


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Among them, particularly preferred are

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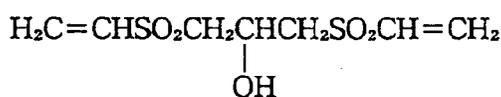


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Representative specific examples of the vinyl sulfone type hardener according to the present invention are shown below.

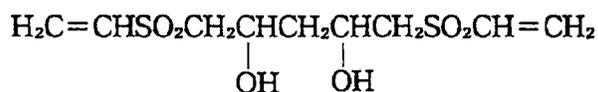
- HA— 1 $\text{H}_2\text{C}=\text{CHSO}_2\text{CH}_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 2 $\text{H}_2\text{C}=\text{CHSO}_2(\text{CH}_2)_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 3 $\text{H}_2\text{C}=\text{CHSO}_2(\text{CH}_2)_3\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 4 $\text{H}_2\text{C}=\text{CHSO}_2\text{CH}_2\text{OCH}_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 5 $\text{H}_2\text{C}=\text{CHSO}_2(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 6

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HA— 7



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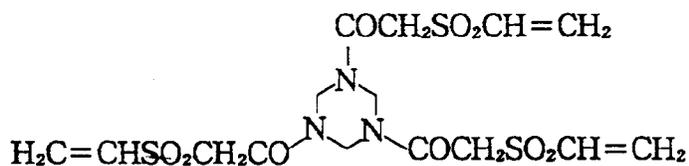
- HA— 8 $\text{H}_2\text{C}=\text{CHSO}_2\text{CH}_2\text{CONHCH}_2\text{NHCOCH}_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 9 $\text{H}_2\text{C}=\text{CHSO}_2\text{CH}_2\text{CONH}(\text{CH}_2)_2\text{NHCOCH}_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 10 $\text{H}_2\text{C}=\text{CHSO}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{NHCOCH}_2\text{SO}_2\text{CH}=\text{CH}_2$
 HA— 11

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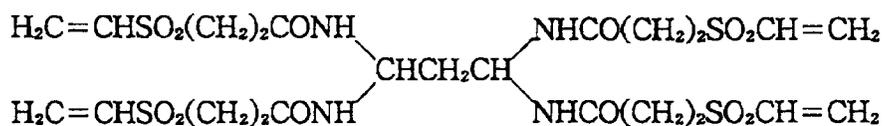
HA— 12



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HA— 13



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HA— 14

HA— 23

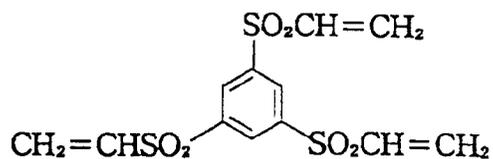
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HA— 24 $(\text{H}_2\text{C}=\text{CHSO}_2\text{CH}_2)_3\text{CC}_2\text{H}_5$

HA— 25

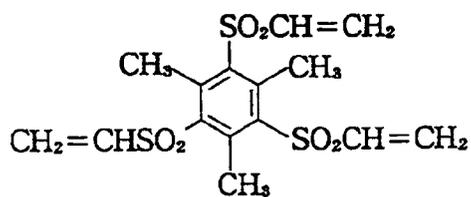
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HA— 26

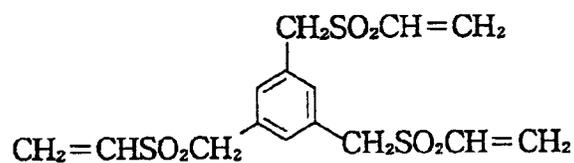
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HA— 27

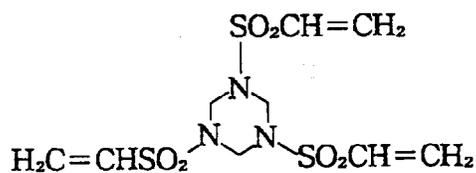
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HA— 28

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HA— 29

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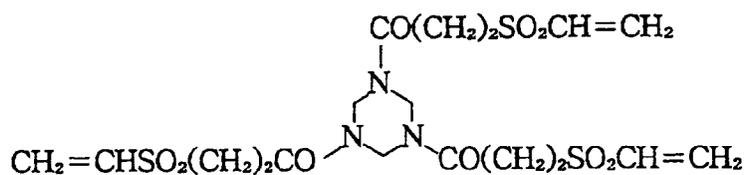
HA— 30 $\text{H}_2\text{C}=\text{CHSO}_2(\text{CH}_2)_2\text{SO}_2(\text{CH}_2)_2\text{SO}_2\text{CH}=\text{CH}_2$

HA— 31 $\text{H}_2\text{C}=\text{CHSO}_2(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{NHONH}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{SO}_2\text{CH}=\text{CH}_2$

HA— 32

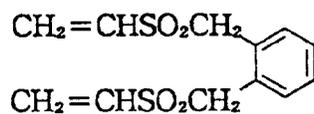
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HA— 33

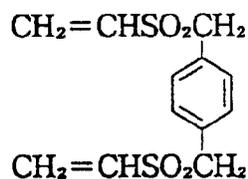
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HA— 34

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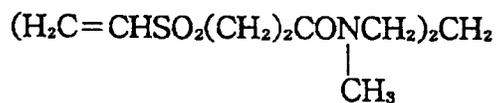
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HA — 35 (H₂C=CHSO₂NH)₂CH₂

HA — 36 H₂C=CHSO₂(CH₂)₂NH(CH₂)₂NH(CH₂)₂SO₂CH=CH₂

HA — 37

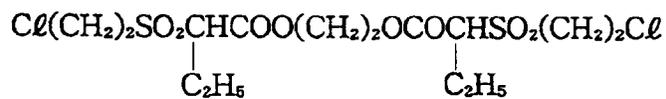
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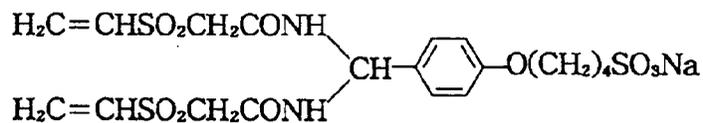
HA — 38

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HA — 39

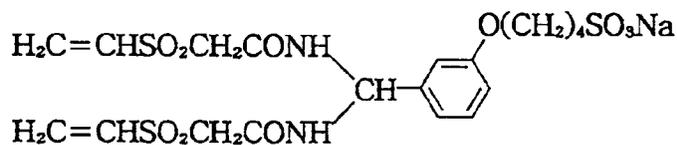
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HA — 40

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and a surface layer have different silver halide compositions with each other.

The silver halide grain may be either a grain of the type in which a latent image is mainly formed on a surface thereof or a grain of the type in which a latent image is mainly formed internally of the grain.

5 The silver halide emulsion may have any grain size distribution. There may be used an emulsion having a wide grain size distribution (called "a polydispersed emulsion") or an emulsion having a narrow grain size distribution (called "a monodispersed emulsion") alone or in combination of several kinds thereof. Further, a mixture of a polydispersed emulsion and a monodispersed emulsion may be used.

As the silver halide emulsion, there may be used a mixture of two or more kinds of silver halide emulsions prepared separately.

10 The silver halide grain to be used in the present invention can be chemically sensitized by a sulfur sensitization method, a selenium sensitization method, a reduction sensitization method and a noble metal sensitization method.

15 Among the silver halide grains to be used in the present invention, the silver halide grains other than the silver halide grains spectrally sensitized by using a combination of the light-sensitive dyes of the present invention can be spectrally sensitized to a desired wavelength region by using a dye which has been known as a sensitizing dye in the photographic field.

To the silver halide emulsion, an antifoggant and a stabilizer may be added.

20 As a binder (or protective colloid) to be used in the emulsion and others of the light-sensitive silver halide photographic material of the present invention, gelatin is advantageously used. In addition, there may be used a gelatin derivative, a graft polymer of gelatin and other polymer, a protein, a sugar derivative, a cellulose derivative and a hydrophilic colloid including a synthetic hydrophilic polymer substance such as a homo- or copolymer.

25 The photographic emulsion layer and other hydrophilic colloidal layers of the light-sensitive silver halide photographic material of the present invention can be hardened by crosslinking binder (or protective colloid) molecules and using a hardener for enhancing film strength alone or in combination thereof.

In the silver halide emulsion, a plasticizer or a dispersion (latex) of a synthetic polymer insoluble or difficultly soluble in water may be contained.

30 In the light-sensitive silver halide photographic material of the present invention, a coupler may be used. Further, there may be used a competitive coupler having an color correction effect, and a compound which releases a photographically useful fragment such as a development accelerator, a bleaching accelerator, a developer, a silver halide solvent, a color adjusting agent, a hardener, a fogging agent, an antifoggant, a chemical sensitizer, a spectral sensitizer and a desensitizer by coupling with an oxidized product of a color developing agent.

35 As a yellow dye-forming coupler, known acylacetanilide type couplers may be preferably used. Among them, benzoylacetylacetanilide type and pivaloylacetylacetanilide type compounds are advantageous.

As a magenta dye-forming coupler, there may be used a 5-pyrazolone type coupler, a pyrazoloazole type coupler, a pyrazolobenzimidazole type coupler, an open chain acylacetone nitrile type coupler and an indazole type coupler.

40 As a cyan dye-forming coupler, a phenol or naphthol type coupler is generally used. When a coupler is incorporated into the light-sensitive material, known techniques used for conventional couplers may be applied. It is preferred that the coupler is dissolved in a high boiling point solvent, if necessary, in combination with a low boiling point solvent, dispersed in the form of fine grains, and added to the silver halide emulsion according to the present invention. Here, if necessary, a hydroquinone derivative, a UV absorber and an antifading agent may be used in combination without any problem.

45 In the light-sensitive silver halide photographic material of the present invention, auxiliary layers such as a filter layer, an antihalation layer and an antiirradiation layer may be provided. In these layers and/or emulsion layer, a dye which flows out from the light-sensitive material during development processing, or bleached may be contained.

50 To the light-sensitive silver halide photographic material of the present invention, there may be added a matting agent, a lubricant, an image stabilizer, a UV absorber, a fluorescent brightener, a surfactant, a development accelerator, a development retarder and a bleaching accelerator.

55 The photographic emulsion layer and other layers of the light-sensitive silver halide photographic material of the present invention may be provided on a baryta paper, a paper on which an α -olefin polymer is laminated, a paper support in which an α -olefin layer and the paper support are easily peeled off, a flexible reflective support such as a synthetic paper, a film comprising a semi-synthetic or synthetic polymer such as cellulose acetate, cellulose nitrate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate and polyamide, a reflective support on which a white pigment is coated, and a rigid material such as glass, metal and ceramics. Or else, they may be provided on a thin type reflective support having a thickness of 120 to 160

μm.

When the light-sensitive silver halide photographic material of the present invention contains a coupler, generally known color photographic processings are carried out after exposure in order to obtain a dye image.

In the present invention, the light-sensitive material may be processed immediately after color development by using a processing solution having bleaching ability and a processing solution having fixing ability, but may be processed by using a processing solution having bleaching ability and fixing ability (the so-called bleach-fixing solution). As a bleaching agent to be used for said bleaching, a metal complex salt of an organic acid is used.

After fixing processing, washing processing is generally carried out. Further, a stabilizing processing substitute for washing processing may be carried out, and both processing steps may be carried out in combination.

EXAMPLES

The present invention is described in detail by referring to Examples, but the embodiments of the present invention are not limited thereby.

Example 1

On a triacetyl cellulose film support, the respective layers having the following compositions were formed successively from a support side to prepare a multilayer light-sensitive color photographic material sample 1.

Amounts in the multilayer light-sensitive color photographic material are represented by gram per 1 m² of the light-sensitive material unless otherwise indicated. Further, silver halide and colloidal silver are represented by calculating them or. silver. Amounts of sensitizing dyes are represented by a molar number per mole of silver.

First layer: antihalation layer (HC)	
Black colloidal silver	0.15
UV absorber (UV-1)	0.20
Colored cyan coupler (CC-1)	0.02
High boiling point solvent (Oil-1)	0.20
High boiling point solvent (Oil-2)	0.20
Gelatin	1.6

Second layer: intermediate layer (IL-1)	
Hardener (HH - 1)	0.09
Gelatin	1.3

Third layer: low sensitivity red-sensitive emulsion layer (RL)	
5	Silver iodobromide emulsion (Em-1) 0.4
	Silver iodobromide emulsion (Em-2) 0.3
	Sensitizing dye (S-1) 3.2×10^{-4}
	Sensitizing dye (S-2) 3.2×10^{-4}
10	Sensitizing dye (S-3) 0.2×10^{-4}
	Cyan coupler (C-1) 0.50
	Cyan coupler (C-2) 0.13
	Colored cyan coupler (CC-1) 0.07
15	DIR compound (D-1) 0.01
	High boiling point solvent (Oil-1) 0.55
	Gelatin 1.0

Fourth layer: high sensitivity red-sensitive emulsion layer (RH)	
20	
25	Silver iodobromide emulsion (Em-3) 0.9
	Sensitizing dye (S-1) 1.7×10^{-4}
	Sensitizing dye (S-2) 1.6×10^{-4}
	Sensitizing dye (S-3) 0.1×10^{-4}
30	Cyan coupler (C-2) 0.23
	Colored cyan coupler (CC-1) 0.03
	DIR compound (D-1) 0.02
35	High boiling point solvent (Oil-1) 0.25
	Gelatin 1.0

Fifth layer: intermediate layer (IL-2)	
40	
	Hardener (HH-1) 0.06
	Gelatin 0.8

45

Sixth layer: low sensitivity green-sensitive emulsion layer (GL)

50	Silver iodobromide emulsion (Em-1)	0.6
	Silver iodobromide emulsion (Em-2)	0.2
	Sensitizing dye (S-4)	6.7×10^{-4}
55	Sensitizing dye (S-5)	0.8×10^{-4}

	Magenta coupler (M-1)	0.47
	Colored magenta coupler (CM - A)	0.10
5	DIR compound (D-3)	0.02
	High boiling point solvent (Oil-2)	0.70
	Gelatin	1.0

10	Seventh layer: high sensitivity green-sensitive emulsion layer (GH)	
	Silver iodobromide emulsion (Em-3)	0.9
15	Sensitizing dye (S-6)	1.1×10^{-4}
	Sensitizing dye (S-7)	2.0×10^{-4}
	Sensitizing dye (S-8)	0.3×10^{-4}
20	Magenta coupler (M-1)	0.15
	Magenta coupler (M-2)	0.06
	Colored magenta coupler (CM-A)	0.04
	DIR compound (D-3)	0.04
25	High boiling point solvent (Oil-2)	0.35
	Gelatin	1.0

30	Eighth layer: yellow filter layer (YC)	
	Yellow colloidal silver	0.1
	Additive (SC-1)	0.12
35	High boiling point solvent (Oil-2)	0.15
	Hardener (HH - 1)	0.05
	Gelatin	1.0

40	Ninth layer: low sensitivity blue-sensitive emulsion layer (BL)	
	Silver iodobromide emulsion (Em-1)	0.25
45	Silver iodobromide emulsion (Em-2)	0.25
	Sensitizing dye (S-9)	5.8×10^{-4}
	Yellow coupler (Y-1)	0.60
50	Yellow coupler (Y-2)	0.32
	DIR compound (D-2)	0.01
	High boiling point solvent (Oil-2)	0.18
55	Gelatin	1.3

	Tenth layer: high sensitivity blue-sensitive emulsion layer (BH)	
5	Silver iodobromide emulsion (Em-4)	0.5
	Sensitizing dye (S-10)	3.0×10^{-4}
	Sensitizing dye (S-11)	1.2×10^{-4}
	Yellow coupler (Y-1)	0.18
10	Yellow coupler (Y-2)	0.10
	High boiling point solvent (Oil-2)	0.05
	Gelatin	1.0

15	Eleventh layer: first protective layer (PRO-1)	
	Silver iodobromide emulsion (Em-5)	0.3
20	UV absorber (UV-1)	0.07
	UV absorber (UV-2)	0.1
	High boiling point solvent (Oil-1)	0.07
	High boiling point solvent (Oil-3)	0.07
25	Hardener (HH-1)	0.06
	Gelatin	0.8

30	Twelfth layer: second protective layer (PRO-2)	
	Alkali-soluble matting agent (average grain size: 2 μm)	0.13
	Polymethyl methacrylate (average grain size: 3 μm)	0.02
35	Gelatin	0.5

In addition to the above compositions, a coating aid SU-2, a dispersing aid SU-1, and dyes AI-1 and AI-2 were suitably added to the respective layers.

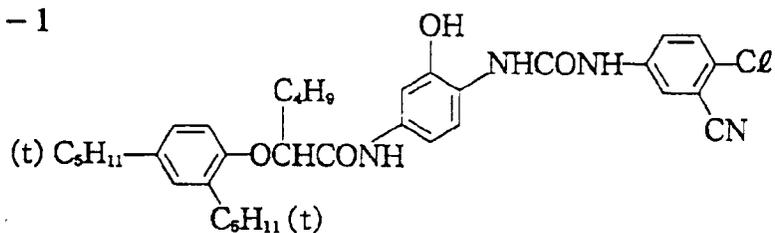
The emulsions used in the above samples are shown below, all of which are monodispersed emulsions having high iodine content in inner portions.

- Em-1: average silver iodide content: 7.5 mole %
 average grain size: 0.55 μm
 grain shape: octahedron
- Em-2: average silver iodide content: 2.5 mole %
 average grain size: 0.36 μm
 grain shape: octahedron
- Em-3: average silver iodide content: 8.0 mole %
 average grain size: 0.84 μm
 grain shape: octahedron
- Em-4: average silver iodide content: 8.5 mole %
 average grain size: 1.02 μm
 grain shape: octahedron
- Em-5: average silver iodide content: 2.0 mole %
 average grain size: 0.08 μm
 grain shape: octahedron

Respective compounds used in the respective layers are as shown below.

C - 1

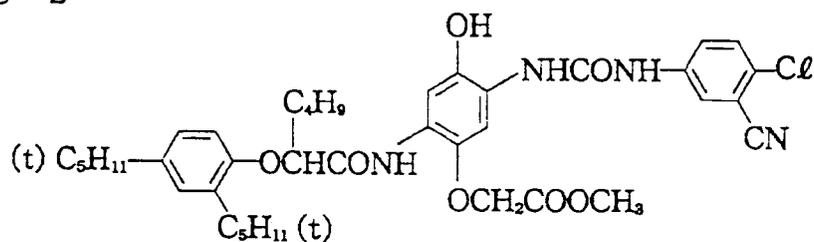
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C - 2

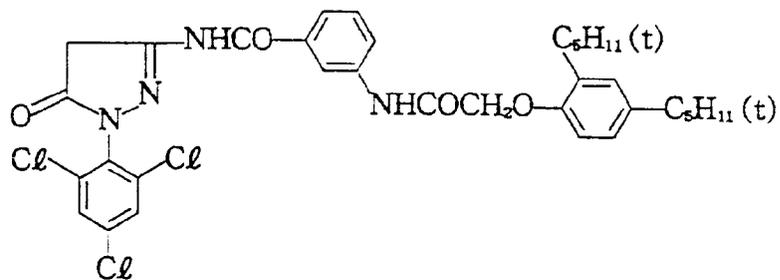
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M - 1

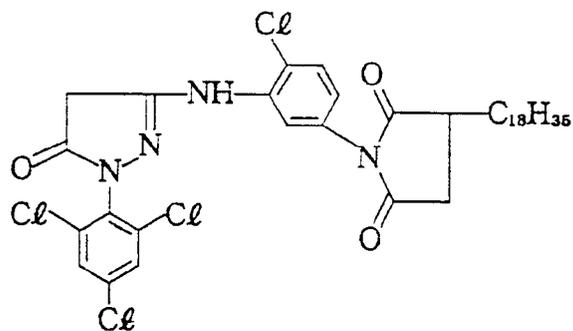
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M - 2

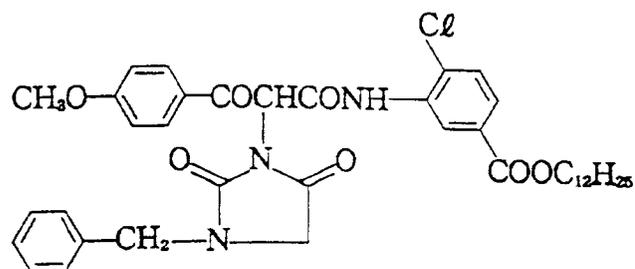
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Y - 1

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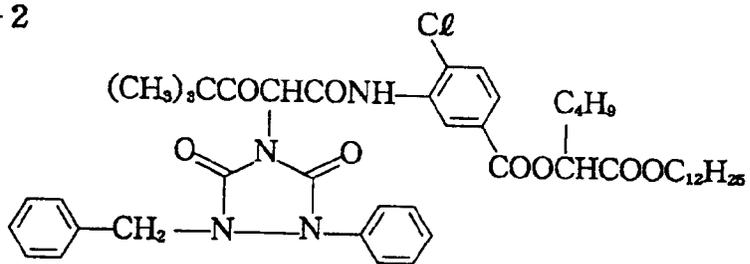
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Y - 2

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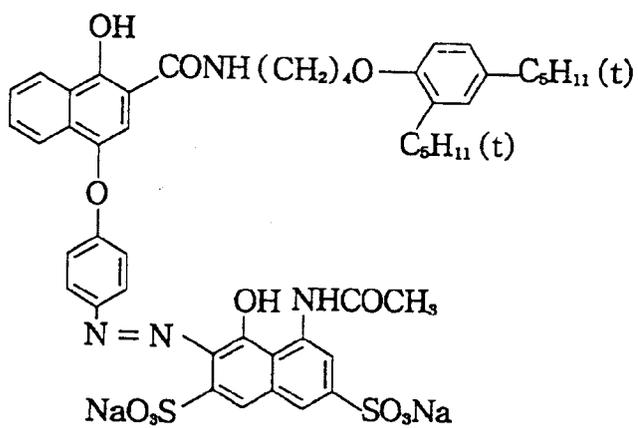


CC - 1

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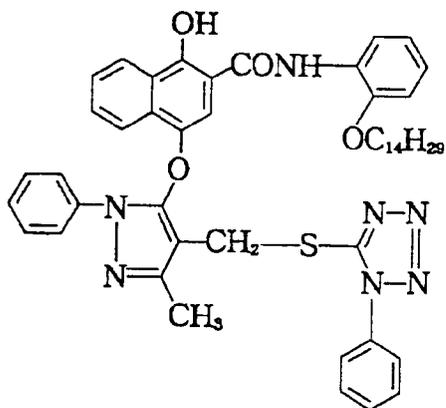


D - 1

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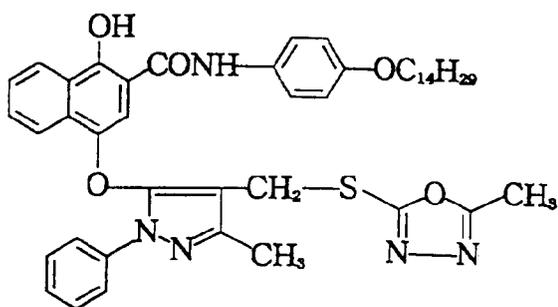


D - 2

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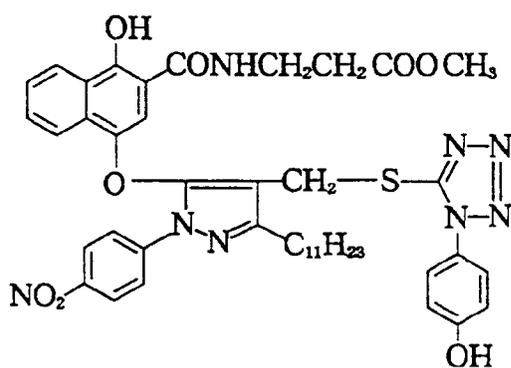
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D - 3

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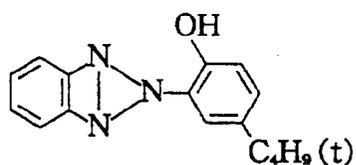
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UV - 1

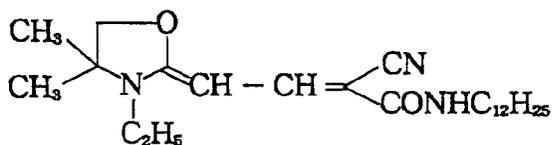
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UV - 2

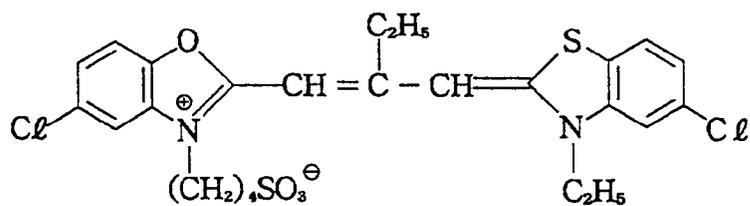
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S - 1

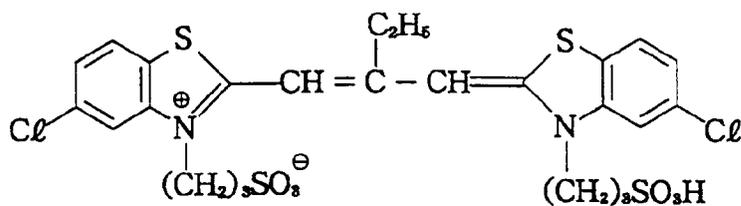
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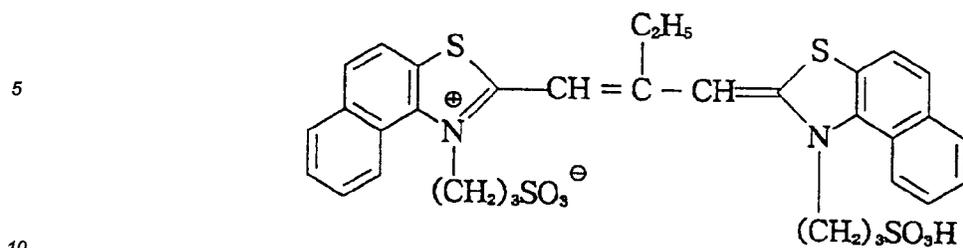
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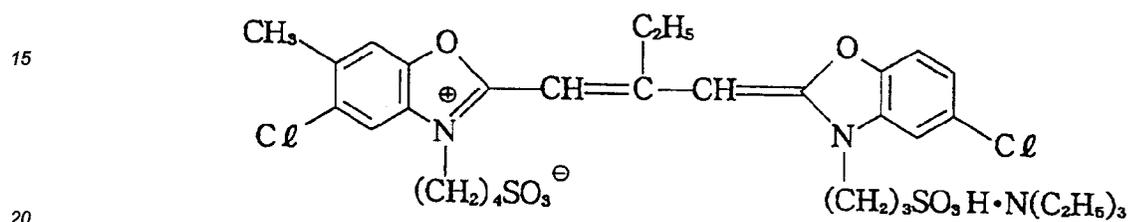


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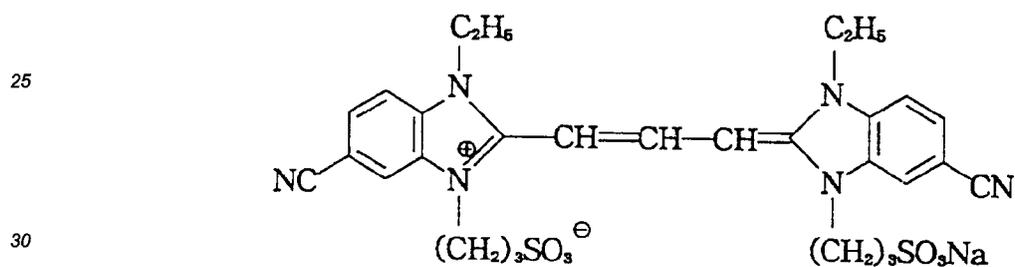
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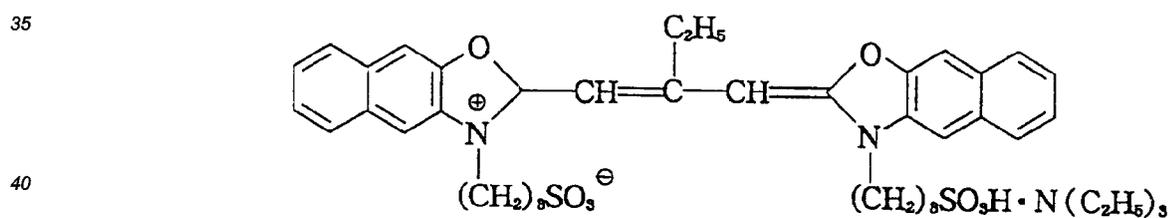
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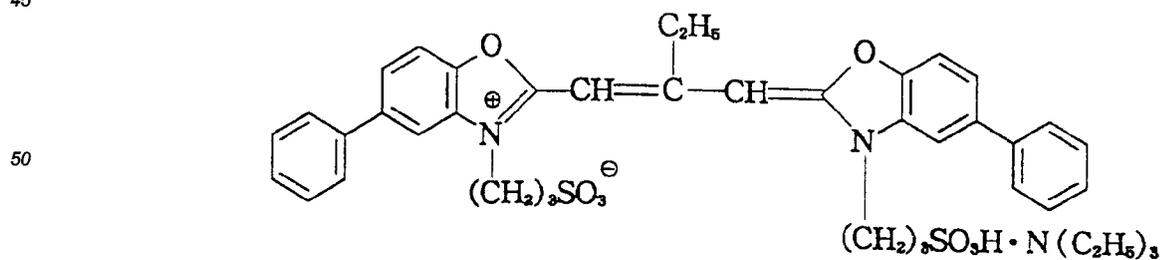
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S - 6



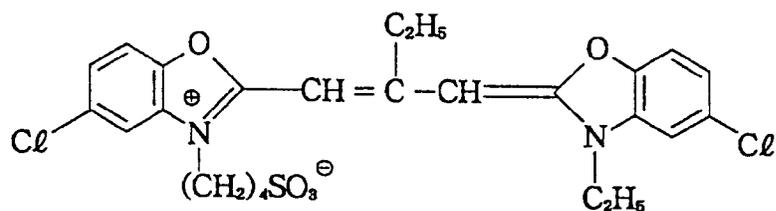
S - 7



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S - 8

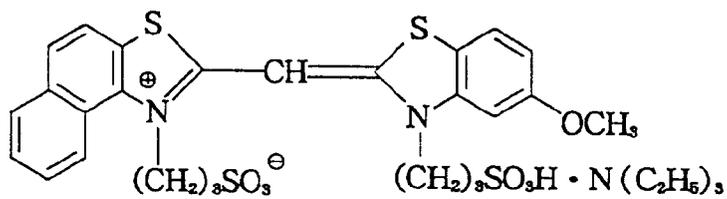
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S - 9

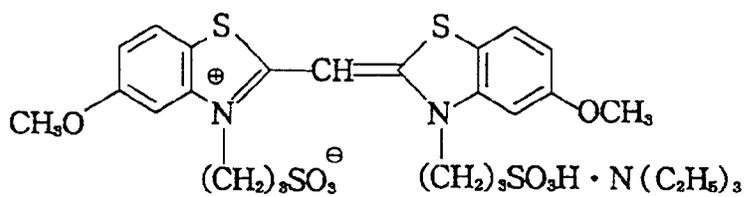
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S - 10

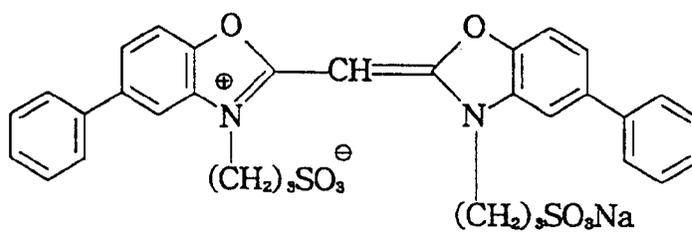
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S - 11

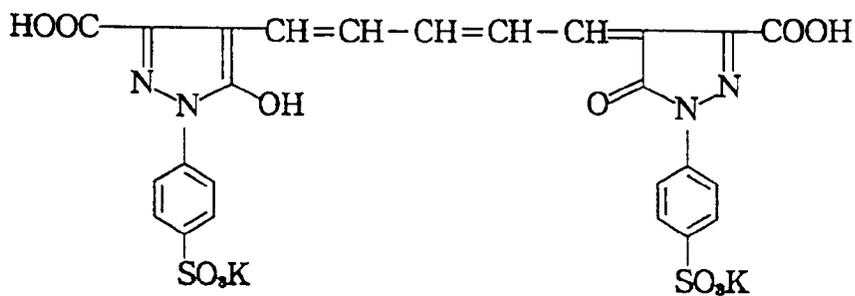
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AI - 1

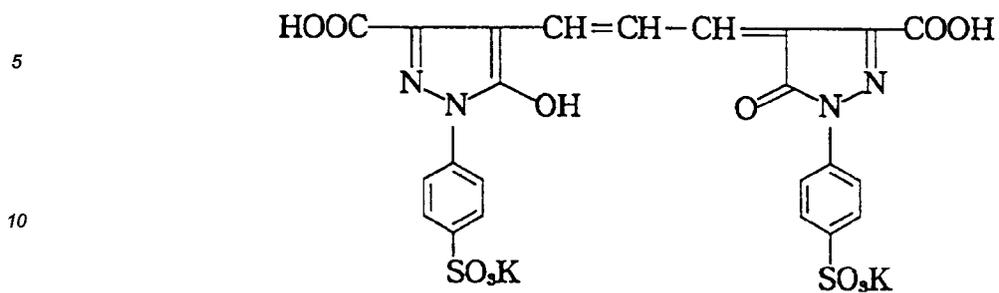
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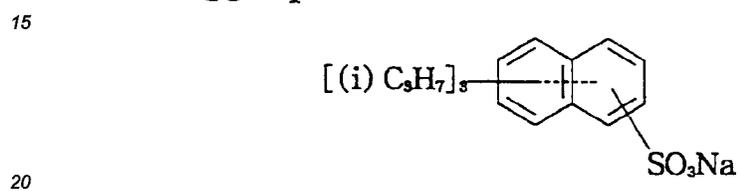
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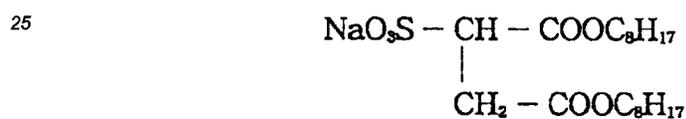
AI - 2



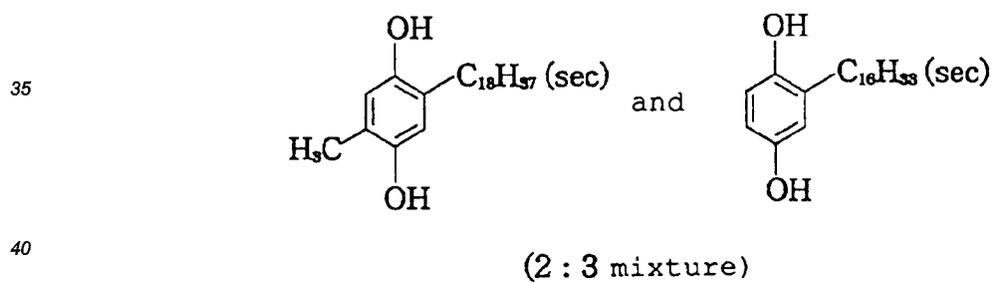
SU - 1



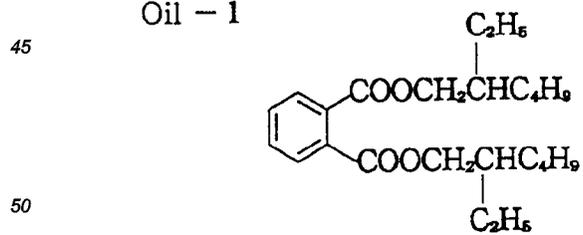
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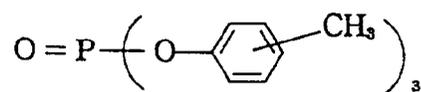
SC - 1



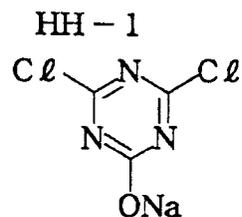
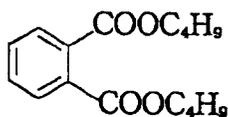
Oil - 1



Oil - 2



Oil - 3

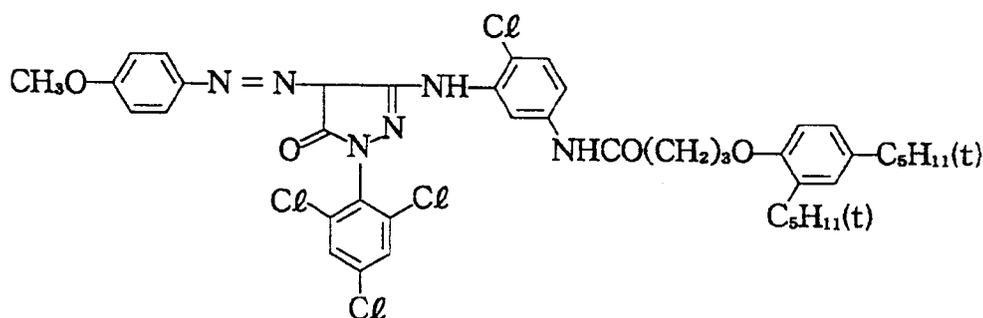


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10 Further, Samples 2 to 18 were prepared in the same manner as in Sample 1 except for changing the colored magenta coupler CM-A in the sixth layer and the seventh layer and the hardener HH-1 in the second layer, the fifth layer, the eighth layer and the eleventh layer to the same amounts of the compounds shown in Table 1, respectively.

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CM - A



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30 By using the respective Samples 1 to 18 thus prepared and a camera KONICA FT-1 MOTOR (trade name, manufactured by KONICA CORPORATION), a color checker produced by MacBeth Co. was photographed, and subsequently, the following development processing was carried out.

Processing A	
Processing step (38 °C)	Processing time
Color development	3 min 15 sec
Bleaching	6 min 30 sec
Washing	3 min 15 sec
40 Fixing	6 min 30 sec
Washing	3 min 15 sec
Stabilizing	1 min 30 sec

45

Drying

The processing solutions used in the respective processing steps had the following compositions.

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< Color developing solution >	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline-sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine-1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Nitrilotriacetic acid-trisodium salt (monohydrate)	2.5 g
Potassium hydroxide	1.0 g

made up to one liter with addition of water (pH = 10.05).

< Bleaching solution >	
Iron (III) ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml

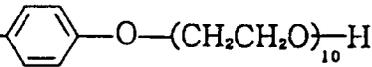
made up to one liter with addition of water and adjusted to pH = 6.0 with aqueous ammonia.

< Fixing solution >	
Ammonium thioisulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metabisulfite	2.3 g

made up to one liter with addition of water and adjusted to pH = 6.0 with acetic acid.

<Stabilizing solution>

Water 900 ml

C_8H_{17} - 2.0 g

Dimethylol urea 0.5 g

Hexamethylenetetramine 0.2 g

1,2-Benzisothiazolin-3-one 0.1 g

Siloxane L-77 (trade name, produced by UCC) 0.1 g

Aqueous ammonia 0.5 ml

made up to one liter with addition of water and adjusted to pH 8.5 with aqueous ammonia or 50 % sulfuric acid.

With regard to the samples obtained, Print samples 1A to 18A were so prepared using Printer A that a gray portion of the color checker became gray with a reflectance of 18 %.

Next, by using Printer B having a detector which is different in a green region from that of Printer A, Print samples 1B to 18B were prepared under the same conditions as in the case of using Printer A, and fluctuation between different printers were judged visually.

5 Samples 1 to 18 were subjected to exposure with white light through step wedge for sensitometry, and then processed according to Processing A described above. Thereafter, the samples were measured by using green light to evaluate fog and sensitivity. The sensitivity was determined by a reciprocal of an exposure amount necessary for giving a density of fog + 0.3, and represented by a relative value when the value of Sample 1 was determined as 100. Further, the respective samples were subjected to exposure with white light through
10 step wedge for sensitometry, and then processed in the same manner as in the above Processing A except for changing pH of the color developing solution in the above Processing A to 10.20 (hereinafter referred to as "Processing B") whereby increase of fog was compared with that in Processing A. The results are all shown in Table 1.

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Table 1

Sample No.	Colored magenta coupler		Hardener	Characteristics on the same day		Processing fluctuation*1 Fog increase in Processing B	Fluctuation between different printers*2
	6th layer	7th layer		Fog	Sensitivity		
1 (Comparison)	CM-A	CM-A	HH-1	0.53	100	0.02	X
2 (Comparison)	CM-29	CM-29	HH-1	0.57	105	0.06	Δ
3 (Present invention)	CM-29	CM-29	HA-6	0.54	104	0.03	O
4 (Present invention)	CM-13	CM-13	HA-6	0.54	105	0.03	O
5 (Present invention)	CM-27	CM-27	HA-6	0.55	104	0.02	O
6 (Present invention)	CM-32	CM-32	HA-6	0.54	103	0.03	O
7 (Present invention)	CM-13	CM-13	HA-4	0.55	103	0.03	O
8 (Present invention)	CM-27	CM-27	HA-4	0.55	104	0.02	O
9 (Present invention)	CM-32	CM-32	HA-4	0.55	104	0.02	O
10 (Present invention)	CM-29	CM-29	HA-4	0.54	103	0.03	O
11 (Present invention)	CM-29	CM-29	HA-2	0.54	104	0.03	O
12 (Present invention)	CM-29	CM-29	HA-9	0.54	103	0.03	O
13 (Present invention)	CM-13	CM-13	HA-10	0.55	103	0.02	O

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Table 1 (cont'd)

Sample No.	Colored magenta coupler		Hardener	Characteristics on the same day		Processing fluctuation*1 Fog increase in Processing B	Fluctuation between different printers*2
	6th layer	7th layer		Fog	Sensitivity		
14 (Present invention)	CM-13	CM-27	HA-11	0.55	104	0.02	0
15 (Present invention)	CM-29	CM-27	HA-13	0.54	104	0.03	0
16 (Present invention)	CM-27	CM-29	HA-25	0.55	104	0.03	0
17 (Present invention)	CM-27	CM-27	HA-28	0.54	103	0.02	0
18 (Present invention)	CM-29	CM-29	HA-28	0.54	104	0.02	0

*1: Processing fluctuation is represented by increase (Δ Fog) in Processing B based on the value in Processing A.

*2: Organoleptic test by ten panels.

Evaluation standard of Fluctuation between different printers:

O: small fluctuation Δ : slightly large fluctuation X: large fluctuation

As clearly seen from Table 1, in Sample 1 which is a comparative sample, increase in fog in Processing B, i.e. processing fluctuation is small, but fluctuation between different printers is extremely large. Also, in Sam-

10. The material of Claim 1 wherein the colored magenta coupler is contained in an amount of 0.01 to 1.0 g/m² based on the light-sensitive silver halide color photographic material.

5 11. The material of Claim 1 wherein the colored magenta coupler is contained in an amount of 0.03 to 0.3 g/m² based on the light-sensitive silver halide color photographic material.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 7859

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X D	EP-A-0 456 443 (KONICA) * page 4, line 1 - page 6, line 32 * * page 23, line 7 - line 11 * * page 40, line 40 * & JP-A-4 016 939 (KONICA) -----	1-11	G03C7/333 G03C1/30
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06 OCTOBER 1992	Examiner MAGRIZOS S.
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