⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 474 166 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **91114764.3**

㉒ Date of filing: **02.09.91**

㊿ Int. Cl.⁵: **G03C 7/30**

㉚ Priority: **03.09.90 JP 232659/90**

(43) Date of publication of application:
11.03.92 Bulletin 92/11

(84) Designated Contracting States:
DE FR GB NL SE

(71) Applicant: **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome Shinjuku-ku
Tokyo(JP)

(72) Inventor: **Iwagaki, Masaru**
Konica Corporation, 1 Sakura-machi
Hino-shi, Tokyo(JP)
Inventor: **Suzuki, Katsutoyo**
Konica Corporation, 1 Sakura-machi
Hino-shi, Tokyo(JP)
Inventor: **Ikeda, Hiroshi**
Konica Corporation, 1 Sakura-machi
Hino-shi, Tokyo(JP)
Inventor: **Ezaki, Atsuo**
Konica Corporation, 1 Sakura-machi
Hino-shi, Tokyo(JP)

(74) Representative: **Henkel, Feiler, Hänzel & Partner**
Möhlstrasse 37
W-8000 München 80(DE)

(54) A silver halide color photographic light-sensitive material.

(57) Disclosed is a silver halide photographic light-sensitive material comprising a support having thereon a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red sensitive emulsion layer, wherein said red-sensitive emulsion layer comprises a high-speed emulsion sublayer, a medium-speed emulsion sublayer and a low-speed emulsion sublayer;

said low-speed emulsion sublayer, said medium-speed emulsion sublayer and said high-speed emulsion sublayer being provided in this order on the support;

said high-speed emulsion sublayer containing a two-equivalent cyan coupler; said medium-speed emulsion sublayer and said low-speed emulsion sublayer each comprising a four-equivalent coupler and a diffusible DIR compound; and the maximum transmission density of cyan dye in said medium-speed emulsion sublayer being not more than 0.35. The silver halide photographic light-sensitive material according to this invention has a high sensitivity, and is capable of forming a high-quality image and having an excellent preservability.

FIELD OF THE INVENTION

The present invention relates to improvement of a silver halide color photographic light-sensitive material, and more particularly to a silver halide color photographic light-sensitive material capable of forming a high-quality image and having an excellent preservability.

BACKGROUND OF THE INVENTION

Recent silver halide color photographic light-sensitive material products are so improved as to form remarkably highquality images. The three major elements of an image quality - graininess, sharpness and color reproducibility - are all on a considerably high level, so that most customers appear to be contended with their prints or slide photos reproduced. Of the three major elements, the color reproducibility has two major factors: the spectral sensitivity distribution and interimage effect.

As for the interimage effect, it is known that the effect can be attained by adding to a silver halide multilayer color photographic light-sensitive material a compound called DIR compound capable of releasing a development inhibitor or a precursor thereof upon its coupling reaction with a color developing agent, wherein the development inhibitor inhibits the development of different color-forming layers to thereby create an interimage effect for color reproducibility improvement.

In a color negative film, it is also possible to render an effect similar to the interimage effect by using a colored coupler in a larger amount than is necessary to cancel a useless absorption.

However, the use of an excessive amount of a color coupler causes the minimum density of the film to increase, which makes it very difficult to judge the color density correction in making prints, sometimes resulting in an inferior color quality of finished prints. The above techniques chiefly contribute to the improvement of color quality rather than color reproducibility.

A compound often used lately which is capable of releasing a highly mobile inhibiting group or a precursor thereof, the so-called diffusible DIR compound, contributes largely to the improvement of color purity. However, it is difficult for the compound to control the directivity of the interimage effect, so that the compound has a drawback of causing color alteration although it can raise color purity. The control of the directivity of the interimage effect is described in U.S. Patent No. 4,725,529.

On the other hand, as for the spectral sensistivity distribution, U.S. Patent No. 3,672,898 discloses a proper spectral sensitivity distribution for reducing the color reproducibility variation due to the different light sources used in photographing.

This, however, is not a means for correcting the aforementioned wrong color reproduction. There is also disclosed a spectral distribution/interimage effect combination technique; for example, JP O.P.I. No. 034541/1986 makes an attempt to improve the foregoing color film's reproduction of certain colors hard to be reproduced, and its effect appears to have been obtained to some extent. The attempt is to exert not only the respective effects of the conventional blue-sensitive layer, green-sensitive layer and red-sensitive layer but also the interimage effect from the outside of the wavelengths to which the above color-sensitive layers are sensitive.

The above technique is considered useful to a certain extent for improving the reproducibility of specific colors, but the technique, for interimage effect generation, needs an interimage effect-generating layer and a light-sensitive silver halide layer in addition to the conventional blue-sensitive, green-sensitive and red-sensitive emulsion layers, which requires increasing the amount of silver and the number of production processes to thus result in a high production cost. Besides, its effect is not sufficient.

The foregoing U.S. Patent No. 3,672,898 discloses a spectral sensitivity distribution for reducing the color reproducibility variation due to different light sources used in photographing; this intends to reduce the color variation by bringing the spectral sensitivity distributions of the blue-sensitive and red-sensitive layers close to that of the green-sensitive layer to thereby lessen the changes in the sensitivities of these layers corresponding to different light sources, particularly different color temperatures, in photographing. In this instance, the three color-sensitive layers are so close to one another as to overlap their spectral sensitivity distributions to cause a color purity deterioration. The color purity deterioration can be prevented to a certain extent, as is well known, by emphasizing the interimage effect by use of the foregoing diffusible DIR compound.

On the other hand, regarding the graininess, British Patent No. 923,045 discloses a method in which a color-sensitive layer is separated into substantially the same color-forming nondiffusible coupler-containing high-speed and low-speed emulsion sublayers, and the high-speed sublayer's maximum color density is set low, whereby the sensitivity of the layer can be raised high without coarsening the grains of the layer. This method, however, is still not sufficient for the graininess.

U.S. Patent No. 3,843,469 discloses a high-sensitivity multilayer color light-sensitive material in which at least one of its red-sensitive, green-sensitive and blue-sensitive layers is comprised of three different-speed sublayers - a high-speed upper sublayer, a medium-speed middle sublayer and a low-speed lower sublayer. This light-sensitive material, however, is still not sufficient, either, although its graininess is improved to some extent.

On the other hand, the two-equivalent coupler having a good color-forming characteristic is conventionally known as one of the sharpness-improving techniques; for example, German Patent No. 1,121,470 describes a light-sensitive material having light-sensitive units each composed of two sublayers each containing a two-equivalent coupler. However, this technique, although useful for improving the sharpness, has the problem of conspicuously deteriorating the graininess and increasing the fog of the light-sensitive unit.

U.S. Patent No. 3,516,831 describes a light-sensitive material comprising emulsion layer units of which at least one emulsion layer unit is comprised of two different-speed sublayers - a high-speed sublayer and a low-speed sublayer each sensitive to the same spectral region, in which the high-speed emulsion sublayer contains a four-equivalent coupler, while the low-speed emulsion sublayer contains a two-equivalent coupler to thereby improve both sharpness and graininess. It is, however, difficult for the above coupler combination to provide a sufficiently high sensitivity.

It has been found that if an attempt is made to obtain a silver halide color photographic light-sensitive material having a high sensitivity and being capable of forming a high-quality image by utilizing the above techniques in combination, its density fluctuation largely occurs during its storage under high-humidity conditions, which is considered attributable to the nondiffusible DIR compound.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a silver halide color photographic light-sensitive material having a high sensitivity, being capable of forming a high-quality image and having an excellent preservability.

The above object is accomplished by a silver halide color photographic light-sensitive material comprising a support having thereon a red-sensitive layer, a green-sensitive layer and a blue-sensitive layer, in which said red-sensitive layer is comprised of a high-speed emulsion sublayer, a medium-speed emulsion sublayer and a low-speed emulsion sublayer, which are provided in the low-speed to high-speed order from the support, wherein said high-speed emulsion sublayer contains a two-equivalent cyan coupler and said medium-speed and low-speed emulsion sublayers each contain a four-equivalent cyan coupler and a diffusible DIR compound, and the maximum cyan color transmission density of said medium-speed emulsion sublayer is not more than 0.35.

In the invention, the high-speed sublayer is preferably adjacent to the medium-speed sublayer, and the medium-speed sublayer adjacent to the low-speed sublayer as well.

In the invention, regarding the differences in the sensitivity between these sublayers, it is preferable that the high-speed sublayer's sensitivity is 0.1 to 1.0 log E higher than the medium-speed sublayer's, while the medium-speed sublayer's sensitivity is 0.1 to 1.0 log E higher than the low-speed sub-layer's.

The high-speed emulsion sublayer in the red-sensitive layer of the invention contains a two-equivalent cyan coupler, and may also contain a four-equivalent cyan coupler. Where the four-equivalent coupler is contained, the amount of the two-equivalent coupler accounts for preferably 50 to 100 mol% of the whole coupler content of the high-speed sublayer and the four-equivalent coupler accounts for the rest; more preferably 80 to 100 mol%; and most preferably 100 mol%.

The whole coupler content of the high-speed emulsion sublayer of the invention is preferably 1x10^{-4} to 1 mol, more preferably 1x10^{-3} to 1 mol, and most preferably 3x10^{-3} to 8x10^{-1} mol per mol of silver.

The two-equivalent coupler used in the invention is repre sented by the following Formula I:

Formula I

$$\begin{array}{c} Cp \\ * \\ | \\ X \end{array}$$

wherein Cp represents a coupler residue, * represents the coupling position of the coupler, and X is a group that splits off upon the coupler's coupling reaction with the oxidation product of an aromatic primary amine developing agent to form a dye.

Typical examples of the cyan coupler residue represented by Cp of the above formula are described in U.S. Patent Nos. 2,367,531, 2,423,730, 2,474,293, 2,772,162, 2,895,826, 3,002,836 and 3,034,892; and Agfa Mitteilung (Band II), pp.156 to 175 (1961).

The preferred among these are phenols and naphthols.

The split-off group represented by X is a monovalent group such as a halogen atom or an alkoxy, aryloxy, heterocyclic oxy, acyloxy, alkylthio, arylthio, heterocyclic thio;

wherein X_1 is a group of atoms necessary to form a 5- or 6-member ring together with at least one atom selected from the group consisting of a carbon atom, an oxygen atom, a nitrogen atom and a sulfur atom; a monovalent group such as acylamino or sulfonamido, or a bivalent group such as alkylene. In the case of a bivalent group, a dimer is formed with X.

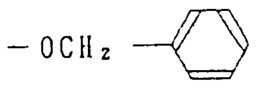
The following are examples of X.

Halogen atom:

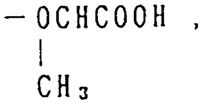
Chlorine, bromine, fluorine

Alkoxy group:

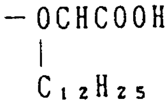
$-OC_2H_5$, $-OCH_2CONHCH_2CH_2OCH_3$,



, $-OCH_2CH_2SO_2CH_3$,

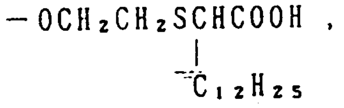


$-\mathrm{O}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCOOH}$,

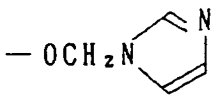


$-\mathrm{O}\underset{\mathrm{C_{12}H_{25}}}{\underset{|}{\mathrm{C}}}\mathrm{HCOOH}$,

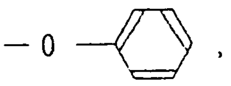
$-OCHCOOH$,

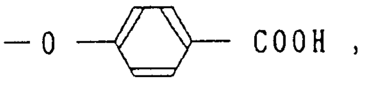


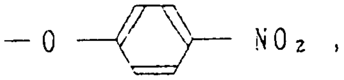
$-\mathrm{OCH_2CH_2S}\underset{\mathrm{C_{12}H_{25}}}{\underset{|}{\mathrm{C}}}\mathrm{HCOOH}$,

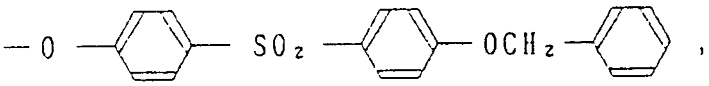


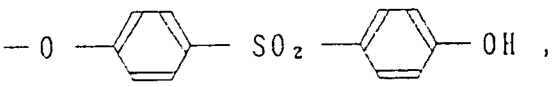
Aryloxy group:

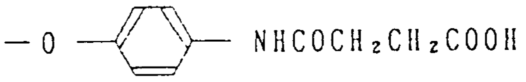


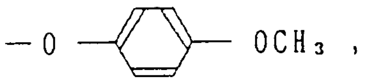


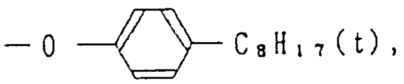


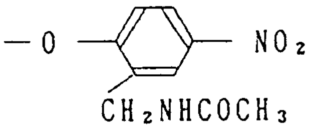




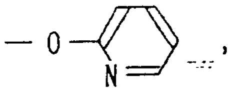


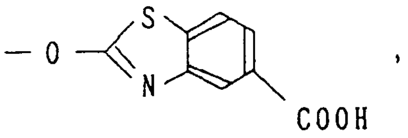


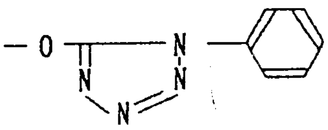




Heterocyclic oxy group:

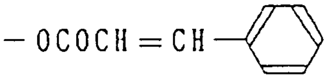




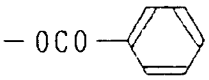


Acyloxy group:

$-OCOCH_3$,



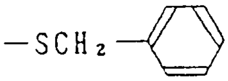
, $-OCOC_4H_9$,



, $-OCOCH_2CH_2COOH$

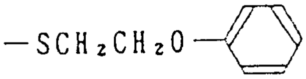
Alkylthio group:

$-SCH_3$, $-SC_2H_5$, $-SC_8H_{17}$, $-SC_{12}H_{25}$,

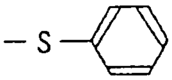


, $-SCH_2CH_2N(C_2H_5)_2$,

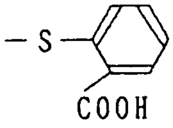
$-SCH_2COOC_2H_5$, $-SCH_2CH_2OC_2H_5$,



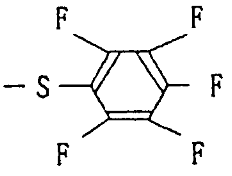
Arylthio group:

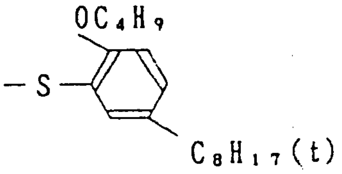


,

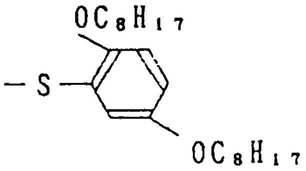


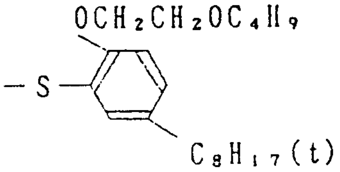
,



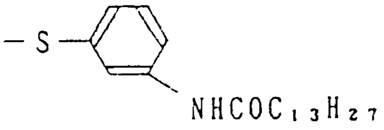


,

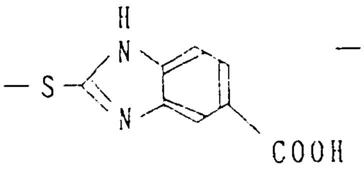




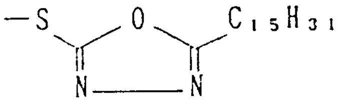
,

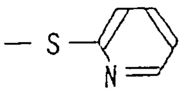


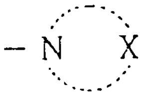
Heterocyclic thio group:



,



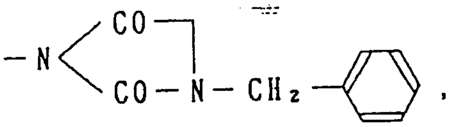


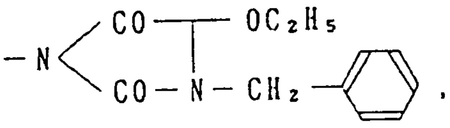


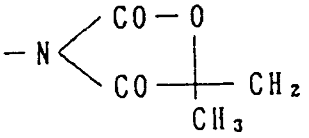
:

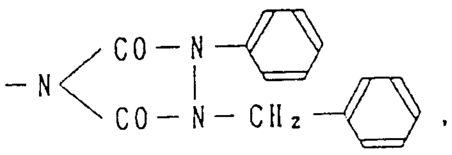
Pyrazolyl group, Imdazolyl group,

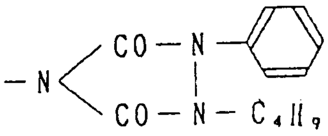
Triazolyl group, Tetrazolyl group,

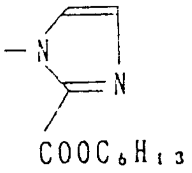


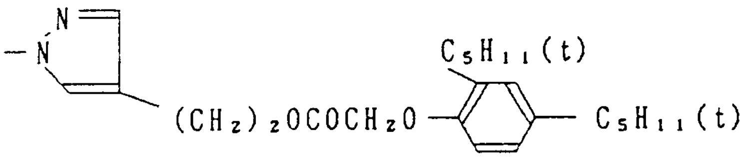


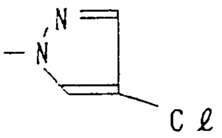




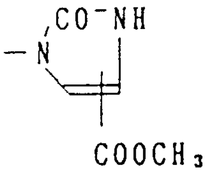




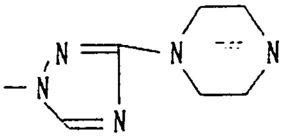




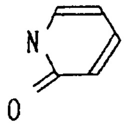
,



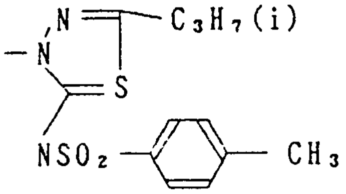
,



,

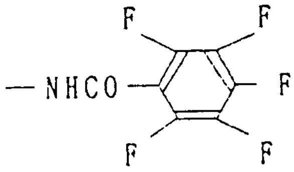


,



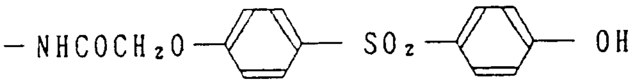
Acylamino group:

$-NHCOCF_3$,



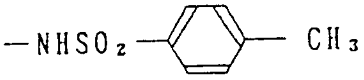
,

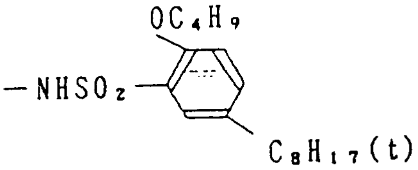
$-NHCO(CF_2CF_2)_2H$,



Sulfonamido group:

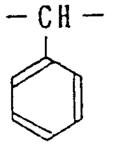
$-NHSO_2CH_3$,



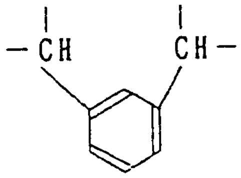


Alkylene group

$-CH_2-$,

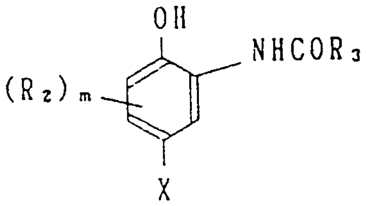


,

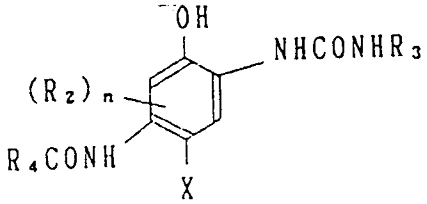


The preferred as the two-equivalent cyan coupler are the compounds having the following Formulas II, III and IV, and the most preferred are those having Formula III.

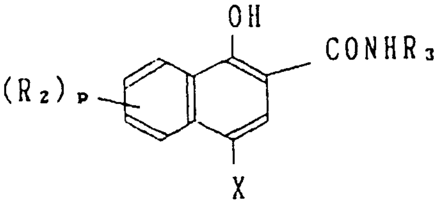
Formula II



Formula III



Formula IV



wherein R_2 and R_3 each represent a hydrogen atom or a substituent, R_4 represents a substituent, m is an integer of 1 to 3, n is an integer of 1 or 2, and p is an integer of 1 to 5, provided that m, n and p each are 2 or more, the respective R_2s may be either the same or different.

The substituent represented by R_4 is a halogen atom or an alkyl, cycloalkyl, aryl or heterocyclic group attached directly or through a bivalent atom or a group to the nucleus.

Examples of the above bivalent atom and group include oxygen, nitrogen and sulfur atoms and groups such as carbonylamino, aminocarbonyl, sulfonylamino, aminosulfonyl, amino, carbonyl, carbonyloxy, oxycarbonyl, ureylene, thioureylene, thiocarbonylamino, sulfonyl and sulfonyloxy.

The above alkyl, cycloalkyl, aryl and heterocyclic groups include those having a substituent such as a halogen atom or a nitro, cyano, alkyl, alkenyl, cycloalkyl, aryl, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, carboxy, sulfo, sulfamoyl, carbamoyl, acylamino, ureido, urethane, sulfonamido, heterocyclic, arylsulfonyl, alkylsulfonyl, arylthio, alkylthio, alkylamino, anilino, hydroxy, imido or acyl group.

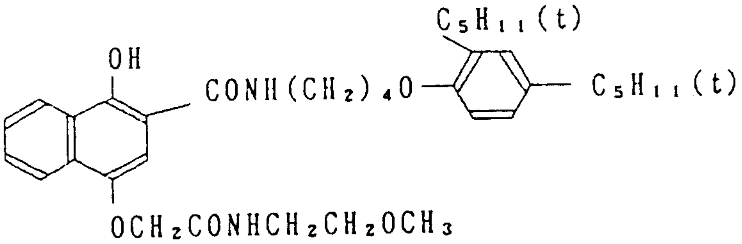
The alkyl, cycloalkyl, aryl and heterocyclic groups each represented by R_3 include those having a substituent, examples of which substituent include those previously exemplified as the substituent to the groups of R_2. R_4 is as defined and exemplified for R_3

In the two-equivalent cyan coupler, X is as previously defined for the X or Formula I, and is preferably a halogen atom or an alkoxy, aryloxy or sulfonamido group. The cyan couplers having Formulas I and II include those forming polymers beyond dimers with R_2, R_3 or X, while the couplers having Formula III include those forming polymers beyond dimers with R_2, R_3, R_4 or X.

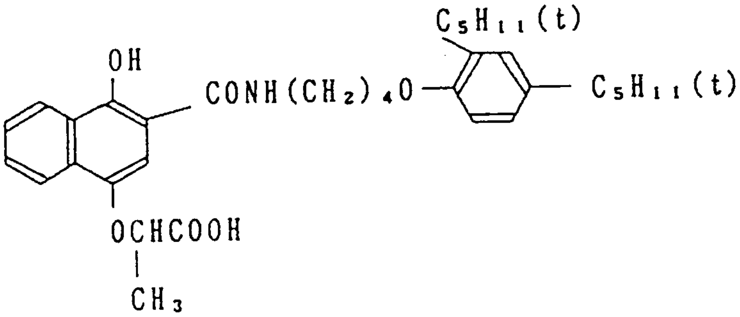
The following are the examples of the two-equivalent cyan couplers usable in the invention, but are not limited thereto.

Exemplified compounds

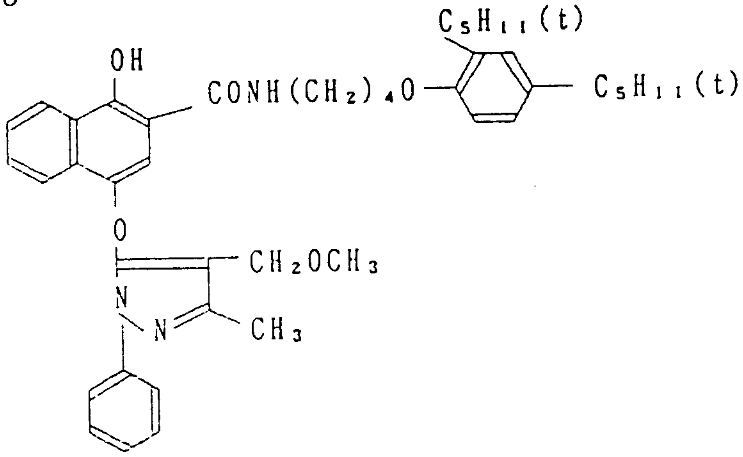
C − 1



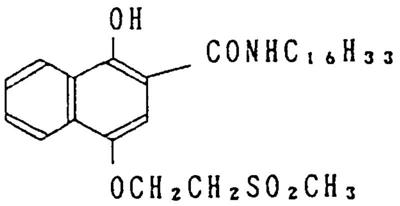
C − 2



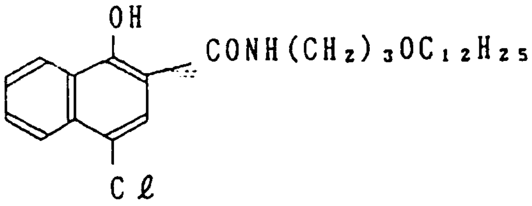
C − 3



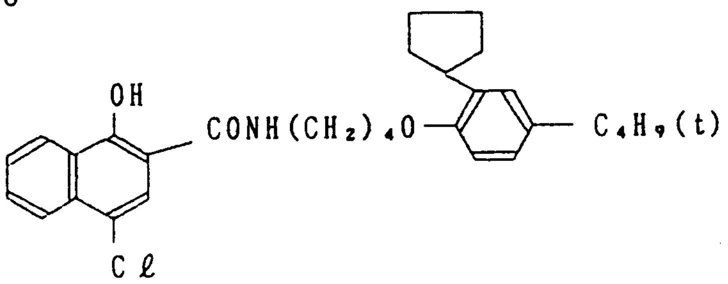
C − 4


OH
CONHC₁₆H₃₃
OCH₂CH₂SO₂CH₃

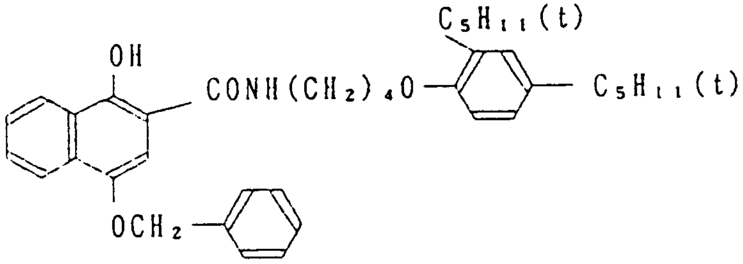
C − 5


OH
CONH(CH₂)₃OC₁₂H₂₅
Cℓ

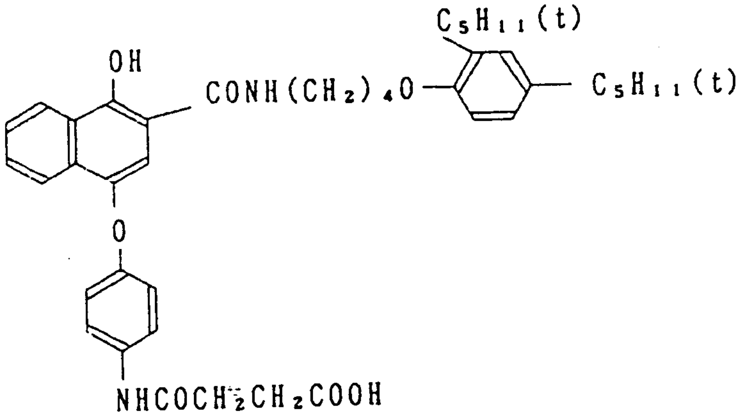
C − 6


OH
CONH(CH₂)₄O
C₄H₉(t)
Cℓ

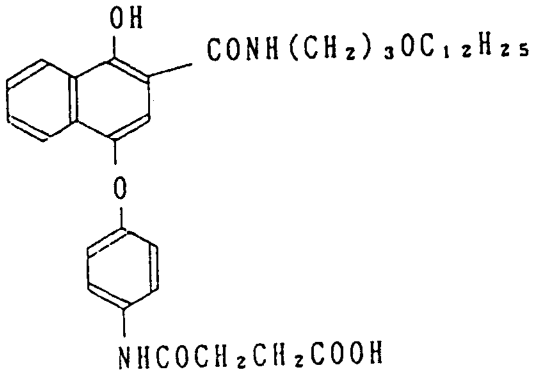
C − 7


C₅H₁₁(t)
OH
CONH(CH₂)₄O
C₅H₁₁(t)
OCH₂

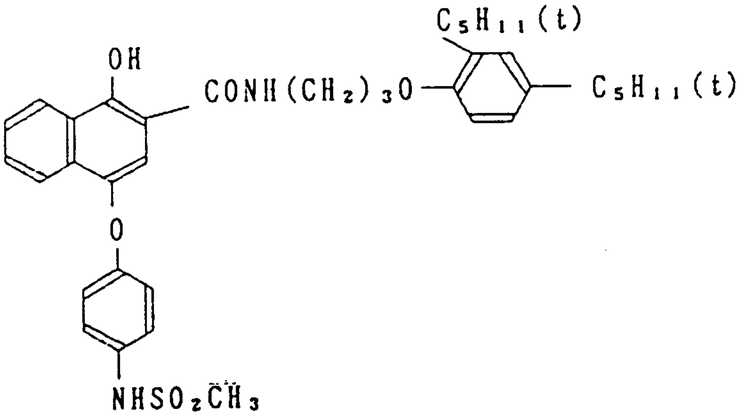
C − 8


OH
CONH(CH2)4O
C5H11(t)
C5H11(t)
O
NHCOCH2CH2COOH

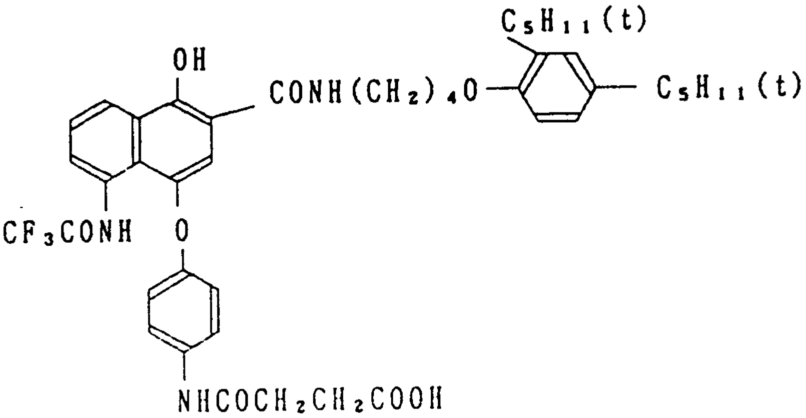
C − 9


OH
CONH(CH2)3OC12H25
O
NHCOCH2CH2COOH

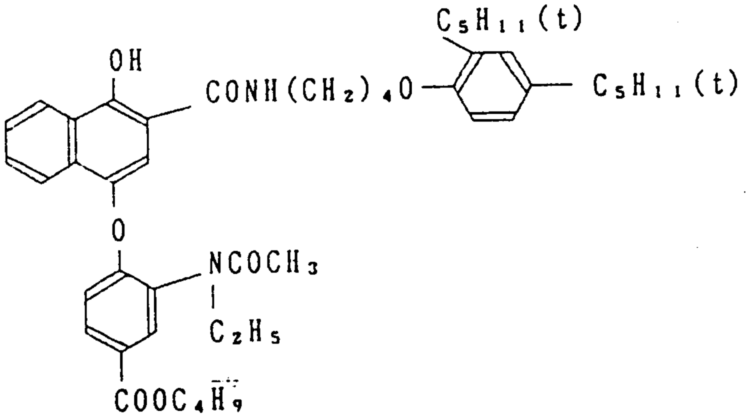
C－10


OH
CONH(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)
O
NHSO₂CH₃

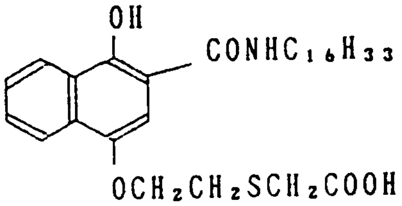
C－11


OH
CONH(CH₂)₄O
C₅H₁₁(t)
C₅H₁₁(t)
CF₃CONH
O
NHCOCH₂CH₂COOH

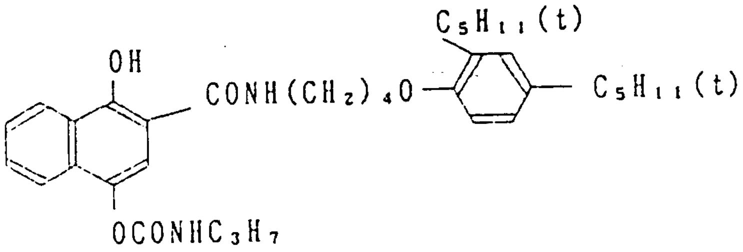
C－１２


C₅H₁₁(t)
OH
CONH(CH₂)₄O
C₅H₁₁(t)
O
NCOCH₃
C₂H₅
COOC₄H₉

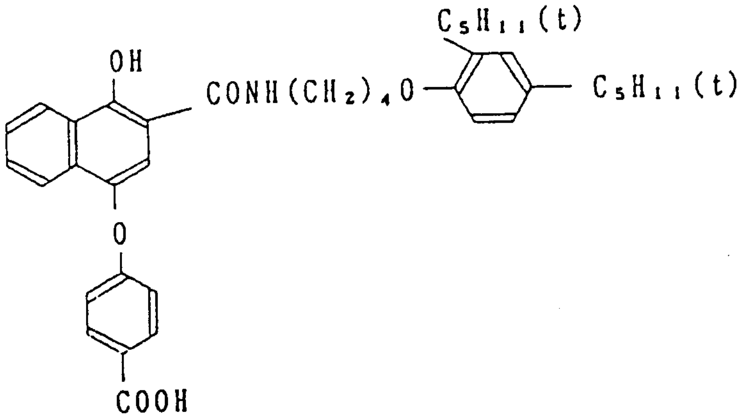
C－１３


OH
CONHC₁₆H₃₃
OCH₂CH₂SCH₂COOH

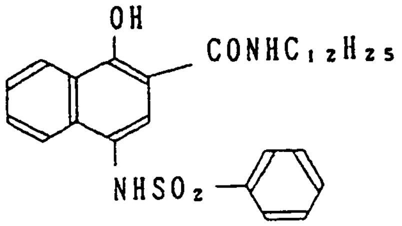
C－１４


C₅H₁₁(t)
OH
CONH(CH₂)₄O
C₅H₁₁(t)
OCONHC₃H₇

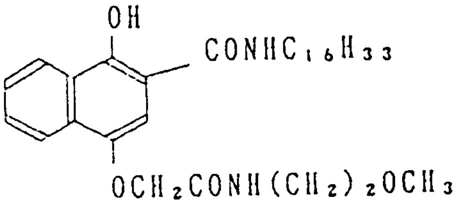
C－１５


OH
CONH(CH₂)₄O
C₅H₁₁(t)
C₅H₁₁(t)
O
COOH

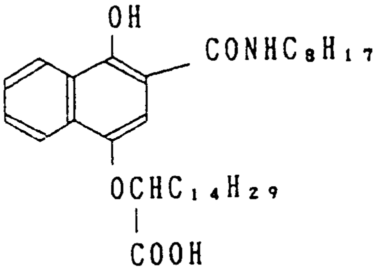
C－１６


OH
CONHC₁₂H₂₅
NHSO₂

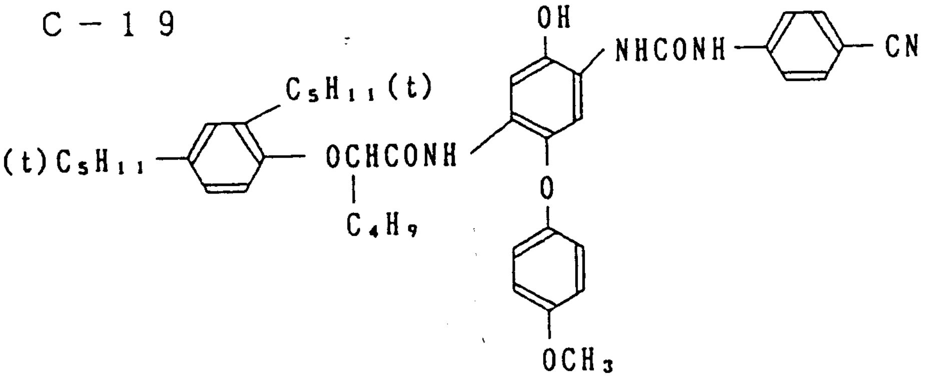
C－１７


OH
CONHC₁₆H₃₃
OCH₂CONH(CH₂)₂OCH₃

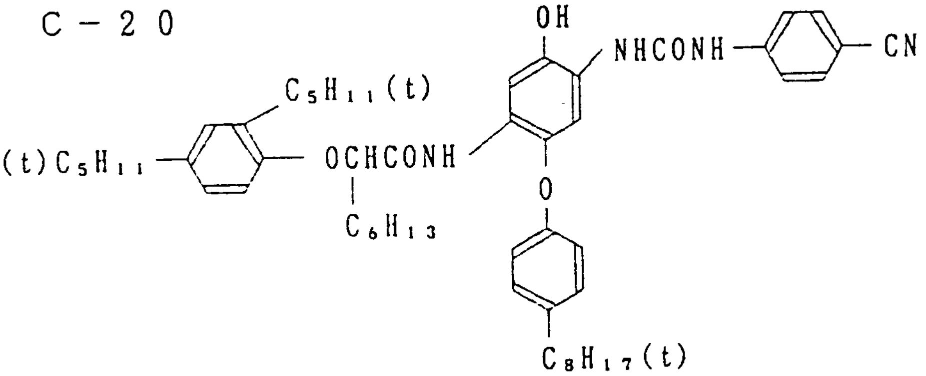
C－１８


OH
CONHC₈H₁₇
OCHC₁₄H₂₉
COOH

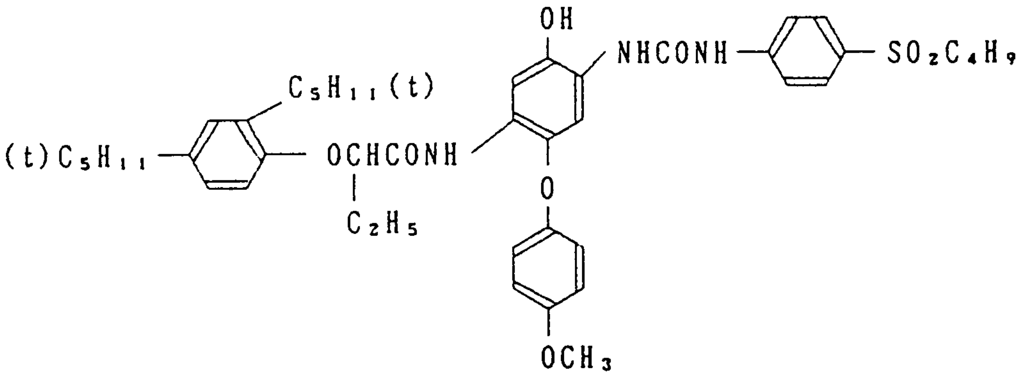
C－１９


OH
NHCONH
CN
C₅H₁₁(t)
(t)C₅H₁₁
OCHCONH
C₄H₉
O
OCH₃

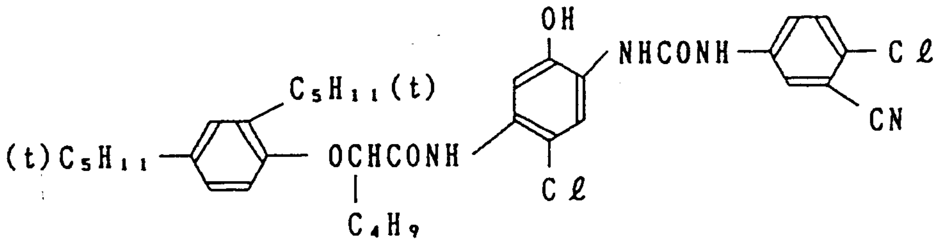
C－２０


OH
NHCONH
CN
C₅H₁₁(t)
(t)C₅H₁₁
OCHCONH
C₆H₁₃
O
C₈H₁₇(t)

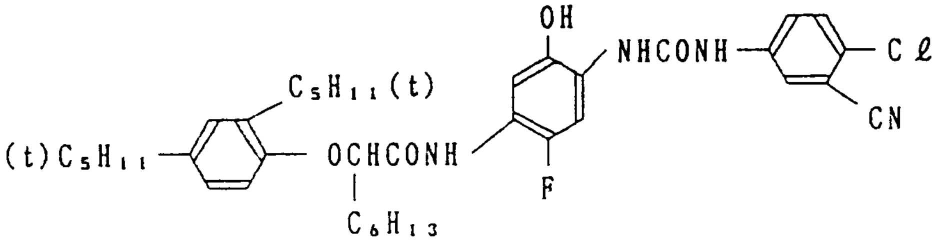
C－21



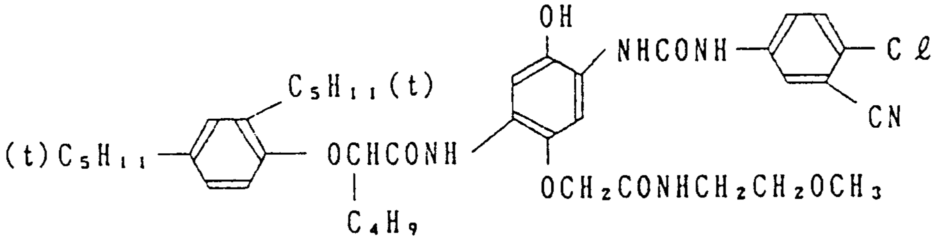
C－22



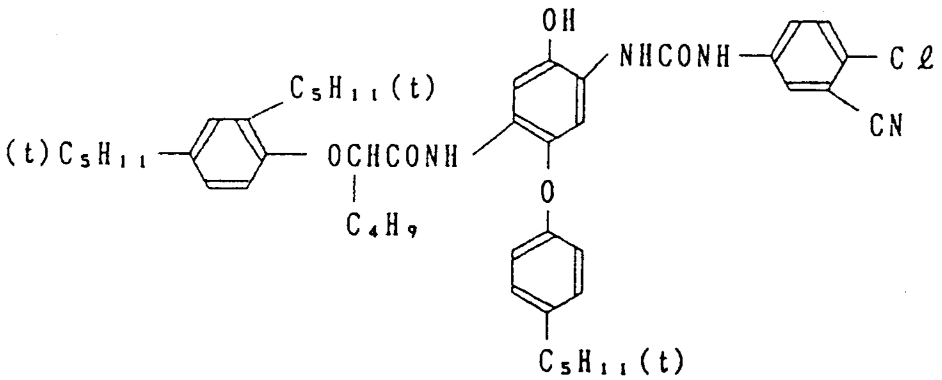
C－23



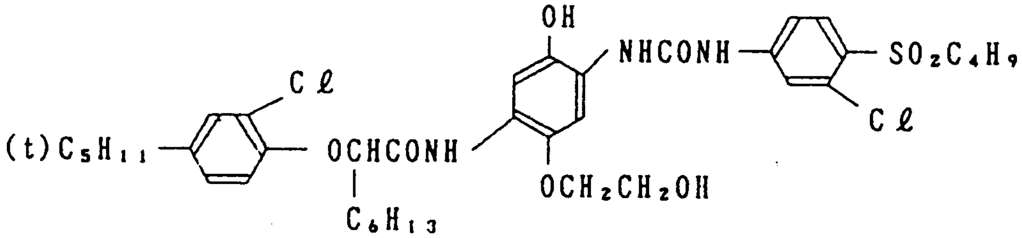
C－24



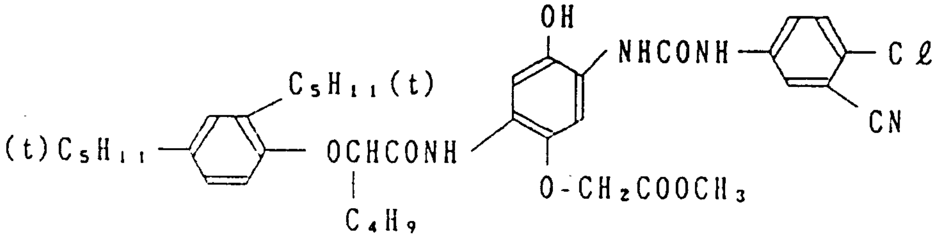
C－２５


OH
NHCONH
Cℓ
CN
$C_5H_{11}(t)$
$(t)C_5H_{11}$
OCHCONH
C_4H_9
O
$C_5H_{11}(t)$

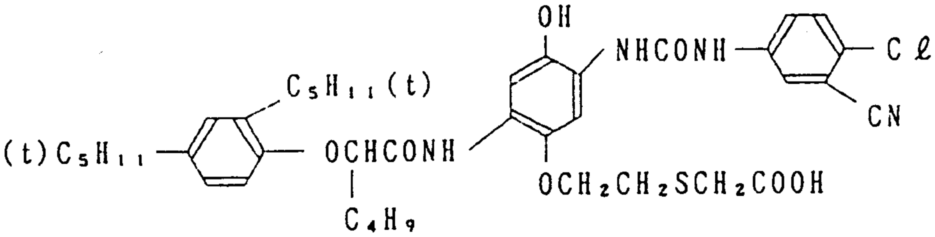
C－２６


OH
NHCONH
$SO_2C_4H_9$
Cℓ
Cℓ
$(t)C_5H_{11}$
OCHCONH
C_6H_{13}
OCH_2CH_2OH

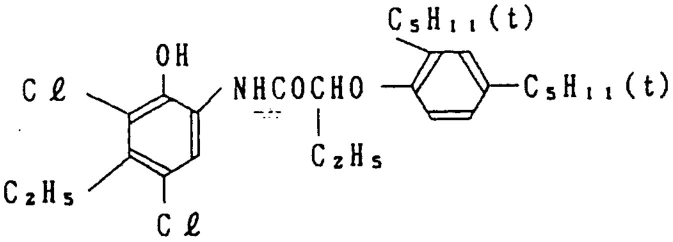
C－２７


OH
NHCONH
Cℓ
CN
$C_5H_{11}(t)$
$(t)C_5H_{11}$
OCHCONH
C_4H_9
$O-CH_2COOCH_3$

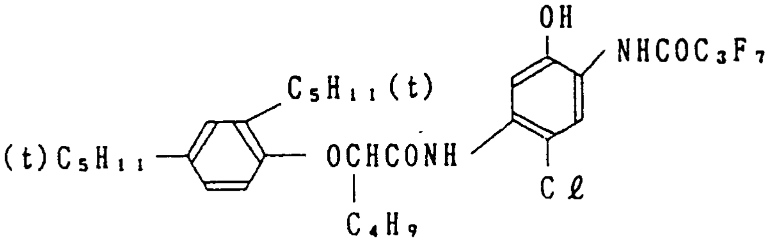
C－28


OH
NHCONH
Cℓ
CN
C5H11(t)
(t)C5H11
OCHCONH
C4H9
OCH2CH2SCH2COOH

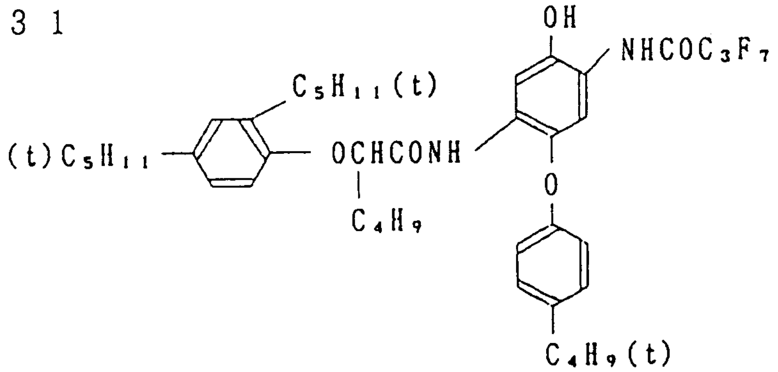
C－29


C5H11(t)
OH
Cℓ
NHCOCHO
C5H11(t)
C2H5
C2H5
Cℓ

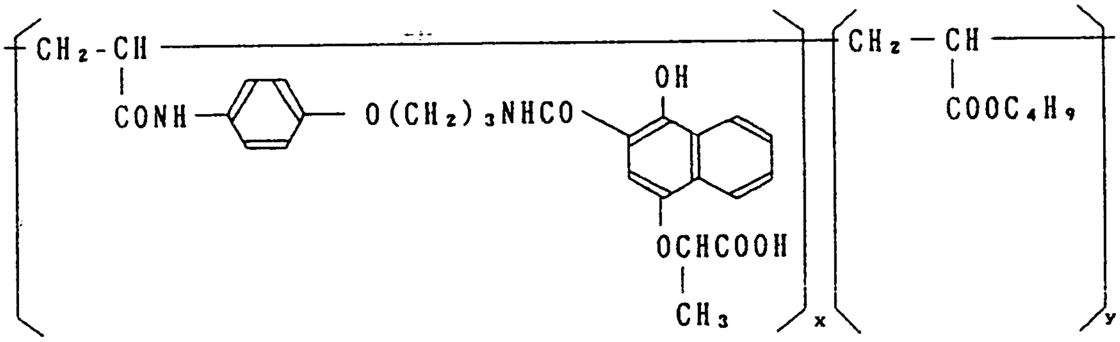
C－30


OH
NHCOC3F7
C5H11(t)
(t)C5H11
OCHCONH
C4H9
Cℓ

C - 3 1

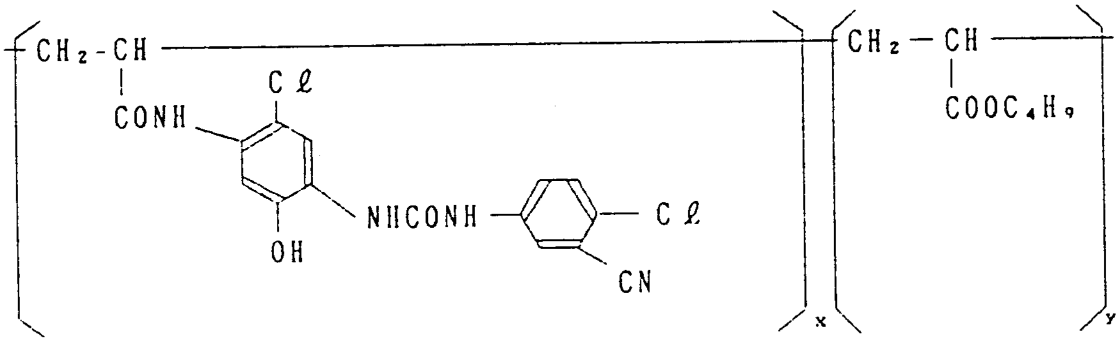


C - 3 2



x:y = 40:60 (ratio by weight)

C - 3 3



x:y = 50:50 (ratio by weight)

In the invention, the four-equivalent cyan coupler used in the red-sensitive medium-speed emulsion sublayer and low-speed emulsion sublayer, is preferably one having Formula I in which the X is a hydrogen atom, and more preferably one having Formula III in which the X is a hydrogen atom.

The medium and low-speed emulsion sublayers of the invention contain a four-equivalent cyan coupler, and may also contain a two-equivalent cyan coupler in combination. In that case, the amount of the four-equivalent cyan coupler used accounts for preferably 50 to 100 mol% of the whole coupler content of the medium and low-speed sublayers and the two-equivalent coupler accounts for the rest, more preferably 80 to 100 mol%, and most preferably 100 mol%, i.e., it is most preferable that the four-equivalent cyan coupler alone be used.

All the coupler amount contained in the medium and low-speed emulsion sublayers of the invention is preferably $1x10^{-4}$ to 1 mol, more preferably $1x10^{-3}$ to 1 mol and most preferably $3x10^{-3}$ to $8x10^{-1}$ mol per mol of silver.

In the invention, a diffusible DIR compound is added to the medium and low-speed emulsion sublayers of the red-sensitive emulsion layer.

The diffusible DIR compound is a compound which is capable of releasing a development inhibitor or a development inhibitor precursor upon its reaction with the oxidation product of a color developing agent and of which the diffusibility according to the following evaluation method is preferably not less than 0.34 and more preferably not less than 0.40.

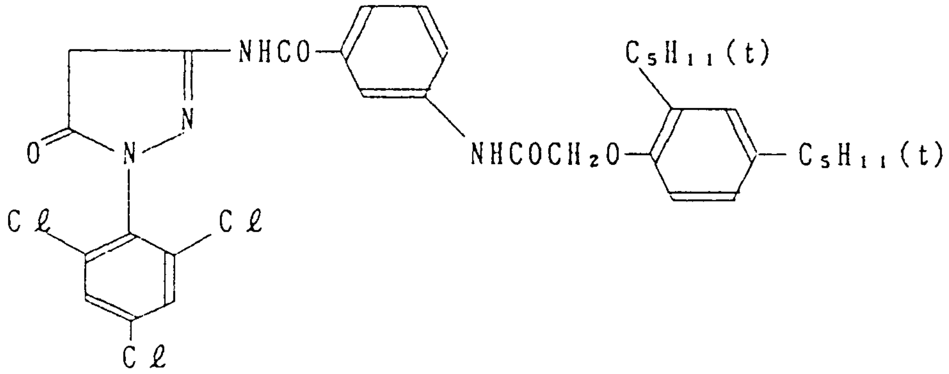
The diffusibility evaluation method is as follows:

Light-sensitive material Samples I and II having the following component layers on a transparent support are prepared.

Sample I: Sample having a Green-sensitive silver halide emulsion layer

A green-sensitive gelatino silver iodobromide emulsion layer (silver iodide content: 6mol%, average grain size: 0.48μm) containing 0.07 mol/mol Ag of the following coupler is coated so as to have a silver coating weight of 1.1g/m^2 and a gelatin coating weight of 3.0g/m^2, and on the emulsion layer is coated a protective gelatin layer containing chemically, spectrally unsensitized silver iodobromide (silver iodide content: 2mol%, average grain size: 0.08μm) so as to have a silver coating weight of 0.1g/m^2 and a gelatin coating weight of 0.8g/m^2.

Coupler:



Sample II: Sample the same as Sample I except that the protective layer contains no silver iodide.

Each of the layers of the above samples contains a gelatin hardener and a surfactant in addition to the above components.

Each of Samples I and II is exposed through an optical wedge to a white light, and then processed in the following manner. In the processing, two different developers are used; one containing various development inhibitors in an amount necessary to decrease the sensitivity of Sample II to 60%, and the other containing no development inhibitor.

Processing step (38° C)	
Color developing	2 min. 40 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 30 sec.
Drying	

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

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

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

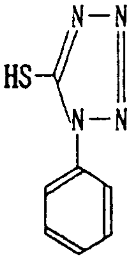
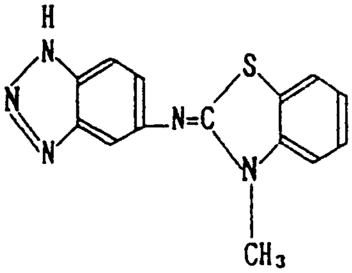
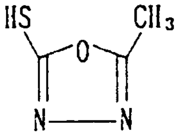
Fixing bath:	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water to make 1 liter.	
Adjust pH to 6.0 with acetic acid.	

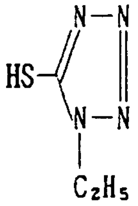
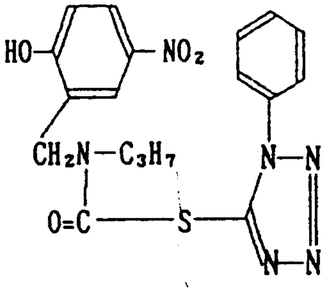
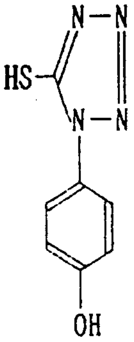
Stabilizing bath:	
Formalin (37% solution)	1.5 ml
Koniducks (product of KONICA Corp.)	7.5 ml
Water to make 1 liter.	

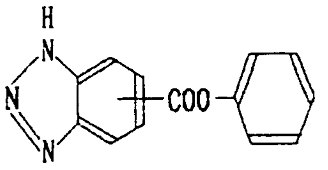
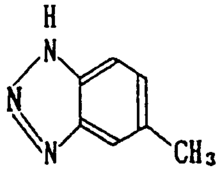
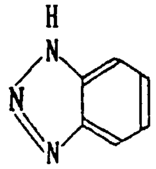
If the sensitivities of Samples I and II when processed in the developer containing no development inhibitor are denoted by S_0 and S_0', respectively, while when processed in the developer containing a development inhibitor are denoted by S_I and S_{II}, respectively, then
the desensitized degree of Sample I: $\Delta S = S_0 - S_I$,
the desensitized degree of Sample II: $\Delta S_0 = S_0' - S_{II}$,
Diffusibility: $\Delta S/\Delta S_0$,
provided that each sensitivity is the logarithm of reciprocal of an exposure amount (-log E) at the fog + 0.3 density point.

The diffusibility values of several development inhibitors obtained according to the above method are given in the following table.

Table

Structural formula	Adding amount	Desensitized degree		Diffusibility
	(mol/ℓ)	ΔS_0	ΔS	$\Delta S/\Delta S_0$
	1.3×10^{-5}	0.22	0.05	0.23
	1.3×10^{-5}	0.23	0.08	0.34
	2.5×10^{-5}	0.22	0.10	0.45

Structural formula	Adding amount	Desensitized degree		Diffusibility
	(mol/ℓ)	ΔS_0	ΔS	$\Delta S/\Delta S_0$
	3.0×10^{-5}	0.21	0.10	0.48
	1.4×10^{-5}	0.23	0.11	0.48
	2.5×10^{-5}	0.22	0.13	0.59

Structural formula	Adding amount	Desenstized degree		Diffusibility
	(mol/ℓ)	ΔS_0	ΔS	$\Delta S/\Delta S_0$
	3.5×10^{-5}	0.23	0.15	0.65
	4.3×10^{-5}	0.22	0.16	0.73
	1.7×10^{-4}	0.21	0.20	0.95

In the invention, there may be used any diffusible DIR compound regardless of its chemical structure as long as the diffusibility of the group released therefrom is in the above prescribed range.

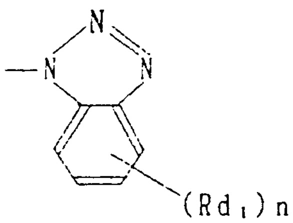
The following is a typical structural formula representing the diffusible DIR compound.

Formula D-1 $A\text{-}(Y)_m$

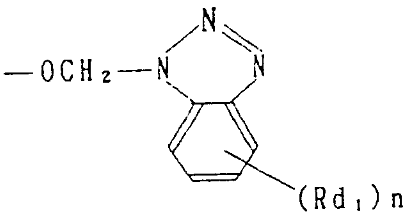
wherein A represents a coupler residue, m is an integer of 1 or 2, and Y represents a group attached to the coupling position of the coupler residue A and capable of splitting off upon the compound's reaction with the oxidation product of a color developing agent to release a development-inhibiting group or a development inhibitor having a diffusibility of more than 0.34.

In Formula D-1, Y is typically represented by the following Formulas D-2 to D-19.

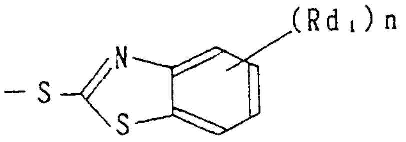
Formula D-2



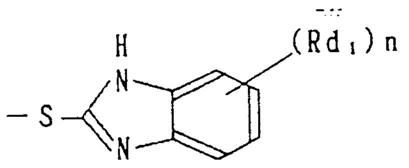
Formula D-3



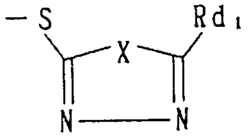
Formula D-4



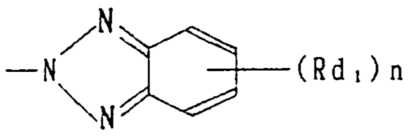
Formula D-5



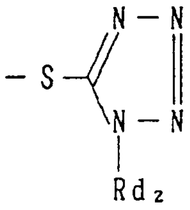
Formula D-6



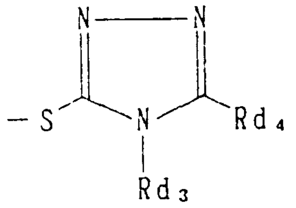
Formula D-7



Formula D-8



Formula D-9



In Formulas D-2 to D-7, Rd_1 is a hydrogen atom, a halogen atom or an alkyl, alkoxy, acylamino, alkoxycarbonyl, thiazolydinilidenamino, aryloxycarbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, N-alkylcarbamoyloxy, hydroxy, alkoxycarbonylamino, alkylthio, arylthio, aryl, heterocyclic, cyano, alkylsulfonyl or aryloxycarbonylamino group; n is an integer of 0, 1 or 2, provided that when n is 2, the Rd_1s may be either the same or different. The total number of carbon atoms contained in the n number of Rd_1s is from 0 to 10, and the number of carbon atoms contained in the Rd_1 of Formula D-6 is 0 to 15.

In Formula D-6, X represents an oxygen atom or a sulfur atom.

In Formula D-8, Rd_2 represents an alkyl group, aryl group or a heterocyclic group.

In Formula D-9, Rd_3 represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group, and Rd_4 represents a hydrogen atom, a halogen atom, or an alkyl, cycloalkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamido, cyano, heterocyclic, alkylthio or amino group.

The alkyl groups represented by Rd_1, Rd_2, Rd_3 and Rd_4 include those having a substituent, which may be either straight-chain or branched-chain.

The aryl groups represented by Rd_1, Rd_2, Rd_3 and Rd_4 include those having a substituent.

The heterocyclic groups represented by Rd_1, Rd_2, Rd_3 and Rd_4 include those having a substituent, and are in the form of preferably a single or condensed 5- or 6-member ring containing at least one hetero atom selected from the group consisting of a nitrogen atom, an oxygen atom and a sulfur atom. Examples of the heterocyclic group include pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, thiazolyl, triazolyl, benzotriazolyl, imido and oxazine groups.

The number of carbon atoms contained in the Rd_2 of Formulas D-6 and D-8 is 0 to 15.

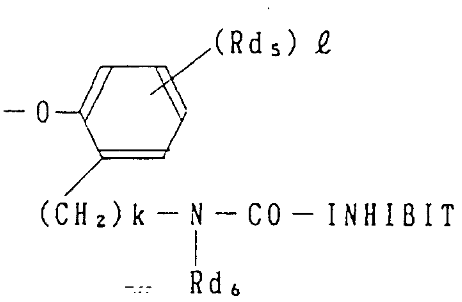
In Formula D-9, the total number of carbon atoms contained in Rd_3 and Rd_4 is 0 to 15.

Formula D-10 -TIME-INHIBIT

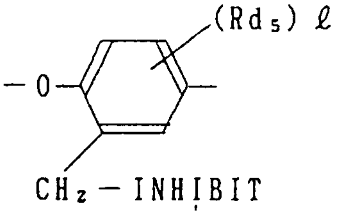
wherein TIME is a group attached to the coupling position of A and cleavable upon the coupler's reaction with the oxidation product of a color developing agent, and thereafter capable of controlling and releasing the INHIBIT group. The INHIBIT group is a group represented by the foregoing Formulas D-2 to D-9 which, after being released, becomes a development inhibitor.

In Formula 10, the -TIME-INHIBIT group is typically represented by the following Formulas D-11 to D-19.

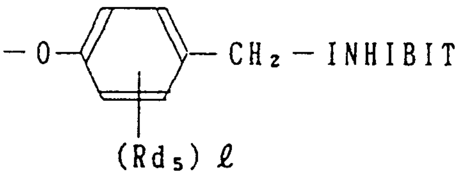
Formula D-11



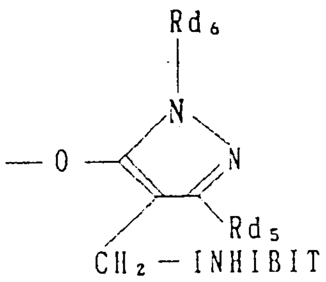
Formula D-12



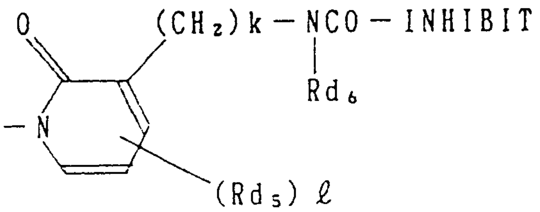
Formula D-13



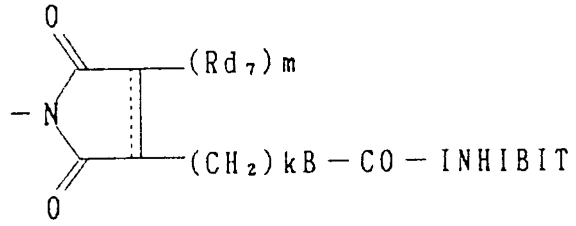
Formula D-14



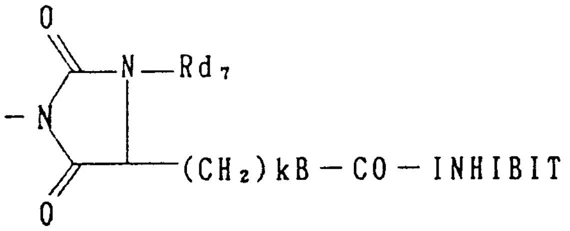
Formula D-15



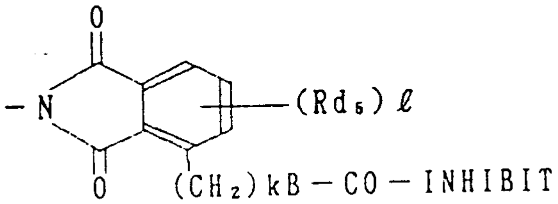
Formula D-16



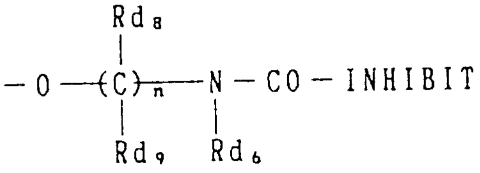
Formula D-17



Formula D-18

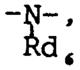


Formula D-19



$$-O-\Big(\underset{Rd_9}{\overset{Rd_8}{C}}\Big)_n-\underset{Rd_6}{N}-CO-INHIBIT$$

In Formulas D-11 to D-15 and D-18, Rd_5 represents a hydrogen atom, a halogen atom or an alkyl, cycloalkyl, alkenyl, aralkyl, alkoxy, alkoxycarbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamido, sulfamoyl, carbamoyl, aryl, carboxy, sulfo, hydroxy or alkanesulfonyl group. In Formulas D-11 to D-13, D-15 and D-18, the Rd_5s may combine with each other to form a condensed ring. In Formulas D-11, D-14, D-15 and D-19, Rd_6 is an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. In Formulas D-16 and D-17, Rd_7 is a hydrogen atom or an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. In Formula D-19, Rd_8 and Rd_9 each represent a hydrogen atom or an alkyl group preferably having 1 to 4 carbon atoms. In Formulas D-11 and D-15 to D-18, k is an integer of 0, 1 or 2. In Formulas D-11 to D-13, D-15 and D-18, 1 is an integer of 1 to 4. In Formula D-16, m is an integer of 1 or 2, provided that when m is 2, the Rd_7s may be either the same or different. In Formula D-19, n is an integer of 2 to 4, provided that the n number of Rd_8s and of Rd_9s may be either the same or different, respectively. In Formulas D-16 to D-18, B represents an oxygen atom or



$$\underset{Rd_6}{-\overset{|}{N}-},$$

wherein Rd_6 is as defined previously, and ---- implies that it may be either a single bond or double bond; in the case of a single bond, m is 2, while in the case of a double bond, m is 1. These INHIBIT groups have all the same meaning except the difference in the formula and the number of carbon atoms as defined in D-2 to D-9.

The total number of carbon atoms contained in the Rd_1s in one molecule of the INHIBIT group represented by Formula D-2 to D-7 is 0 to 32, the number of carbon atoms contained in the Rd_2 of Formula D-8 is 1 to 32, and the total number of carbon atoms contained in the Rd_3 and Rd_4 of Formula D-9 is 0 to 32.

The alkyl, aryl and cycloalkyl groups represented by Rd_5, Rd_6 and Rd_7 include those having a substituent.

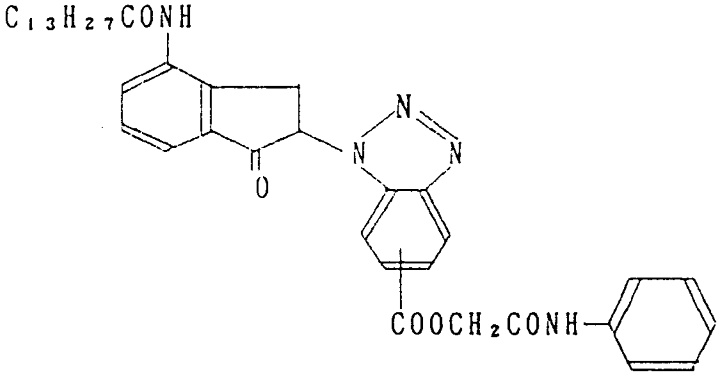
The preferred among the diffusible DIR compounds are those in which Y is represented by Formulas D-2, D-3 and D-10, and the preferred among the Y groups of Formula D-10 are those of which the INHIBIT group is represented by Formulas D-2, D-6 in which X is an oxygen atom, and D-8 in which Rd_2 is hydroxyaryl or alkyl having 1 to 5 carbon atoms.

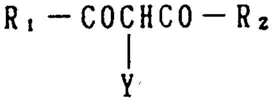
Examples of the coupler component represented by A of Formula D-1 include a yellow dye-image forming coupler residue, a magenta dye-image forming coupler residue, a cyan dye-image forming coupler residue and a colorless coupler residue.

The following are the examples of the useful DIR compounds for the invention, but are not limited thereto.

Exemplified compounds:

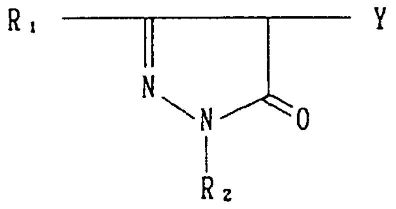
D - 1



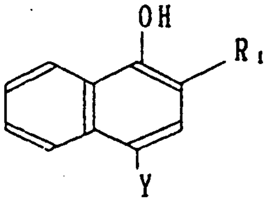


$$R_1-CO\underset{\underset{Y}{|}}{C}HCO-R_2$$

Exemplified compound No.	R_1	R_2	Y
D - 2	(1)	(1)	(30)
D - 3	(2)	(3)	(30)
D - 4	(2)	(4)	(30)
D - 5	(7)	(6)	(31)
D - 6	(2)	(4)	(32)
D - 7	(2)	(5)	(36)
D - 8	(7)	(8)	(33)
D - 33	(2)	(4)	(55)



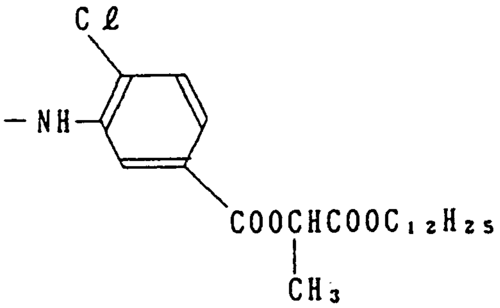
Exemplified compound No.	R_1	R_2	Y
D − 9	(9)	(10)	(30)
D − 10	(11)	(10)	(30)
D − 11	(12)	(7)	(34)
D − 12	(12)	(13)	(35)
D − 13	(9)	(14)	(36)
D − 14	(15)	(16)	(37)



Exemplified compound No.	R_1	Y
D－15	(17)	(38)
D－16	(17)	(39)
D－17	(18)	(40)
D－18	(19)	(41)
D－19	(18)	(42)
D－20	(18)	(43)
D－21	(18)	(44)
D－22	(19)	(45)
D－23	(18)	(46)
D－24	(21)	(47)
D－25	(21)	(48)
D－26	(22)	(49)
D－27	(22)	(50)

D－28	(22)	(51)
D－29	(23)	(52)
D－30	(18)	(53)
D－31	(18)	(54)
D－32	(23)	(49)
D－33	(18)	(55)
D－34	(18)	(56)

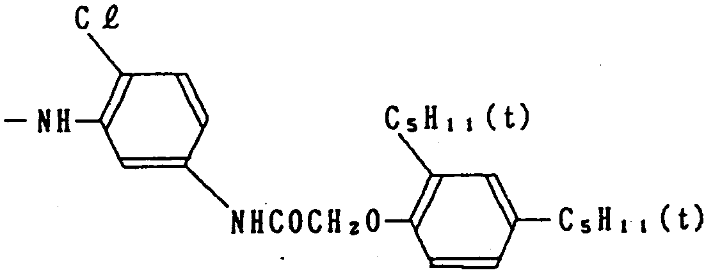
1


Cℓ
—NH
COOCHCOOC₁₂H₂₅
CH₃

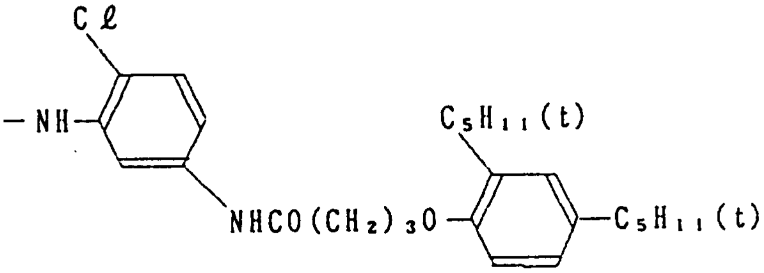
2

$-C(CH_3)_3$

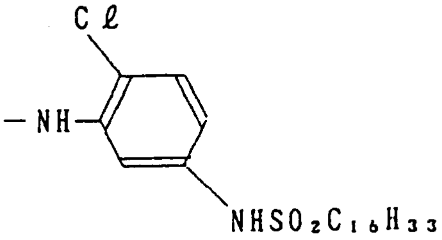
3


Cℓ
—NH
NHCOCH₂O
C₅H₁₁(t)
C₅H₁₁(t)

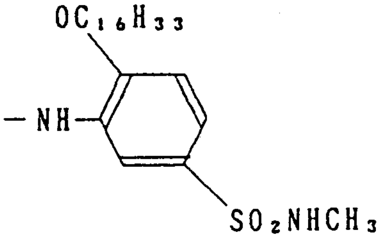
4


Cℓ
—NH
NHCO(CH₂)₃O
C₅H₁₁(t)
C₅H₁₁(t)

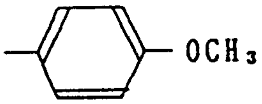
5


Cℓ
—NH—
NHSO₂C₁₆H₃₃

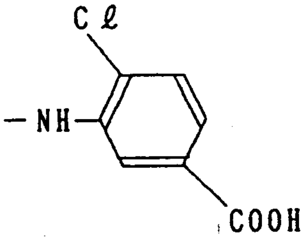
6


OC₁₆H₃₃
—NH—
SO₂NHCH₃

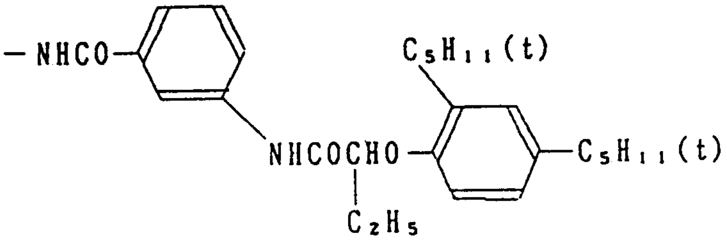
7


OCH₃

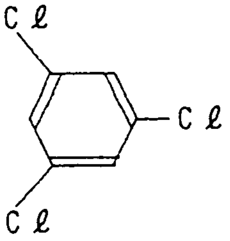
8


Cℓ
—NH—
COOH

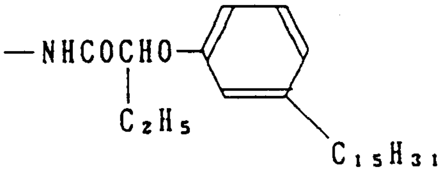
9


—NHCO—
C₅H₁₁(t)
NHCOCHO—
C₅H₁₁(t)
C₂H₅

10



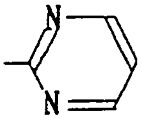
11



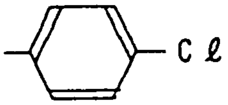
12

$-C_{17}H_{35}$

13



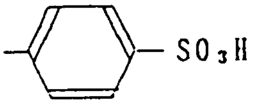
14



15

$-CH_3$

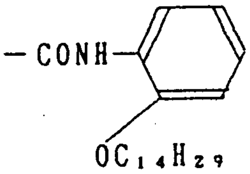
16



17

$-CONHC_{18}H_{37}$

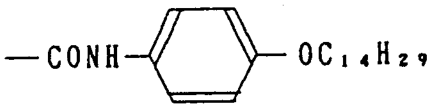
18



19

$-CONHC_{16}H_{33}$

20



21

$-CONHCH_2CH_2COOH$

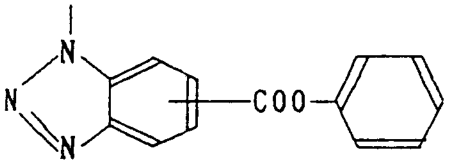
22

$-CONHCH_2CH_2COOCH_3$

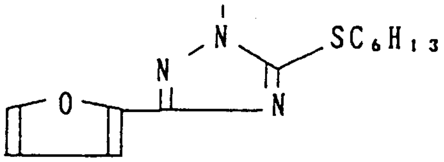
23

$-CONHCH_2CH_2COOCH_3$

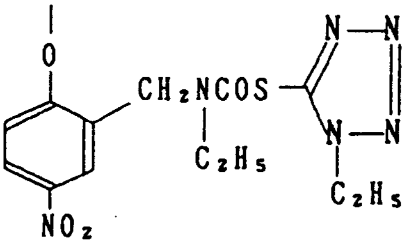
３０



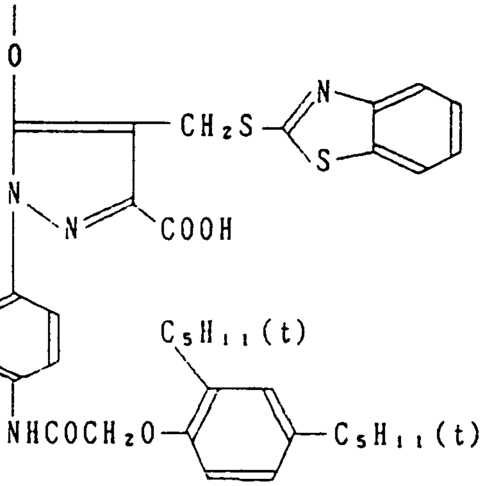
３１



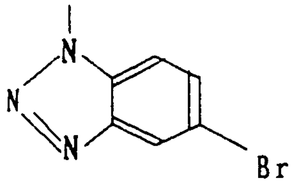
３２



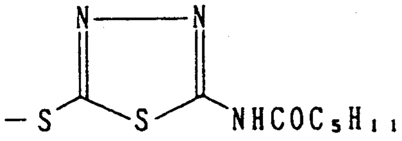
３３



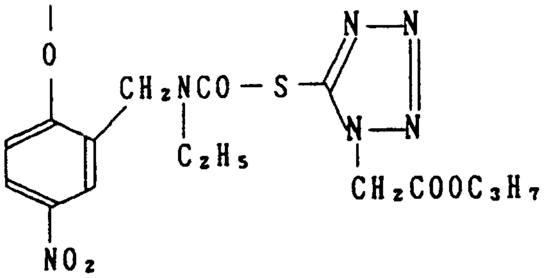
3 4


N
N
N
Br

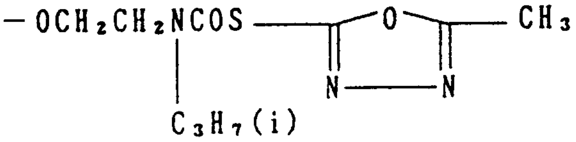
3 5


N
N
S
S
NHCOC₅H₁₁

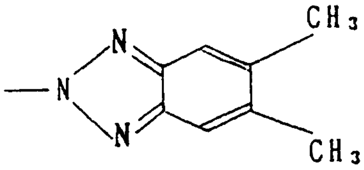
3 6


O
CH₂NCO — S
C₂H₅
N
N
N
N
CH₂COOC₃H₇
NO₂

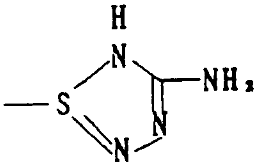
3 7


— OCH₂CH₂NCOS
O
CH₃
N
N
C₃H₇(i)

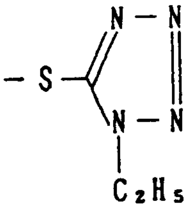
3 8



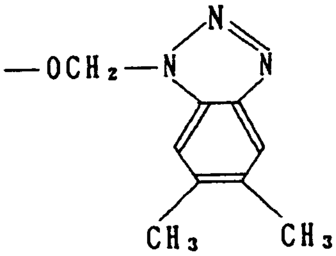
3 9



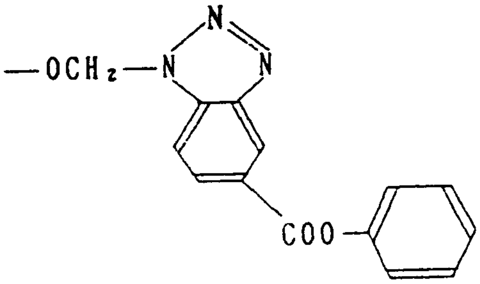
4 0



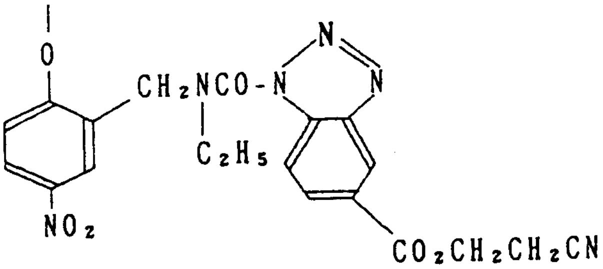
4 1



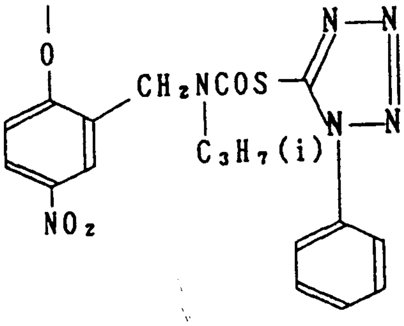
4 2



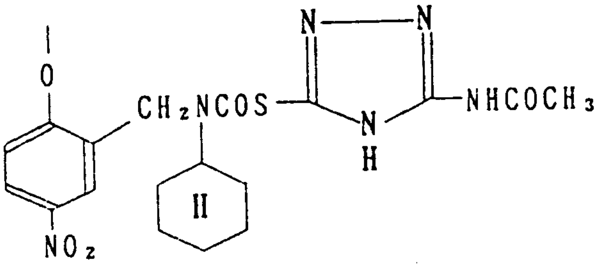
4 3



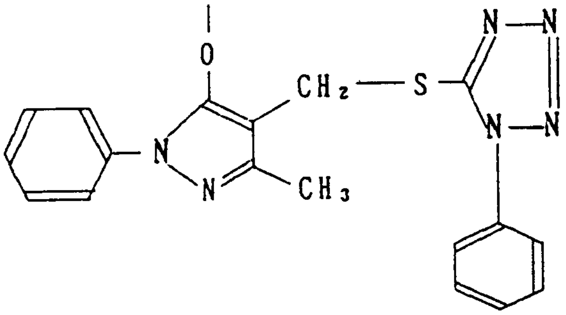
4 4



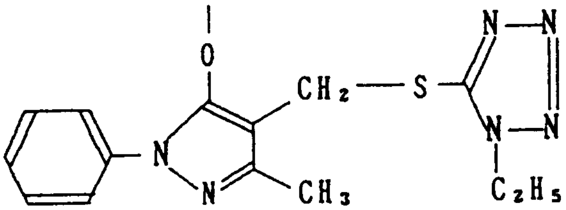
4 5



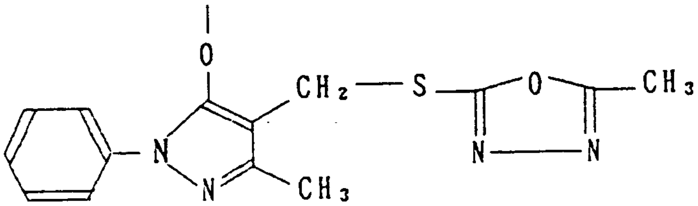
4 6



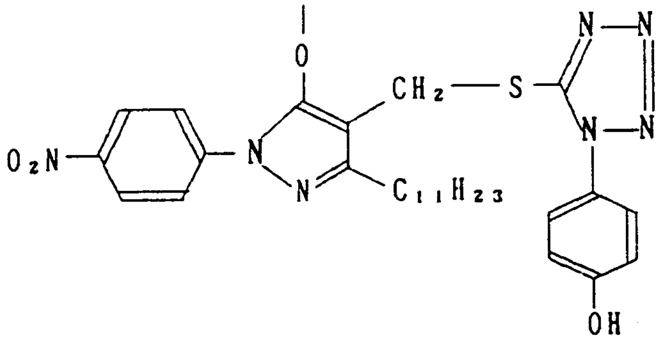
4 7



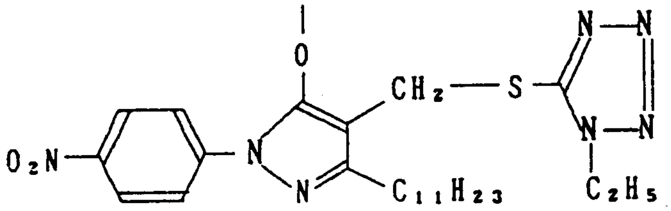
4 8



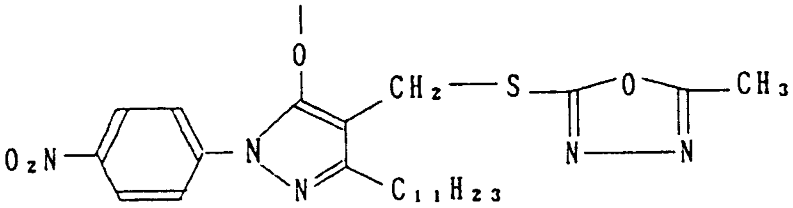
4 9



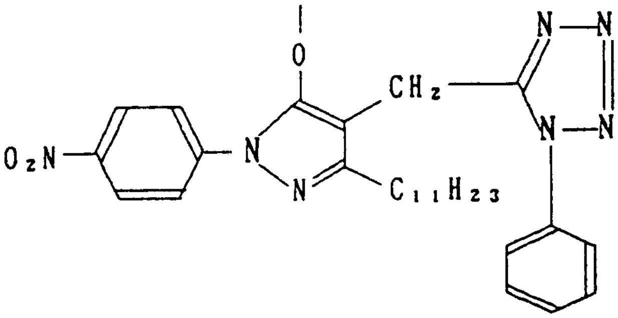
5 0



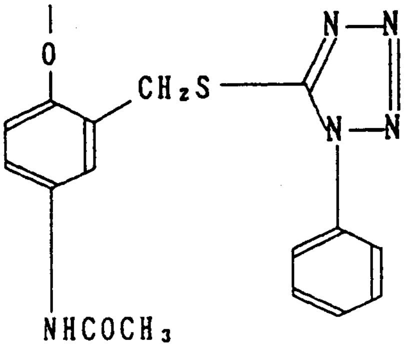
5 1



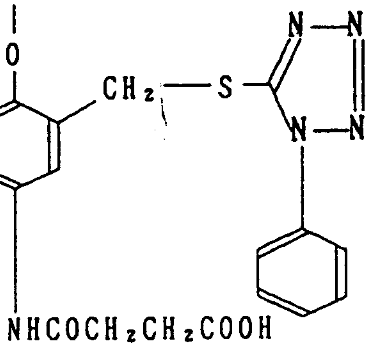
5 2



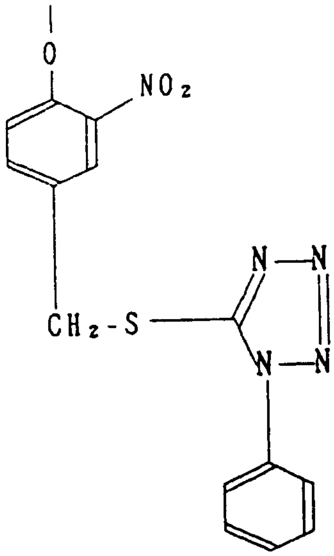
5 3



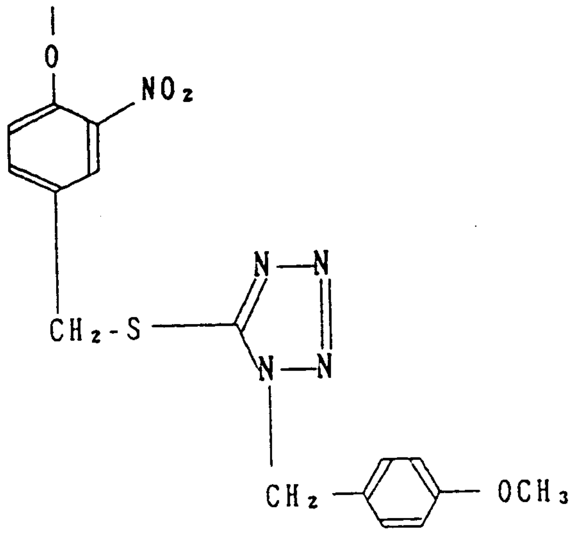
5 4



5 5



5 6



Including the above exemplified compounds, examples of the diffusible DIR compounds usable in the invention are described in U.S. Patent Nos. 4,234,678, 3,227,544, 3,617,291, 3,958,993, 4,149,866, 3,933,500, 2,072,363 and 2,070,266; JP O.P.I. Nos. 56837/1982 and 13239/1976; and Research Disclosure No. 21228, Dec. 1981.

The diffusible DIR compound is used in the amount range of preferably 0.0001 to 0.1 mol, and more preferably 0.001 to 0.05 mol per mol of silver halide.

The incorporation of the foregoing two-equivalent cyan coupler, four-equivalent cyan coupler and diffusible DIR compound into the emulsion layer may be carried out by adding to the emulsion a solution of them dissolved in a water-miscible organic solvent; adding to the emulsion an oil-in-water-type dispersion prepared by dissolving them in a water-nonmiscible organic solvent, particularly a high-boiling solvent, and dispersedly mixing the solution with a hydrophilic colloid liquid; adding to the emulsion a suspension/dispersion of them in the milled solid state; or by the deposition-precipitation dispersion method as disclosed in JP O.P.I. No. 120848/1990, European Patent No. 374,837 and World Patent No. 90/08345.

In the invention, the maximum cyan color transmission density of the medium-speed emulsion sublayer of the red-sensitive layer is obtained in the following manner:

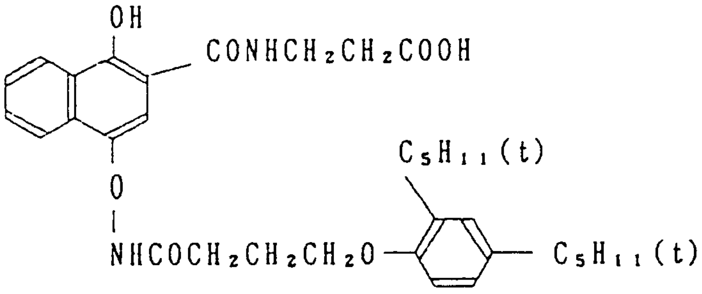
A sample is prepared in the same manner as in the foregoing sample except that the medium-speed emulsion sublayer of the red-sensitive layer thereof has the silver halide and coupler removed therefrom and instead contains 0.08g/m^2 of the following compound C-X thereby to be replaced by a non-color forming layer comprised substantially of gelatin alone, provided that the gelatin amount is adjusted so as not to change the whole layer thickness. The obtained sample is exposed for 1/100 sec. through an optical wedge with a W-26 filter, manufactured by Eastman Kodak Company, to a white light, and then subjected to the hereinafter described Processing A to thereby obtain a characteristic curve. Further, a standard sample (such as one of Samples 101 to 108 in Table 1 and Samples 201 to 208 in Table 3, which will be described hereinafter) also is exposed and processed likewise to obtain its characteristic curve. And the difference between both the samples is found, which is regarded as the maximum color density of the medium-speed emulsion sublayer.

In the invention, the maximum cyan color transmission density of the medium-speed red-sensitive emulsion layer is preferably not more than 0.35, more preferably 0.05 to 0.30, and most preferably 0.10 to 0.25.

The maximum color transmission density of the high-speed emulsion sublayer of the red-sensitive layer of the invention is preferably 0.3 to 1.0, and more preferably 0.4 to 0.9.

And, the maximum color transmission density of the low-speed emulsion sublayer of the red-sensitive layer is preferably 0.6 to 2.0, and more preferably 0.7 to 1.8.

C-X



Processing A (38 ° C)	
Color developing	1 min. 45 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 30 sec.
Drying	

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

Color developer	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.75g
Anhydrous sodium sulfite	4.25g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate, monohydrate	2.5 g
Potassium hydroxide	1.0 g
Water to make 1 liter (pH = 10.1)	

Bleaching bath	
Ferric-ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetatraacetate	1.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 ml
Water to make 1 liter.	
Adjust pH to 6.0 with ammonia water.	

Fixing bath	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water to make 1 liter.	
Adjust pH to 6.0 with acetic acid.	

Stabilizing bath	
Formalin (37% solution)	1.5 ml
Koniducks (product of KONICA Corp.)	7.5 ml
Water to make 1 liter	

The silver halide color photographic light-sensitive material of the invention preferably has an ISO speed of not less than 100. The method for determining an ISO speed is specified in JIS K 7614-1981.

The silver halide color photographic light-sensitive material of the invention preferably has a monodisperse silver halide emulsion. The monodisperse silver halide emulsion is an emulsion comprising silver halide grains, in which the weight of the silver halide grains confined within the average grain diameter $\bar{d}$ ±20% range accounts for preferably 70% or more, more preferably 80% or more, and most preferably 90% or more of the whole silver halide weight.

The average grain diameter $\bar{d}$ is defined by the grain diameter di in the case where $n_i \times d_i^3$, the product of the frequency n_i of grains having a grain diameter d_i and d_i^3, is the maximum (rounded to three decimal places).

The grain diameter herein is the diameter of a circular image equivalent in the areal to the projection image of a grain.

The grain diameter can be obtained by actually measuring the diameter or the area of the grain image formed on a photographic print or projected on a screen by magnifying a silver halide grain 10,000 to 50,000 times through an electron microscope (the number of grains subjected to the measurement shall be 1000 or more selected at random).

The highly monodisperse emulsion suitable for the invention has a grain diameter distribution width of preferably not more than 20%, and more preferably not more than 15%, wherein the grain diameter distribution width is defined by

$$\frac{\text{Grain diamter's standard deviation}}{\text{Average grain diameter}} \times 100 = \text{distribution width (\%)}$$

Herein, the method for measuring grain diameters complies with the aforementioned method, and the average grain diameter is an arithmetic mean.

$$\text{Average grain diameter} = \frac{\sum d_i n_i}{\sum n_i}$$

The silver halide emulsion of the invention comprises silver iodobromide emulsion of which the average silver iodide content is preferably 4 to 20 mol%, and more preferably 5 to 15 mol%.

The silver halide emulsion used in the invention may contain silver chloride in an amount not to impair the effect of the invention.

The silver halide grain used in the invention has thereinside a high silver halide-content phase.

The silver halide content of the high silver iodide-content phase is preferably 15 to 45 mol%, more preferably 20 to 42 mol%, and most preferably 25 to 40 mol%.

The silver halide grain of the invention has the internal high silver iodide-content phase covered with an external low silver iodide-content phase.

The average silver iodide content of the external low silver iodide-content phase that forms the outermost phase of the grain is preferably not more than 6 mol%, and more preferably 0 to 4 mol%. A medium silver iodide-content phase (intermediate phase) may be present between the outermost phase and the internal high silver iodide-content phase.

The silver iodide content of the intermediate phase is preferably 10 to 22 mol%, and more preferably 12 to 20 mol%.

Each of the differences in the silver iodide content between the outermost phase and the intermediate phase and between the intermediate phase and the high silver iodide-content phase is preferably not less than 6 mol%, and more preferably not less than 10 mol%.

In the above embodiment, there may be present another silver halide phase as the core of the high silver iodide-content phase, still another silver halide phase between the high silver iodide-content phase and the intermediate phase and a further silver halide phase between the intermediate phase and the outermost phase.

The volume of the outermost phase accounts for preferably 4 to 70%, more prefeably 10 to 50%, that of the high silver iodide-content phase accounts for preferably 10 to 80%, more preferably 20 to 50% and most preferably 20 to 45%, and that of the intermediate phase accounts for 5 to 60%, and more preferably 20 to 55% of the whole volume of the grain.

The above phases each may be a single phase of a homogeneous composition, a complex phase of a homogeneous composition or a group of phases having stepwise varied compositions, and besides arbitrary one of these phases may have a continuously varied composition.

Another embodiment of the silver halide emulsion of the invention is such that the silver iodide content continuously changes from the core toward the external of the grain rather than the silver iodide present locally forms substantially stepwise uniform phases. In this instant, the silver iodide content preferably decreases monotonously from its maximum content point inside the core to the external of the grain.

The silver iodide content at its maximum content point is preferably 15 to 45 mol%, and more preferably 25 to 40 mol%.

The silver iodide content of the surface phase of the silver iodobromide grain is preferably not more than 6 mol%, and more preferably 0 to 4 mol%.

The silver halide emulsion used in the invention preferably satisfies at least one of the following requirements (1) to (4):

(1) When the average silver iodide content J_1 obtained by an X-ray fluorescence analysis and the average silver iodide content J_2 by an X-ray photoelectron spectral analysis are compared, the emulsion shall satisfy the relation of $J_1>J_2$.

The grain diameter herein is the diameter of the circumcircle where the projection image area of the grain is maximum.

The X-ray photoelectron spectral analysis is explained.

The emulsion is pretreated as follows prior to measurement by the X-ray photoelectron spectral analysis. Firstly, the emulsion, after adding a pronase solution thereto, is stirred for one hour at 40°C for gelatin decomposition, and then centrifuged to deposit the emulsion grains. After removing the supernatant in the decantation manner, the pronase solution is added to the grains to repeat gelatin decomposition under the same conditions as the above. This sample is again centrifuged to remove its supernatant therefrom, then distilled water is added thereto to redisperse the emulsion grains into water, then again centrifuged to remove its supernatant therefrom...., thus repeating this washing operation three times. After that, the emulsion grains are redispersed into ethanol, which is then thinly coated on a mirror-like polished silicon wafer to thereby prepare a sample for measurement.

For the measurement according to the X-ray photoelectrone spectral analysis there may be used a measuring instrument such as an ESCA/SAM560, manufactured by PHI Co., provided with Mg-Kα rays as an excitation X-ray source, which is operated under conditions of an X-ray source power of 15KV, an X-ray source current of 40mA and a pass energy of 50eV.

In order to find the surface halide composition, Ag3d, Br3d and I3d3/2 electrons are detected. The composition ratio is calculated according to a relative speed coefficient method by using the respective peaks' integral intensities. The composition ratio is rendered in atomic percentages by using 5.10, 0.81 and 4.592 as the relative speed coefficients of Ag3d, Br3d and I3d3/2.

(2) When the average silver iodide content J_1 obtained by the foregoing X-ray fluorescent analysis and the average silver iodide content J_3 measured on the silver halide crystal 80% or more apart in the direction of the grain diameter from the center of the grain by using an X-ray microanalysis method are compared, the emulsion shall satisfay the relation of $J_1 > J_3$.

The X-ray microanalysis method is explained.

Silver halide grains are dispersed in an electron-microscopic observation grid of an electron microscope equipped with an energy-dispersion-type X-ray analyzer, the grid is cooled by liquid nitrogen, the magnification is set so as to get one grain in the CRT field of view, and the intensities of AgLα and ILα rays are integrated for a given period of time. From the intensity ratio of ILα/AgLα and an in advance prepared calibration curve, a silver iodide content can be calculated.

(3) At the maximum peak height x 0.13 of a (420) X-ray diffraction signal with CuKα rays as an X-ray source, the emulsion is characterized by having a continuous signal over a diffraction angle of more than 1.5; preferably has a continuous signal over a diffraction angle of more than 1.5 at the signal's maximum peak height x 0.15; more preferably has a continuous signal over a diffraction angle of more than 1.8; and most preferably has a continuous signal over a diffraction angle of more than 2.0. That the emulsion has the signal means that at the maximum peak height x 0.13 or 0.15, it has a signal intensity more than the height.

A more preferred embodiment of the silver halide emulsion of the invention is such that it has two or three peaks, more preferably three peaks, in the above (420) X-ray diffraction signal with CuKα rays as the X-ray source.

The X-ray diffractometry is known as a method useful for examining the structure of silver halide crystals.

As the X-ray source for the method there may be used various characteristics-having X rays. Particularly. CuLα rays with Cu used as a target is most widely used.

Silver iodobromide has a rock-salt structure, which shows a diffraction angle 2 of 71 to 74° in the (420) X-ray diffraction signal with CuKα rays. The X-ray diffractometry generates a relatively high-intensity signal at a high angle and a good resolution, so that it is suitable for examining crystal structures.

In the X-ray diffractometry of the photographic emulsion, it is necessary to remove gelatin from and mix a reference sample such as silicon with the emulsion and to perform the measurement of the emulsion in a powder state.

For the measurement reference can be made to the Kiso-Bunseki Kagaku Koza 24 'X-sen Bunseki' (Basic Analytical Chemistry Course 24 'X-ray Analysis'), published by Kyoritsu Publishing Co.

(4) When the average silver iodide content of the individual silver halide grains of the emulsion is measured according to the aforementioned X-ray microanalysis method, the measured values' relative standard deviation shall be preferably not more than 20%, more preferably not more than 15%, and most preferably not more than 12%.

The above relative standard deviation is

$$\frac{\text{Standard deviation of silver iodide content values*}}{\text{Average silver iodide content}} \times 100$$

Note * The values obtained by measuring at least 100 emulsions.

The silver halide crystal used in the invention may be a regular crystal such as a cubic, tetradecahedral or octadecahedral crystal, or a tabular twin crystal, or a mixture of these crystals.

In the case of the tabular twin crystal, the projected image area of ones each in which the ratio of the diameter of a circular image equivalent in the area to that of its projection image and its thickness is in the range of from 1 to 20 accounts for preferably more than 60% of the whole projected image area of the twin crystal grains in a scene. And the above ratio range is preferably less than 8.0, and more preferably not less than 1.5 and less than 5.0.

The monodisperse regular crystal grains-containing emulsion of the invention can be prepared by making reference to the methods described in JP O.P.I. Nos. 177535/1984, 138538/1985, 52238/1984, 143331/1985, 35726/1985, 258536/1985 and 14636/1986.

The monodisperse twin crystals emulsion may be prepared making reference to the spherical seed grains growing method disclosed in JP O.P.I. No. 14636/1986.

In growing seed grains, it is preferable to add a silver nitrate aqueous solution and a halide aqueous solution by a double-jet process. An iodide may be provided in the form of silver iodide to the system. The addition should be made at a speed not to generate new nuclei and not to cause a grain size distribution extension due to Ostwald ripening: i.e., at a speed in the range of from 30 to 100% of the speed to generate new nuclei.

For the growth of the seed grains there is a method in which silver halide grains are added thereto to dissolve, recrystalize and thereby grow the seed grains as described in p.88 of the book of the gists of papers presented to the annual convention '83 of the Society of Photographic Science and Technology of Japan.

The growth of the silver halide emulsion is preferably carried out under conditions of a pAg of 5 to 11, a temperature of 40 to 85 ° C and a pH of 1.5 to 12.

In the invention, the silver halide emulsion is subjected to physical ripening, chemical ripening and spectral sensitization.

The additives used in these processes are described in Research Disclosure (hereinafter abbreviated to RD) Nos.17643, 18716 and 308119. The relevant items and pages in these publications are listed below.

Item	RD308119	Rd17643	RD 18716
Chemical sensitizers	996 III-A	23	648
Spectral sensitizers	996 IV-A-A,B,C,D, H,H,I,J	23-24	648-9
Supersensitizers	996 IV-A-E, J	23-24	648-9
Antifoggants	998 VI	24-25	649
Stabilizers	998 VI		

The known photographic additives usable in the invention also are described in the above publications, in which the relevant items and pages are listed below.

Item	RD308119	RD17643	RD18716
Anti-color-cross-over agents	1002 VII-I	25	650
Dye image stabilizers	1001 VII-J	25	
Brightening agents	998 V	24	
UV absorbents	1003 VIII-C, XIIIC	25-26	
Light absorbents	1003 VIII	25-26	
Light scattering agents	1003 VIII		
Filter dyes	1003 VIII	25-26	
Binders	1003 IX	26	651
Antistatic agents	1006 XIII	27	650
Hardeners	1004 X	26	651
Plasticizers	1006 XII	27	650
Lubricants	1006 XII	27	650
Activators	1005 XI	26-27	650
Coating aids			
Mattings agents	1007 X VI		
In-emulsion developing agents	1011 XXB		

Various couplers may be used in the invention, examples of which are described in the above publications.

Item	RD11308119	RD17643 RD 18716
Yellow couplers	1001 VII-D	VII-C - G
Magenta couplers	1001 VII-D	VII-C - G
Cyan couplers	1001 VII-D	VII-C - G
Colored couplers	1002 VII-G	VII-G
DIR couplers	1001 VII-F	VII-F
BAR couplers	1002 VII-F	
Useful residue-releasing couplers	1001 VII-F	
Alkali-soluble couplers	1001 VII-E	

The additives used in the invention can be added according to the dispersing method described in RD308119 X IV.

As the support of the light-sensitive material of the invention there may be used one of the materials described in the foregoing RD17643 p.28, RD18716 p.647-8, and RD308119 XVII.

The light-sensitive material of the invention may have auxiliary layers such as the filter layer and intermediate layer described in RD308119 VII-K.

The light-sensitive material of the invention may take various layer structures such as the normal layer structure, inverted layer structure and unit structure described in RD 308119 VII-K.

The invention may apply to various color light-sensitive materials such as color negative films for general or movie use, color reversal films for slide or TV use, color photographic papers, color positive films and color reversal papers.

The light-sensitive material of the invention may be processed in the usual manner as described in RD17643 p.28-29, RD18716 p.647, and RD308119 XVII.

EXAMPLES

In all the following examples, adding amounts to the silver halide light-sensitive material are shown in grams per m^2 except that those of silver halide and colloidal silver are shown in silver equivalents and those of sensitizing dyes in mols per mol of silver halide.

Example 1

On a subbed triacetyl cellulose film support were formed the following compositions-having layers in order from the support side, whereby a multilayer color photographic material sample 101 was prepared.

Layer 1: Antihalation layer HC	
Black colloidal silver	0.15
UV absorbent UV-1	0.20
Colored coupler CC-1	0.02
High-boiling solvent Oil-1	0.20
High-boiling solvent Oil-2	0.20
Gelatin	1.6

Layer 2: Intermediate layer IL-1	
Gelatin	1.3

Layer 3: Low-speed red-sensitive emulsion layer RL	
Silver iodobromide emulsion (average grain diameter: 0.3μm)	0.4
Silver iodobromide emulsion (average grain diameter: 0.4μm)	0.3
Sensitizing dye S-1	$3.2\text{x}10^{-4}$
Sensitizing dye S-2	$3.2\text{x}10^{-4}$
Sensitizing dye S-3	$0.2\text{x}10^{-4}$
Cyan coupler C-1	0.5
Cyan coupler C-2	0.13
Colored cyan coupler CC-1	0.07
DIR compound D-1	0.006
DIR compound D-2	0.01
High-boiling solvent Oil-1	0.55
Gelatin	1.0

Layer 4: High-speed red-sensitive emulsion layer RH	
Silver iodobromide emulsion (average grain diameter: 0.7μm)	0.9
Sensitizing dye S-1	$1.7\text{x}10^{-4}$
Sensitizing dye S-2	$1.6\text{x}10^{-4}$
Sensitizing dye S-2	$0.1\text{x}10^{-4}$
Cyan coupler C-2	0.23
Colored cyan coupler CC-1	0.03
DIR compound D-1	0.01
High-boiling solvent Oil-1	0.25
Gelatin	1.0

Layer 5: Intermediate layer IL-2	
Gelatin	0.8

Layer 6: Low-speed green-sensitive emulsion layer GL	
Silver iodobromide emulsion (average grain diameter: 0.4μm)	0.6
Silver iodobromide emulsion (average grain diameter: 0.3μm)	0.2
Sensitizing dye S-4	$6.7\text{x}10^{-4}$
Sensitizing dye S-5	$0.8\text{x}10^{-4}$
Magenta coupler M-1	0.17
Magenta coupler M-2	0.43
Colored magenta coupler CM-1	0.10
DIR compound D-3	0.02
High-boiling solvent Oil-2	0.7
Gelatin	1.0

Layer 7: High-speed green-sensitive emulsion layer GH	
Silver iodobromide emulsion (average grain diameter: 0.7µm)	0.9
Sensitizing dye S-6	$1.1x10^{-4}$
Sensitizing dye S-7	$2.0x10^{-4}$
Sensitizing dye S-8	$0.3x10^{-4}$
Magenta coupler M-1	0.03
Magenta coupler M-2	0.13
Colored magenta coupler CM-1	0.04
DIR compound D-3	0.004
High-boiling solvent Oil-2	0.35
Gelatin	1.0

Layer 8: Yellow filter layer YC	
Yellow colloidal silver	0.1
Additive HS-1	0.07
Additive HS-2	0.07
Additive SC-1	0.12
High-boiling solvent Oil-2	0.15
Gelatin	1.0

Layer 9: Low-speed blue-sensitive emulsion layer BL	
Silver iodobromide emulsion (average grain diameter: 0.3µm)	0.25
Silver iodobromide emulsion (average grain diameter: 0.4µm)	0.25
Sensitizing dye S-9	$5.8x10^{-4}$
Yellow coupler Y-1	0.6
Yellow coupler Y-2	0.32
DIR compound D-1	0.003
DIR compound D-2	0.006
High-boiling solvent Oil-2	0.18
Gelatin	1.3

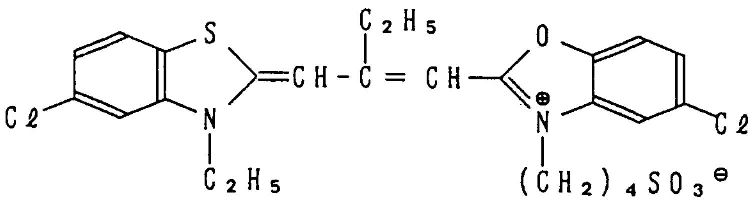
Layer 10: High-speed blue-sensitive emulsion layer BH	
Silver iodobromide emulsion (average grain diameter: 0.8µm)	0.50
Sensitizing dye S-10	$3x10^{-4}$
Sensitizing dye S-11	$1.2x10^{-4}$
Yellow coupler Y-1	0.18
Yellow coupler Y-2	0.10
High-boiling solvent Oil-2	0.05
Gelatin	1.0

Layer 11: First protective layer Pro-1	
Silver iodobromide emulsion (average grain diameter: 0.08μm)	0.3
UV absorbent UV-1	0.07
UV absorbent UV-2	0.10
Additive HS-1	0.2
Additive HS-2	0.1
High-boiling solvent Oil-1	0.07
High-boiling solvent Oil-3	0.07
Gelatin	0.8

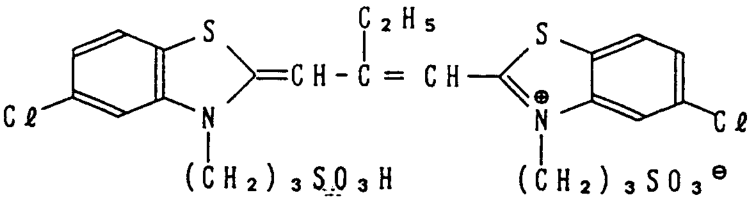
Layer 12: Second protective layer Pro-2	
Alkali-soluble matting agent (average particle size: 2μm)	0.13
Polymethyl methacrylate (average particle size: 3μm)	0.02
Gelatin	0.5

Besides, to each of the above layers were added a coating aid Su-2, a dispersing aid Su-1, hardeners H-1 and H-2, dyes AI-1 and AI-2, a stabilizer ST-1, antifoggants AF-1 and AF-2 and an antiseptic DI-1 in addition to the above compounds.

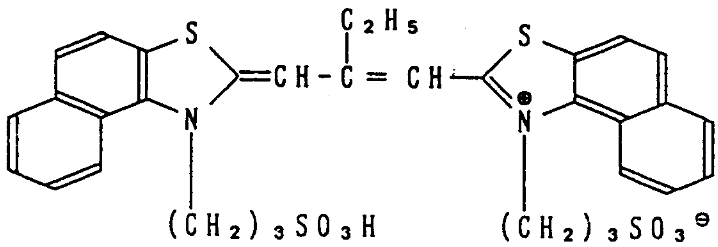
S − 1



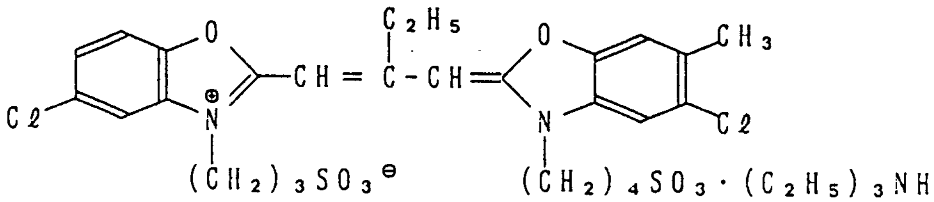
S − 2



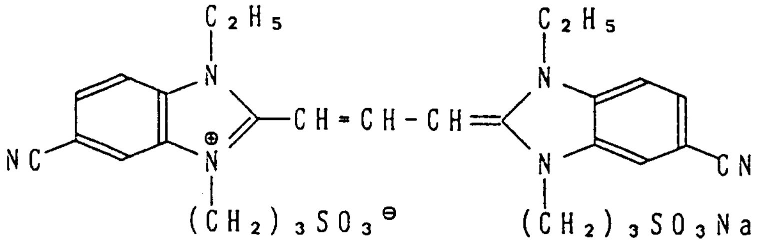
S − 3



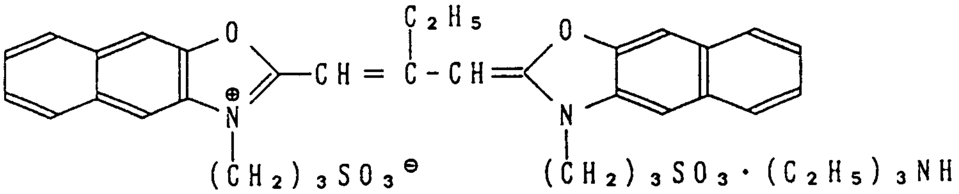
S − 4



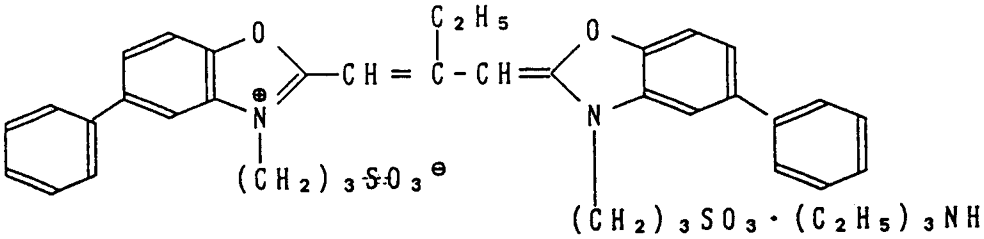
S − 5



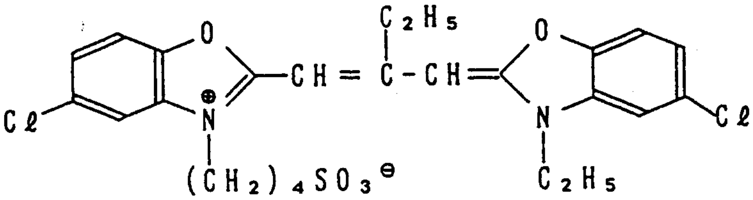
S－6


C₂H₅
O
CH = C - CH
N
(CH₂)₃SO₃⊖
(CH₂)₃SO₃·(C₂H₅)₃NH

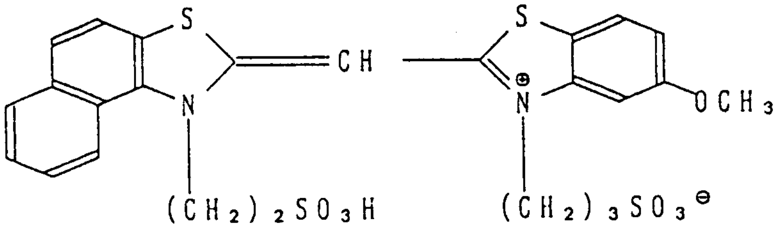
S－7


C₂H₅
O
CH = C - CH
N
(CH₂)₃SO₃⊖
(CH₂)₃SO₃·(C₂H₅)₃NH

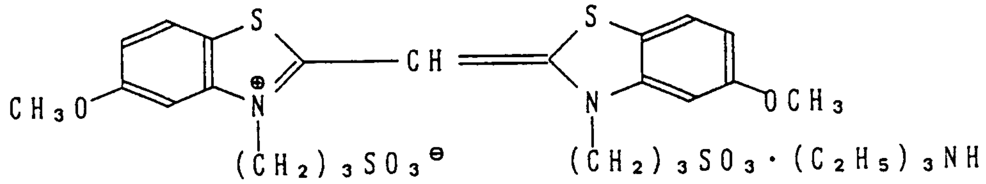
S－8


C₂H₅
O
CH = C - CH
N
Cℓ
(CH₂)₄SO₃⊖
C₂H₅

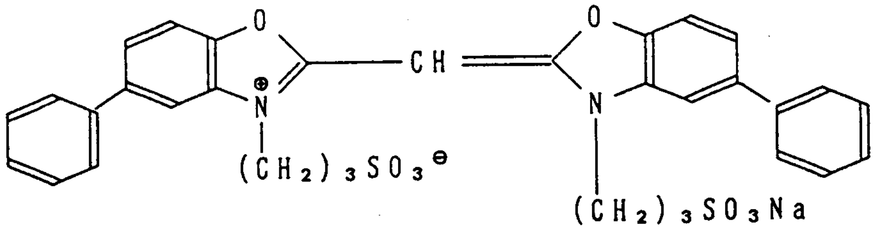
S－9


S
CH
N
OCH₃
(CH₂)₂SO₃H
(CH₂)₃SO₃⊖

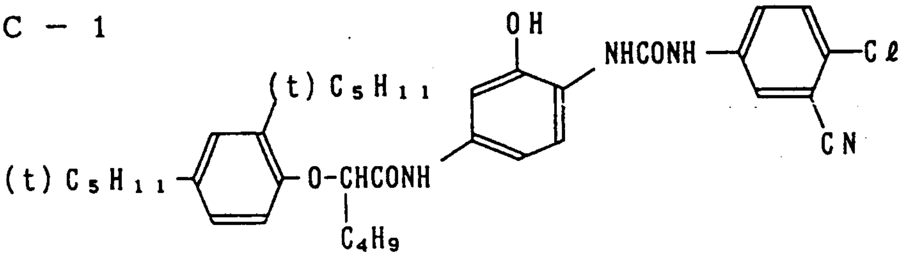
S－１０


S
S
CH
CH₃O
OCH₃
N
N
(CH₂)₃SO₃⊖
(CH₂)₃SO₃·(C₂H₅)₃NH

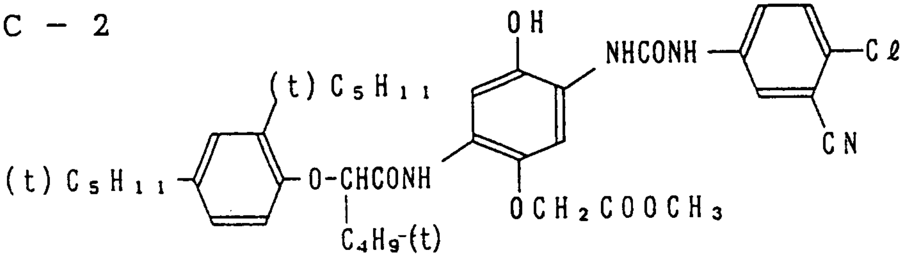
S－１１


O
O
CH
N
N
(CH₂)₃SO₃⊖
(CH₂)₃SO₃Na

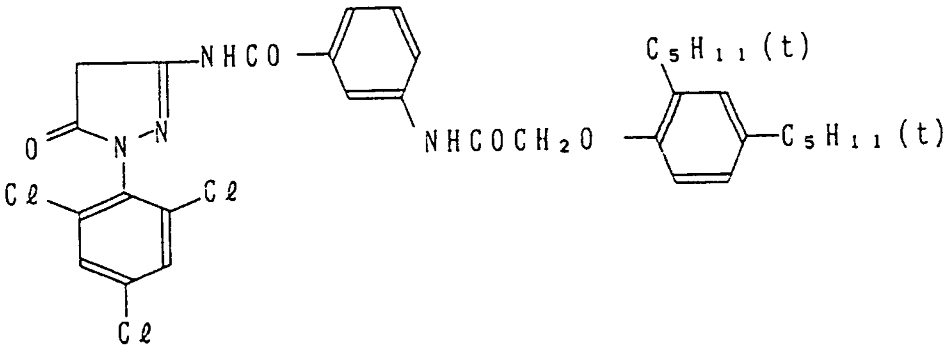
C－１


OH
NHCONH
Cℓ
CN
(t)C₅H₁₁
(t)C₅H₁₁
O-CHCONH
C₄H₉

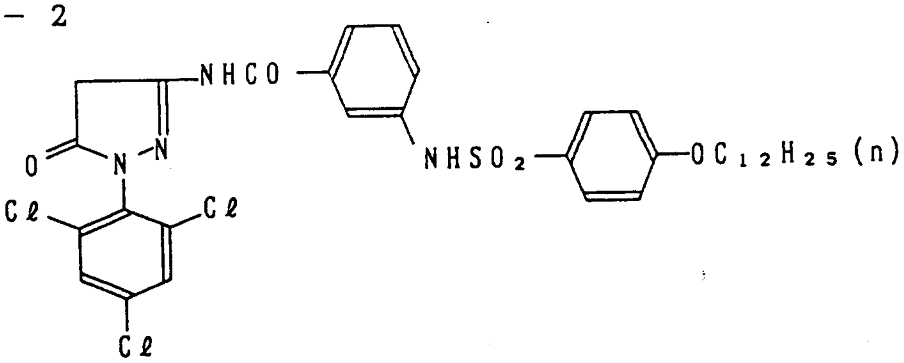
C－２


OH
NHCONH
Cℓ
CN
(t)C₅H₁₁
(t)C₅H₁₁
O-CHCONH
C₄H₉-(t)
OCH₂COOCH₃

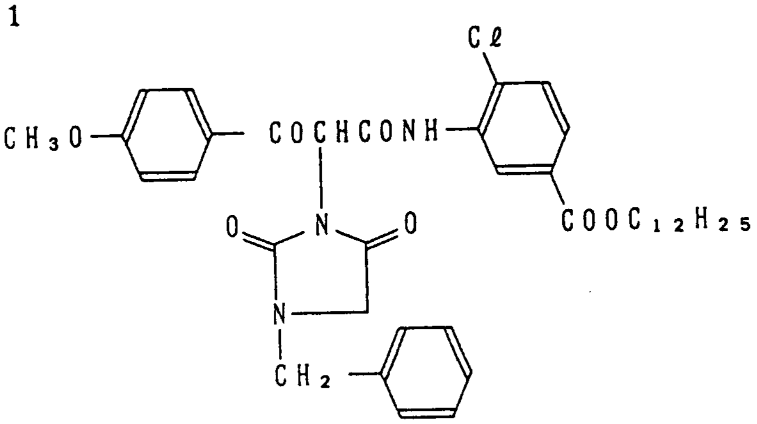
M − 1



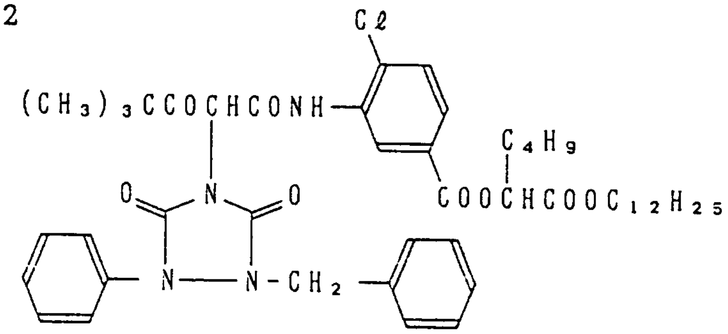
M − 2



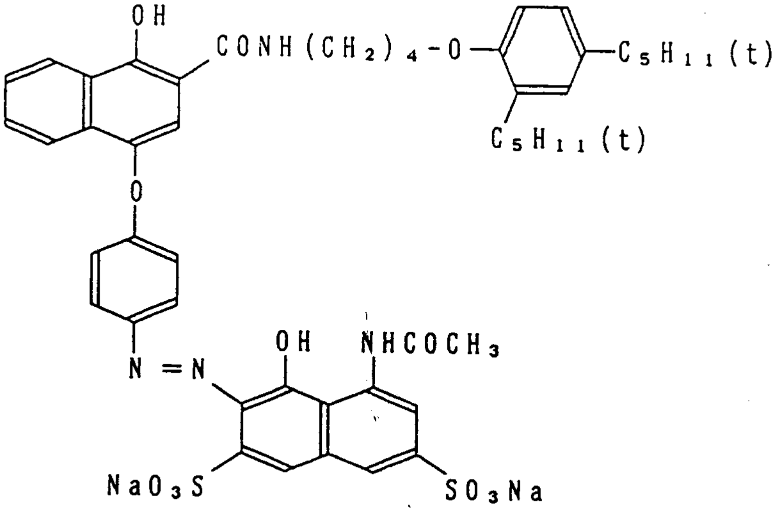
Y − 1



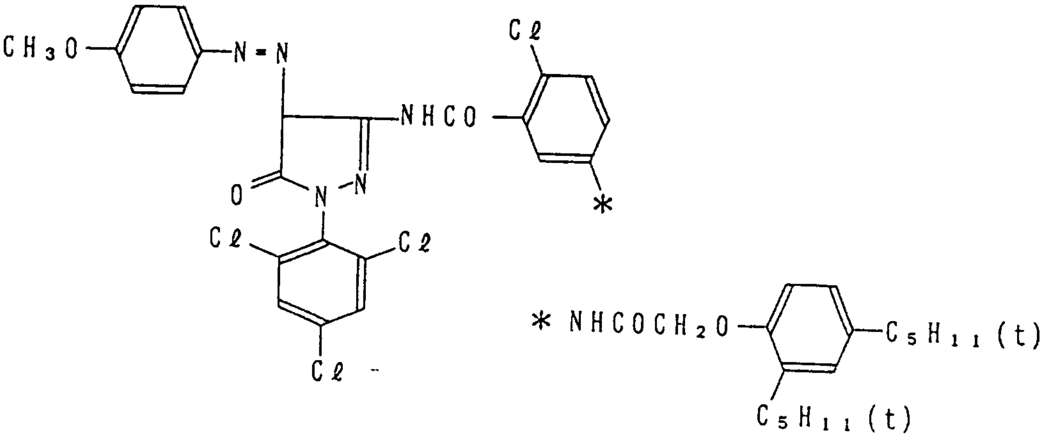
Y－2


Cℓ
(CH₃)₃CCOCHCONH
C₄H₉
COOCHCOOC₁₂H₂₅
O
N
O
N
N-CH₂

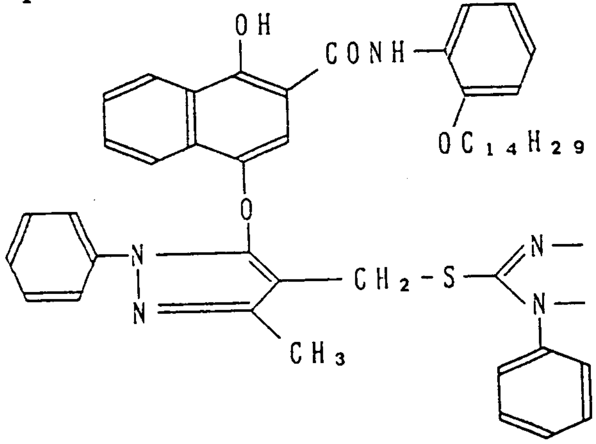
CC－1


OH
CONH(CH₂)₄-O
C₅H₁₁(t)
C₅H₁₁(t)
O
N=N
OH
NHCOCH₃
NaO₃S
SO₃Na

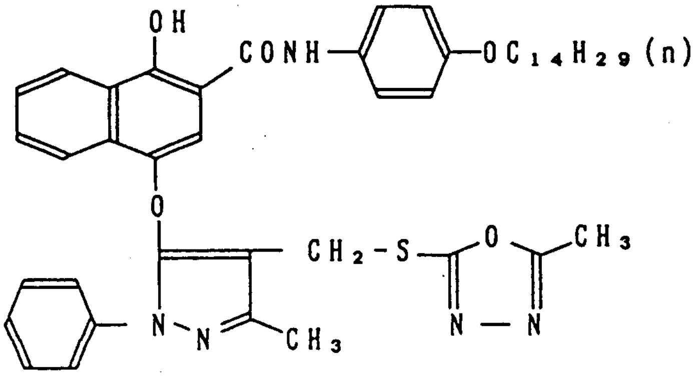
CM－1


CH₃O
N=N
Cℓ
NHCO
*
O
N-N
Cℓ
Cℓ
Cℓ
* NHCOCH₂O
C₅H₁₁(t)
C₅H₁₁(t)

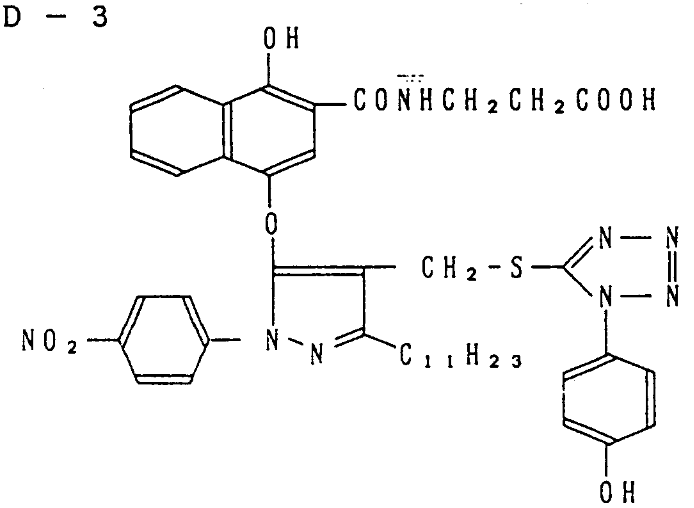
D − 1



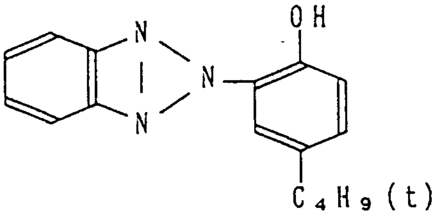
D − 2



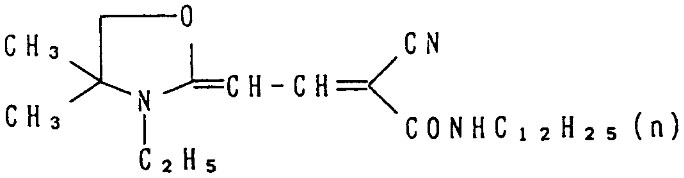
D − 3



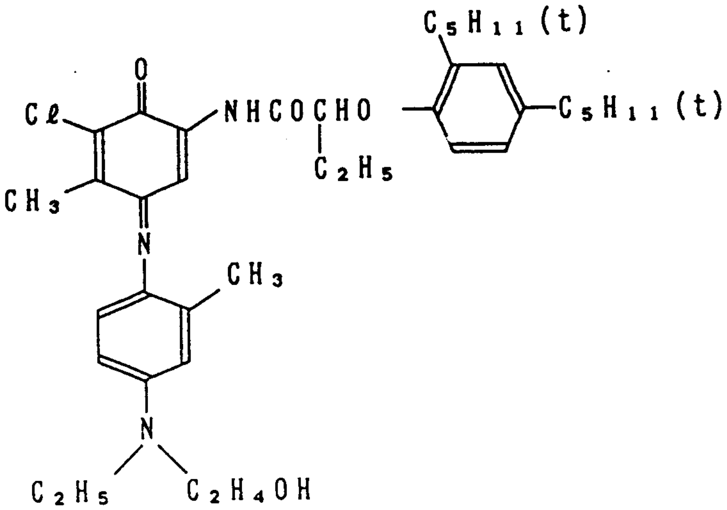
UV-1



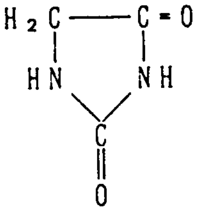
UV-2



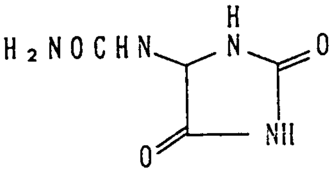
DY-1



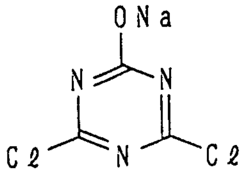
HS-1



HS-2



H - 1



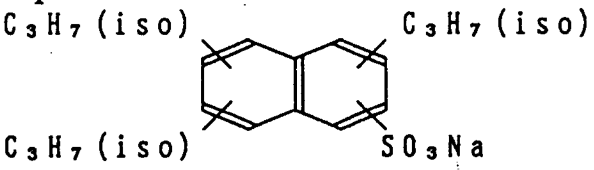
H - 2

$[(CH_2=CHSO_2CH_2)_3CCH_2SO_2(CH_2)_2]_2N(CH_2)_2SO_3K$

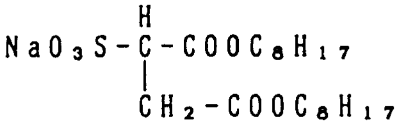
H - 3

$(CH_2=CHSO_2CH_2)_2O$

Su - 1

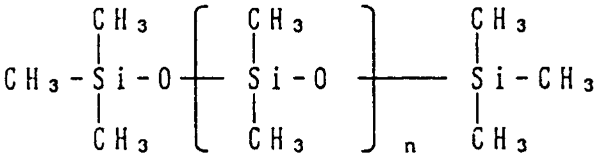


Su - 2



$$NaO_3S-\underset{\displaystyle CH_2-COOC_8H_{17}}{\overset{H}{C}}-COOC_8H_{17}$$

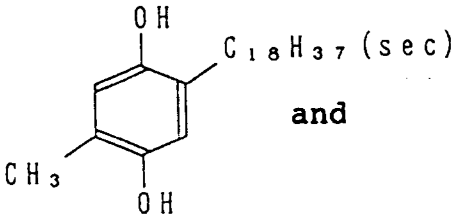
WAX - 1



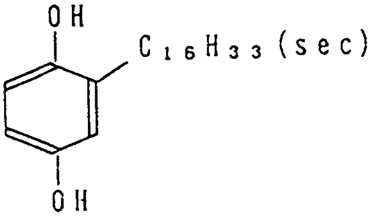
$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

Weight average molecular weight Mw = 3,000

Sc-1

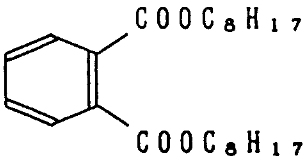


and

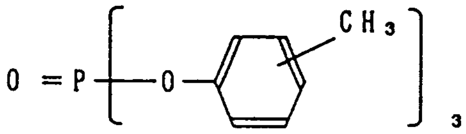


(Mixture in the ratio of 2 : 3)

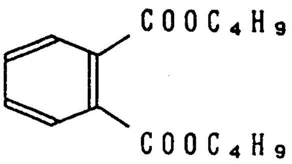
Oil-1



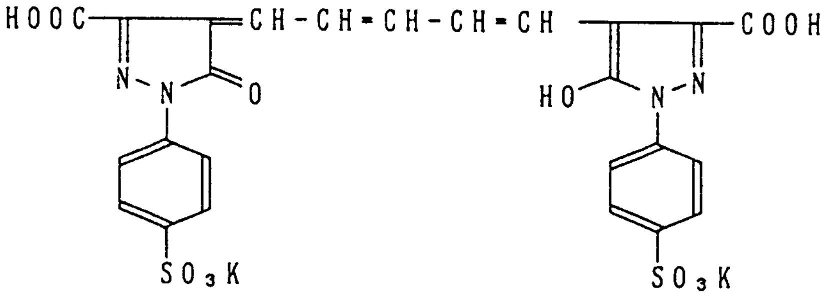
Oil-2



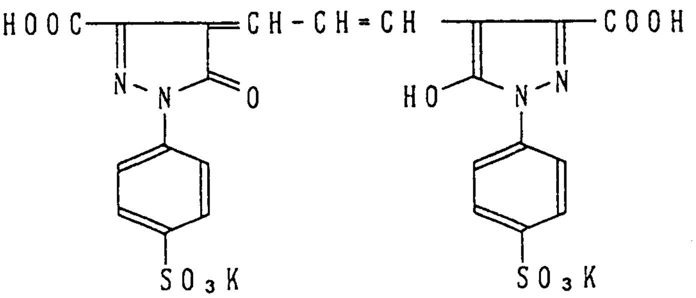
Oil-3



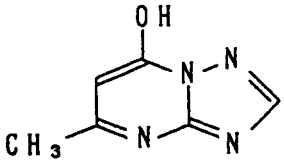
AI-1



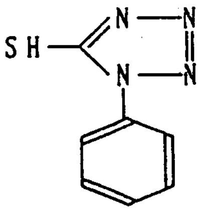
A I - 2



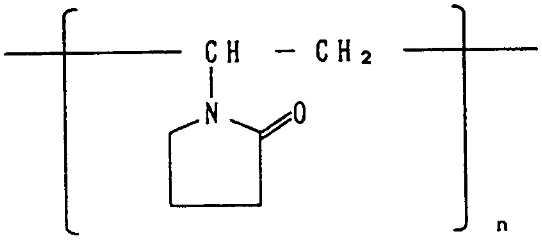
S T - 1



A F - 1



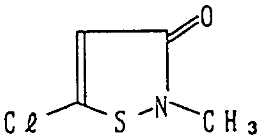
A F - 2



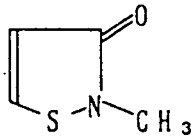
n: Polymerization degree

D I - 1

A mixture of



and



A sample 102 was prepared in the same manner as in Sample 101 except that the DIR compound of Layer 4 of Sample 101 was removed and the following Layer 3A was provided between the Layer 3 and Layer 4 of Sample 101.

Layer 3A: Medium-speed red-sensitive emulsion layer RM	
Silver iodobromide emulsion (average grain diameter: 0.5μm)	0.5
Sensitizing dye S-1	2.5×10^{-4}
Sensitizing dye S-2	2.3×10^{-4}
Sensitizing dye S-3	0.2×10^{-4}
Cyan coupler C-1	0.45
Colored cyan coupler CC-1	0.05
High-boiling solvent Oil-1	0.26
Gelatin	0.6

Samples 103 to 108 were prepared in the same manner as in Sample 102 except that the coating weights (g/m^2) of the cyan coupler C-1 and the DIR compound D-1 contained in Layer 3A of Sample 102 were varied as shown in Table 1.

Table 1

	Layer 3A, Coated weight(g/m^2)	
Sample No.	Cyan coupler C-1	DIR compound D-1
102	0.45	--
103	0.45	0.004
104	0.38	0.004
105	0.27	--
106	0.27	0.004
107	0.20	0.004
108	0.10	0.004

Each of Samples 101 to 108 was exposed through an optical stepwedge for sensitometric evaluation; imagewise exposed for image-quality evaluation; and then processed in the following procedure. In addition, a separate set of the samples, prepared for different sensitometric evaluation, were allowed to stand for 20 days under atmospheric conditions of 35° C/70%RH, and then exposed and processed in like manner.

Processing step (38° C)	
Color developing	3 min. 15 sec.
Bleaching	6 min. 30 sec.
Washing	3 min. 15 sec.
Fixing	6 min. 30 sec.
Washing	3 min. 15 sec.
Stabilizing	1 min. 30 sec.
Drying	

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

Color developer	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline sulfate	4.75g
Anhydrous sodium sulfite	4.25g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Sodium bromide	1.3 g
Trisodium nitrilotriacetate, monohydrate	2.5 g
Potassium hydroxide	1.0 g
Water to make 1 liter.	
Adjust pH to 10.0 with potassium hydroxide.	

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

Fixing bath	
Ammonium thiosulfate	175.0 g
Anhydrous sodium sulfite	8.5 g
Sodium metasulfite	2.3 g
Water to make 1 liter.	
Adjust pH to 6.0 with acetic acid.	

Stabilizing bath	
Formalin (37% solution)	1.5 ml
Koniducks (product of KONICA Corp.)	1.5 ml
Water to make 1 liter.	

The graininess of each sample was evaluated in terms of an RMS granularity value. The RMS value is the standard deviation of the fluctuation of density values obtained when measuring the red density + 0.5 area with a SAKURA microdensitometer PDM-5AR having a head slit opening of 250µm^2, manufactured by KONICA Corp. In Table 2, the RMS values of the samples are shown in relative values to the value of Sample 101 set at 100.

The smaller the value, the more excellent the graininess.

The sharpness was evaluated in terms of MTF (modulation transfer function). The density of the image formed on each sample by photographing a square wave chart was measured with a microdensitometer having a 300x2µm slit, and the percentage of the output resolution to the input chart image was found, from which a MTF value was obtained. In Table 2, the MTF values of the samples for a spatial frequency of 20 lines/m^2 are shown in relative values to the value of Sample 101 set at 100.

The larger the value, the more excellent the sharpness.

For evaluation of the preservability, percentage of the sensitivity (measured at the Dmin + 0.2 density point) of each sample subjected to the foregoing high temperature/high humidity treatment to that of the same sample untreated is shown in Table 2. The larger the value, the more excellent the preservability.

The thus obtained results of the respective red-sensitive layers (cyan image-forming layers) of the samples are collectively shown in Table 2.

As is apparent from Table 2, the samples having the construction of the invention have better improved graininess, sharpness and preservability than the comparative samples.

Table 2

Sample No.	Cyan density of Layer 3A	Cyan image evaluation		
		Graininess	Sharpness	Preservability(%)
101 (Comp.)	-	100	100	89
102 (Comp.)	0.57	98	90	96
103 (Comp.)	0.54	94	98	90
104 (Comp.)	0.42	93	98	92
105 (Comp.)	0.32	97	92	98
106 (Inv.)	0.30	92	102	96
107 (Inv.)	0.23	91	102	97
108 (Inv.)	0.15	92	100	97

Example 2

On a subbed triacetyl cellulose film support were coated the following compositions-having layers in order from the support side, whereby a multilayer color photographic light-sensitive material sample 201 was prepared.

Layer 1: Antihalation layer HC	
Black colloidal silver	0.18
UV absorbent UV-1	0.18
Cyan dye DY-1	0.022
High-boiling solvent Oil-1	0.18
High-boiling solvent Oil-2	0.02
Gelatin	1.6

Layer 2: Intermediate layer IL-1	
Gelatin	1.3

Layer 3: Low-speed red-sensitive emulsion layer RL	
Silver iodobromide emulsion (average grain diameter: 0.4μm)	0.40
Silver iodobromide emulsion (average grain diameter: 0.3μm)	0.20
Sensitizing dye S-1	$2.2\text{x}10^{-4}$
Sensitizing dye S-2	$4.0\text{x}10^{-4}$
Sensitizing dye S-3	$1.9\text{x}10^{-5}$
Sensitizing dye S-5	$9.1\text{x}10^{-5}$
Cyan coupler C-2	0.47
Colored cyan coupler CC-1	0.038
DIR compound D-1	0.005
High-boiling solvent Oil-1	0.57
Gelatin	1.1

Layer 4: Medium-speed red-sensitive emulsion layer RM	
Silver iodobromide emulsion (average grain diameter: 0.7μm)	0.62
Sensitizing dye S-3	$2.0\text{x}10^{-6}$
Sensitizing dye S-2	$1.8\text{x}10^{-4}$
Sensitizing dye S-1	$9.3\text{x}10^{-5}$
Sensitizing dye S-5	$9.0\text{x}10^{-5}$
Cyan coupler C-2	0.30
Colored cyan coupler CC-1	0.023
High-boiling solvent Oil-1	0.25
Gelatin	0.6

Layer 5: High-speed red-sensitive emulsion layer RH	
Silver iodobromide emulsion (average grain diameter: 0.8μm)	1.40
Sensitizing dye S-3	$1.9\text{x}10^{-5}$
Sensitizing dye S-2	$1.7\text{x}10^{-4}$
Sensitizing dye S-1	$1.7\text{x}10^{-4}$
Cyan coupler C-2	0.13
Colored cyan coupler CC-1	0.023
DIR compound D-1	0.025
High-boiling solvent Oil-1	0.21
Gelatin	1.1

Lyer 6: Intermediate layer IL-2	
Gelatin	0.8

Layer 7: Low-speed green-sensitive emulsion layer GL	
Silver iodobromide emulsion (average grain diameter: 0.4µm)	0.65
Silver iodobromide emulsion (average grain diameter: 0.3µm)	0.11
Sensitizing dye S-4	6.4×10^{-4}
Sensitizing dye S-5	7.0×10^{-5}
Magenta coupler M-1	0.17
Magenta coupler M-2	0.54
Colored magenta coupler CM-1	0.048
High-boiling solvent Oil-2	0.75
Gelatin	1.7

Layer 8: Medium-speed green-sensitive emulsion layer GM	
Silver iodobromide emulsion (average grain diameter: 0.7µm)	0.54
Sensitizing dye S-5	7.8×10^{-5}
Sensitizing dye S-6	1.1×10^{-4}
Sensitizing dye S-7	1.8×10^{-4}
Sensitizing dye S-8	1.4×10^{-5}
Magenta coupler M-1	0.034
Magenta coupler M-2	0.074
Colored magenta coupler CM-1	0.043
DIR compound D-2	0.018
High-boiling solvent Oil-2	0.30
Gelatin	0.6

Layer 9: High-speed green-sensitive emulsion layer GH	
Silver iodobromide emulsion (average grain diameter: 0.9µm)	1.3
Sensitizing dye S-5	2.4×10^{-5}
Sensitizing dye S-6	1.2×10^{-4}
Sensitizing dye S-7	1.5×10^{-4}
Sensitizing dye S-8	3.8×10^{-6}
Magenta coupler M-1	0.033
Magenta coupler M-2	0.14
Colored magenta coupler CM-1	0.038
High-boiling solvent Oil-2	0.39
Gelatin	1.0

Layer 10: Yellow filter layer YC	
Yellow colloidal silver	0.08
Antistain agent SC-1	0.1
High-boiling solvent Oil-2	0.13
Gelatin	0.8
Formalin scavenger HS-2	0.042
Formalin scavenger HS-1	0.042

Layer 11: Intermediate layer	
Formalin scavenger HS-2	0.056
Formalin scavenger HS-1	0.046
Gelatin	0.5

Layer 12: Low-speed blue-sensitive emulsion layer BL	
Silver iodobromide emulsion (average grain diameter: 0.3µm)	0.17
Silver iodobromide emulsion (average grain diameter: 0.4µm)	0.17
Silver iodobromide emulsion (average grain diameter: 0.7µm)	0.038
Sensitizing dye S-9	5.3×10^{-4}
Sensitizing dye S-11	7.2×10^{-6}
Yellow coupler Y-1	0.61
Yellow coupler Y-2	0.24
High-boiling solvent Oil-2	0.17
Gelatin	1.3
Formalin scavenger HS-2	0.073
Formalin scavenger HS-1	0.16

Layer 13: High-speed blue-sensitive emulsion layer BH	
Silver iodobromide emulsion (average grain diameter: 0.7µm)	0.32
Silver iodobromide emulsion (average grain diameter: 1.0µm)	0.32
Sensitizing dye S-9	2.1×10^{-4}
Sensitizing dye S-11	7.6×10^{-5}
Yellow coupler Y-1	0.17
High-boiling solvent Oil-2	0.068
Gelatin	0.9
Formalin scavenger HS-2	0.024
Formalin scavenger HS-1	0.079

Layer 14: First protective layer Pro-1	
Fine-grained silver iodobromide emulsion (average grain diameter: 0.08µm, AgI: 1 mol%)	0.4
UV absorbent UV-1	0.065
UV absorbent UV-2	0.10
High-boiling solvent Oil-1	0.07
High-boiling solvent Oil-3	0.07
Formalin scavenger HS-2	0.13
Formalin scavenger HS-1	0.37
Gelatin	1.3

Layer 15: Second protective layer Pro-2	
Alkali-soluble matting agent (average particle size: 2µm)	0.15
Polymethyl methacrylate (average particle size: 3µm)	0.04
Lubricant WAX-1	0.04
Gelatin	0.6

In addition to the above compounds, to each of the above layers were added a coating aid Su-2, a dispersing aid Su-1, a viscosity-control agent, hardeners H-1 and H-2, a stabilizer ST-1, two different antifoggants AF-1 having a $\overline{Mw}$ of 10,000 and AF-2 having a $\overline{Mw}$ of 1,100,000 and an antiseptic DI-1.

Samples 202 to 208 were prepared in the same manner as in Sample 201 except that the cyan coupler and DIR compound contained in the Layers 3, 4 and 5 of Sample 201 were changed as shown in Table 3, provided that cyan coupler C-1 was added in an amount of 0.8g/m^3 to layer 3 and in an amount of 0.56g/m^2 to Layer 4 of each of Samples 203, 204 and 205, and added as shown in Table 3 to Samples 206, 207 and 208; and DIR compound D-1 was added in an amount of 0.003g/m^2 to Layer 4.

Samples 201 to 208 were exposed, processed and evaluated in the same manner as in Example 1. The results are shown in Table 4.

As is apparent from Table 4, the samples having the construction of the invention have better improved graininess, sharpness and preservability than the comparative samples.

Table 3

Sample No.	Layer 5 RH	Layer 4 RM	Layer 3 RL
201	C-2 D-1	C-2	C-2 D-1
202	C-2 D-1	C-2	C-1 D-1
203	C-2 D-1	C-1	C-1 D-1
204	C-2	C-1 D-1	C-1 D-1
205	C-2 D-1	C-1 D-1	C-1
206	C-2	C-1 (0.38g/m^2) D-1	C-1 D-1
207	C-2	C-1 (0.28g/m^2) D-1	C-1 D-1
208	C-2	C-1 (0.11g/m^2) D-1	C-1 D-1

Table 4

Sample No.	Layer 4 cyan density	Cyan image evaluation		
		graininess	Sharpness	Preservability(%)
201 (Comp.)	0.60	100	100	91
202 (Comp.)	0.64	96	98	92
203 (Comp.)	0.60	94	96	92
204 (Comp.)	0.58	94	97	94
205 (Comp.)	0.57	93	99	92
206 (Inv.)	0.35	91	102	95
207 (Inv.)	0.25	90	104	96
208 (Inv.)	0.08	91	103	96

Claims

1. A silver halide photographic light-sensitive material which comprises a support having thereon a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red sensitive emulsion layer, wherein said red-sensitive emulsion layer comprises a high-speed emulsion sublayer, a medium-speed emulsion sublayer and a low-speed emulsion sublayer;

   said low-speed emulsion sublayer, said medium-speed emulsion sublayer and said high-speed emulsion sublayer being provided in this order on the support;

   said high-speed emulsion sublayer containing a two-equivalent cyan coupler; said medium-speed emulsion sublayer and said low-speed emulsion sublayer each comprising a four-equivalent coupler and a diffusible DIR compound; and the maximum transmission density of cyan dye in said medium-speed emulsion sublayer being not more than 0.35.

2. The material of claim 1, wherein said high-speed emulsion sublayer is adjacent to said medium-speed emulsion sublayer and said medium-speed emulsion sublayer is adjacent to said low-speed emulsion sublayer.

3. The material of claim 1, the sensitivity of said high-speed emulsion sublayer is higher 0.1 to 1.0 log E than said medium-speed emulsion sublayer in sensitivity, wherein E is exposure amount.

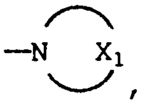
4. The material of claim 1, wherein the sensitivity of said medium-speed emulsion sublayer is higher 0.1 to 1.0 log E than said low-speed emulsion sublayer in sensitivity, wherein E is exposure amount.

5. The material of claim 1, wherein said the two-equivalent coupler is represented by Formula I:

$$\begin{array}{c}\mathrm{Cp}\\ * \\ | \\ \mathrm{X}\end{array}$$

wherein Cp represents a Coupler residual, * represents the coupling position of the coupler, X represents a group capable of being split off upon reaction with the oxidized product of a color developing agent.

6. The material of claim 5, wherein X in Formula I is selected from the group consisting of a halogen atom, an alkoxy group, an aryloxy group, a heterocyclicoxy group, an acyloxy group, an alkylthio group, an arylthio group, a heterocyclicthio group,

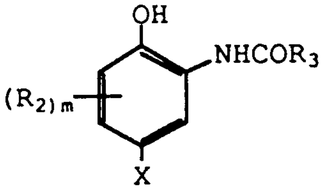


in which X_1 represents a group of non-metalic atoms necessary to complete an atom-containing 5-members to 6-members heterocyclic ring which may have a substituent, wherein said atom is selected from a carbon atom, an oxygen atom, a nitrogen atom, a sulfur atom; an acylamino group, a sulfonamido.

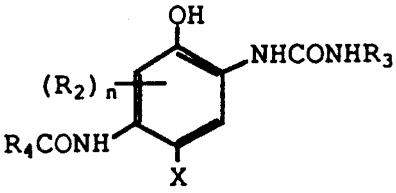
7. The material of claim 5, wherein X in Formula I is selected from a divalentgroup, the two-equivalent coupler forms a dimer with X.

8. The material of claim 5, wherein the two-equivalent coupler is represented by the following Formula II, Formula III, Formula IV;

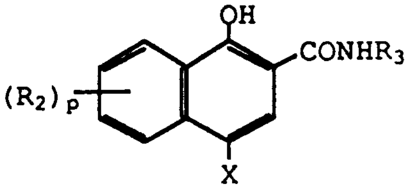
Formula II



Formula III



Formula IV



wherein R_2 and R_3 each represents a hydrogen atom or a substituent, R_4 represents a substituent, m is an integer of 1 to 3, n is an integer of 1 to 2, p is integer of 1 to 5, wherein m, n and p are 2 or more, R_2s may be the same or the different.

9. The material of claim 1, wherein said diffusible DIR compound is represented by Formula D-1:

Formula D-1: $A\text{-}(Y)_m$;

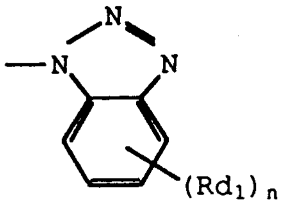
wherein A represents a coupler residue, m is an integer of 1 to 2, Y represents a group capable of being split off upon reaction with oxidized product of a color developing agent.

10. The material of claim 9, Y represents a development-inhibiting substituent that has a diffusibility of more than 0.34.

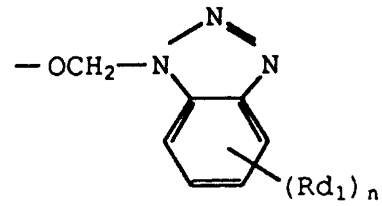
11. The material of claim 9, Y represents a development inhibitor releasing substituent that has a diffusibility of more than 0.34.

12. The material of claim 9, wherein Y is represented by the following Formulae D-2, D-3, D-4, D-5, D-6, D-7, D-8 or D-9;

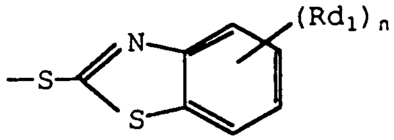
Formula D-2



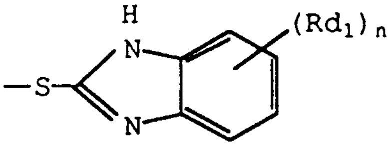
Formula D-3



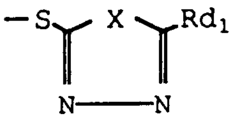
Formula D-4,



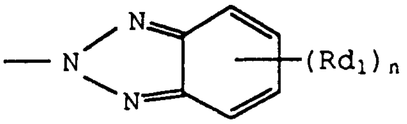
Formula D-5



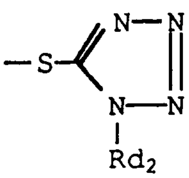
Formula D-6,



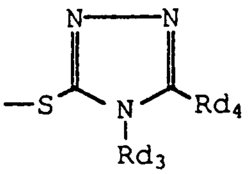
Formula D-7



Formula D-8,



Formula D-9



wherein Rd_1 is a hydrogen atom, a halogen atom or an alkyl, an alkoxy, an acylamino, an alkoxycarbonyl, a thiazolydinilidenamino, an aryloxycarbonyl, an acyloxy, a carbamoyl, a N-alkylcarbamoyl, a N,N-dialkylcarbamoyl, a nitro, an amino, a N-arylcarbamoyloxy, a sulfamoyl, a N-alkylcarbamoyloxy, a hydroxy, an alkoxycarbonylamino, an alkylthio, an arylthio, an aryl, a heterocyclic, a cyano, an alkylsulfonyl, or an aryloxycarbonylamino group; n is an integer of 0 to 2, provided that when n is 2, the Rd_1s may be either the same or different and the total number of carbon atoms contained in the n number of Rd_1s is from 0 to 10, and the number of carbon atoms contained in the Rd_1 of Formula D-6 is 0 to 15, X represents an oxygen atom or a sulfur atom, and Rd_2 represents an alkyl group, an aryl group or a heterocyclic group, and Rd_3 represents a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group or a heterocyclic group; Rd_4 represents a hydrogen atom, a halogen atom, or an alkyl, a cycloalkyl, an aryl, an acylamino, an alkoxycarbonylamino, an aryloxycarbonylamino, an alkanesulfonamido, a cyano, a heterocyclic, an alkylthio, or an amino group.

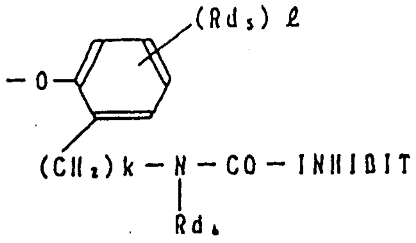
13. The material of claim 9, wherein Y is represented by Formula D-10:

Formula D-10 **-TIME-INHIBIT**

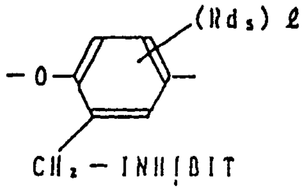
wherein TIME is a group attached to the coupling position of A, and the INHIBIT is a group represented by Formulae D-2 to D-9.

14. The material of claim 13, wherein Formula D-10 is represented by the following Formula D-11 to D-19:

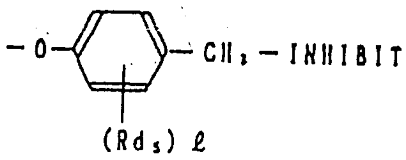
Formula D-11



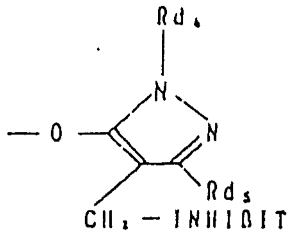
Formula D-12,



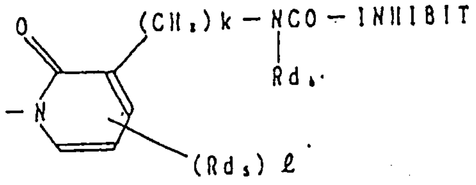
Formula D-13



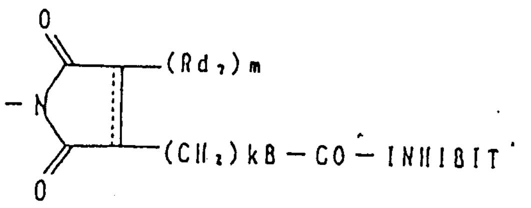
Formula D-14,



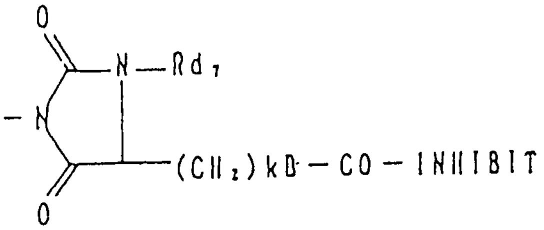
Formula D-15



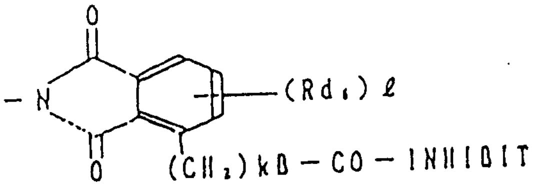
Formula D-16



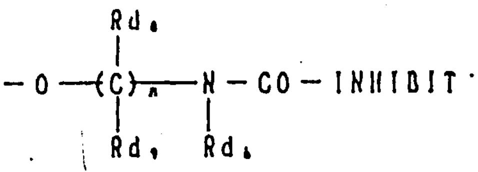
Formula D-17



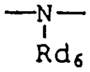
Formula D-18



Formula D-19



wherein, Rd$_5$ represents a hydrogen atom, a halogen atom or an alkyl atom, a cycloalkyl, an alkenyl, an aralkyl, an alkoxy, an alkoxycarbonyl, an anilino, an acylamino, an ureido, a cyano, a nitro, a sulfonamido, a sulfamoyl, a carbamoyl, an aryl, a carboxy, a sulfo, a hydroxy or an alkanesulfonyl group; Rd$_6$ is an alkyl, an alkenyl, an aralkyl, a cycloalkyl, a heterocyclic or an aryl group; and Rd$_7$ is a hydrogen atom or an alkyl, an alkenyl, an aralkyl, a cycloalkyl, a heterocyclic or an aryl group; Rd$_8$,Rd$_9$ each represents a hydrogen atom or an alkyl group, and k is an integer of 0, 1 or 2, and m is an integer of 1 or 2; and n is an integer 2 to 4; B is an oxygen atom or



$$-\underset{Rd_6}{\underset{|}{N}}-$$

and ----is a single bond or a double bond.

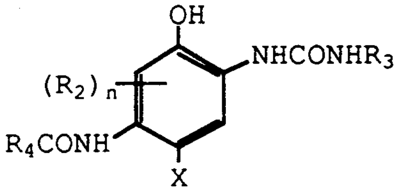
15. A silver halide photographic light-sensitive material which comprises a support having thereon a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red sensitive emulsion layer, wherein said red-sensitive emulsion layer comprises a high-speed emulsion sublayer, a medium-speed emulsion sublayer and a low-speed emulsion sublayer;

said low-speed emulsion sublayer, said medium-speed emulsion sublayer and said high-speed emulsion sublayer being provided in this order on the support;

said high-speed emulsion sublayer is adjacent to said medium-speed emulsion sublayer and said medium-speed emulsion sublayer is adjacent to said low-speed emulsion sublayer.

said high-speed emulsion sublayer containing a two-equivalent cyan coupler represented by Formula III; said medium-speed emulsion sublayer and said low-speed emulsion sublayer each comprising a four-equivalent coupler and a diffusible DIR compound represented by Formula D-1; and the maximum transmission density of cyan dye in said medium-speed emulsion sublayer being not more than 0.35:

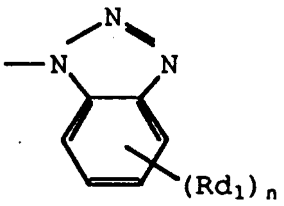
Formula III



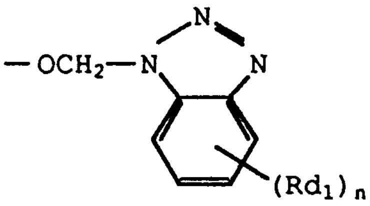
wherein R_2 and R_3 each represents a hydrogen atom or a substituent, R_4 represents a substituent, n is an integer of 1 to 2, wherein n are 2 or more, R_2s may be the same or the different, X represents a group capable of being split off upon reaction with the oxidized product of a color developing agent;

Formula D-1: A-$(Y)_m$, wherein A represents a coupler residue, m is an integer of 1 to 2, Y represents a group capable of being split off upon reaction with oxidized product of a color developing agent, and Y is represented by Formula D-2, D-3, D-10;

Formula D-2



Formula D-3

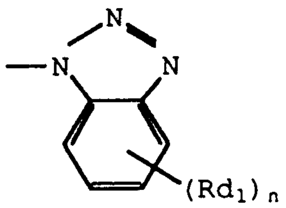


wherein Rd_1 is a hydrogen atom, a halogen atom or an alkyl, an alkoxy, an acylamino, an alkoxycarbonyl, a thiazolydinilidenamino, an aryloxycarbonyl, an acyloxy, a carbamoyl, a N-alkylcarbamoyl, a N,N-dialkylcarbamoyl, a nitro, an amino, a N-arylcarbamoyloxy, a sulfamoyl, a N-alkylcarbamoyloxy, a hydroxy, an alkoxycarbonylamino, an alkylthio, an arylthio, an aryl, a heterocyclic, a cyano, an alkylsulfonyl, or an aryloxycarbonylamino group; n is an integer of 0 to 2, provided that when n is 2, the Rd_1s may be either the same or different and the total number of carbon atoms contained in the n number of Rd_1s is from 0 to 10,

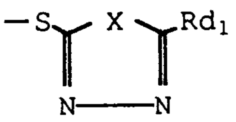
Formula D-10 -TIME-INHIBIT;

wherein TIME is a group attached to the coupling position of A, and the INHIBIT is a group represented by Formula D-2, D-6, D-8;

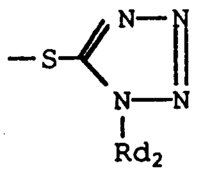
Formula D-2



Formula D-6



Formula D-8



wherein Rd_1 is a hydrogen atom, a halogen atom or an alkyl, an alkoxy, an acylamino, an alkoxycarbonyl, a thiazolydinilidenamino, an aryloxycarbonyl, an acyloxy, a carbamoyl, a N-alkylcarbamoyl, a N,N-dialkylcarbamoyl, a nitro, an amino, a N-arylcarbamoyloxy, a sulfamoyl, a N-alkylcarbamoyloxy, a hydroxy, an alkoxycarbonylamino, an alkylthio, an arylthio, an aryl, a heterocyclic, a cyano, an alkylsulfonyl, or an aryloxycarbonylamino group; n is an integer of 0 to 2, provided that when n is 2, the Rd_1s may be either the same or different and the total number of carbon atoms contained in the n number of Rd_1s is from 0 to 10, and the number of carbon atoms contained in the Rd_1 of Formula D-6 is 0 to 15, X represents an oxygen atom or a sulfur atom, and Rd_2 represents an alkyl group, an aryl group or a heterocyclic group,

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 4764

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 365 246 (KONICA) * page 3, line 44 - line 46 * * * page 8, line 26 - page 23, line 52 * * * page 25, line 31 - page 28, line 9 * * * page 42, line 23 - page 45, line 30; claim 3 * * – – –	1-15	G 03 C 7/30
Y	EP-A-0 106 306 (FUJI) * page 3, line 21 - page 4, line 3 * * * page 8; example 2 * * * page 33, line 5 - page 34, line 16 * * * page 38; example C1 * * * page 43; example D * * – – –	1-15	
Y	EP-A-0 136 603 (3M) * page 11, line 12 - page 12, line 3 * * * page 14, line 1 - line 9 * * – – – – –	1-15	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	12 November 91	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention

E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document