⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 383 623 A2**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **90301714.3**

(51) Int. Cl.^{5}: **G03C 7/30, G03C 7/305**

㉒ Date of filing: **16.02.90**

㉚ Priority: **17.02.89 JP 38044/89**

㊸ Date of publication of application:
22.08.90 Bulletin 90/34

(84) Designated Contracting States:
DE GB

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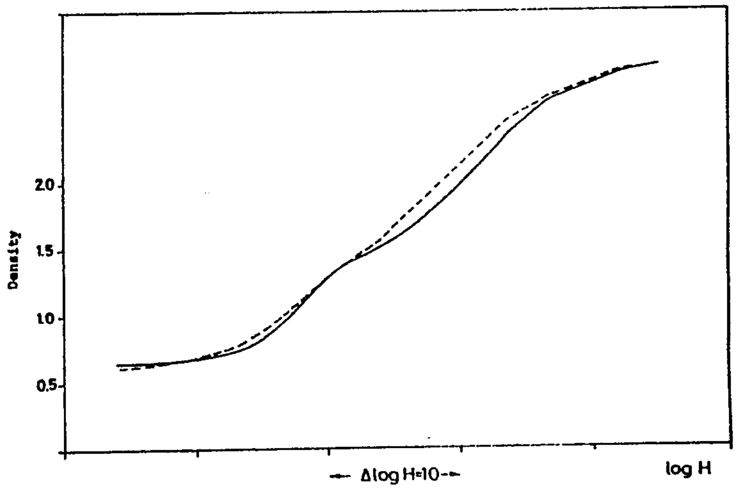
(54) **Light-sensitive silver halide color photographic material.**

(57) Disclosed is a light-sensitive silver halide color photographic material, comprising a support, silver halide emulsion layers, which are respectively a blue-sensitive, green-sensitive and red-sensitive, and a yellow filter layer which are provided on the support, wherein the material has a DIR compound, the yellow filter layer contains a yellow dye, and at least one of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers has a single layer constitution. According to the present invention, a light-sensitive color photographic material suitable for full color photographing can be prepared.

FIG. 1



EP 0 383 623 A2

Light-sensitive silver halide color photographic material

BACKGROUND OF THE INVENTION

This invention relates to a light-sensitive color photographic material suitable for full color photographing, particularly to a negative-type light-sensitive silver halide color photographic material of which at least one color sensitive layer is a single layer.

Presently, color photography widely spread is the so-called negative-positive system in which photographing is practiced with a color negative film and color print is effected by enlarging onto a color paper. One of the reasons is that a color negative film has very broad exposure latitude, with very little probability of failure during photographing, and even users in general having no special knowledge can take color photographs without any particular concern.

"Having broad exposure latitude" refers to the fact that the gradation is good over wide exposure amount range from the shadow portion with little exposure amount to the highlight portion with much exposure amount in the so-called characteristic curve in which the exposure amount is taken on the axis of abscissa and the color formed density on the axis of ordinate.

If the gradation is inferior, color reproducibility, tone reproducibility will be deteriorated.

Color negative film, as different from color reversal film or color paper, is a light-sensitive material for which gradation is demanded to be strictly controlled over wider range of exposure amount, and for this reason, color negative films for photography commercially available at the present time are made to have an overlaid constitution comprising a plurality of emulsion layers of higher sensitivity layer containing greater grain sizes and lower sensitivity layer containing smaller grain sizes for the respective color sensitive layers to the light of blue color, green color and red color. Further, the so-called DIR compound for forming consequently a developing inhibitor through the reaction with the oxidized product of the developing agent is employed.

Such technique is inherent in color negative film, and particularly the DIR compound improves not only gradation but also sharpness, graininess and color reproducibility, and is essential in color negative film.

As the technique for improving the so-called gradation stability which strictly controls such gradation is disclosed in, for example, Japanese Unexamined Patent Publication No. 244944/1985. Specifically, there is disclosed the method in which after chemical sensitization of the silver halide emulsion with equal mean grain size, sensitizing dyes are added to the respective emulsions with various molar ratios, and the emulsions are again mixed.

Further, color negative film is subjected to developing processing in various laboratories as compared with color reversal film, and hence to developing processing under processing conditions with greater fluctuation width.

Accordingly, color negative film has been demanded to have higher stability to fluctuation in processing conditions.

However, as described above, color negative film has an overlaid constitution by use of a plurality of emulsion layers containing silver halide grains with different grain sizes, and further gradation is strictly controlled by use of DIR compound, whereby storability of the light-sensitive photographic material before photogaphing to external conditions such as temperature, humidity, etc. (hereinafter abbreviated as stability of light-sensitive material) is inferior, and also inferior in stability of the light-sensitive photographic material after photographing (hereinafter abbreviated as latent image stability) against external conditions. Further, as described above, in spite of the demand for high degree of stability to processing conditions, processing stability has not been solved. For the reasons that the processing condition is inferior, etc., deterioration in gradation occurs, thus involving the drawbacks of deterioration of color reproducibility and tone reproducibility. Further, according to the method disclosed in Japanese Unexamined Patent Publication No. 244944/1985, there is the problem that adsorption equilibrium of the dyes between grains occurs undesirably during the stagnation period before coating of the remixed emulsion.

SUMMARY OF THE INVENTION

Accordingly, the present inventors have examined about the causes of deterioration in gradation, color reproducibility and tone reproducibility, and consequently found that they are also caused by yellow colloidal silver in the yellow filter which has been used in the prior art for the purpose of improving color reproducibility.

A first object of the present invention is to provide a light-sensitive silver halide color photographic material, which is excellent in storage stability of light-sensitive material, and also excellent in storate stability of latent image.

A second object of the present invention is to provide a light-sensitive silver halide color photographic material excellent in stability to fluctuations of processing conditions.

The above respective objects of the present invention is accomplished by a light-sensitive silver halide color photographic material, comprising a support, silver halide emulsion layers, which are respectively blue-sensitive, green-sensitive or red-sensitive, and a yellow filter layer which are provided on the support, wherein said material has a DIR compound, said yellow filter layer contains a yellow dye, and at least one of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers has a single layer constitution.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a characteristic curve as a standard (broken line) and a characteristic curve which is to be evaluated (solid line) of a light-sensitive photographic material. Fig. 2 is a graph showing a point gamma of the light-sensitive photographic material of the characteristic curve as a standard (broken line) and the characteristic curve which is to be evaluated (solid line).

DETAILED DESCRIPTION OF THE INVENTION

The DIR compound to be used in the present invention is shown below, and use of the DIR compound offers very good result in view of graininess.

In the present invention, the DIR compound refers to a compound which eliminates a developing inhibitor or a compound capable of releasing a developing inhibitor through the reaction with the oxidized product of the color developing agent.

The above-mentioned compound capable of releasing a developing inhibitor may be one which releases the developing inhibitor either imagewise or non-imagewise.

Imagewise release may be effected by, for example, the reaction with the oxidized product of the developing agent, while non-imagewise release by utilizing, for example, the TIME group as described below.

In the following, representative structural formulae are shown.

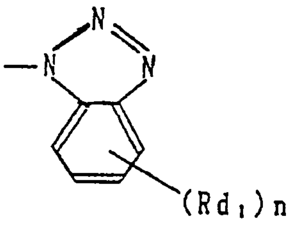
Formula (D-1)

$A - (Y)_m$

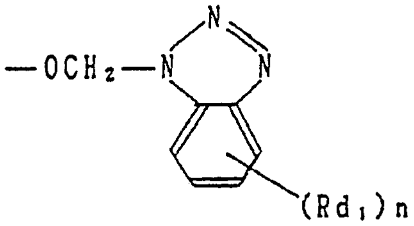
wherein A represents a coupler residue, m represents 1 or 2, Y represents a group bonded to the coupling position of the coupler residue A and eliminatable through the reaction with the oxidized product of the color developing agent, which is a developing inhibitor group or a group capable of releasing a developing inhibitor.

In the formula (D-1), Y may be typically represented by the formulae (D-2) to (D-9) and (D-20) set forth below.

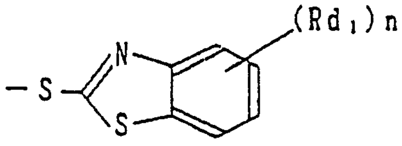
Formula (D-2)



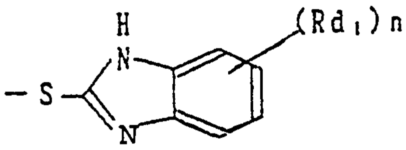
Formula (D-3)



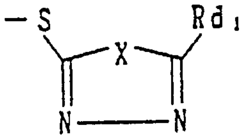
Formula (D-4)



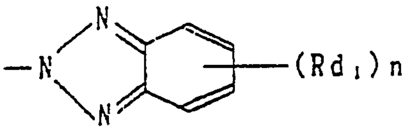
Formula (D-5)



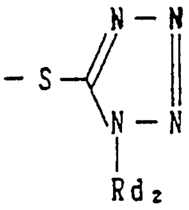
Formula (D-6)



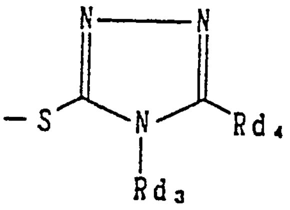
Formula (D-7)



Formula (D-8)



Formula (D-9)



In the formulae (D-2) to (D-7), Rd_1 represents hydrogen atom, a halogen atom or an alkyl, alkoxy, acylamino, alkoxycarbonyl, thiazolidinylideneamino, 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 represents 0, 1 or 2, and when n is 2, the respective Rd_1's may be either the same or different. The total carbon atoms contained in n Rd_1's may be 0 to 10. On the other hand, the total number of the carbon atoms contained in Rd_1 in the formula (D-6) may be 0 to 15.

In the above formula (D-6), X represents oxygen atom or sulfur atom.

In the formula (D-8), Rd_2 represents an alkyl group, an aryl group or a heterocyclic group.

In the formula (D-9), Rd_3 represents hydrogen atom, or an alkyl, cycloalkyl, aryl or heterocyclic group, Rd_4 represents hydrogen atom, a halogen atom or an alkyl, cycloalkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamide, cyano, heterocyclic, alkylthio or amino group.

When Rd_1, Rd_2, Rd_3 or Rd_4 represents an alkyl group, the alkyl group may include those having substituents, and may be either straight or branched.

When Rd_1, Rd_2, Rd_3 or Rd_4 represents an aryl group, the aryl group may include those having substituents.

When Rd_1, Rd_2, Rd_3 or Rd_4 represents a heterocyclic group, the heterocyclic group may include those having substituents, preferably 5- or 6-membered monocyclic or fused rings containing at least one selected from nitrogen atom, oxygen atom and sulfur atom as the hetero atom, that may be selected from the groups of, for example, pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, thiazolyl, triazolyl, benzotriazolyl, imide, oxazine.

The carbon atoms contained in Rd_2 in the formula (D-8) may be 0 to 15.

In the above formula (D-9), the total carbon atoms contained in Rd_3 and Rd_4 may be 0 to 15.

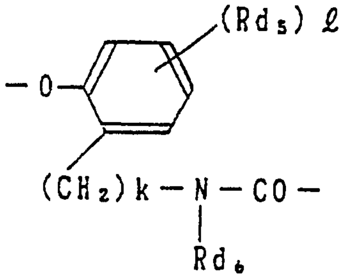
Formula (D-10)

- (TIME)n - INHIBIT

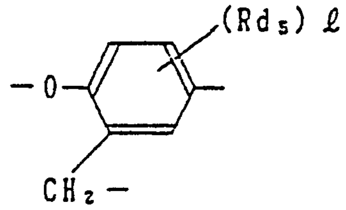
wherein the TIME group is a group, bound to the coupling position of A and being cleavable through the reaction with the oxidized product of the color developing agent, which is a group cleaved successively after cleavage from the coupler and until finally can release the INHIBIT groups with adequate control; n is 1 to 3, and when it is 2 or 3, the respective TIME groups may be either the same or different. The INHIBIT group is a group which becomes a developing inhibitor by the above-mentioned release (e.g. the group represented by the above formulae (D-2) to (D-9)).

In the formula (D-10), the -TIME group may be typically represented by the formulae (D-11) to (D-19) set forth below.

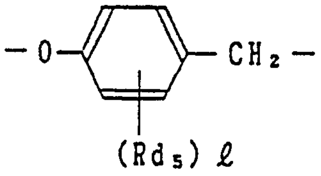
Formula (D-11)



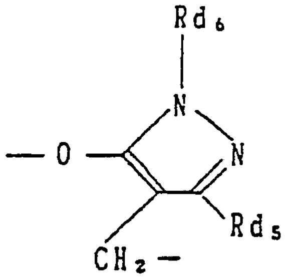
Formula (D-12)



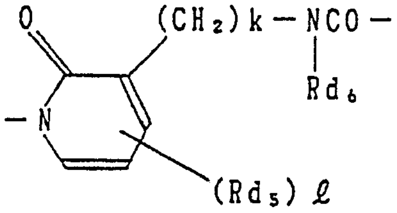
Formula (D-13)



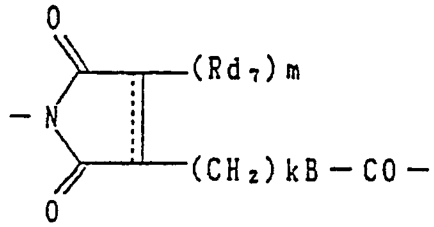
Formula (D-14)



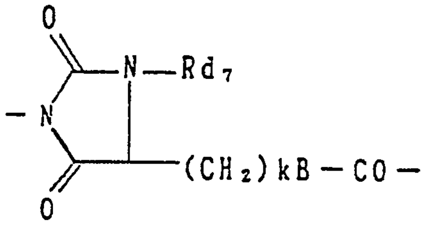
Formula (D-15)



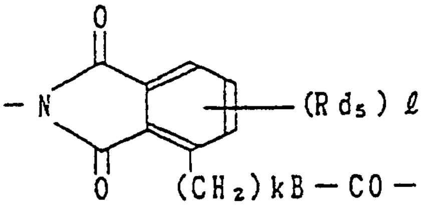
Formula (D-16)



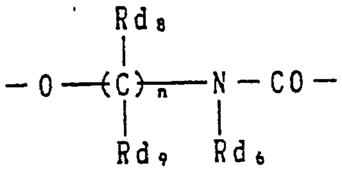
Formula (D-17)



Formula (D-18)



Formula (D-19)



In the formulae (D-11) to (D-15) and (D-18), Rd_5 represents hydrogen atom, a halogen atom or an alkyl, cycloalkyl, alkenyl, aralkyl, alkoxy, alkoxycarbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamide, sulfamoyl, carbamoyl, aryl, carboxy, sulfo, hydroxy or alkanesulfonyl group. In the formulae (D-11) to (D-13), (D-15) and (D-18), Rd_5's may be mutually bonded together to form a fused ring. In the formulae (D-11), (D-14), (D-15) and (D-19), Rd_6 represents an aralkyl, alkenyl, alkyl, cycloalkyl, heterocyclic or aryl group. In the formulae (D-16) and (D- 17), Rd_7 represents a hydrogen atom or an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. Each of Rd_8 and Rd_9 in the formulae (D-19) represents hydrogen atom or an alkyl group (preferably an alkyl group having 1 to 4 carbon atoms), k in the formulae (D-11) and (D-15) to (D-18) represents an integer of 0, 1 or 2, ℓ in the formulae (D-11) to (D-13). (D-15) and (D-18) represents an integer of 1 to 4, m in the formula (D-16) represents an integer of 1 or 2. When ℓ and m are 2 or more, the respective Rd_5 and Rd_7 may be either the same or different. n in the formula (D-19) represents an integer of 2 to 4, and Rd_8 and Rd_9 in number of n may be each the same or different. B in the formulae (D-16) to (D-18) represents oxygen atom or $-\underset{Rd6}{\underset{|}{N}}$ (Rd_6 represents the same meaning as already defined), and $\overset{\rule{2em}{0.4pt}}{\cdots\cdots}$ in the formula (D-16) may be either a single bond or a double bond, and m is 2 in the case of the single bond and m is 1 in the case of the double bond.

Formula (D-20)

$(T_1)_{\ell}$-SR$(T_2)_m$-INHIBIT

wherein T_1 represents a component which cleaves SR$(T_2)_m$ INHIBIT, SR a component which forms $(T_2)_m$INHIBIT through the reaction with the oxidized product of the developing agent after formation of SR$(T_2)_m$INHIBIT, T_2 a component which cleaves INHIBIT after formation of $(T_2)_m$INHIBIT, INHIBIT a developing inhibitor and ℓ and m each 0 or 1.

The component represented by SR may be one which can form the component as mentioned above through the reaction with the oxidized product of the developing agent, and may include, for example, a coupler component which undergoes the coupling reaction with the oxidized product of the developing agent or a redox component which undergoes the redox reaction with the oxidized product of the developing agent.

As the coupler component, there may be included yellow couplers, magenta couplers, cyan couplers such as acylacetanilides, 5-pyrazolones, pyrazoloazoles, phenols, naphthols, acetophenones, indanones, carbamoylacetanilides, 2(5H)-imidazolones, 5-isoxazolones, uracils, homophthalimides, oxazolones, 2,5-thiadiazoline-1,1-dioxides, triazolothiadiazines, indoles, etc., and otherwise those which form various dyes or form no dye.

The $(T_1)_{\ell}$SR$(T_2)_m$ INHIBIT should be preferably bonded to the active site of the component A of the formula (D-1).

When SR is a coupler component, SR is bonded to $(T_1)_{\ell}$ and $(T_2)_m$ INHIBIT so as to function for the first time as the coupler after cleavage from $(T_1)_{\ell}$.

For example, when the coupler component is a phenol or a naphthol and the oxygen atom of hydroxyl group is a 5-pyrazolone, the oxygen atom at the 5-position, or the nitrogen atom at the 2-position of the enantiomer, and also the oxygen atom of hydroxyl group of the enantiomer in acetophenones or indanones should be preferably bonded to $(T_1)_{\ell}$, and $(T_2)_m$ INHIBIT to the active site of the coupler.

In the case when SR is a redox component, its examples may include hydroquinones, catechols, pyrogallols, aminophenols (e.g. p-aminophenols, o-aminophenols), naphthalenediols (e.g. 1,2-naphthalenediols, 1,4-naphthalenediols, 2,6-naphthalenediols), or aminonaphthols (e.g. 1,2-aminonaphthols, 1,4-aminonaphthols, 2,6-aminonaphthols), etc.

In the case when SR is a redox component, SR is bonded to $(T_1)_{\ell}$and $(T_2)_m$INHIBIT so as to function for the first time as the redox component after cleavage from $(T_1)_{\ell}$.

Examples of the group represented by T_1 and T_2 may include those represented by the formulae (D-11) to (D-19) as described above.

As the developing inhibitor represented by INHIBITOR, for example, those represented by the formulae (D-2) to (D-9) as described above may be included.

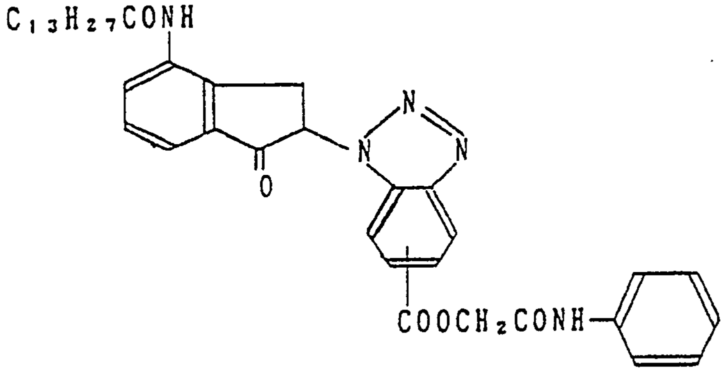
Among the DIR compounds, preferable are those wherein Y is represented by the formula (D-2), (D-3), (D-8), (D-10) or (D-20), and among (D-10) and (D-20), those wherein INHIBIT is represented by the formula (D-2), (D-3), (D-6) (particularly when X of (D-6) is oxygen atom), or (D-8) are preferred.

As the coupler component represented by A in the formula (D-1), yellow color image forming coupler residues, magenta color image forming coupler residues, cyan color image forming coupler residues and no color exhibiting coupler residues may be included.

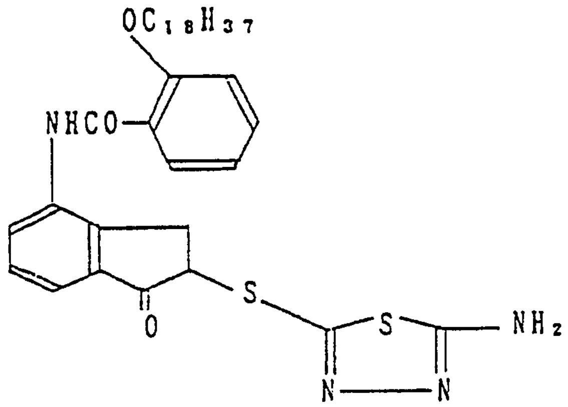
As preferable DIR compounds to be used in the present invention, the compounds as shown below may be included, but these are not limitative of the invention.

Exemplary compounds

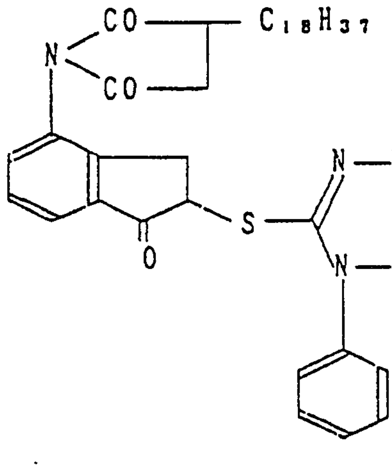
E − 1

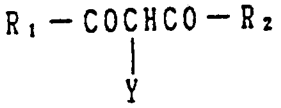


E − 36



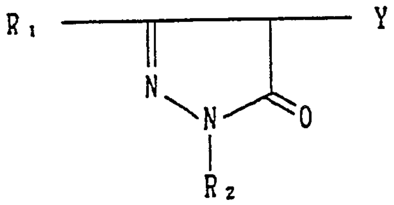
E − 37



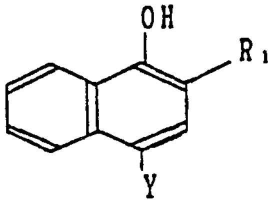


$$R_1-\underset{\displaystyle Y}{\underset{|}{\mathrm{COCHCO}}}-R_2$$

Exemplary compound No.	R_1	R_2	Y
E − 2	(1)	(1)	(30)
E − 3	(2)	(3)	(30)
E − 4	(2)	(4)	(30)
E − 5	(5)	(6)	(31)
E − 6	(2)	(4)	(32)
E − 7	(2)	(3)	(32)
E − 8	(7)	(8)	(33)
E −33	(2)	(4)	(55)
E −40	(2)	(4)	(56)
E −43	(2)	(25)	(59)



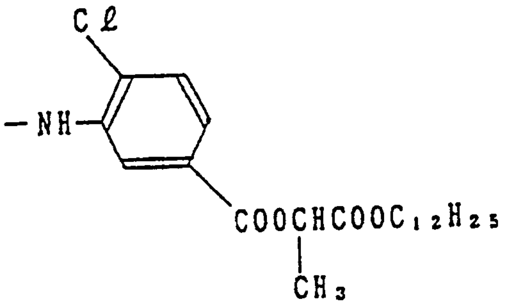
Exemplary compound No.	R_1	R_2	Y
E − 9	(9)	(10)	(30)
E −10	(11)	(10)	(30)
E −11	(12)	(7)	(34)
E −12	(12)	(13)	(35)
E −13	(9)	(14)	(36)
E −14	(15)	(16)	(37)
E −35	(56)	(24)	(23)



Exemplary compound No.	R₁	Y
E－15	(17)	(38)
E－16	(17)	(39)
E－17	(18)	(40)
E－18	(19)	(41)
E－19	(18)	(42)
E－20	(18)	(43)
E－21	(18)	(44)
E－22	(18)	(45)
E－23	(18)	(46)
E－24	(20)	(47)
E－25	(20)	(48)
E－26	(21)	(49)
E－27	(21)	(50)
E－28	(21)	(51)
E－29	(22)	(52)
E－30	(18)	(53)
E－31	(18)	(54)
E－32	(22)	(49)
E－34	(18)	(56)
E－38	(19)	(46)

Exemplary compound No.	R_1	Y
E －39	(18)	(57)
E －41	(18)	(60)
E －42	(18)	(48)
E －44	(18)	(58)

1



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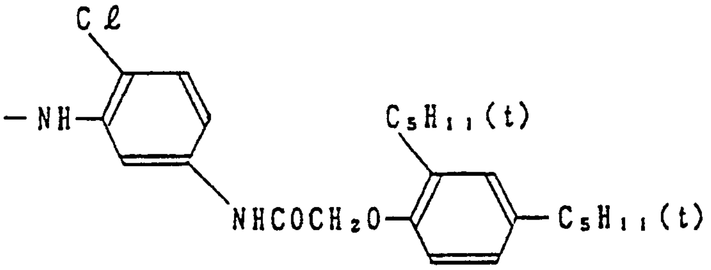
$-C(CH_3)_3$

3



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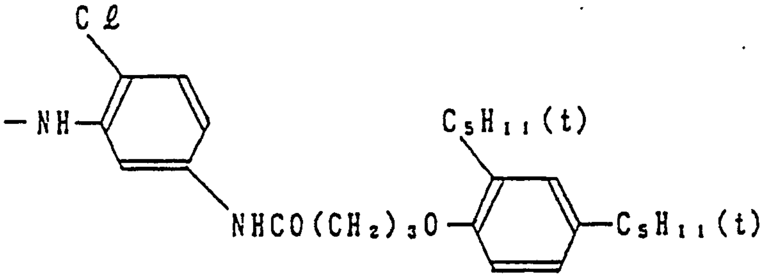
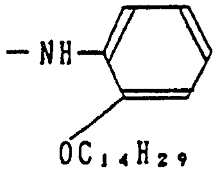


5

$-OCH_3$

6



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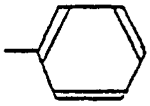

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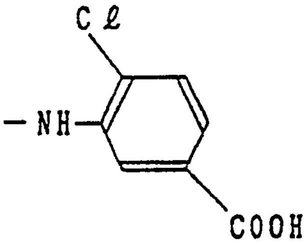

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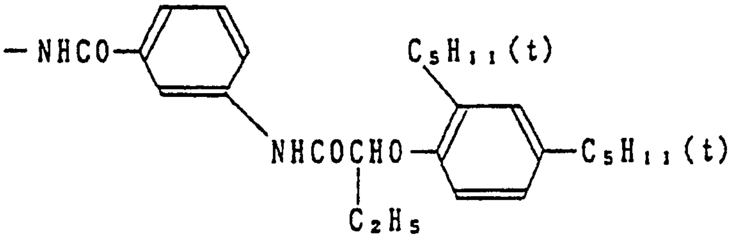

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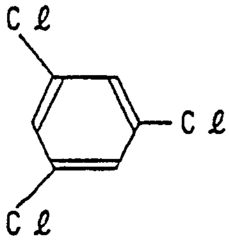

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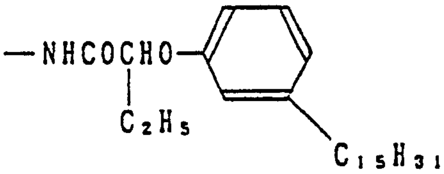
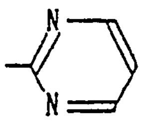


12

$-C_{17}H_{35}$

13



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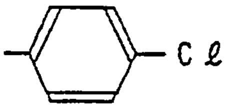
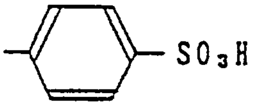


15

$-CH_3$

16



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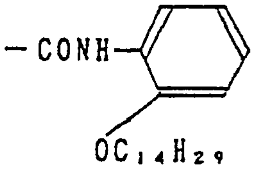
$-CONHC_{18}H_{37}$

18



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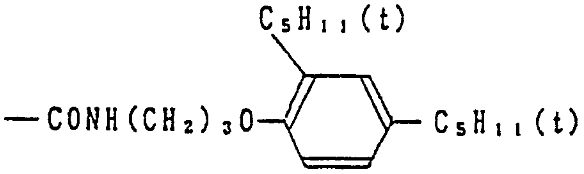

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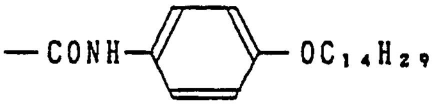


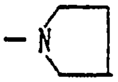
21

$-CONHCH_2CH_2COOH$

22

$-CONHCH_2CH_2COOCH_3$

23



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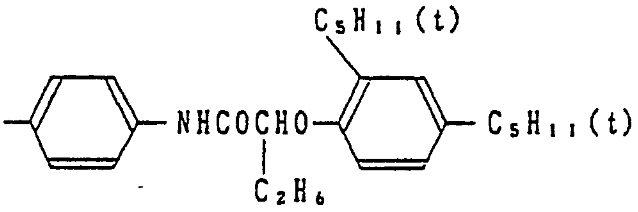

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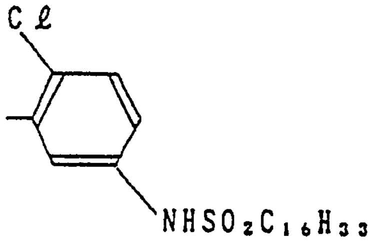

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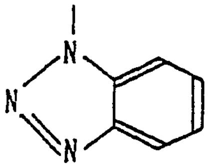

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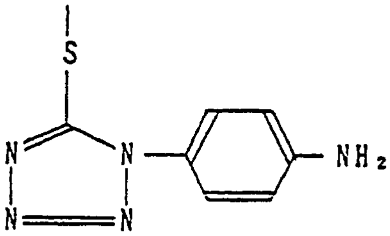

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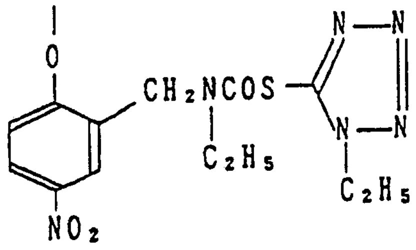

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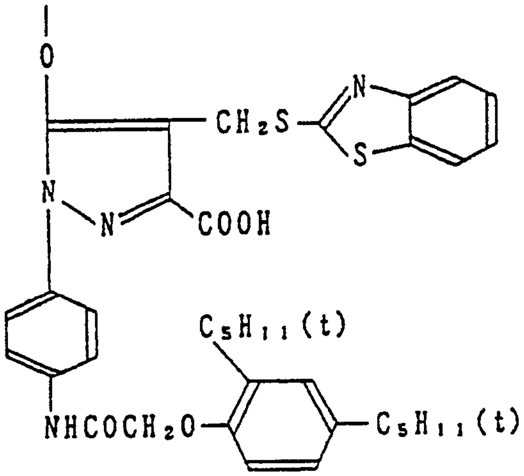

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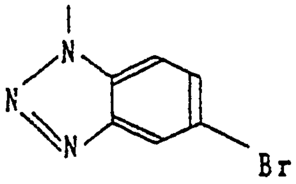

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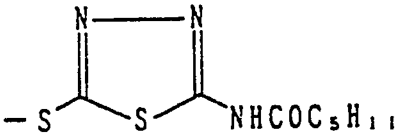

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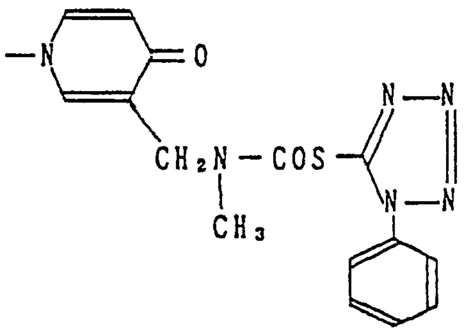

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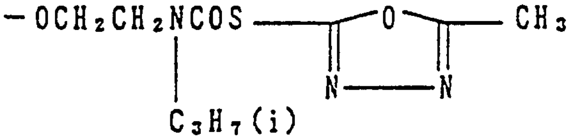

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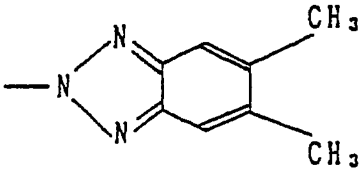

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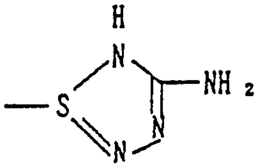

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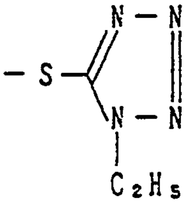

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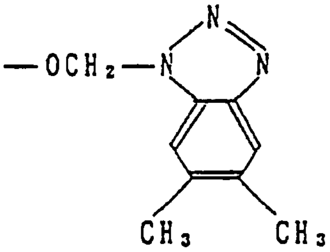

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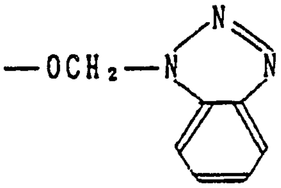

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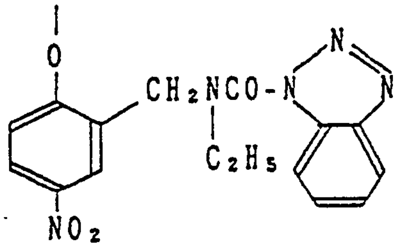

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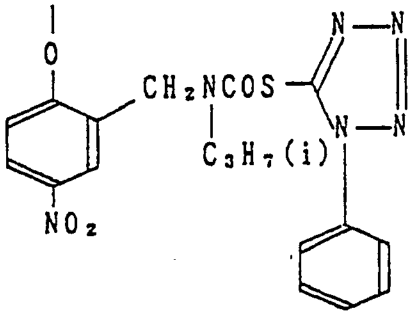

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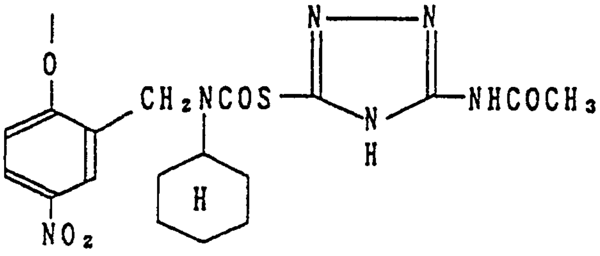
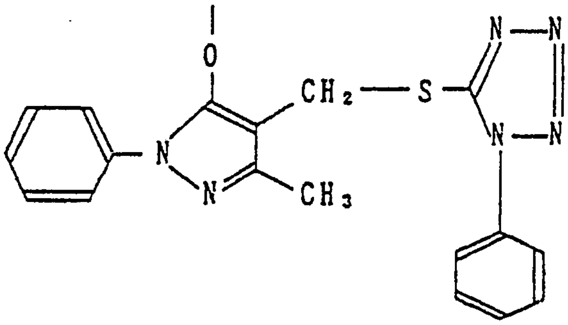
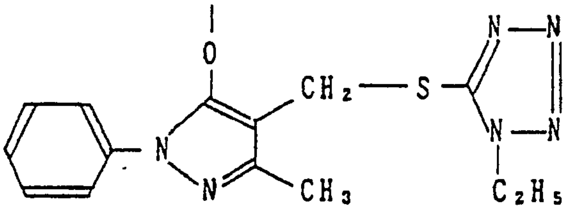

O
CH₂NCOS
N
N
N
H
NHCOCH₃
H
NO₂

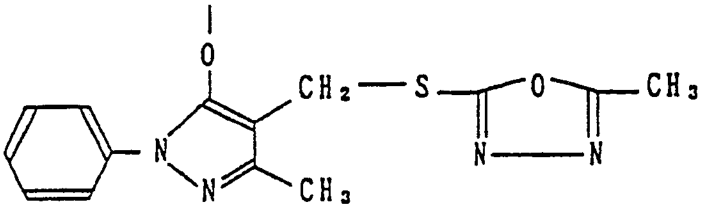
4 6


O
CH₂
S
N
N
N
N
N
N
CH₃

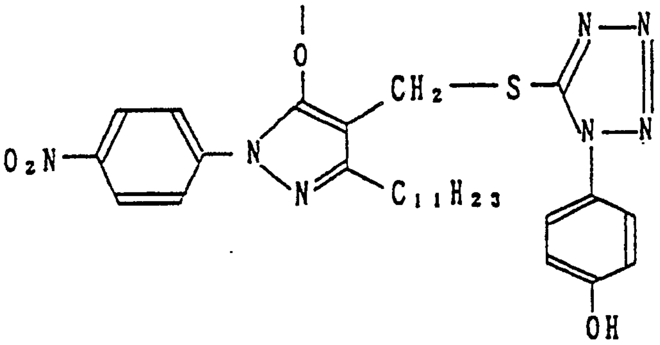
4 7


O
CH₂
S
N
N
N
N
N
N
CH₃
C₂H₅

4 8



4 9



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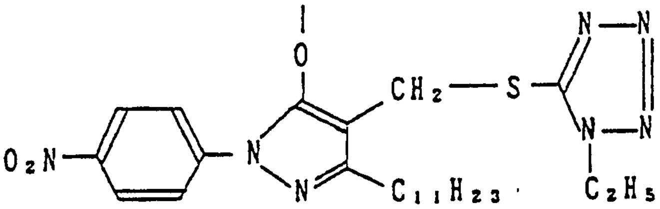
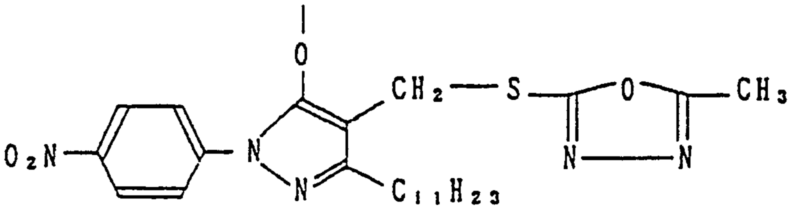


5 1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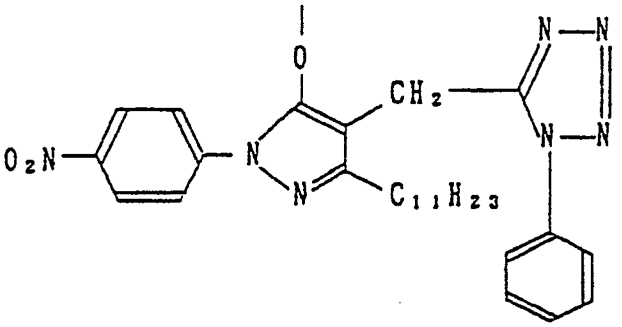
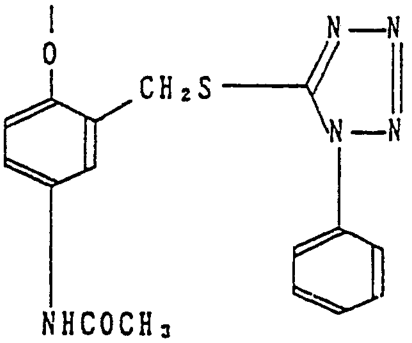
S
O
CH₃
O₂N
N
N
N
N
C₁₁H₂₃

5 2


O
N
N
CH₂
N
N
O₂N
N
N
C₁₁H₂₃

5 3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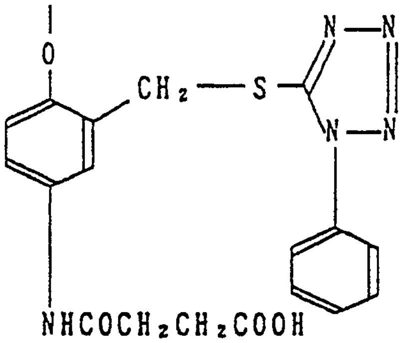
N
N
N
N
NHCOCH₃

5 4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S
N
N
N
N
NHCOCH₂CH₂COOH

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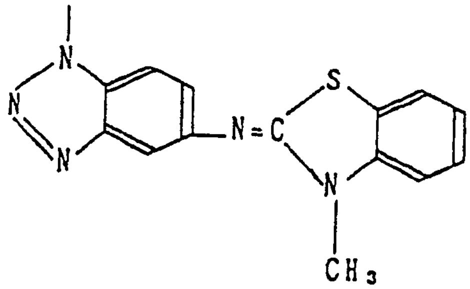

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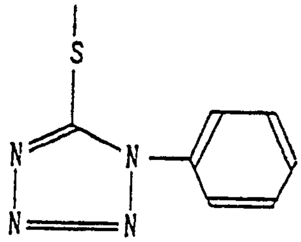

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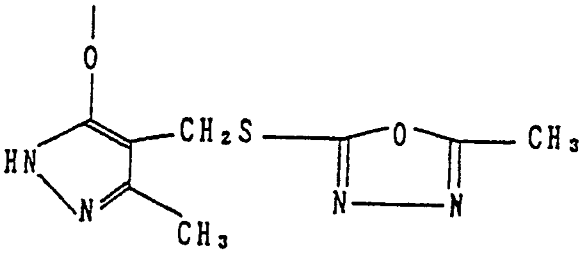

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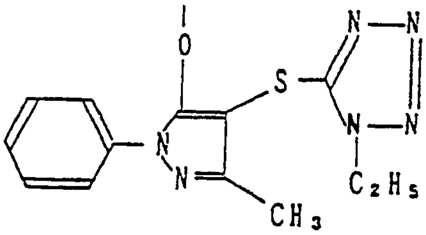

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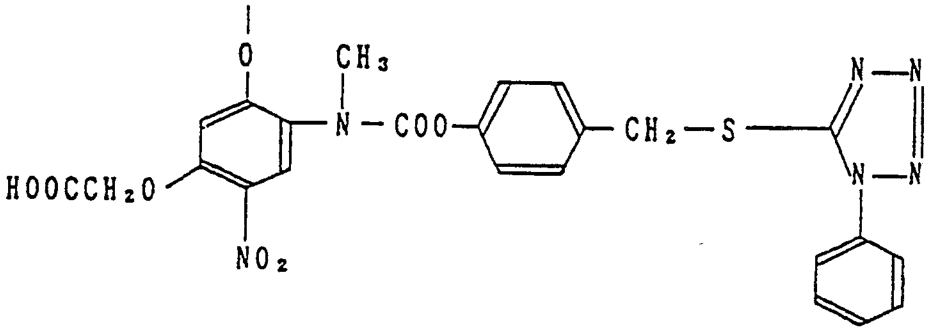

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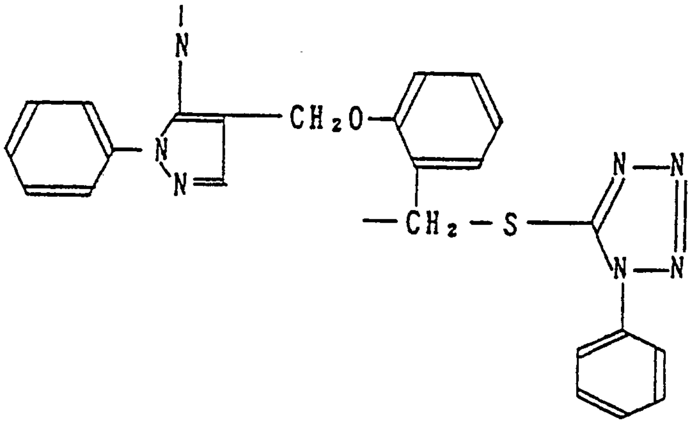


Specific examples of the DIR compounds which can be used in the present invention, including these are described in U.S. Patents 4,234,678, 3,227,544, 3,617,291, 3,958,993, 4,149,866, 3,933,500, Japanese Unexamined Patent Publications Nos. 56837/1982 and 13239/1976, U.S. Patents 2,072,363 and 2,070,266, Research Disclosure No. 21228, December, 1981, etc.

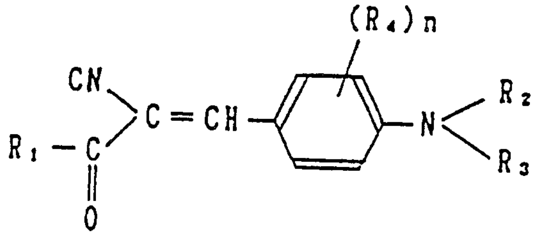
The DIR compound should be preferably used in an amount of 0.0001 to 0.1 mole, particularly 0.001 to 0.05 mole, per mole of silver halide.

The place in which the DIR compound to be used in the present invention is added may be any place which can affect developing of the silver halide in the emulsion layers having a single layer constitution as described above, preferably a silver halide emulsion layer, more preferably an emulsion layer having a single layer constitution.

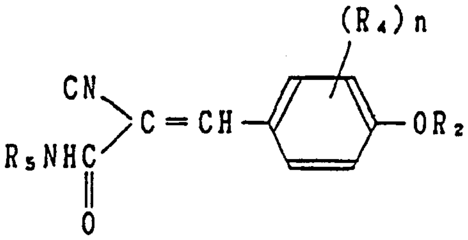
The position of the yellow filter layer in the photographic light-sensitive material in the present invention may be at a position that the light for exposure reaches prior to the green-sensitive layer and the red-sensitive layer, and the light for exposure reaches later than at least one blue-sensitive layer.

As the yellow dye contained in the yellow filter layer, those represented by the following formula (A) or (B) are preferred.

Formula (A)



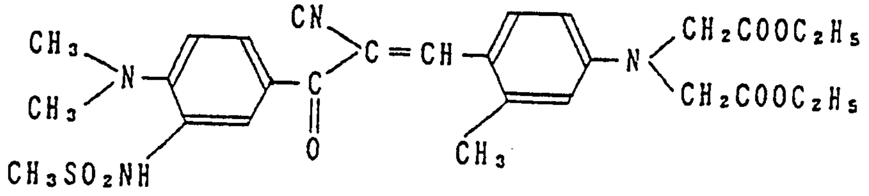
Formula (B)



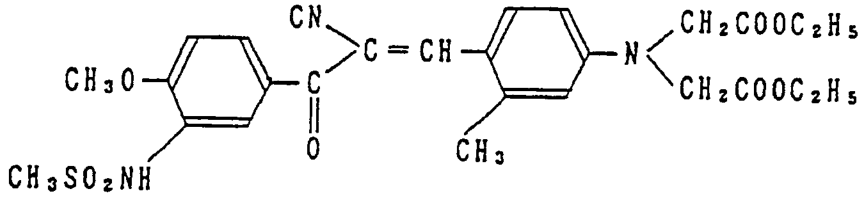
In the formulae, R_1 represents an aryl group or an alkoxy group, R_2 and R_3 alkyl groups, R_4 hydrogen atom or a substituent, R_5 an aryl group, respectively, and n represents an integer of 1 to 4. As the aryl group represented by R_1 or R_5, phenyl grcup, naphthyl group, etc. may be included, preferably phenyl group.

Said aryl group is inclusive of those containing substituents, and examples of said substituent may include sulfo group (including salts such as potassium salt, sodium salt, etc.), amino groups (dimethylamino group, etc.), sulfonylamino groups (alkylsulfonylamino groups such as methanesulfonylamino, ethanesulfonylamino, dodecanesulfonylamino groups, etc.), alkoxy groups (methoxy group, ethoxy group, etc.). As R_1, a phenyl group having at least an alkylsulfonylamino group is preferable, and as R_5, a phenyl group having at least sulfo group is preferable.

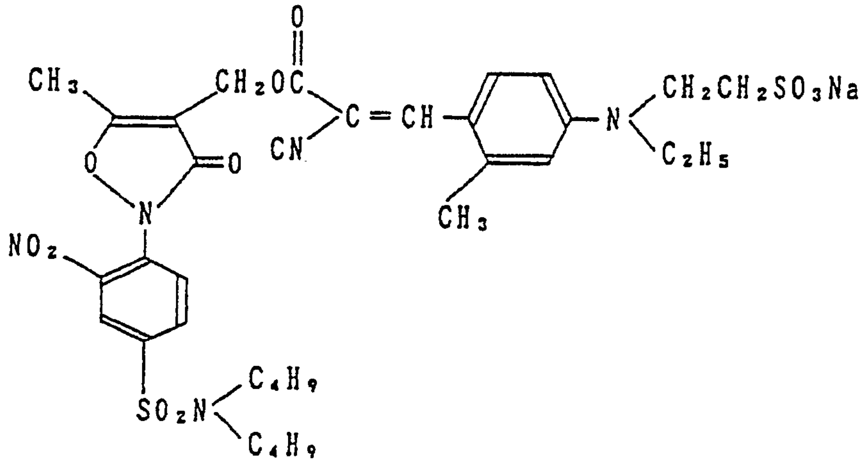
Y I - 1



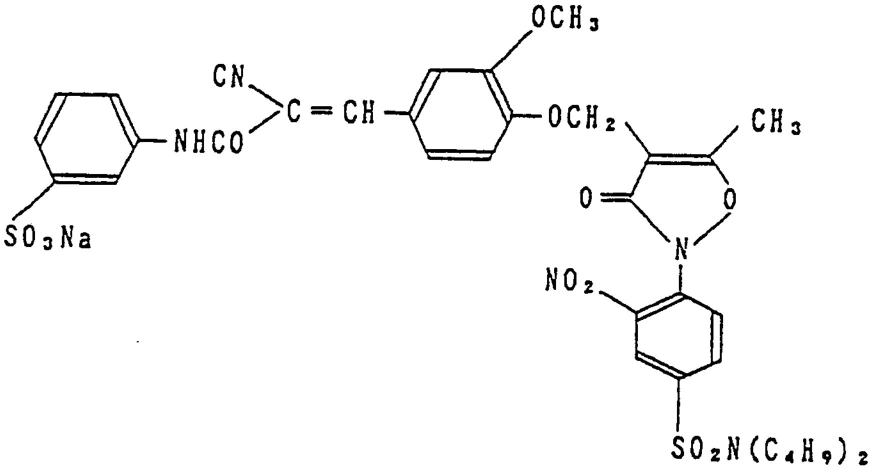
Y I - 2



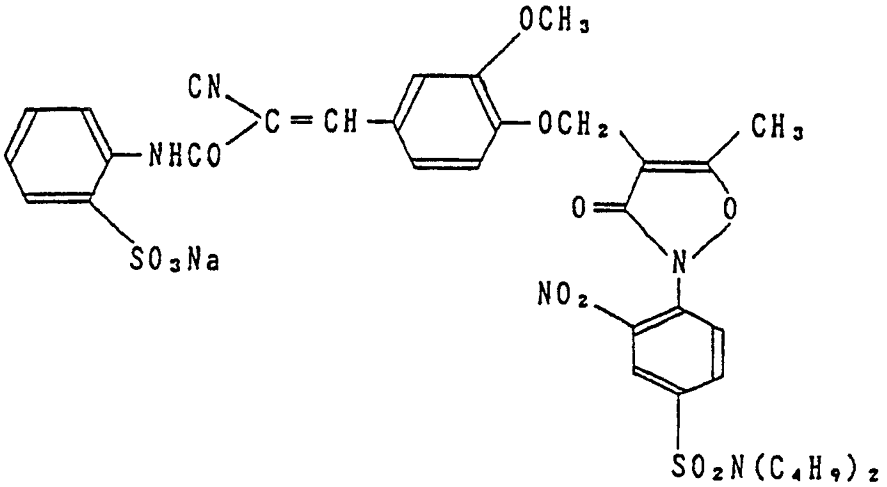
Y I - 3



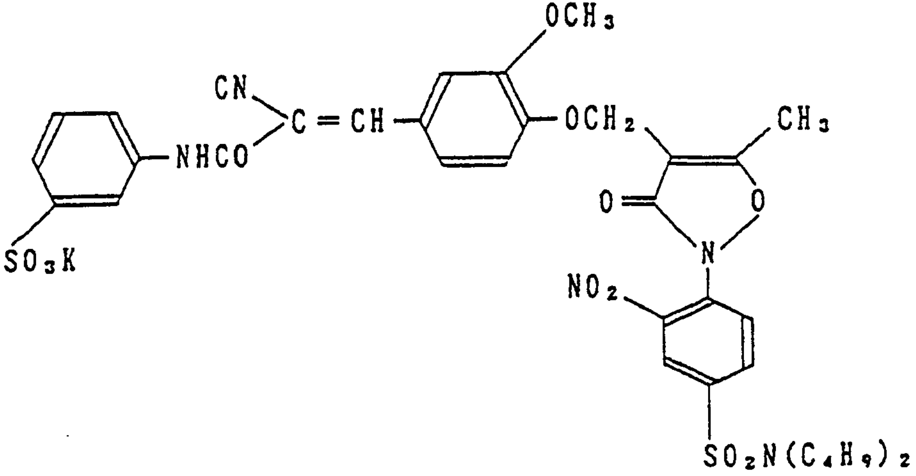
Y I - 4



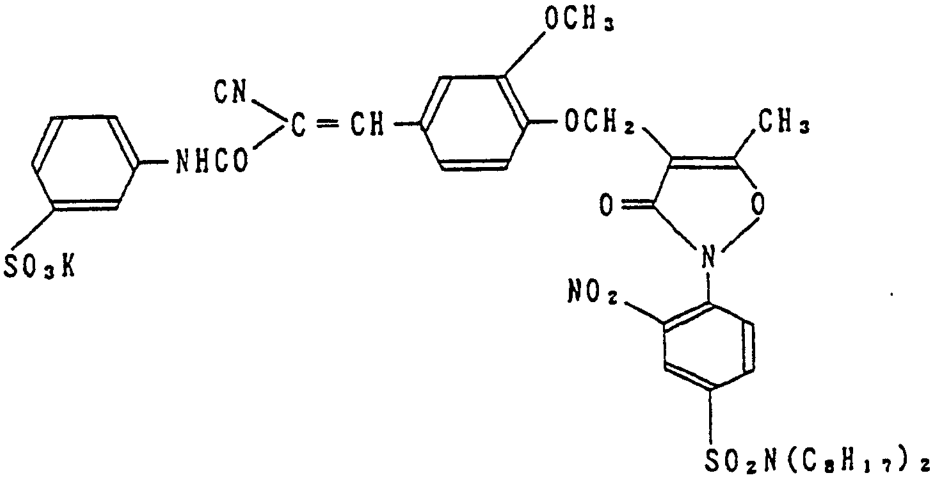
YI－5



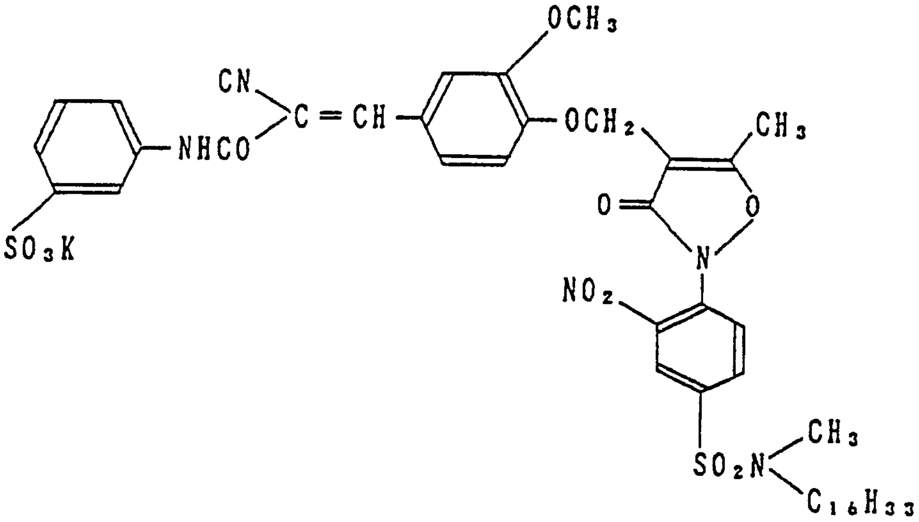
YI－6



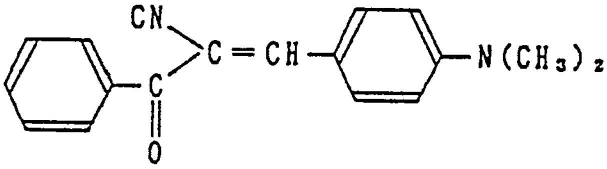
YI－7



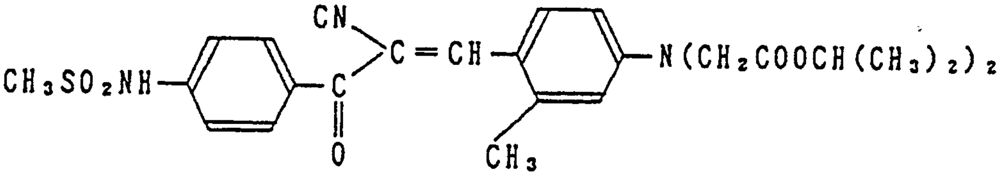
Y I − 8



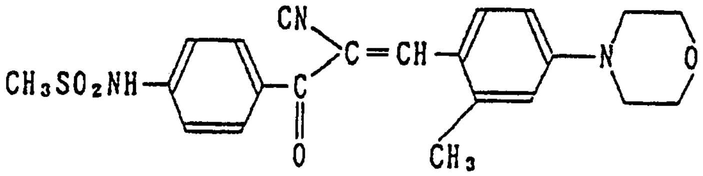
Y I − 9



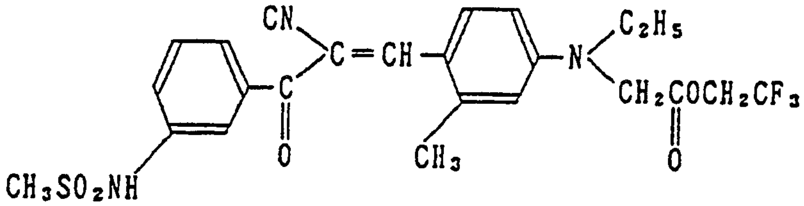
Y I − 1 0



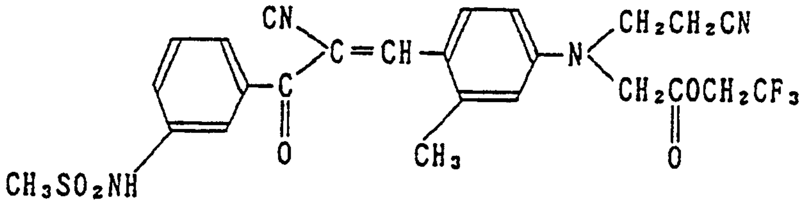
YI-11



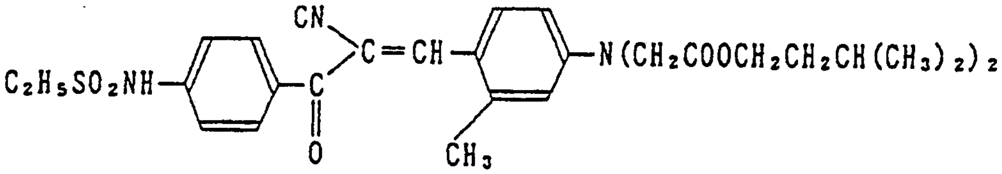
YI-12



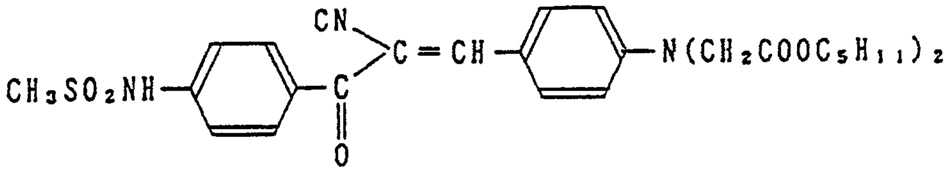
YI-13



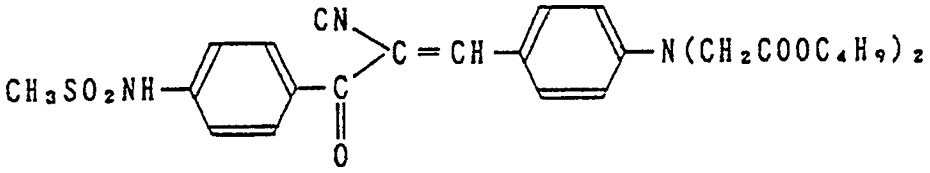
YI-14



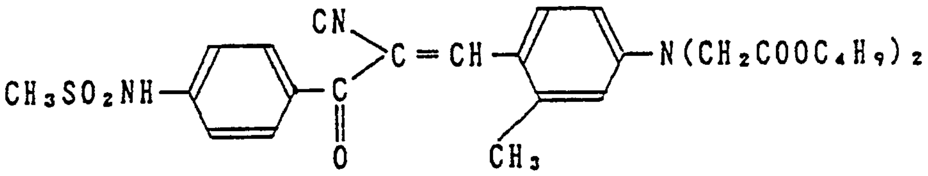
YI-15



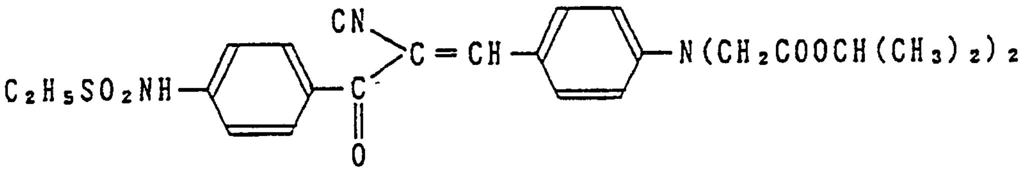
YI-16



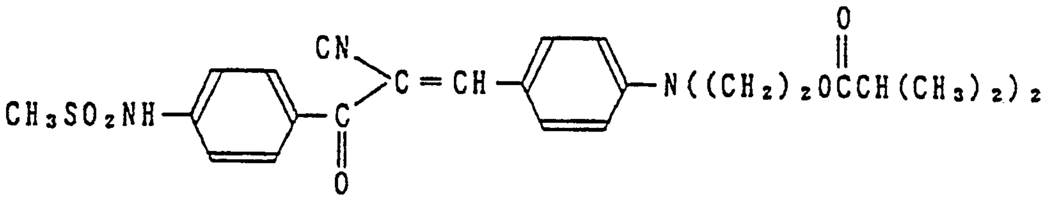
YI-17



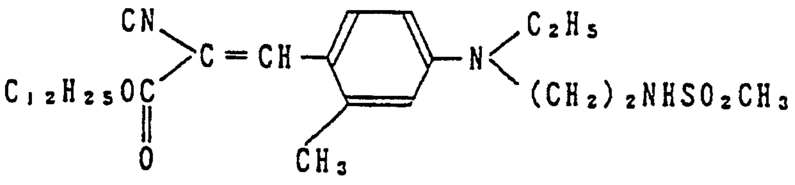
YI-18



YI-19



YI-20



Other than these, as the yellow dye, those disclosed in Japanese Unexamined Patent Publications Nos. 204630/1986, 32460/1987, 222248/1987, 184769/1988, 271351/1988, 282738/1988, 296039/1988, U.S. Patent 4,420,555, etc. may be included.

The yellow dye should be preferably used in an amount of 1 to 1,000 mg/m^2 in the light-sensitive material, preferably so that the optical density may be in the range from 0.05 to 3.0. The timing when the yellow dye is added in the coating solution is not particularly limited.

The constitution that the color sensitive layer is a single layer is also inclusive of the case when a plurality of emulsion layers which are the same in color sensitivity, being the same in the kind of the couplers contained in the emulsion layers, grain sizes of the silver halide grains, the halogen compositions and crystal habits, and also the ratio of the coupler to the silver halide, are arranged as continuous layers.

Here, "the same in color sensitivity" or "the same color sensitivity" may be the same in the point of, for example, blue sensitivity, green sensitivity, red sensitivity, and is not required to be totally the same in spectral sensitivity characteristics.

In the present invention, the blue-sensitive layer should be preferably a single layer, and further preferably, both the blue-sensitive layer and the green-sensitive layer should be single layers. Particularly, all of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers should be preferably single layers, respectively.

When the same color sensitive layer has a single layer constitution, the number of the layers coated of the light- sensitive layer can be reduced as compared with the overlaid constitution of the prior art, whereby the film can be made thinner. Therefore, production efficiency, sharpness are improved, and graininess is also improved. The thickness of all the layers coated should be preferably to 3 µm, particularly 15 to 5 µm, after drying.

The exposure latitude is the width of light received at which the exposure effect with a significant difference can be exhibited, particularly the exposure region from the highlight to the deep shadow in the characteristic curve, and is determined by the method defined in "Shashin no Kagaku", p. 393 (Shashin Kogyo Shuppansha, 1982).

More specifically, it is the difference in log H between the two points where the slope of the tangential line at the toe portion and the shoulder portion of the characteristic curve represented with log H as the axis of abscissa and the transmission density as the axis of ordinate becomes 0.2.

The light-sensitive material should be preferably one having an exposure latitude measured according to the method as described above of 3.0 or more, particularly 3.0 to 8.0.

As the means for making the exposure latitude of the silver halide emulsion layer which is a single layer wide, e.g. 3.0 or more, it is possible to use the method in which silver halide grains with different sensitivities are used as a mixture. Specifically, there may be included for example, the method in which silver halide grains with different grain sizes are used as a mixture, and the method in which the desensitizer is contained in at least a part of the silver halide grains.

One of the methods for obtaining wide exposure latitude is a method using two kinds of mono-emulsified grains which are different in mean grain size and sensitized. In this instance, the grain group having a larger mean grain size should preferably be 0.2 to 2.0 µm and the grain group having a smaller mean grain size, 0.05 to 1.0 µm, and the mean grain size of the latter group is smaller than the former group. Also, one or more of silver halide grains having an intermediate mean grain size may be combined.

Also, the mean grain size of the silver halide grains with the maximum mean grain size should be preferably 1.5 to 40 times as that of the silver halide grain with the minimum mean grain size.

For obtaining a broad exposure latitude, silver halide grains with different mean grain sizes can be also used as a mixture, but by using silver halide grains containing a desensitizer in place of the low sensitivity silver halide grains with small grain sizes, the mean grain size difference can be made smaller without changing the sensitivity of the silver halide grains, and further it becomes possible to use silver halide grains with equal mean grain size and different sensitivities.

Thus, by use of silver halide grains containing a desensitizer, the exposure latitude can be obtained even if the fluctuation coefficient of the grains as a whole may be made smaller.

Therefore, these silver halide grains with small fluctuation coefficient exposed to the same environment are preferably stabilized in photographic performances relative to changes with lapse of time and fluctuations in developing processing. Further, in aspect of production technique, it becomes also possible to sensitize chemically a mixed system of silver halide grains with different sensitivities in the same batch.

As the desensitizer, in addition to metal ions, various ones such as antifoggants, stabilizers, desensitizing dyes, etc. can be used.

In the present invention, the metal ion doping method is preferred. As the metal ion to be used for doping, there may be included the metal ions of the groups Ib, IIb, IIIa, IIIb, IVb, Va, VIII in the periodic table of elements. Preferable metal ions may include Au, Zn, Cd, Tl, Sc, Y, Bi, Fe, Ru, Os, Rh, Ir, Pd, Pr, Sm and Yb. Particularly, Rh, Ru, Os and Ir are preferred. These metal ions can be used as, for example, halogeno complexes, etc., and the pH of the AgX system during doping should be preferably 5 or less.

The amount of these metal ions doped will differ variously depending on the kind of the metal ion, the grain size of the silver halide grains, the doping position of the metal ion, the desired sensitivity, etc., but may be preferably 10^{-17} to 10^{-2} mole, further 10^{-12} to 10^{-3} mole, particularly 10^{-9} to 10^{-4} mole, per mole of AgX.

Further, by selection of the kind of the metal ion, the doping position and the doping amount, various different qualities can be given to the silver halide grains.

With a doping amount of 10^{-2} mole/AgX or less, no great influence will be scarcely given to the growth of the grains, and hence silver halide grains with small grain size distribution can be prepared under the same grain growth conditions, even by growth in the same batch.

After the silver halide grains with different doping conditions are adjusted in conditions to be provided for practical application, these can be also made up in the same batch by mixing at a predetermined ratio and subjected to chemical sensitization. The respective silver halide gains receive the sensitizing effects based on their qualities, whereby an emulsion having a broad exposure latitude depending on the sensitivity difference and the mixing ratio can be obtained.

As the above-mentioned antifoggants or stabilizers, there may be included azoles, (e.g. benzothiazolium salt, indazoles, triazoles, benztriazoles, benzimidazoles, etc.), heterocyclic mercapto compounds (e.g. mercaptotetrazoles, mercaptothiazoles, mercaptothiadiazoles, mercaptobenzthiazoles, mercaptobenzimidazoles, mercaptopyrimidines, etc.), azaindenes (e.g. tetraazaindenes, pentaazaindenes, etc.), decomposed products of nucleic acids (e.g. adenine, guanine, etc.), benzenethiosulfonates, thioketo compounds, and others.

As the desensitizing dyes, there may be included cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes, etc.

As the position where the desensitizer exists, in viewpoint of storability of the light-sensitive material, digestion stability of the coating liquid and the like, it should be preferably mixed internally of the silver halide grains, and its distribution may be either uniform, localized at the central portion of grain or the intermediate positions, etc., or also gradually reduced from the central portion of grain toward outside.

From the standpoint of production efficiency, the case where the desensitizer exists as localized at the central portion of grain is preferable, and by use of the system in which seed grains with small fluctuation coefficient are used, the steps of grain growth *et seq* can be proceeded in the same batch.

The light-sensitive material of the present invention should desirably have at least one color sensitive layer (e.g. blue-sensitive layer) containing AgX grains containing a desensitizer. Preferably, it is the case when the blue-sensitive layer contains AgX grains containing a desensitizer, more preferably when the blue-sensitive layer and the green-sensitive layer contain them, most preferably when all of the color sensitive layers contain them.

Also, the fluctuation coefficient defined by the ratio $S/\bar{r}$ of the standard deviation of grain size (S) as the silver halide grains contained in the respective silver halide emulsion layers and the mean grain size ($\bar{r}$) should be preferably 0.4 or less, more preferably 0.33 or less, further preferably 0.25 or less, particularly preferably

0.20 or less.

$$S = \sqrt{\frac{\Sigma (\bar{r} - ri)^2 ni}{\Sigma ni}}$$

The mean grain size ($\bar{r}$) is defined by the following formula when the number of grains with a grain size ri (in the case of a cubic silver halide grain, its length of one side, or in the case of a grain with other shape than cubic, the length of one side of the cube calculated to have the same volume) is ni:

$$\bar{r} = \frac{\Sigma\, ni \cdot ri}{\Sigma\, ni}$$

The relationship of grain size distribution can be determined according to the method described in the essay of Tribel and Smith in "Empirical Relationship between Sensitometry Distribution and Grain Size Distribution in Photography", The Photographic Journal, vol. LXXIX (1949), p.p. 330 - 338.

As the silver halide emulsion to be used in the light-sensitive material of the present invention, any of conventional silver halide emulsions can be used, but a silver halide containing substantially iodine in the halogen composition (e.g. silver iodobromide, silver iodochlorobromide) may be preferable, particularly preferably silver iodobromide with respect to sensitivity. The amount of iodine may be preferably 1 mole % or more and 20 mole % or less, particularly 3.5 mole % or more 12 mole % or less.

A core/shell type silver halide emulsion to be used in the present invention preferably has a grain structure comprising two or more phases different in silver iodide content and comprises silver halide grains in which a phase containing a maximum silver iodide content (referred to as "core") is other than the outermost surface layer (referred to as "shell").

The content of silver iodide in an inner phase (core) having the maximum silver iodide content is preferably 6 to mole %, more preferably 8 to 40 mole %, particularly preferably 10 to 40 mole %. The content of silver iodide in the outermost surface layer is preferably less than 6 mole %, more preferably 0 to 4.0 mole %.

A ratio of the shell portion in the core/shell type silver halide grains is preferably 10 to 80 %, more preferably 15 to 70 %, particularly preferably 20 to 60 % in terms of volume.

Also, a ratio of the core portion is preferably, in terms of volume, 10 to 80 %, more preferably 20 to 50 % based on the whole grains.

Difference of silver iodide content between the core portion having higher silver iodide content and the shell portion having less silver iodide content of the silver halide grains may be clear with sharp boundary or may be hazy where boundary is not clear and the content continuously changes. Also, those having an intermediate phase with silver iodide content between those of the core portion and the shell portion, between the core and the shell, may be preferably used.

In case of the core/shell type silver halide grains having the above intermediate phase, a volume of the intermediate phase is preferably 5 to 60 %, more preferably 20 to 55 % based on the whole grain. Differences of the silver iodide content between the shell and the intermediate phase, and between the intermediate phase and the core are each preferably 3 mole % or more and the difference of the silver iodide content between the shell and the core is preferably 6 mole % or more.

The core/shell type silver halide emulsion can be prepared according to the known methods as disclosed in Japanese Provisional Patent Publications No. 177535/1984, No. 138538/1985, No. 52238/1984, No. 143331/1985, No. 35726/1985 and No. 258536/1985.

For producing silver iodobromide or silver bromide, soluble silver salt and soluble halide are generally used, but as clear from the examples mentioned below, iodide salts are preferably used in the form of silver iodide fine crystals in the point of preservability and processing stability of the light-sensitive material.

Also, silver iodobromide fine crystals having high AgI content are similarly and preferably used as the silver iodide fine crystals.

Distribution condition of the silver iodide in the above core/shell type silver halide grains can be determined by various physical measuring method and, for example, it can be examined by the measurement of luminescence at low temperature or X-ray diffraction method as described in Lecture Summary of Annual Meeting, Japanese Photographic Association, 1981.

The core/shell type silver halide grain may be any shape of normal crystal such as cubic, tetradecahedral and octahedral, or twinned crystal, or mixtures thereof, but preferably normal crystal grains.

Said emulsion can be chemically sensitized in conventional manner, and optically sensitized to a desired wavelength region by use of a sensitizing dye.

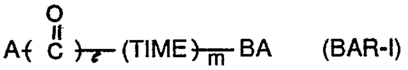
In the silver halide emulsion, antifoggants, stabilizers, etc. can be added. As the binder for said emulsion, gelatin can be advantageously used.

The emulsion layer and other hydrophilic colloid layers can be hardened, and also a plasticizer and a dispersion (latex) of a water-soluble or difficultly soluble synthetic polymer can be contained therein.

In the emulsion layer of a light-sensitive material for color photography, couplers are used.

Further, there can be used colored couplers having the effect of color correction, competitive couplers and compounds releasing photographically useful fragments such as developer, silver halide solvent, toning agents, film hardeners, antifoggants, chemical sensitizers, spectral sensitizers and desensitizers through the coupling with the oxidized product of the developing agent.

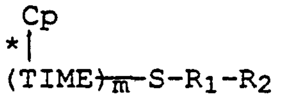
The bleaching accelerator releasing compound (BAR compound) may preferably be represented by the following formula (BAR-I).



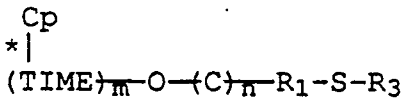
$$A\!\left(\overset{O}{\overset{\|}{C}}\right)_{\ell}\!\!-\!(TIME)_m\!-BA \qquad \text{(BAR-I)}$$

wherein A is a coupler residue which can be subjected to a coupling reaction with an oxidized product of a color developing agent, or a residue of an oxidation-reduction nucleus which can be cross-oxidized with an oxidized product of a color developing agent; TIME is a timing group; BA is a bleaching accelerator or its precursor; m is 0 or 1; and when A is a coupler residue, ℓ is 0, and when A is a residue of an oxidation-reduction nucleus, ℓ is 0 or 1.

Of the BAR compound represented by the formula (BAR-I), preferred are those represented by the formulae (BAR-II) and (BAR-III).

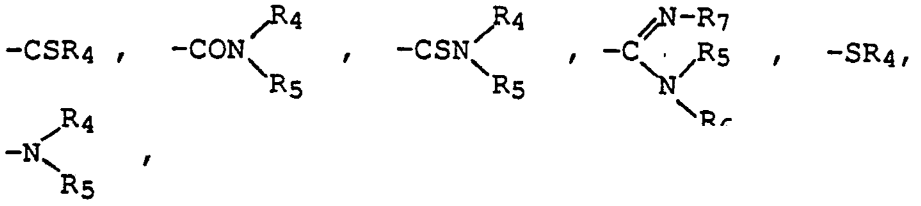


$$\overset{\overset{Cp}{*|}}{(TIME)_m}\!-S-R_1-R_2 \qquad \text{(BAR-II)}$$



$$\overset{\overset{Cp}{*|}}{(TIME)_m}\!-O\!-\!(C)_n\!-R_1-S-R_3 \qquad \text{(BAR-III)}$$

wherein Cp is a coupler residue which can be subjected to a coupling reaction with an oxidized product of a color developing agent; * is a coupling position of a coupler; TIME is a timing group; R_1 is an aliphatic group, an aromatic group, a saturated heterocyclic group or a 5- or 6-membered aromatic nitrogen-containing heterocyclic group; R_2 is a water solubilizing substituent or its precursor; R_3 is a hydrogen atom a cyano group, $-COR_4$,



or a heterocyclic group, in which R_4 is an aliphatic group or an aromatic group, R_5, R_6 and R_7 each are a hydrogen atom, an aliphatic group or an aromatic group; and m and n each are 0 or 1.

As the coupler residue represented by Cp, there may be mentioned residues capable of forming yellow, magenta or cyan dyes and residues forming substantially colorless products by the coupling reaction.

The representative examples of a yellow coupler residue are described in U.S. Patents No. 2,298,443, No. 2,407,210, No. 2,875,057, No. 3,048,194, No. 3,265,506 and No. 3,447,928, and Farbkuppler eine Literaturuverisiecht Agfa Mitteilung (Band II), pp. 112 to 126 (1961). Of these, acylacetoanilides such as benzoylacetoanilide and pyvaloylacetoanilide are preferred.

The representative examples of a magenta coupler residue are described in U.S. Patents No. 2,369,489, No. 2,343,703, No. 2,311,182, No. 2,600,788, No. 2,908,573, No. 3,062,653, No. 3,152,986, No. 3,519,429, No. 3,725,067 and No. 4,540,654, Japanese Provisional Patent Publication No. 162548/1984 and in the above-mentioned Agfa Mitteilung (Band II), pp. 126 to 156 (1961). Of these, pyrazolone and pyrazoloazoles, e.g. pyrazoloimidazole and pyrazolotriazole are preferred.

The representative examples of a cyan coupler residue are described in U.S. Patents No. 2,367,531, No. 2,423,730, No. 2,474,293, No. 2,772,162, No. 2,395,826, No. 3,002,836, No. 3,034,892, No. 3,041,236 and No. 4,666,999 and in the above-mentioned Agfa Mitteilung (Band II), pp. 156 to 175 (1961). Of these, phenols and naphthols are preferred.

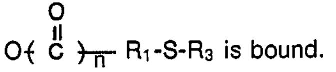
The representative examples of a coupler residue which forms substantially colorless products are described in British Patent No. 861,138 and U.S. Patents No. 3,632,345, No. 3,928,041, No. 3,958,993 and No. 3,961,959. Of these, a cyclic carbonyl compound is preferred.

A timing group represented by TIME is a group which allows a bleaching accelerator and its precursor (BA) to be split-off from Cp, while controlling time. This group may contain a group capable of controlling the rate of a reaction between Cp and an oxidized product of a color developing agent, the rate of diffusion of -TIME-BA split-off from Cp, and the rate of splitting off of BA.

The representative examples of a timing group are the following known timing groups.

(*) is a portion to be bounded to an active position of Cp;

and (*)(*) is a portion to which $-S-R_1-R_2$ or

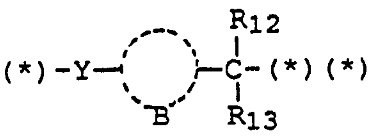


$O\left(\overset{O}{\overset{\|}{C}}\right)_{\overline{n}} R_1\text{-}S\text{-}R_3$ is bound.

(1) A group which causes a cleavage reaction by using an electron transfer reaction along with a conjugated system.

Examples of such a group include those described in Japanese Provisional Patent Publications No. 114,946/1981, No. 154,234/1982, No. 188,035/1982, No. 98,728/1983, No. 160,954/1983, No. 162,949/1983, No. 209,736/1983, No. 209,737/1983, No. 209,738/1983, No. 209,739/1983, No. 209,740/1983, No. 86,361/1987 and No. 87,958/1987.

Of these, groups represented by the following formulae (TIME-I) and (TIME-II) are preferred.



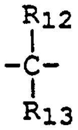
(TIME-I)

wherein B is a group of atoms necessary for the formation of a benzene ring or a naphthalene ring; Y is -O-, -S- or

$\overset{R_{14}}{\overset{|}{-N-}}$;

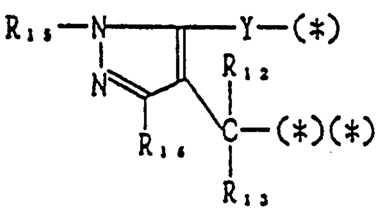
and R_{12}, R_{13} and R_{14} each are a hydrogen atom, an alkyl group or an aryl group.

The above-described



$\underset{R_{13}}{\underset{|}{\overset{R_{12}}{\overset{|}{-C-}}}}$

group is substituted at the ortho-or para-position relative to Y.

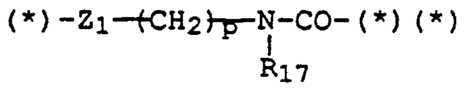


(TIME-II)

wherein Y, R_{12} and R_{13} are as described above; R_{15} is a hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfon group, an alkoxycarbonyl group or a heterocyclic group; and R16 is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an amino group, an acylamino group, a sulfonamido group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group or a cyano group.

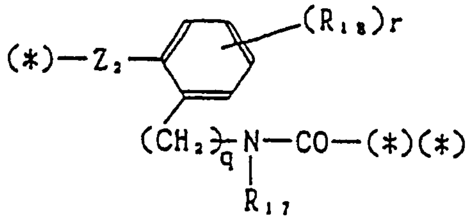
(2) A group which causes a cleavage reaction by using an intramolecular nucleophilic substitution reaction.

Examples of such a group include those described in U.S. Patent No. 4,248,962 and Japanese Provisional Patent Publication No. 56,837/1982. Of these, preferred are those represented by the formulae (TIME-III), (TIME-IV) and (TIME-V).

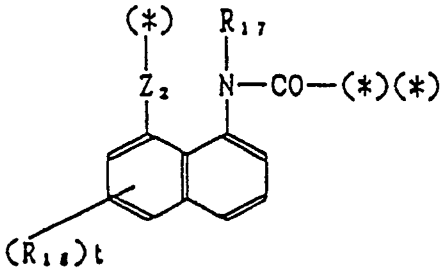


$$(*)\text{-}Z_1\text{-}(CH_2)_p\text{-}\underset{R_{17}}{\underset{|}{N}}\text{-}CO\text{-}(*)(*)$$

(TIME-III)



(TIME-IV)



(TIME-V)

wherein Z_1 is (*)-O-, (*)-O-CO-,

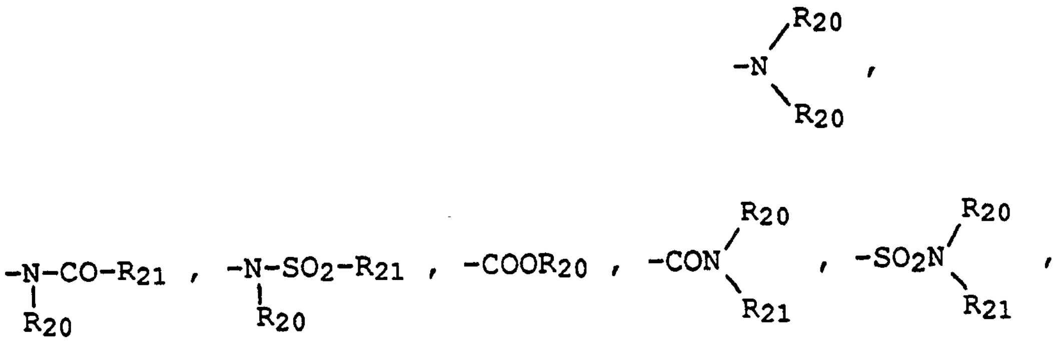
wherein Z_1 is $(*)\text{-}O\text{-}$, $(*)\text{-}O\text{-}CO\text{-}$, $(*)\text{-}O\text{-}CO\underset{R_{19}}{\underset{|}{N}}\text{-}$, $(*)\text{-}S\text{-}$,

$(*)\text{-}\underset{R_{19}}{\underset{|}{N}}\text{-}SO_2\text{-}$, $(*)\text{-}\underset{R_{19}}{\underset{|}{N}}\text{-}CO\text{-}$, $(*)\text{-}O\text{-}\underset{R_{19}}{\underset{|}{N}}SO_2\text{-}$, $(*)\text{-}\underset{SO_2R_{19}}{\underset{|}{N}}\text{-}$, $(*)\text{-}\underset{COR_{19}}{\underset{|}{N}}\text{-}$,

$(*)\text{-}OCOO\text{-}$, $(*)\text{-}OCO\text{-}S\text{-}$ or $(*)\text{-}O\text{-}\underset{R_{19}}{\underset{|}{N}}\text{-}CO\text{-}$; and Z_2 is

$(*)\text{-}O\text{-}$, $(*)\text{-}O\text{-}CH_2\text{-}$, $(*)\text{-}O\text{-}CO\text{-}$, $(*)\text{-}S\text{-}$, $(*)\text{-}\underset{SO_2R_{19}}{\underset{|}{N}}\text{-}$ or $(*)\text{-}\underset{COR_{19}}{\underset{|}{N}}\text{-}$,

wherein R_{19} is a hydrogen atom, an alkyl group, an aryl group or a heterocyclic group; R_{17} is a hydrogen atom, an alkyl group or an aryl group; and R_{18} is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group,
$-O-R_{20}$, $-S-R_{20}$, $-OCO-R_{20}$, $-OSO_2R_{20}$,



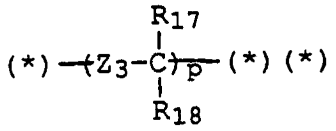
$$-N(R_{20})(R_{20}),\quad -N(R_{20})-CO-R_{21},\quad -N(R_{20})-SO_2-R_{21},\quad -COOR_{20},\quad -CON(R_{20})(R_{21}),\quad -SO_2N(R_{20})(R_{21}),$$

a cyano group, a halogen atom or a nitro group. R_{20} and R_{21} may be either identical or different and each are the same group as that represented by R_{19}; p is an integer of 1 to 4, q is 0, 1 or 2; r is an integer of 1 to 4; t is an integer of 1 to 3; when r or t is 2 or more, R_{18} may be either the same or different; and when r or t is 2 or more, R_{18}s may be combined each other to form a ring.

(3) A group which uses a cleavage reaction of hemiacetal

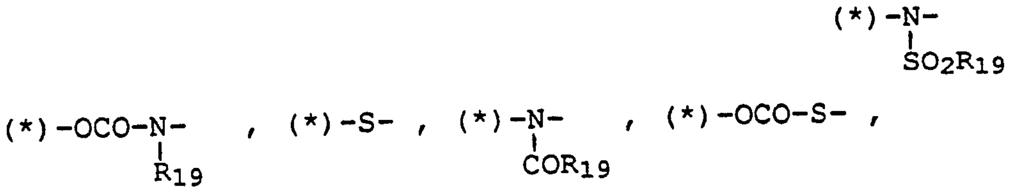
Examples of such a group include those described in U.S. Patent No. 4,146,396 and Japanese Provisional Patent Publications No. 249,148/1985 and No. 249,149/1985.

Of these, groups represented by the following formula (TIME-VI) are preferred.



$$(*)\!-\!\left(Z_3-\underset{R_{18}}{\overset{R_{17}}{\overset{|}{\underset{|}{C}}}}\right)_p\!-\!(*)\,(*) \qquad \text{(TIME-VI)}$$

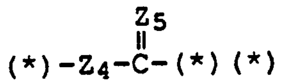
wherein Z3 represents (*)-O- , (*)-OCO-O- ,



$$(*)-N(SO_2R_{19})-,\quad (*)-OCO-N(R_{19})-,\quad (*)-S-,\quad (*)-N(COR_{19})-,\quad (*)-OCO-S-,$$

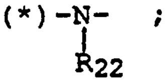
(*)-OCH$_2$-O- or (*)-OCH$_2$-S- ; R_{17}, R_{18} and R_{19} each have the same meaning as that mentioned in the formulae (TIME-III), (TIME-IV) and (TIME-V).

(4) A group represented by the following formula (TIME-VII) and described in German Patent (OLS) No. 2,626,315 and U.S. Patent No. 4,546,073.



$$(*)-Z_4-\overset{Z_5}{\overset{\|}{C}}-(*)\,(*) \qquad \text{(TIME-VII)}$$

wherein Z_4 represents (*)-O- , (*)-S- or



$$(*)-\underset{R_{22}}{\underset{|}{N}}-\;;$$

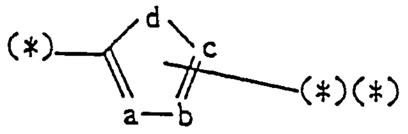
Z_5 represents an oxygen atom, a sulfur atom or $=N-R_{22}$; and R_{22} represents a hydrogen atom or a substituent.

The aliphatic group represented by R_1 of the formula (BAR-II) and (BAR-III) may be a saturated or unsaturated, straight-chain, branched-chain or cyclic aliphatic group having a carbon number of 1 to 8. This group may be either substituted or unsubstituted.

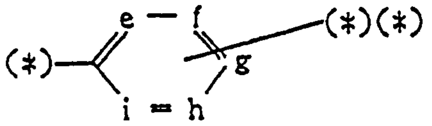
The aromatic group represented by R_1 may preferably be an aromatic group having a carbon number of 6 to 10, more preferably a substituted or unsubstituted phenylene group.

The saturated heterocyclic group represented by R_1 may be a 3- to 8-membered, preferably a 4- to 6-membered saturated heterocyclic group having a carbon number of 1 to 7, preferably 1 to 5, and containing at least one selected from an oxygen atom, a nitrogen atom and a sulfur atom.

The 5- or 6-membered aromatic nitrogen-containing heterocyclic group represented by R_1 may preferably be represented by the following formulae (H-I) and (H-II).



(H-I)



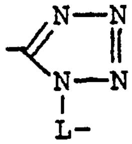
(H-II)

wherein a, b, c, e, f, g, h and i each are a nitrogen atom or a methyn group; d is an oxygen atom, a sulfur atom or an imino group; (*) is a position to which $Cp\text{-}(TIME)_{m}\text{-}S\text{-}$ or

$Cp\text{-}(TIME)_{m}O(\overset{O}{\overset{\|}{C}})_{n}$ is bound; and (*)(*) is a position to which R_3-S- or R_2 is bound.

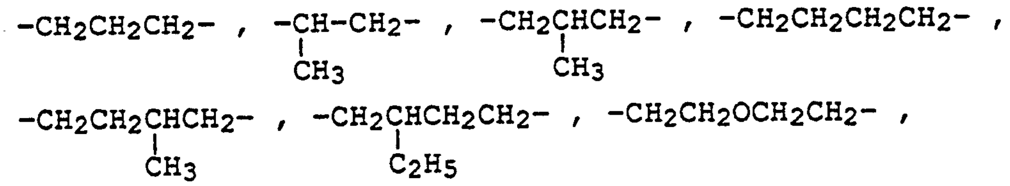
In the above formula, at least one of e, f, g, i and h is a nitrogen atom.

R_1 may more preferably be an aliphatic group or



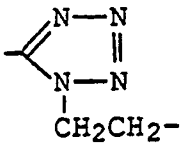
wherein L represents a divalent aliphatic group or a phenylene group having a carbon number of 1 to 8.

The preferred examples of R_1 include $-CH_2-$, $-CH_2CH_2-$,

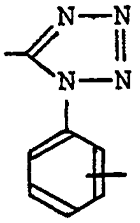


$$-CH_2CH_2CH_2- , -\underset{CH_3}{\underset{|}{C}}H-CH_2- , -CH_2\underset{CH_3}{\underset{|}{C}}HCH_2- , -CH_2CH_2CH_2CH_2- ,$$

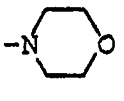
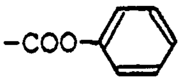
$$-CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_2- , -CH_2\underset{C_2H_5}{\underset{|}{C}}HCH_2CH_2- , -CH_2CH_2OCH_2CH_2- ,$$



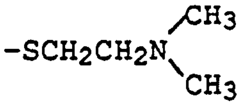
and



The preferred examples of an water-solubilizing substituent or its precursor represented by R_2 include $-COOH$, $-COONa$, $-COOCH_3$, $-COOC_2H_5$, $-NHSO_2CH_3$, $-NHCOOCH_3$, $-NHCOOC_2H_5$, $-SO_3H$, $-SO_3K$, $-OH$,

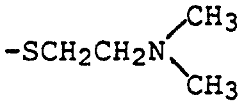
 ,  ,

$-SO_2NH_2$, $-NR_{10}R_{11}$,
wherein R_{10} ad R_{11} each are a hydrogen atom or an alkyl group having a carbon number of 1 to 4,
$-CONH_2$, $-COCH_3$, $-NHCOCH_3$, $-CH_2CH_2COOH$, $-CH_2CH_2NH_2$, $-SCH_2COOH$,

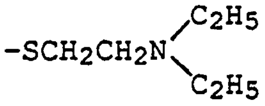


$-SCH_2CH_2N(CH_3)_2$,

$-CH_2COOH$, $-SCH_2CONH_2$, $-SCH_2COCH_3$ and $-SCH_2CH_2COOH$;
and the particularly preferred examples of the bleaching accelerator or precursor thereof represented by $-S-R_1-R_2$ include
$-SCH_2CH_2COOH$, $-SCH_2CH_2CH_2COOH$,

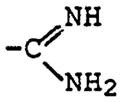


$-SCH_2CH_2N(CH_3)_2$ and



$-SCH_2CH_2N(C_2H_5)_2$.

The preferred examples of R_3 include
H , -CN , -COH , $-COCH_3$, $-COCH_2OCH_3$, $-COCF_3$, $-CSCH_3$, $-CON(CH_3)_2$, $-CON(C_2H_5)_2$, $-CSN(CH_3)_2$,

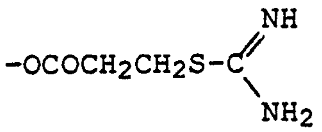


$-C(=NH)NH_2$

$-SCH_3$, $-SCH_2CH_2N(CH_3)_2$, $-SCH_2CH_2OH$, $-SCH_2CH_2COOH$, $-NHCH_3$, $-NHCH_2CH_2COOH$ and

 .

The particularly preferred examples of a bleaching accelerator or its precursor represented by $-O\left(\overset{O}{\overset{\|}{C}}\right)_{n}R_1\text{-}S\text{-}R_3$ include
$-OCOCH_2CH_2SH$, $-OCH_2CH_2SH$,

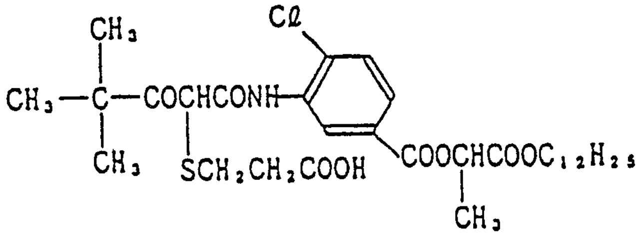


$-OCOCH_2CH_2S-C(=NH)NH_2$,

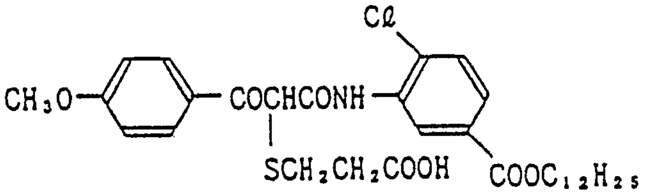
$-OCOCH_2CH_2SCOCH_3$, $-OCOCH_2CH_2SCSCH_3$, $-OCOCH_2CH_2SSCH_2CH_2COOH$, $-OCH_2CH_2SSCH_2CH_2OH$ and $-OCOCH_2CH_2SCN$.

The specific examples of a BAR compound to be used in the present invention are given below. These examples are given only for the purpose of illustration.

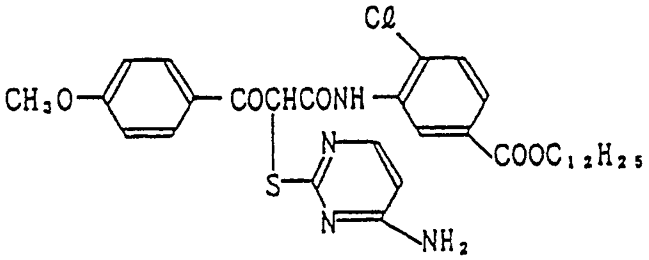
BAR-1



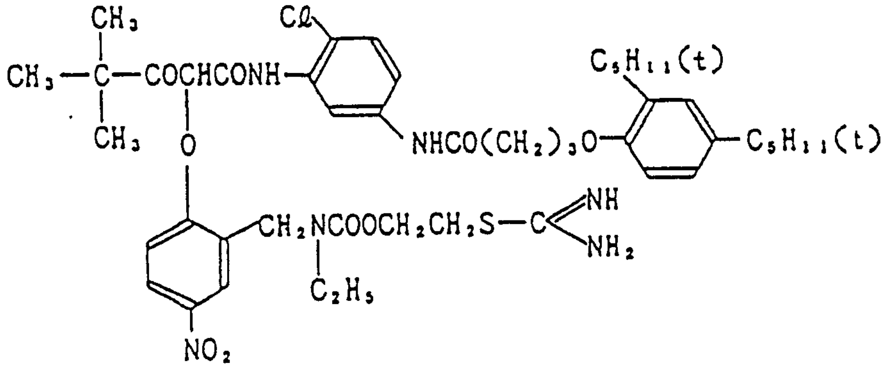
BAR-2



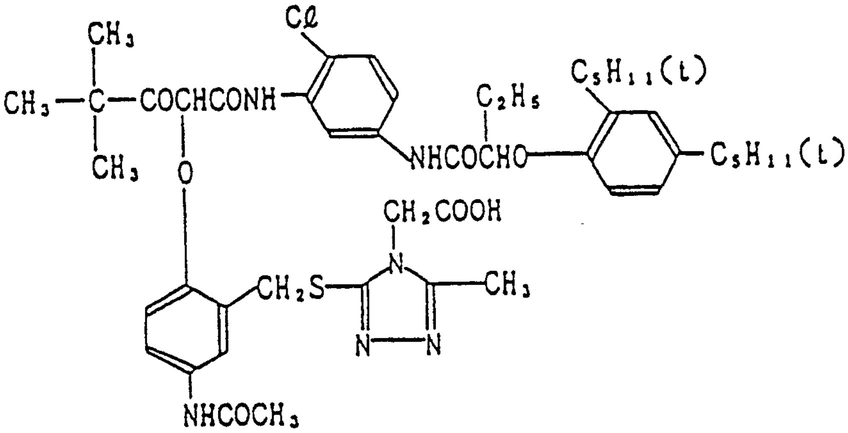
BAR-3



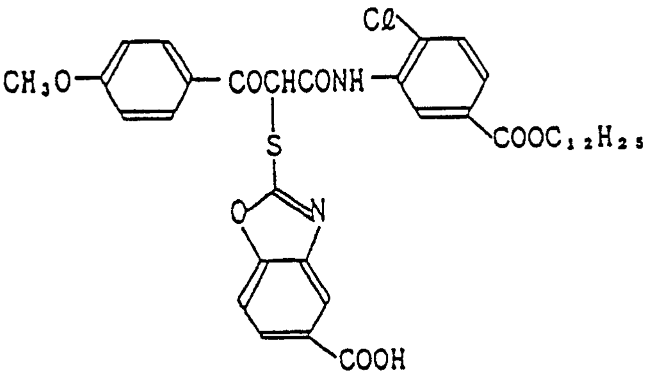
BAR-4



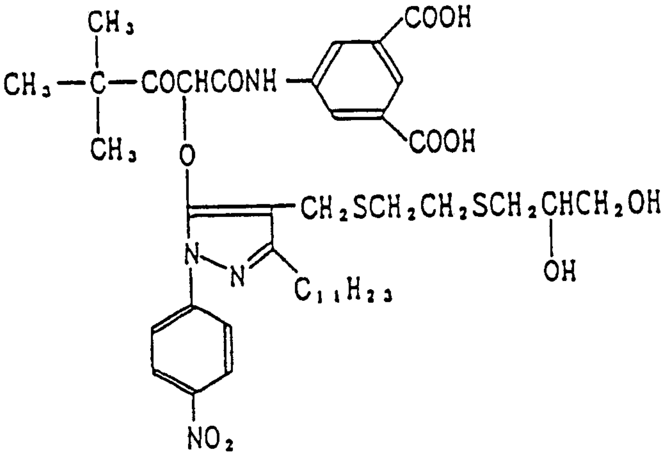
BAR-5



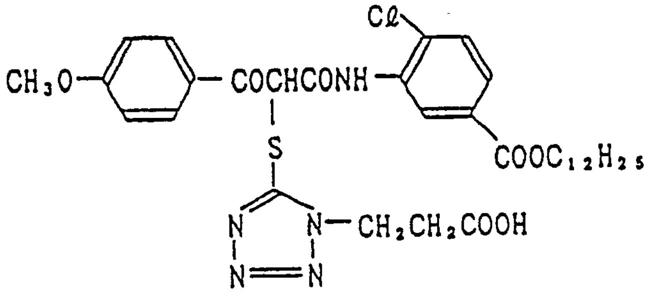
BAR-6



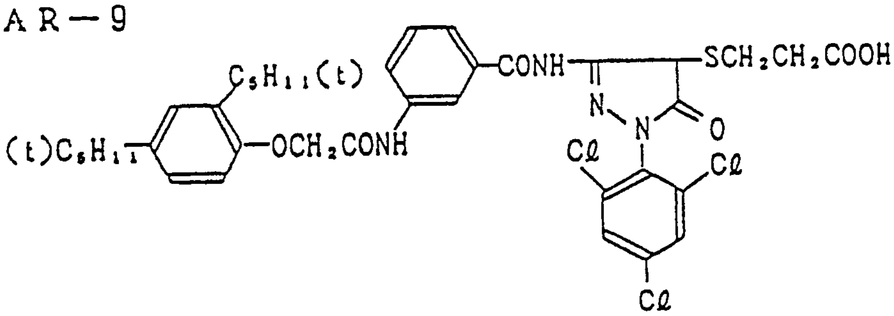
BAR-7



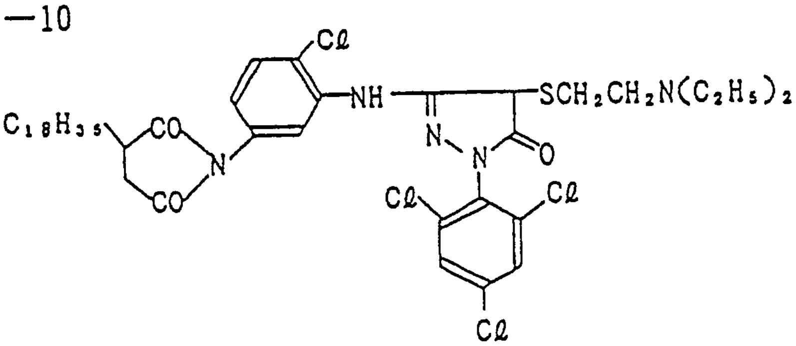
BAR−8



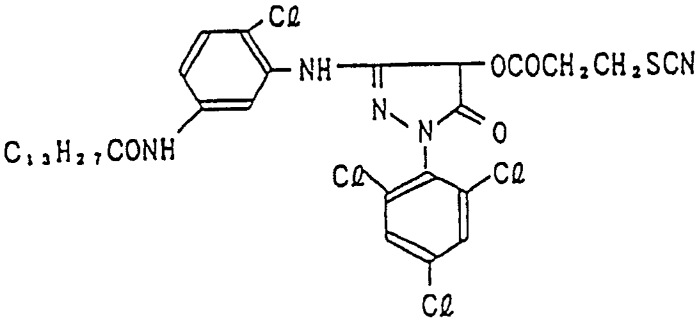
BAR−9



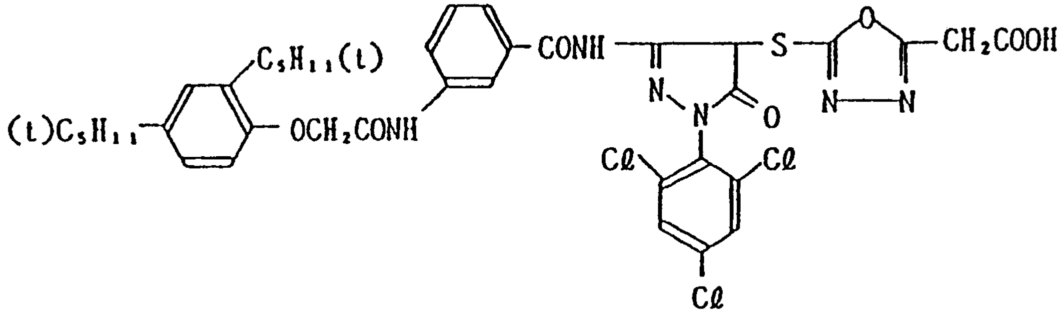
BAR−10



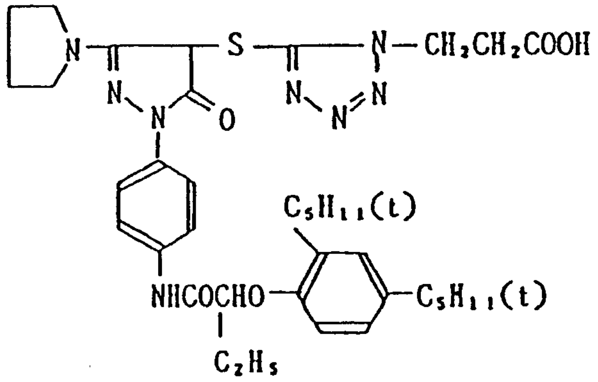
BAR−11



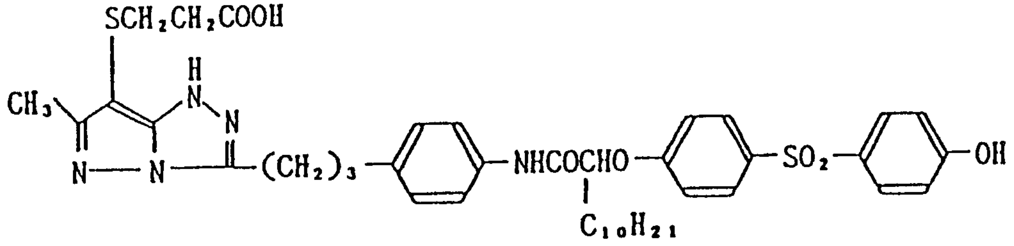
BAR-12


(t)C₅H₁₁
C₅H₁₁(t)
OCH₂CONH
CONH
S
CH₂COOH
N
N
O
N
N
O
Cℓ
Cℓ
Cℓ

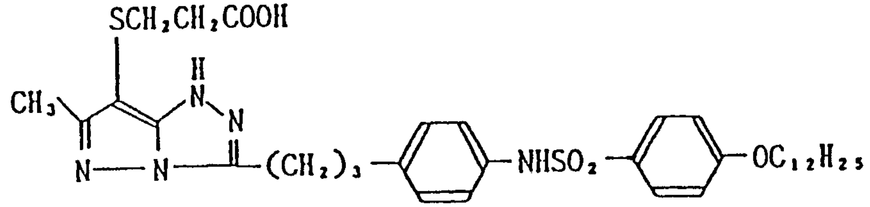
BAR-13


N
S
N—CH₂CH₂COOH
N
N
O
N
N
N
C₅H₁₁(t)
NHCOCHO
C₅H₁₁(t)
C₂H₅

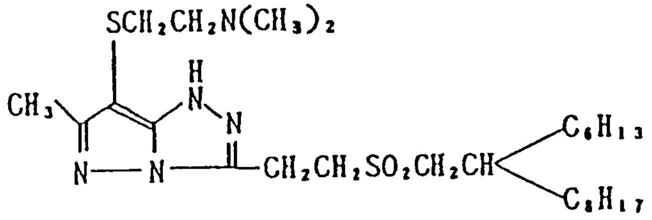
BAR—14



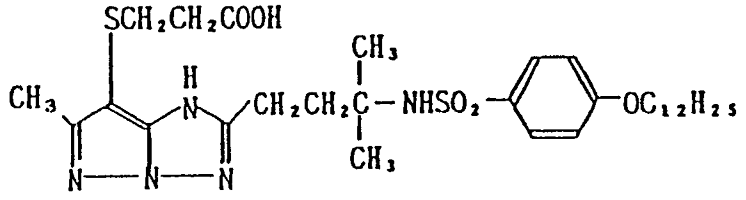
BAR—15



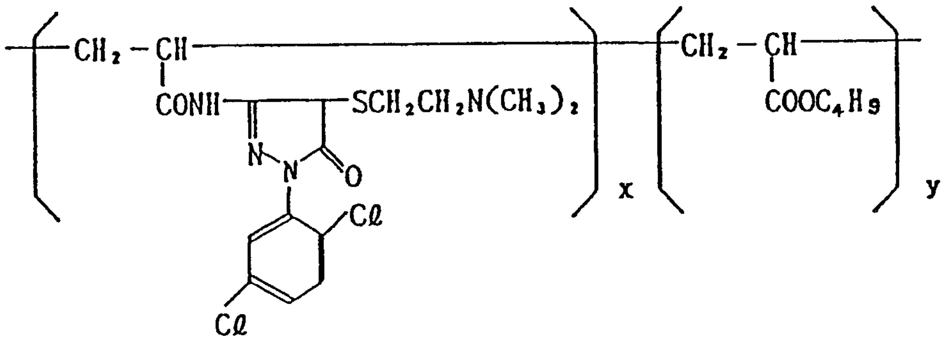
BAR—16



BAR−17

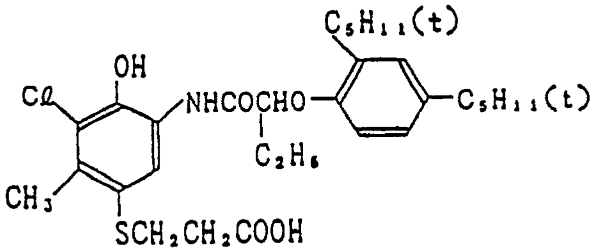


BAR−18

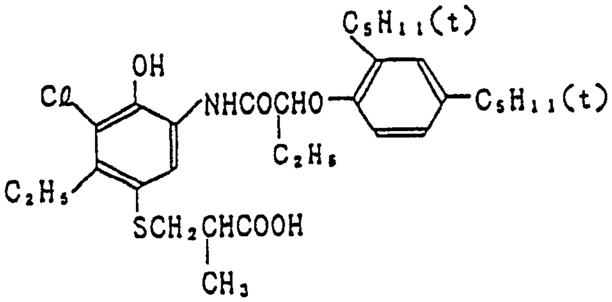


x:y=50:50 (weight ratio)

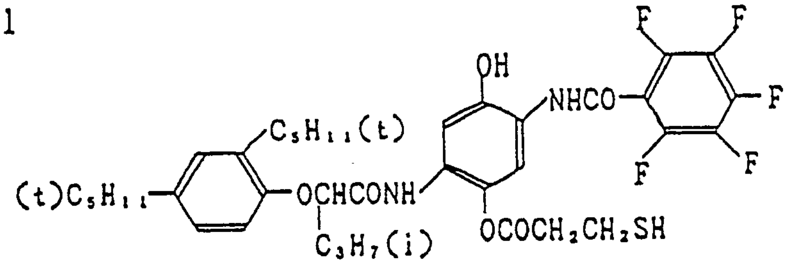
BAR-19



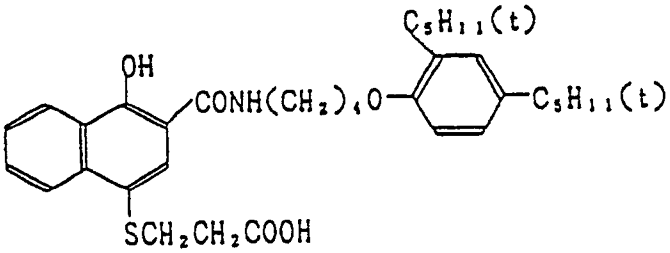
BAR-20



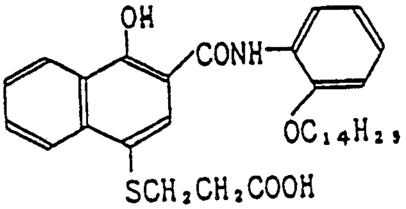
BAR-21



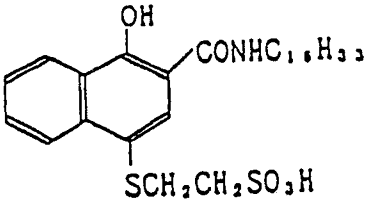
BAR-22



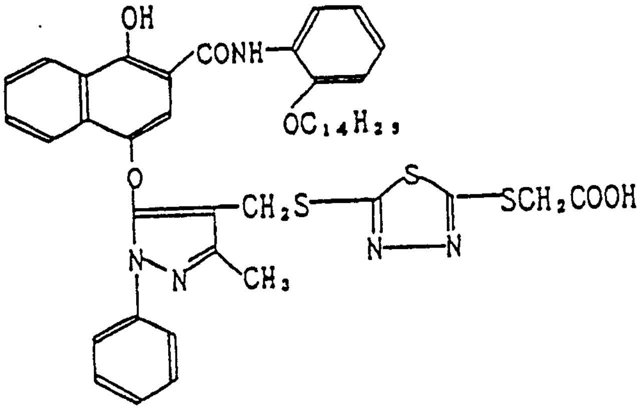
BAR-23



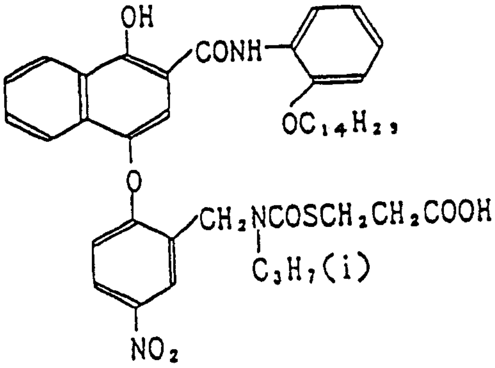
BAR-24



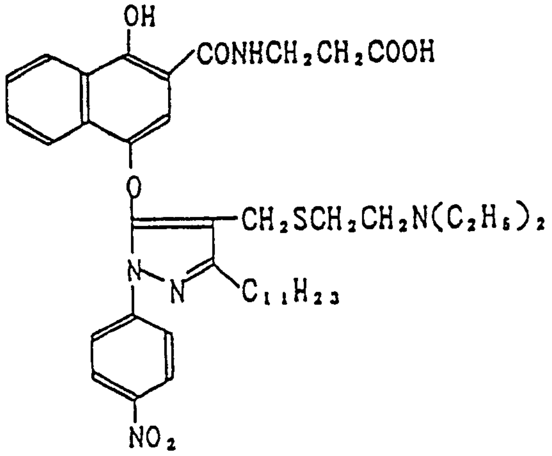
BAR-25



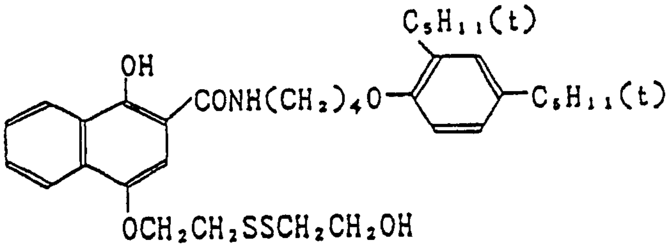
BAR-26



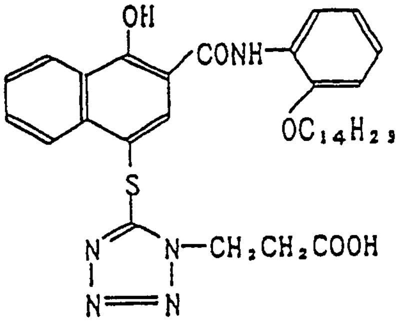
BAR-27



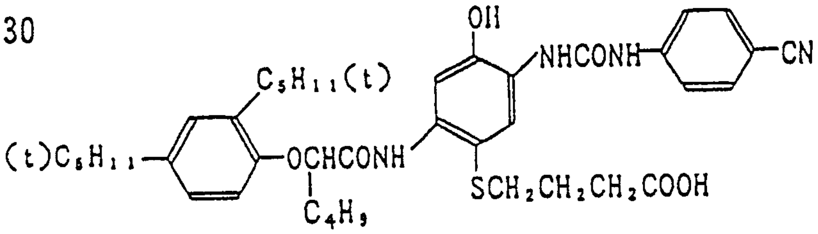
BAR-28



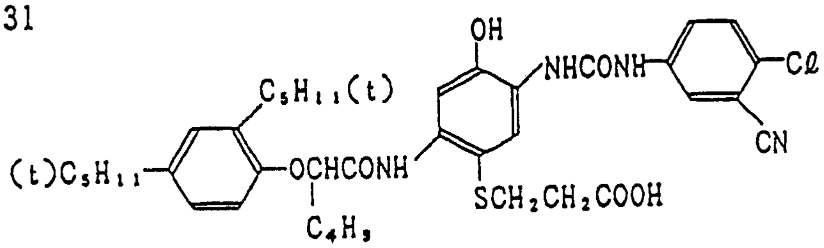
BAR-29



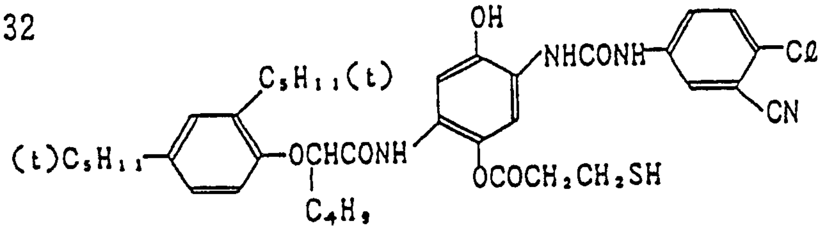
BAR-30



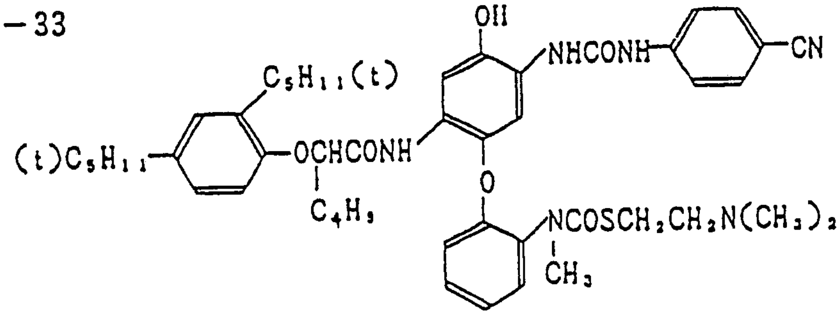
BAR-31



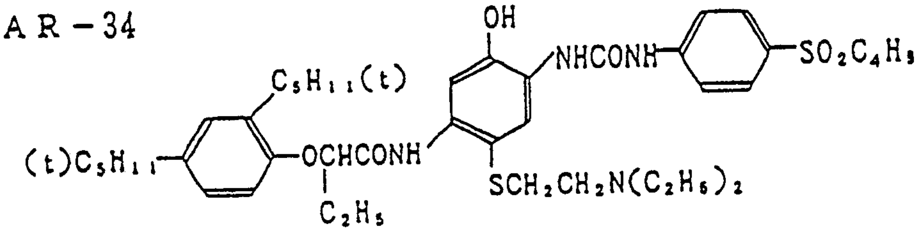
BAR-32



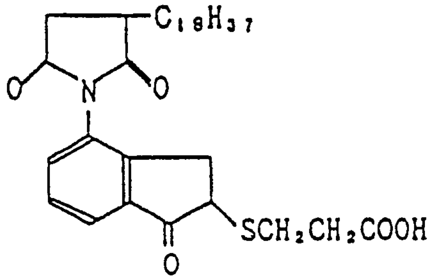
BAR-33



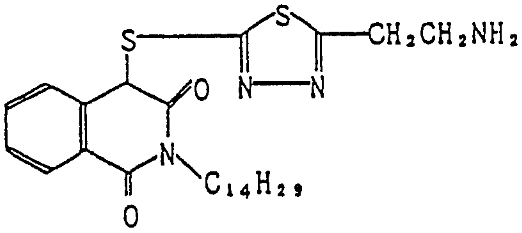
BAR-34



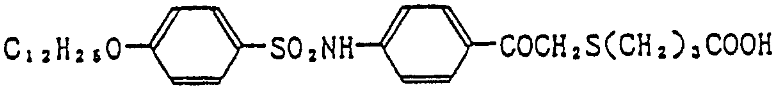
BAR-35



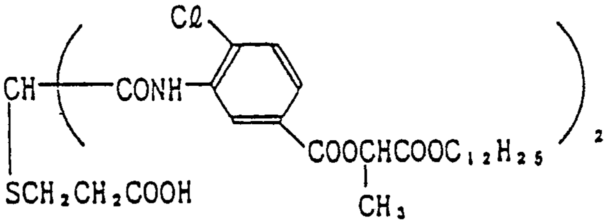
BAR-36



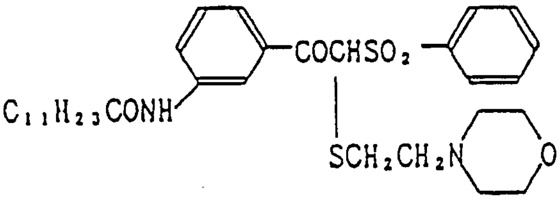
BAR-37



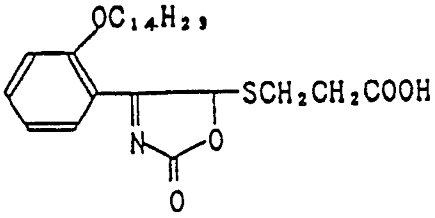
BAR-38



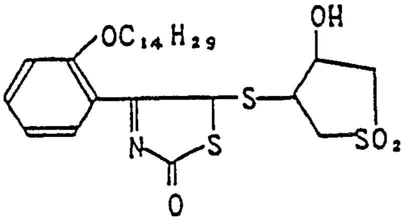
BAR-39



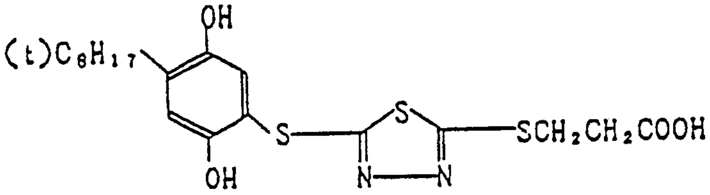
BAR-40



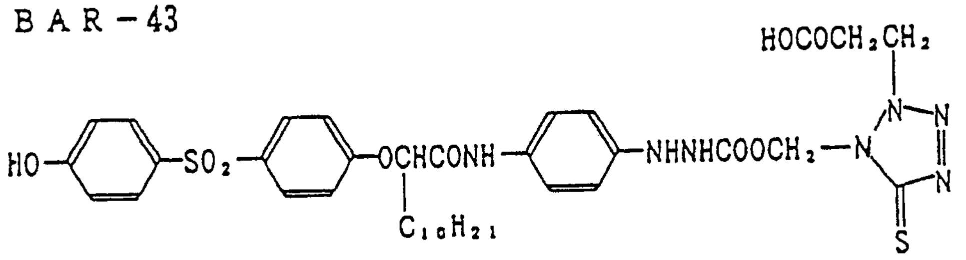
BAR-41



BAR-42



BAR-43



There is no restriction as to the kind of layers to which a BAR compound is added. The BAR compound may be added to not only a silver halide light-sensitive emulsion layer but also an anti-halation layer, an intermediate layer, a yellow colloidal silver filter layer and a protective layer. However, the BAR compound may preferably be added to a silver halide photosensitive emulsion layer.

The BAR compound can be added to a hydrophilic colloidal layer of a light-sensitive material for color photography by the following method: The BAR compound is dissolved, singly or in combination with another kinds of a BAR compound, to a mixture of a high-boiling point solvent such as dibutyl phthalate, tricresyl phosphate and dinonyl phenol and a low-boiling point solvent such as butyl acetate and propionic acid. The resultant is mixed with an aqueous solution of gelatin containing a surface active agent, and subsequently emulsified by means of a high-speed revolution mixer, a colloid mill or an ultrasonic dispersing machine. The resultant may be directly added to a coating liquid. Alternatively, it may be coagulated, cut into small pieces, washed with water and then added to a coating liquid.

The amount of the BAR compound to be added may preferably be 0.0005 mole to 5.0 mole, more preferably 0.005 mole to 1.0 mole, per mole of a silver halide.

The BAR compound may be employed either singly or in combination.

In the light-sensitive material, auxiliary layers such as filter layer, antihalation layer, anti-irradiation layer, etc. can be provided. In these layers and/or emulsion layers, a dye which flows out from the light-sensitive material or bleached during developing processing may be also contained.

In the light-sensitive material, formalin scavenger, fluorescent brightener, matte agent, lubricant, image stabilizer, surfactant, color fog preventive, developing accelerator, developing retarder, bleaching accelerator, etc. can be added.

For the support, papers laminated with polyethylene, etc., polyethylene terephthalate film, baryta film, cellulose triacetate, etc. can be used.

The light-sensitive material of the present invention is particularly useful as the negative-type light-sensitive material.

For obtaining a dye image by use of the light-sensitive material of the present invention, after exposure, color photographic processings generally known in the art can be performed.

Also, a light-sensitive photographic material-containing package unit in which a light-sensitive silver halide color photographic material is built-in and photographing function is provided, which is produced by the present applicant or assignee in the trade name of "Torezo-Kun", has spread in recent years.

These package units have been sold mainly at a sightseeing spot so that their storage circumstance is markedly wrong whereby further improvement in storage stability has been demanded.

The package units in which a light-sensitive silver halide color photographic material of the present invention is built-in and photographing function is provided are excellent in stability to long period of preservation even under bad outer conditions, and also excellent in gradation, color reproducibility and tone reproducibility.

The above-mentioned light-sensitive photographic package unit to which photographing function is provided comprises, for example, a first receiving room put a wound and unphotographed light-sensitive photographic material away therein, a second receiving room (e.g. patrone room) which receives a photographed light-sensitive photographic material and those having a function necessary for photographing such as a lens and a shutter.

The unphotographed light-sensitive photographic material is directly or indirectly (for example, in the state of once received in patrone or cartridge) received in the first receiving room.

The size of the light-sensitive photographic material may be any size such as 110 size, 135 size, 126 size, and so-called disc type size.

Examples

The present invention will be described in more detail by referring to examples, but the present invention is not limited to these examples at all. Prior to examples, the silver halide emulsions to be used in examples were prepared.

Preparation of mono-dispersed emulsion

Into a reaction vessel in which an aqueous gelatin had been thrown, while controlling the pAg and the pH in the reaction vessel and also controlling the addition time, were added at the same time an aqueous silver nitrate, an aqueous potassium iodide solution and an aqueous potassium bromide solution, and then precipitation and desalting were practiced by use of a pH coagulatable gelatin, followed by addition of gelatin to prepare a seed emulsion. The emulsion obtained is called NE-1.

Also, a seed emulsion was prepared in the same manner as described above except for adding K_3RhCl_6 in the reaction vessel (NE-2). The emulsions and their contents are shown in Table 1.

Table 1

Seed emulsion No.	Kind of additive	Amount added mol/mol-silver	Grain size (μm)
NE-1	-	-	0.093
NE-2	K_3RhCl_6	5×10^{-5}	0.093

In a reaction vessel in which the above seed emulsion and an aqueous gelatin had been added, while controlling the pAg and the pH in the reaction vessel, were added an aqueous ammoniacal silver nitrate solution, an aqueous potassium iodide solution and an aqueous potassium bromide solution in proportion to the surface area during the grain growth, followed by subsequent addition in place of the aqueous potassium bromide solution at an adequate grain size. After precipitation and desalting were practiced similarly as in the case of seed emulsion, gelatin was added to effect re-dispersion to give emulsions of pAg 7.8 and pH 6.0. Thus, silver iodobromide emulsions EM-1 to EM-4 with high iodine contents internally of grains were prepared.

The emulsions and their contents are shown in Table 2.

Table 2

Emulsion No.	Mean grain size (μm)	Mean Ag content (mol %)	Seed emulsion	Fluctuation coefficient
EM-1	0.65	6.5	NE-1	0.20
EM-2	0.40	7.5	NE-1	0.19
EM-3	0.40	7.5	NE-2	0.19
EM-4	0.40	7.5	NE-1 (*1) NE-2	0.19

*1 Equal amounts of NE-1 and NE-2 were employed.

Example 1

<u>Preparation of Sample No. 101 (Control)</u>

On a cellulose acetate support applied with subbing working, was prepared a multi-layer color light-sensitive material No. 101 with an overlaid constitution comprising the composition shown below.

The amounts coated are indicated in the amount represented in g/m^2 unit calculated on silver for silver halide and colloidal silver, the amount represented in g/m^2 unit for the additive and gelatin, and further in moles per mole of silver within the same layer for sensitizing dye, coupler and DIR compound. The emulsion contained in each color sensitive emulsion layer was applied with optimum sensitization with sodium thiosulfate and chloroauric acid.

Layer	Main composition	Amount used
First layer (HC) (halation preventive layer)	Black colloidal silver	0.20
	Gelatin	1.5
	UV-ray absorber UV-1	0.1
	UV-ray absorber UV-2	0.2
	Dioctyl phthalate (abbreviated as DOP)	0.03

Second layer(IL-1) (Intermediate layer)	Gelatin	2.0
	Antistaining agent (AS-1)	0.1
	DOP	0.1

Third layer(R-1) (First red-sensitive emulsion layer)	EM-2	1.2
	Gelatin	1.1
	Sensitizing dye I	6×10^{-4}
	Sensitizing dye II	1×10^{-4}
	Coupler (C-1)	0.085
	Coupler (CC-1)	0.005
	DIR compound (E-23)	0.0015
	DIR compound (E-42)	0.002
	DOP	0.6

Fourth layer(R-2) (Second red-sensitive emulsion layer)	EM-1	1.3
	Gelatin	1.1
	Sensitizing dye I	3×10^{-4}
	Sensitizing dye II	1×10^{-4}
	Coupler (C-2)	0.007
	Coupler (C-3)	0.027
	Coupler (CC-1)	0.0015
	DIR compound (E-42)	0.001
	DOP	0.2

Fifth layer(IL-2) (Intermediate layer)	Gelatin	0.8
	AS-1	0.03
	DOP	0.1

Sixth layer(G-1) (First green-sensitive emulsion layer)	EM-2 Gelatin Sensitizing dye III Sensitizing dye IV Coupler (M-2) Coupler (CM-1) DIR compound (E-23) DIR compound (E-26) Tricresyl phosphate (abbreviated as TCP)	1.3 1.2 2.5×10^{-4} 1.2×10^{-4} 0.09 0.004 0.001 0.003 0.5

Seventh layer(G-2) (Second green-sensitive emulsion layer)	EM-1 Gelatin Sensitizing dye III Sensitizing dye IV Coupler (M-1) Coupler (CM-1) DIR compound (E-26) TCP	1.4 0.8 1.5×10^{-4} 1.0×10^{-4} 0.03 0.002 0.001 0.3

Eighth layer (YC) (Yellow filter layer)	Gelatin Yellow colloidal silver AS-1 DOP	0.6 0.08 0.1 0.3

Ninth layer (B-1) (First blue-sensitive emulsion layer)	EM-2 Gelatin Sensitizing dye V Coupler (Y-1) TCP	0.5 1.1 1.3×10^{-4} 0.29 0.2

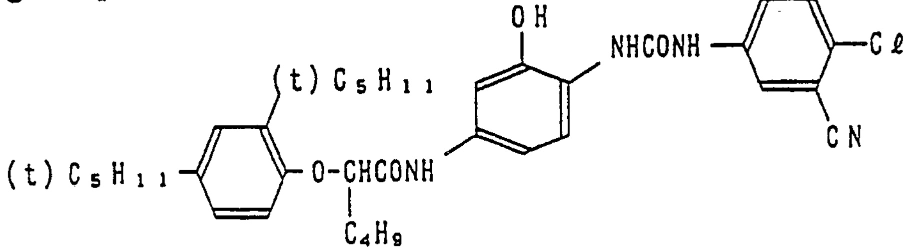
Tenth layer (B-2) (Second blue-sensitive emulsion layer)	EM-1 Gelatin Sensitizing dye V Coupler (Y-1) DIR compound (E-42) TCP	0.5 1.2 1×10^{-4} 0.08 0.003 0.1

Eleventh layer (Pro-1) (First protective layer)	Gelatin	0.55
	UV-ray absorber UV-1	0.1
	UV-ray absorber UV-2	0.2
	DOP	0.03
	Silver iodobromide AgI	0.5
	1 mol% (mean grain size 0.07 µm)	

Twelfth layer (Pro-2) (Second protective layer)	Gelatin	0.5
	Polymethyl methacrylate grains (diameter 1.5 µm)	0.2
	Formalin scavenger (HS-1)	3.0
	Film hardener (H-1)	0.4

In the respective layers, other than the above components, surfactants were added as the coating aid.

C − 1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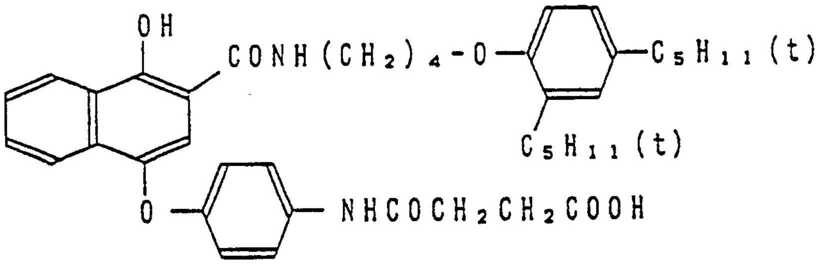
Cℓ
CN
(t)C₅H₁₁
(t)C₅H₁₁
O-CHCONH
C₄H₉

C − 2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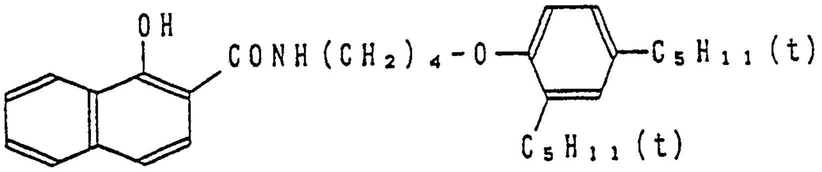
C − 3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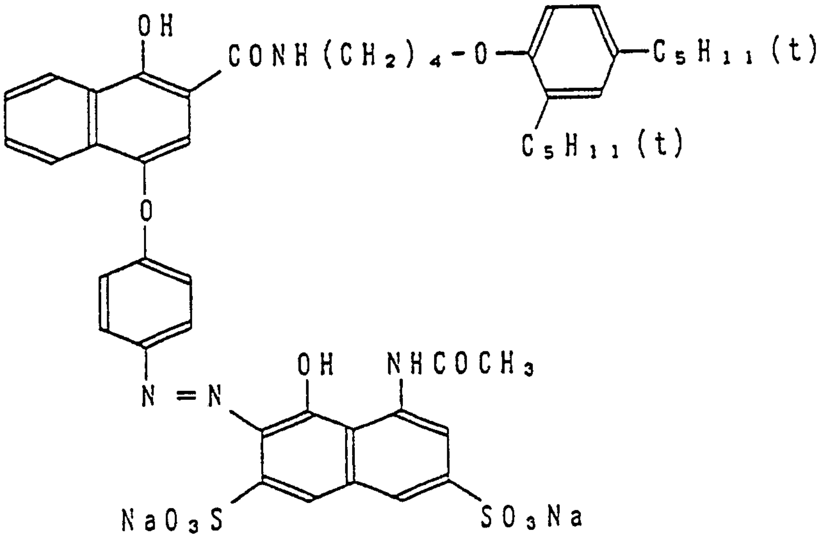
CONH(CH₂)₄-O
C₅H₁₁(t)
C₅H₁₁(t)

C C − 1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CONH(CH₂)₄-O
C₅H₁₁(t)
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O
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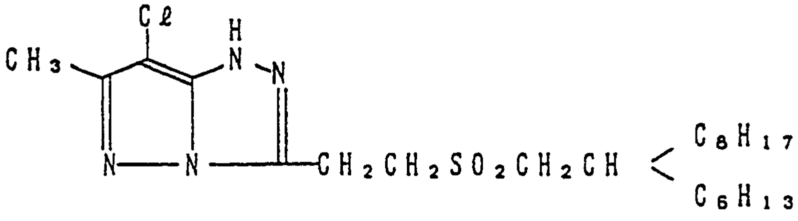
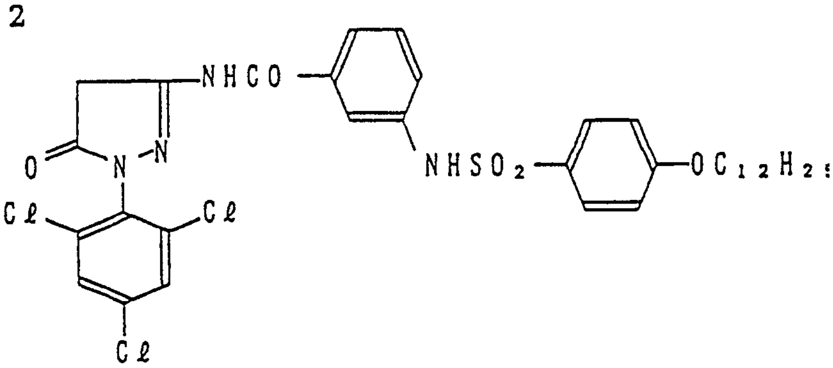
OH
NHCOCH₃
NaO₃S
SO₃Na

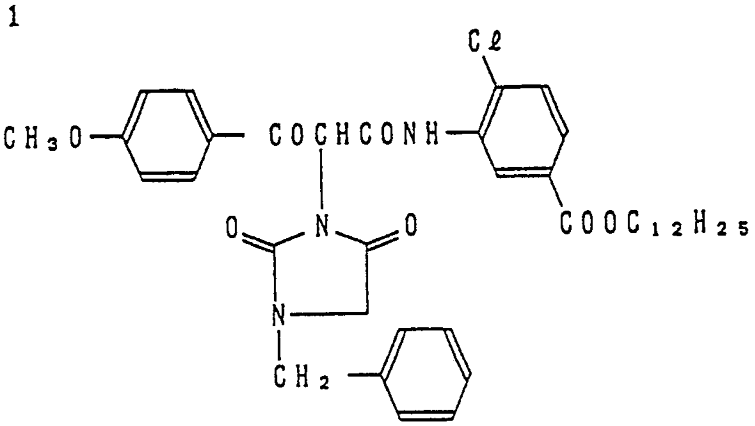
M − 1



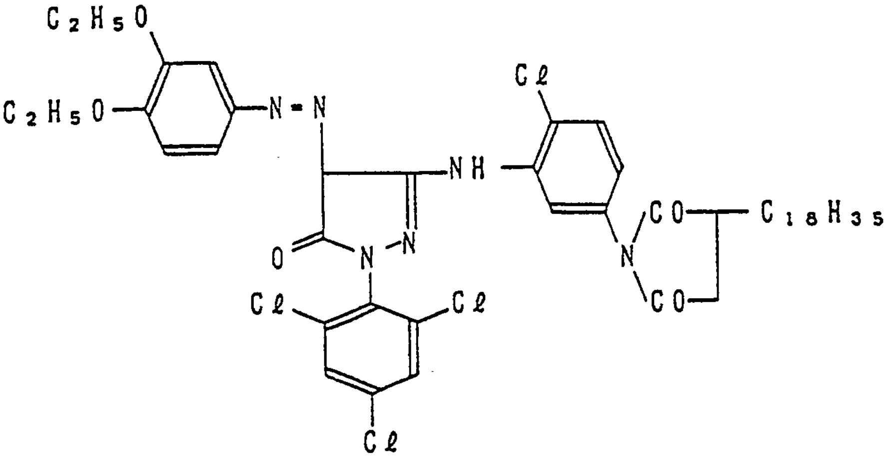
M − 2



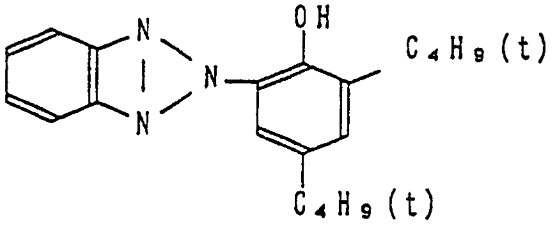
Y − 1



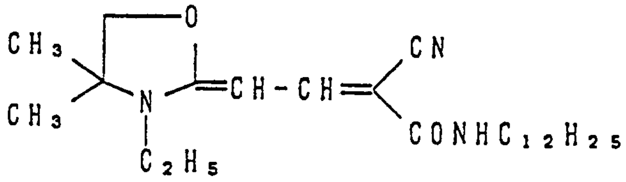
C M − 1



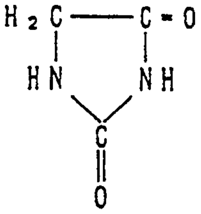
UV-1



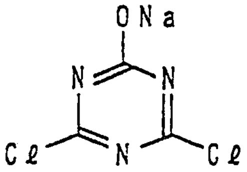
UV-2



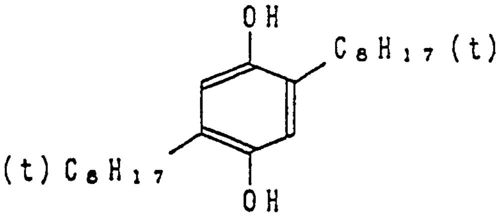
HS-1



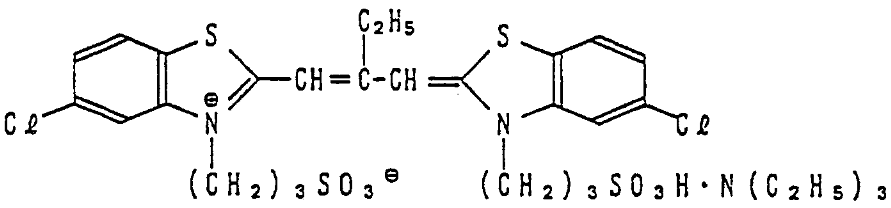
H-1



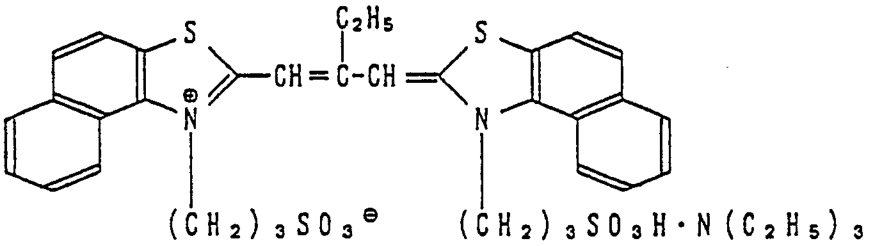
AS-1



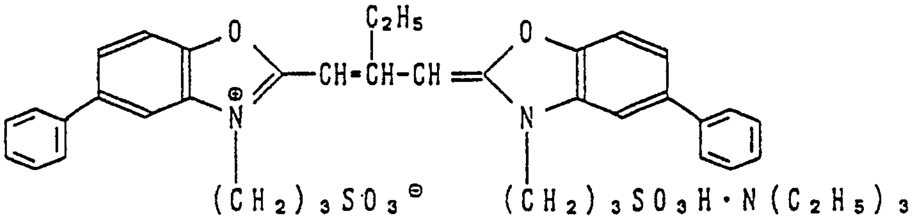
Sensitizing dye I



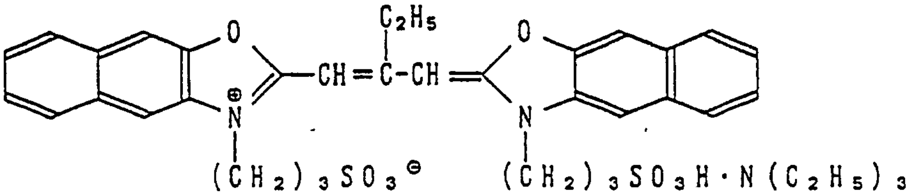
Sensitizing dye II



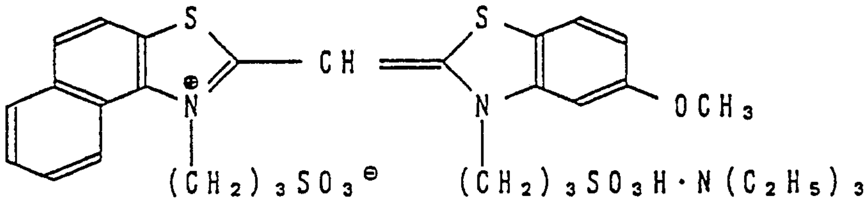
Sensitizing dye III



Sensitizing dye IV



Sensitizing dye V



In the following description, the respective layers with the above compositions are referred to under the abbreviations indicated such as HC, IL-1, R-1, R-2, IL-2, G-1, G-2, YC, B-1, B-2, Pro-1, Pro-2, etc.

Next, Samples No. 102 to No. 115 were prepared.Sample No. 102 was prepared in the same manner as Sample No. 101 except for adding the yellow dye according to the present invention of the kind and the amount indicated in Table 3 in place of the yellow colloidal silver of YC in Sample No. 101.

Sample No 103 was prepared in the same manner as Sample No. 101 except for omitting B-2 in Sample No. 101, changing the emulsion contained in B-1 to a mixture of equal moles of EM-1 and EM-2, increasing the amounts used of the emulsion, the gelatin and TCP contained in B-1 by 15 % (the amounts of the sensitizing dye, coupler and DIR compound of B-1 per mole of silver halide are the same as in Sample No. 101).

Samples No. 104 and No. 108 were prepared in the same manner as Sample No. 103 except for adding the yellow dyes according to the present invention of the kinds and amounts indicated in Table 3 in palce of the yellow colloidal silver of YC in Sample No. 103.

Samples No. 109 was prepared in the same manner as Sample No. 104 except for changing the emulsion contained in B-1 in Sample No. 104 to a mixture of equal moles of EM-2 and EM-3.

Sample No. 110 was prepared in the same manner as Sample No. 104 except for changing the emulsion contained in Sample No. 104 to EM-4.

Sample Nos. 111 to 114 were prepared in the same manner as in Sample Nos. 101, 102, 104 and 110, respectively, excepting for each adding BAR compounds as shown in Table 3 to the R-1 layers.

Sample No. 115 was prepared in the same manner as Sample No. 114 excepting for changing BAR-22 of Sample No. 114 to BAR-23.

The samples thus prepared and their contents are shown in Table 3.

Table 3

Sample No.	Constitution of light-sensitive layer			Yellow dye contained in YC layer		BAR compound contained in R-1 layer		Emulsion used in blue-sensitive emulsion layer
	B	G	R	Kind	Added amount	Kind	Added amount	
Control:								
101	Double	Double	Double	-	-	-	-	EM-1 (B-2) and EM-2 (B-1)
102	Double	Double	Double	YI-5	5×10^{-4}	-	-	EM-1 (B-2) and EM-2 (B-1)
103	Single	Double	Double	-	-	-	-	EM-1 and EM-2
Present Invention:								
104	Single	Double	Double	YI-5	5×10^{-4}	-	-	EM-1 and EM-2
105	Single	Double	Double	YI-12	5×10^{-4}	-	-	EM-1 and EM-2
106	Single	Double	Double	YI-17	5×10^{-4}	-	-	EM-1 and EM-2
107	Single	Double	Double	YI-10	5×10^{-4}	-	-	EM-1 and EM-2
108	Single	Double	Double	YI-20	5×10^{-4}	-	-	EM-1 and EM-2
109	Single	Double	Double	YI-5	5×10^{-4}	-	-	EM-2 and EM-3
110	Single	Double	Double	YI-5	5×10^{-4}	-	-	EM-4

Table 3 (cont'd)

Sample No.	Constitution of light-sensitive layer			Yellow dye contained in YC layer		BAR compound contained in R-1 layer		Emulsion used in blue-sensitive emulsion layer
	B	G	R	Kind	Added amount	Kind	Added amount	
Control:								
111	Double	Double	Double	-	-	BAR-22	0.03	EM-1 (B-2) and EM-2 (B-1)
112	Double	Double	Double	YI-5	5×10^{-4}	BAR-22	0.03	EM-1 (B-2) and EM-2 (B-1)
Present invention:								
113	Single	Double	Double	YI-5	5×10^{-4}	BAR-22	0.03	EM-1 and EM-2
114	Single	Double	Double	YI-5	5×10^{-4}	BAR-22	0.03	EM-4
115	Single	Double	Double	YI-5	5×10^{-4}	BAR-23	0.03	EM-4

B = blue-sensitive layer, G = green-sensitive layer, R = red-sensitive layer,

Amount of yellow dye added is represented in mol/m^2 (hereinafter the same)

Amount of BAR compound added is represented in mol/mol AgX (hereinafter the same)

For the samples No. 101 to 115 thus obtained, stability of light-sensitive material and stability of latent image were evaluated.

Evaluation method of light-sensitive material stability

Sample was divided into two, and a part was stored under the conditions of 50 °C and a relative humidity of 80% for 7 days, and the other part in a refrigerator (5 °C) for 7 days, then subjected to wedge exposure in conventional manner, followed by processing according to the processing steps as described below, and gradation stability in storage of light-sensitive material as described below was evaluated.

Evaluation method of latent image stability

Sample was divided into two, and after wedge exposure in conventional manner, a part was stored under the conditions of 25 °C and a relative humidity of 80%, and the other part in a refrigerator (5 °C) for 15 days, respectively, followed by processing according to processing steps as described below, and gradation stability in latent image storage as also described below was evaluated.

Evaluation method of silver removability

Silver removability was determined by defining the silver removability of Sample No. 101 as 100. The measurement was carried out by use of a fluorescent X-ray analysis. Larger the value is, superior the effect of improvement in the silver removability is.

The results obtained for the blue-sensitive layers are shown in Table 4.

The evaluation method of gradation stability is to be described by use of drawings. Fig. 1 shows the characteristic curve which is the standard (broken line) and the characteristic curve (solid line) to be evaluated. Fig. 2 shows the point gamma values of the respective exposure points from the exposure point which gives +0.1 to a density of the minimum density in Fig. 1 to the exposure point of $\Delta \log H = +3.0$ ($\Delta \log H = 0.15$ between the respective exposure points).

From Fig. 2, the absolute values $\Delta\gamma$ of the difference of the point gamma values at the respective exposure points of the characteristic curve which is the standard and the characteristic curve to be evaluated are determined. Then, the gradation stability is represented by the mean value of $\Delta\gamma$ multiplied by 1,000 ($\Delta\bar{\gamma}$) and value of Σ of the standard deviation σ of $\Delta\gamma$ multiplied by 1,000. Thus, the difference in point gamma between the both characteristic curves is greater as the value of $\Delta\bar{\gamma}$is greater, and the gradation change is not uniform indicating poor gradation stability as the value of Σ is greater.

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

The processing liquor compositions used in the respective processing steps are shown below.

(Color developing solution)	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline•sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Potassium bromide	1.3 g
Nitrilotriacetic acid•trisodium salt (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
made up to one liter with addition of water (pH = 10.2)	

(Bleaching solution)	
Iron (III) ammonium ethylenediaminetetraacetate	100.0 g
Iron diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
(made up to one liter with addition of water, and adjusted to pH 6.0 with ammonia water)	

(Fixing solution)	
Ammonium thiosulfate	175.0 g
Anhydrous ammonium sulfite	8.6 g
Sodium metasulfite	2.3 g
(made up to one liter with addition of water, and adjusted to pH 6.0 with acetic acid)	

(Stabilizing solution)	
Formalin (37 % aqueous solution)	1.5 ml
Konidax (manufactured by Konika K.K.)	7.5 ml
(made up to one lither with addition of water)	

Table 4

Sample No.	Gradation stability				Silver removability
	Stability of light-sensitive material		Latent image stability		
	$\Delta\bar{\gamma}$	Σ	$\Delta\bar{\gamma}$	Σ	
Control:					
101	92	82	108	94	100
102	90	81	105	90	100
103	89	79	101	88	100
Present invention:					
104	73	62	93	70	110
105	72	61	92	70	110
106	73	61	90	73	110
107	73	60	94	73	110
108	72	62	91	72	110
109	61	55	82	69	115
110	63	54	80	67	120
Control:					
111	92	82	108	94	100
112	90	81	105	90	100
Present invention:					
113	73	62	93	70	120
114	63	54	80	67	130
115	63	54	80	67	135

As is apparent from Table 4, the samples of the present invention were found to have excellent gradation stability with little fluctuation of gradation from the highlight to the shadow of the characteristic curve in storage of light-sensitive material and storage of latent image. The yellow dye according to the present invention can be understood to have very great effect when the blue-sensitive layer has a single layer constitution (comparison between Sample No. 103 and Sample No. 104), although the effect is small when it is a double layer (comparison between Sample No. 101 and Sample No. 102).

Such fact was also unexpected to the present inventors.

Also, Sample No. 110 is preferable with respect to production efficiency as compared with other samples, because physical aging and chemical aging can be done each at one time in preparation of the emulsion.

It has been also found that there is the effect of the present invention even when 40 mole% of the yellow dye contained in YC of Sample No. 104 is replaced with yellow colloidal silver.

Also, the effects of the present invention could be recognized in the respective samples by use of YI-2, YI-3 or YI-11 in place of the yellow dye YI-5 of Sample No. 104, and the respective samples by use of YI-9, YI-13 or YI-19 in place of the yellow dye YI-5 of Sample No. 109.

Sample Nos. 113 to 115, in which BAR compounds were used in combination in the single layer, showed excellent silver removability. Further, the samples of the present invention showed small variation in gradation from the highlight portion through the shadow portion of the characteristic curve, good tone reproducibility, and wide exposure latitude as the exposure latitude indicated by Δlog H was 3.0 or more.

Next, Sample No. 102 of which the blue-sensitive emulsion layer was a double constitution layer and Sample No. 105 of which the blue-sensitive emulsion layer was a single constitution layer were respectively cut into a length corresponding to 24 frames with a size of 35 mm. The cut samples were rolled so that the light-sensitive layer side becomes the inner side and taken in a film-housing room of a packaging unit with a lense as described in Fig. 1 of U.S. Patent 4,827,298. The end portion of the film was set to a patrone for

35 mm size and then taken in a patrone room to prepare a light-sensitive photographic material packaging unit provided with a photographing function with a fixed-focus of F:8 and a shutter speed of 1/100 second.

A group of two kinds of units containing the light-sensitive photographic materials obtained above was stored in a refrigerator of 5 °C (standard) for 1 month and another group was stored under the condition of a temperature of 37 °C and a relative humidity of 80 % for 1 month.

After the storage, the light-sensitive materials were used for photographing an object of a continuous wedge, and the exposed films were processed according to the processing steps as shown in Example 1.

The results are shown below.

Sample No.	Gradation stability Σ
102 (Control)	85
104 (Present invention)	65

As is apparent from the above result, even if the sample was packaged in the packaging unit, the Sample No. 105 of the present invention showed small variation in gradation from the highlight protion through the shadow portion of the characteristic curve and good tone reproducibility during storage with lapse of time. Further, it had a wide exposure latitude as the exposure latitude indicated by Δlog H was 3.0 or more.

Example 2

Samples No. 101 and 104 prepared in Example 1 were used as such to provide Samples No. 201 and No. 202, respectively.

Sample No. 203 was prepared in the same manner as Sample No. 202 except for omitting G-2, changing the emulsion contained in G-1 to a mixture of equal moles of EM-1 and EM-2, and further increasing the amounts used of the emulsion, gelatin and TCP contained in G-1 by 30% (the amounts of the sensitizing dye, coupler and DIR compound per mole of silver halide in G-1 are the same as in Sample No. 202).

Sample No. 204 was prepared in the same manner as Sample No. 203 except for omitting R-2, changing the emulsion contained in R-1 to a mixture of equal moles of EM-1 and EM-2, and further increasing the amounts used of the emulsion, gelatin and DOP contained in R-1 by 25% (the amounts of the sensitizing dye, coupler and DIR compound per mole of silver halide in R-1 are the same as in Sample No. 203).

Samples No. 205 to No. 208 were prepared in the same manner as Sample No. 204 except for changing the emulsion contained in Sample No. 204 to those as shown in Table 5, and changing the yellow dye contained in YC to those as shown in Table 5.

The samples thus prepared and their contents are shown in Table 5.

Table 5

Sample No.	Constitution of light-sensititve layer			Yellow dye contained in YC layer		Emulsion used in light-sensitive layers		
	B	G	R	Kind	Added amount	B	G	R
Control:								
201	Double	Double	Double	-	-	EM-1 (B-2) EM-2 (B-1)	EM-1 (G-2) EM-2 (G-1)	EM-1 (R-2) EM-2 (R-1)
Present Invention:								
202	Single	Double	Double	YI-5	5 x 10^{-4}	EM-1 and EM-2	EM-1 (G-2) EM-2 (G-1)	EM-1 (R-2) EM-2 (R-1)
203	Single	Single	Double	YI-5	5 x 10^{-4}	EM-1 and EM-2	EM-1 and EM-2	EM-1 (R-2) EM-2 (R-1)
204	Single	Single	Single	YI-5	5 x 10^{-4}	EM-1 and EM-2	EM-1 and EM-2	EM-1 and EM-2
205	Single	Single	Single	YI-5	5 x 10^{-4}	EM-2 and EM-3	EM-2 and EM-3	EM-2 and EM-3
206	Single	Single	Single	YI-5	5 x 10^{-4}	EM-4	EM-4	EM-4
207	Single	Single	Single	YI-17	5 x 10^{-4}	EM-4	EM-4	EM-4
208	Single	Single	Single	YI-20	5 x 10^{-4}	EM-4	EM-4	EM-4
EM-2 and EM-3 of B-1, G-1 and R-1 in Sample No. 205 are equimolar mixtures.								

For the samples thus prepared, gradation stability in storage of light-sensitive material and latent image storage was evaluated in the same manner as in Example 1.

Also, the sample was divided into two, of which a part was subjected to wedge exposure similarly as in Example 1 and then processed in the same manner except for changing the pH of the developer to 9.8, and gradation stability to fluctuations in processing conditions was evaluated similarly as in Example 1.

The results of the blue-sensitive layers are shown in Table 6.

Table 6

Sample No.	Gradation stability					
	Stability of light-sensitive material		Latent image stability		Processing stability	
	$\Delta\bar{\gamma}$	Σ	$\Delta\bar{\gamma}$	Σ	$\Delta\bar{\gamma}$	Σ
Control:						
201	91	83	108	94	105	77
Present invention:						
202	73	62	93	71	84	68
203	68	57	88	67	78	65
204	61	52	77	61	71	57
205	55	47	68	54	62	51
206	54	47	68	53	61	50
207	53	47	67	52	60	51
208	54	48	68	53	60	51

As is apparent from Table 6, it can be understood that the samples of the present invention have excellent stability of light-sensitive material, latent image stability, and also remarkably excellent gradation stability to processing fluctuations.

The effect of gradation stability of the yellow dye according to the present invention is greater when the light-sensitive emulsion layer is a single layer than when it is a double layer, and processing stability is more effective when it is a single layer.

When comparison is made among the samples of the present invention, those having the blue-sensitive layer and the green-sensitive layer which are made single layers have preferably great improvement effects for storage stability, processing stability, and those having all the color sensitive emulsion layers which have been made single layers are more preferable with greater improvement effects.

It has also been found that the samples No. 205 to No. 208 are preferred embodiments of the present invention, because gradation stability to processing fluctuation is particularly improved due to narrow grain size distribution of the silver halide grains of the respective light-sensitive layers because of containing emulsions having Rh doped internally of the grains.

In the above examples, emulsions with fluctuation coefficients of 19 to 20 % were employed, but the effect of the present invention could be also recognized when an emulsion with a fluctuation coefficient of 29% was employed.

Also, the effects of the present invention could be recognized in the respective samples by use of E-4, E-2 or E-29 in place of the DIR compound E-23 of B-1 in Sample No. 208, the respective samples by use of E-6, E-2 or E-10 in place of E-23 in G-1, and the respective samples by use of E-17, E-19 or E-21 in place of E-42 in R-1.

Also, in the respective samples by use of emulsions each containing seed emulsions, which were prepared by addition of $RuCl_2$, $OsCl_3$ or $Pb(NO_3)_2$ in place of K_3RhCl_6, as a substituent of NE-2, in place of EM-3 in Sample No. 205 and EM-4 in Samples Nos. 206 to No. 208, the effects of the present invention could be recognized.

The light-sensitive material obtained by the present invention is excellent in its storage stability, excellent in latent image stability, and also excellent in stability to fluctuations in processing conditions.

Claims

1. A light-sensitive silver halide color photographic material, comprising a support, silver halide emulsion layers, which are respectively a blue-sensitive, green-sensitive or red-sensitive, and a yellow filter layer which are provided on the support, wherein said material has a DIR compound, said yellow filter layer contains a yellow dye, and at least one of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers has a single layer constitution.

2. The light-sensitive silver halide color photographic material according to Claim 1, wherein the DIR compound is contained in an amount of 0.0001 to 0.1 mol per mol of a silver halide in the material.

3. The light-sensitive silver halide color photographic material according to Claim 2, wherein the DIR compound is contained in an amount of 0.001 to 0.05 mol per mol of a silver halide in the material.

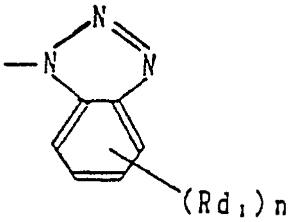
4. The light-sensitive silver halide color photographic material according to Claim 1, wherein the DIR compound is a compound represented by Formula (D-1):

A - (Y)m

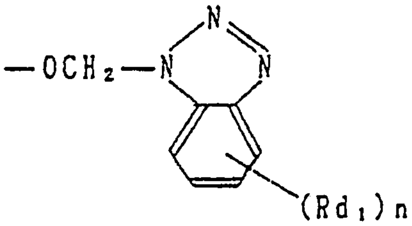
wherein A represents a coupler residue, m represents 1 or 2, Y represents a group bonded to the coupling position of the coupler residue A and eliminatable through the reaction with the oxidized product of a color developing agent, which is a developing inhibitor group or a group capable of releasing a developing inhibitor.

5. The light-sensitive silver halide color photographic material according to Claim 4, wherein the group represented by Y is represented by at least one selected from the group consisting of Formulae (D-2) to (D-9) set forth below:

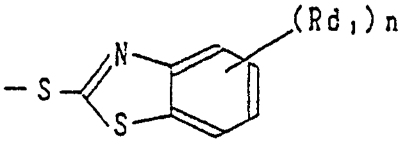
Formula (D-2)



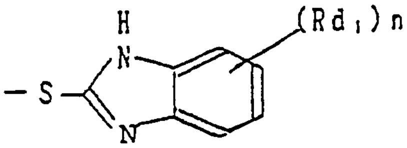
Formula (D-3)



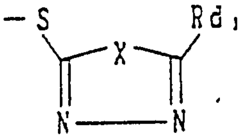
Formula (D-4)



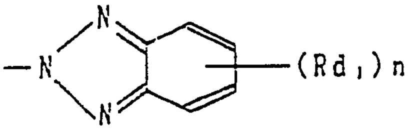
Formula (D-5)



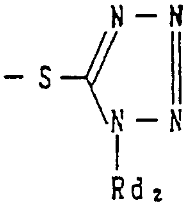
Formula (D-6)



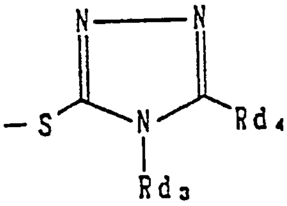
Formula (D-7)



Formula (D-8)



Formula (D-9)

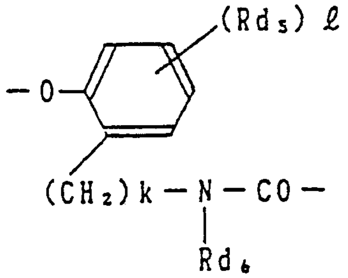


in Formulae (D-2) to (D-7), Rd_1 represents at least one selected from the group consisting of hydrogen atom, a halogen atom and an alkyl, alkoxy, acylamino, alkoxycarbonyl, thiazolidinylideneamino, aryloxycarbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, N-alkylcarbamoyloxy, hydroxy, alkoxycarbonylamino, alkylthio, arylthio, aryl, heterocyclic, cyano, alkylsulfonyl and aryloxycarbonylamino groups, n represents 0, 1 or 2, and when n is 2, the respective Rd_1's may be either the same or different, the total carbon atoms contained in n Rd_1's may be 0 to 10, the total number of the carbon atoms contained in Rd_1 in the formula (D-6) is 0 to 15;
in Formula (D-6), X represents oxygen atom or sulfur atom;
in Formula (D-8), Rd_2 represents at least one selected from the group consisting of an alkyl group, an aryl group and a heterocyclic group;
in Formula (D-9), Rd_3 represents selected from the group consisting of hydrogen atom, and an alkyl, cycloalkyl, aryl and heterocyclic group, Rd_4 represents at least one selected from the group consisting of hydrogen atom, a halogen atom and an alkyl, cycloalkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamide, cyano, heterocyclic, alkylthio and amino group;
when at least one of Rd_1, Rd_2, Rd_3 and Rd_4 represents an alkyl group, the alkyl group may include those having substituents, and may be either straight or branched;
when at least one of Rd_1, Rd_2, Rd_3 and Rd_4 represents an aryl group, the aryl group may include those having substituents;
when at least one of Rd_1, Rd_2, Rd_3 and Rd_4 represents a heterocyclic group, the heterocyclic group may include those having substituents;
The carbon atoms contained in Rd_2 in Formula (D-8) is 0 to 15; and
in Formula (D-9), the total carbon atoms contained in Rd_3 and Rd_4 is 0 to 15.

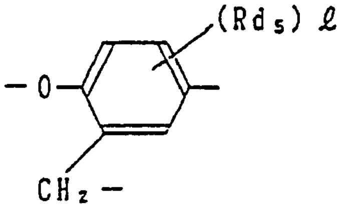
6. The light-sensitive silver halide color photographic material according to Claim 4, wherein the group represented by Y is a compound represented by Formula (D-10) set forth below:
$-(TIME)_n-INHIBIT$
wherein the TIME group is a group, bound to the coupling position of A and being cleavable through the reaction with the oxidized product of a color developing agent, which is a group cleaved successively after cleavage from the coupler and until finally can release the INHIBIT groups with adequate control; n is 1 to 3, and when it is 2 or 3, the respective TIME groups is either the same or different; and the INHIBIT group is a group which becomes a developing inhibitor by the release.

7. The light-sensitive silver halide color photographic material according to Claim 6, wherein the -TIME group of Formula (D-10) is represented by at least one of Formulae (D-11) to (D-19) set forth below:

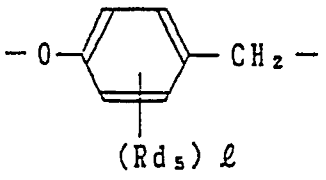
Formulae (D-11)



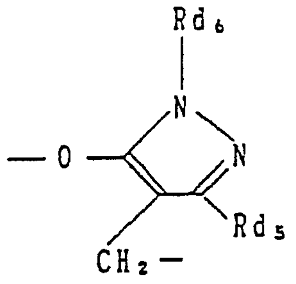
Formulae (D-12)



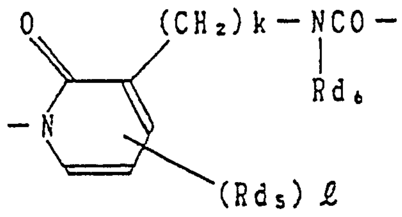
Formulae (D-13)



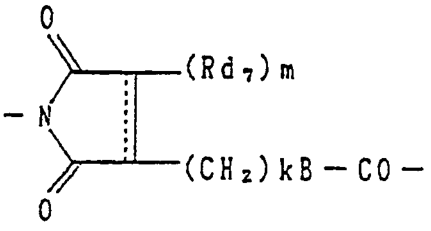
Formulae (D-14)



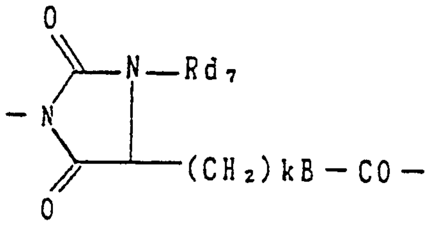
Formulae (D-15)



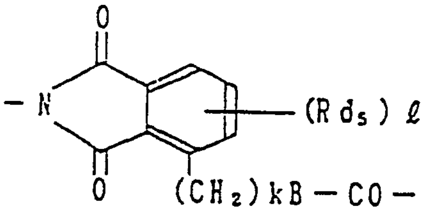
Formulae (D-16)



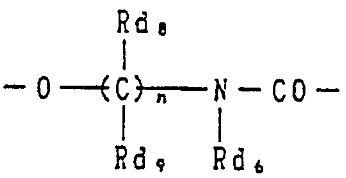
Formulae (D-17)



Formulae (D-18)



Formulae (D-19)



in Formulae (D-11) to (D-15) and (D-18), Rd_5 represents at least one selected from the group consisting of hydrogen atom, a halogen atom and an alkyl, cycloalkyl, alkenyl, aralkyl, alkoxy, alkoxycarbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamide, sulfamoyl, carbamoyl, aryl, carboxy, sulfo, hydroxy and alkanesulfonyl group;

in Formulae (D-11) to (D-13), (D-15) and (D-18), Rd_5's may be mutually bonded together to form a fused ring;

in Formulae (D-11), (D-14), (D-15) and (D-19), Rd_6 represents at least one selected from the group consisting of an aralkyl, alkenyl, alkyl, cycloalkyl, heterocyclic and aryl group; in Formulae (D-16) and (D-17), Rd_7 represents at least one selected from the group consisting of hydrogen atom and an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic and aryl group;

each of Rd_8 and Rd_9 in Formula (D-19) represents at least one of hydrogen atom and an alkyl group, k in Formulae (D-11) and (D-15) to (D-18) represents an integer of 0, 1 or 2, ℓ in Formulae (D-11) to (D-13), (D-

15) and (D-18) represents an integer of 1 to 4, m in the formula (D-16) represents an integer of 1 or 2; when ℓ and m are 2 or more, the respective Rd_5 and Rd_7 may be either the same or different; n in Formula (D-19) represents an integer of 2 to 4, and Rd_8 and Rd_9 in number of n may be each the same or different; B in Formulae (D-16) to (D-18) represents oxygen atom or $-\underset{Rd\,6}{\underset{|}{N}}$ (Rd_6 represents the same meaning as already defined); and $\overline{\text{- - - - - - -}}$ in Formula (D-16) may be either a single bond or a double bond, and m is 2 in the case of the single bond and m is 1 in the case of the double bond.

8. The light-sensitive silver halide color photographic material according to Claim 5, wherein the group represented by Y is a compound represented by Formula (D-20) set forth below:

$(T_1)_{\ell}$ SR$(T_2)_m$ INHIBIT

wherein T_1 represents a component which cleaves SR$(T_2)_m$INHIBIT, SR a component which forms $(T_2)_m$INHIBIT through the reaction with the oxidized product of a developing agent after formation of SR$(T_2)_m$ INHIBIT, T_2 a component which cleaves INHIBIT after formation of $(T_2)_m$ INHIBIT, INHIBIT a developing inhibitor and ℓ and m are each 0 or 1.

9. The light-sensitive silver halide color photographic material according to Claim 8, wherein the component represented by SR is at least one selected from the group consisting of a coupler component which undergoes the coupling reaction with a oxidized product of a developing agent and a redox component which undergoes a redox reaction with a oxidized product of the developing agent.

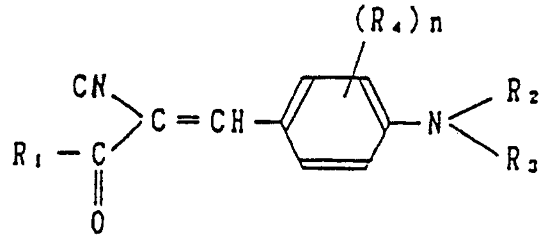
10. The light-sensitive silver halide color photographic material according to Claim 9, wherein the coupler component is at least one selected from the group consisting of acylacetanilides, 5-pyrazolones, pyrazoloazoles, phenols, naphthols, acetophenones, indanones, carbamoylacetanilides, 2(5H)-imidazolones, 5-isoxazolones, uracils, homophthalimides, oxazolones, 2,5-thiadiazoline-1,1-dioxides, triazolothiadiazines and indoles.

11. The light-sensitive silver halide color photographic material according to Claim 9, wherein the component represented by SR is at least one selected from the group consinsting of hydroquinones, catechols, pyrogallols, aminophenols, naphthalenediols and aminonaphthols.

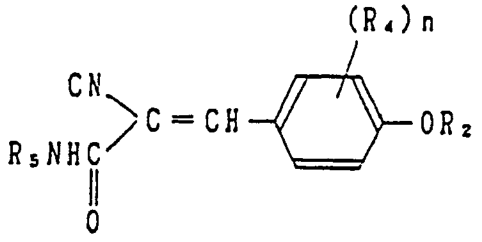
12. The light-sensitive silver halide color photographic material according to Claim 1, wherein the position of the yellow filter layer in the photographic light-sensitive material is at a position that the light for exposure reaches prior to the green-sensitive layer and the red-sensitive layer, and the light for exposure reaches later than at least one blue-sensitive layer.

13. The light-sensitive silver halide color photographic material according to Claim 12, wherein the yellow dye contained in the yellow filter layer is a compound represented by at least one of Formulae (A) and (B);

Formula (A)



Formula (B)



in the formulae, R_1 represents an aryl group or an alkoxy group, R_2 and R_3 alkyl groups, R_4 at least one of hydrogen atom and a substituent, R_5 an aryl group, and n represents an integer of 1 to 4.

14. The light-sensitive silver halide color photographic material according to Claim 13, wherein the aryl group represented by R_1 or R_5 is at least one of a phenyl group and a naphthyl group.

15. The light-sensitive silver halide color photographic material according to Claim 12, wherein the aryl

group contains at least one substituent selected from the group consisting of sulfo group, amino groups, sulfonylamino groups and alkoxy groups.

16. The light-sensitive silver halide color photographic material according to Claim 12, wherein R_1 is a phenyl group having at least an alkylsulfonylamino group and R_5 is a phenyl group having at least sulfo group.

17. The light-sensitive silver halide color photographic material according to Claim 1, wherein the yellow dye contained in the yellow filter layer is used in an amount of 1 to 1,000 mg/m^2 in the light-sensitive silver halide color photographic material.

18. The light-sensitive silver halide color photographic material according to Claim 1, wherein the yellow dye contained in the yellow filter layer is used so that the optical density may be in the range from 0.05 to 3.0.

19. The light-sensitive silver halide color photographic material according to Claim 1, wherein the blue-sensitive layer is a single layer.

20. The light-sensitive silver halide color photographic material according to Claim 19, wherein the both the blue-sensitive layer and the green-sensitive layer is single layers.

21. The light-sensitive silver halide color photographic material according to Claim 1, wherein the all of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers are single layers.

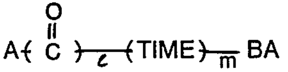
22. The light-sensitive silver halide color photographic material according to Claim 1, wherein the film thickness of the single layer is 20 to 3 µm, after drying.

23. The light-sensitive silver halide color photographic material according to Claim 22, wherein the film thickness of the single layer is 15 to 5 µm, after drying.

24. The light-sensitive silver halide color photographic material according to Claim 1, wherein the silver halide emulsion layer having the single layer constitution comprises silver halide grains containing a desensitizer and silver halide grains containing no desensitizer.

25. The light-sensitive silver halide color photographic material according to Claim 1, wherein the silver halide emulsion layer having the single layer constitution contains a BAR compound.

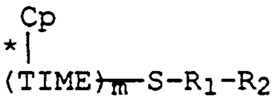
26. The light-sensitive silver halide color photographic material according to Claim 25, wherein the BAR compound is a compound represented by Formula (BAR-I):


(BAR-I)

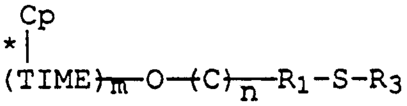
$$A\!\left(\overset{\overset{O}{\|}}{C}\right)_{\ell}\!\left(TIME\right)_{m}BA$$

wherein A is a coupler residue which can be subjected to a coupling reaction with an oxidized product of a color developing agent, or a residue of an oxidation-reduction nucleus which can be cross-oxidized with an oxidized product of a color developing agent; TIME is a timing group; BA is a bleaching accelerator or its precursor; m is 0 or 1; and when A is a coupler residue, ℓ is 0, and when A is a residue of an oxidation-reduction nucleus, ℓ is 0 or 1.

27. The light-sensitive silver halide color photographic material according to Claim 26, wherein the BAR compound is a compound represented by at least one of Formulae (BAR-II) and (BAR-III):

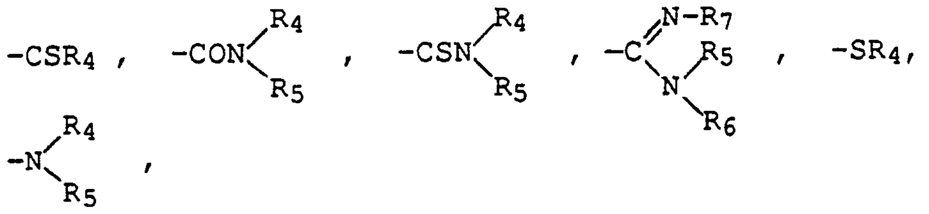

(BAR-II)

$$\begin{array}{l} \;\;Cp \\ *| \\ (TIME)_{m}\text{-}S\text{-}R_1\text{-}R_2 \end{array}$$


(BAR-III)

$$\begin{array}{l} \;\;Cp \\ *| \\ (TIME)_{m}\text{-}O\text{-}(C)_{n}\text{-}R_1\text{-}S\text{-}R_3 \end{array}$$

wherein Cp is a coupler residue which can be subjected to a coupling reaction with an oxidized product of a color developing agent; * is a coupling position of a coupler; TIME is a timing group; R_1 is at least one selected from the group consisting of an aliphatic group, an aromatic group, a saturated heterocyclic group and a 5- or 6-membered aromatic nitrogen-containing heterocyclic group; R_2 is a water solubilizing substituent or its precursor; R_3 is a hydrogen atom, a cyano group, $-COR_4$,



$-CSR_4$, $-CON(R_4)R_5$, $-CSN(R_4)R_5$, $-C(=N-R_7)N(R_5)R_6$, $-SR_4$, $-N(R_4)R_5$,

or a heterocyclic group, in which R_4 is an aliphatic group or an aromatic group, R_5, R_6 and R_7 each are a hydrogen atom, an aliphatic group or an aromatic group; and m and n each are 0 or 1.

28. The light-sensitive silver halide color photographic material according to Claim 1, wherein the silver halide emulsion layer having the single layer constitution contains two or more groups of silver halide grains with different mean diameters.

FIG. 1

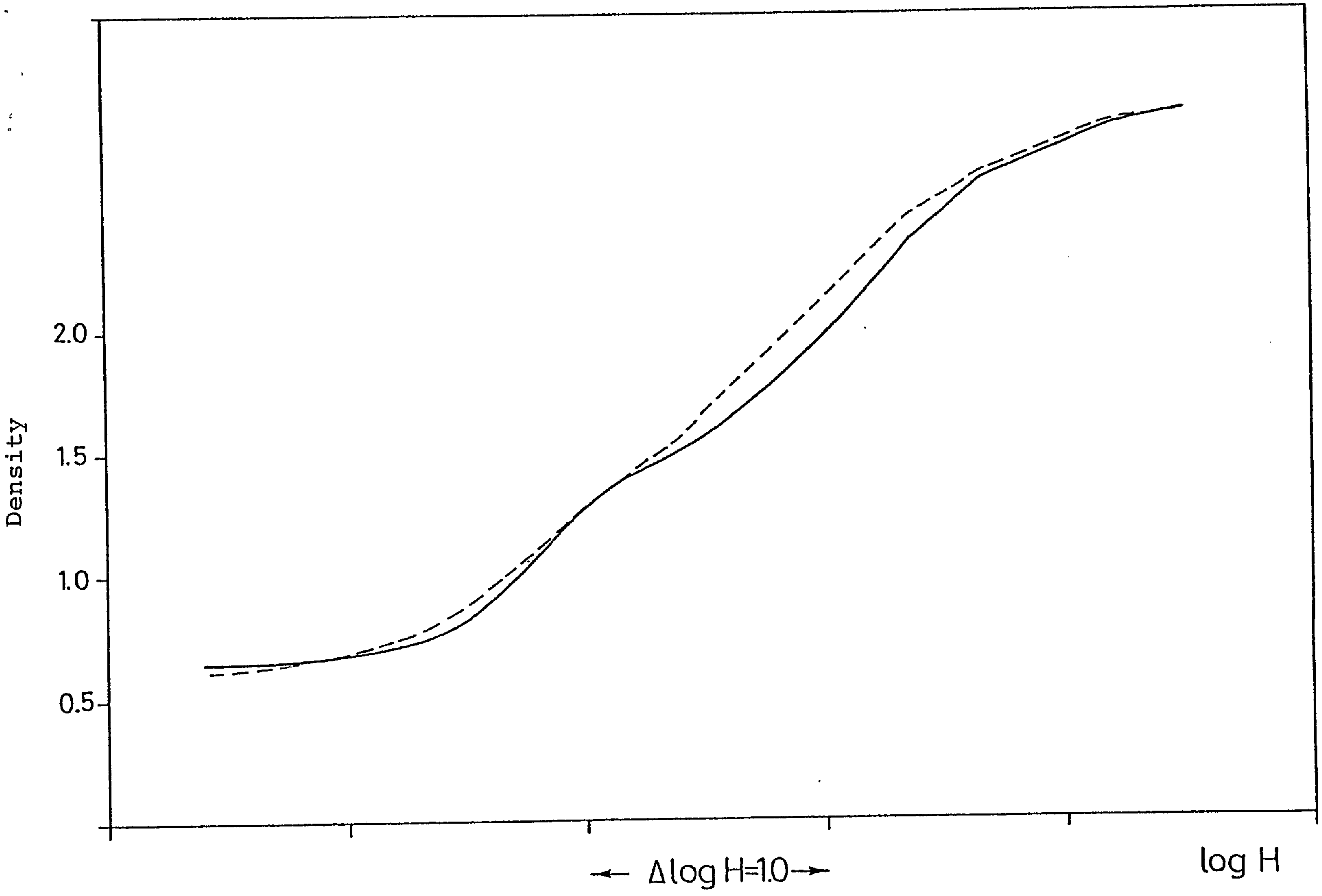


FIG. 2