

12

EUROPEAN PATENT APPLICATION

21 Application number: **90301756.4**

51 Int. Cl.⁵: **G03C 7/30, G03C 7/305**

22 Date of filing: **16.02.90**

30 Priority: **16.02.89 JP 36995/89**

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

64 Designated Contracting States:
DE GB

71 Applicant: **KONICA CORPORATION**
No. 26-2, Nishishinjuku 1-chome Shinjuku-ku
Tokyo(JP)

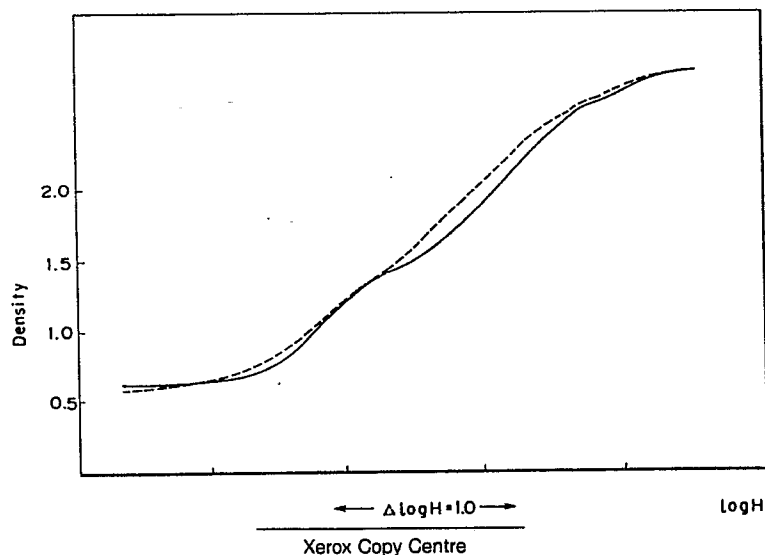
72 Inventor: **Okusa, Hiroshi**
Konnica Corporation, 1, Sakuramachi
Hino-shi, Tokyo(JP)
Inventor: **Hirabayashi, Shigeto**
Konnica Corporation, 1, Sakuramachi
Hino-shi, Tokyo(JP)
Inventor: **Ohya, Yukio**
Konnica Corporation, 1, Sakuramachi
Hino-shi, Tokyo(JP)

74 Representative: **Ellis-Jones, Patrick George**
Armine et al
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5LX(GB)

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

57 There is disclosed a light-sensitive silver halide color photographic material, which comprises on a support material at least silver halide emulsion layers which are respectively blue-sensitive, green-sensitive and red-sensitive, wherein a compound which can react with an oxidized product of a developing agent to scavenge the oxidized product or a compound which can release a precursor thereof is contained, and also at least one of the blue-, green- and red-sensitive layers has a single layer constitution.

FIG. 1



Light-sensitive silver halide color photographic materialBACKGROUND 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 dose range from the shadow portion with little exposure dose to the highlight portion with much exposure dose in the so-called characteristic curve in which the exposure dose is taken on the axis of abscissa and the color formed density on the axis of ordinate.

If the gradation is inferior, color reproducibility and tone reproducibility of a dye image 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 dose. For that 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 of silver halide grains and lower sensitivity layer containing smaller grain sizes of silver halide grains for the respective color sensitive layers to the lights 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 of a dye image, 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 Provisional 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 particularly 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 a DIR compound, whereby storability of the light-sensitive photographic material before photographing to external conditions such as temperature, humidity, etc. is inferior, and also in spite of the demand for high degree of stability to processing conditions, processing stability has not been solved to be inferior in stability to processing conditions. For such reasons, deterioration in gradation occurs, thus involving the drawbacks of deterioration of color reproducibility and tone reproducibility, and also with respect to sensitivity, it cannot be said to be yet satisfactory. Further, according to the method disclosed in Japanese Provisional Patent Publication No. 244944/1985, there is the problem that adsorption equilibrium of the dyes between grains occurs undesirably during the standing period before coating of the remixed emulsion.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive silver halide color photographic material, which is excellent in sensitivity and storability before photographing, and also excellent in stability to

fluctuations in processing conditions.

The object of the present invention has been accomplished by a light-sensitive silver halide color photographic material, comprising on a support material at least silver halide emulsion layers which are respectively blue-sensitive, green-sensitive and red-sensitive, wherein a compound which can react with the oxidized product of the developing agent to scavenge said oxidized product or a compound which can release a precursor thereof is contained, and also at least one of said blue-, green- and red-sensitive layers has a single layer constitution.

BRIEF DESCRIPTION OF THE DRAWING

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

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

DESCRIPTION OF THE PREFERRED EMBODIMENTS

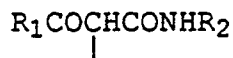
The compound which can react with the oxidized product of the developing agent to scavenge said oxidized product or the compound which can release a precursor thereof in the present invention (hereinafter called "DSR compound") may be preferably represented by the formula (DSR-I):

Coup-(Time)₁-Sc (DSR-I)

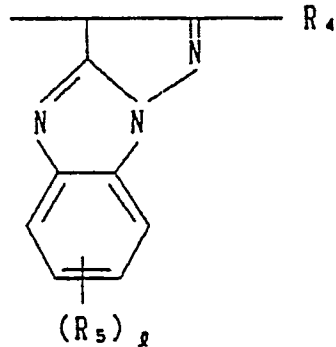
In the above formula (DSR-I), Coup represents the coupler residue which can release the (Time)₁-Sc through the reaction with the oxidized product of the color developing agent, Time represents a timing group which can release Sc after Time-Sc is released from Coup, Sc represents the scavenger of the oxidized product of the color developing agent which can scavenge the oxidized product of the color developing agent through redox reaction or coupling reaction after released from Coup or Time-Sc or a precursor thereof, and ₁ represents 0 or 1.

Further, to describe the compound represented by the formula (DSR-I) in more detail, the coupler residue represented by Coup is generally a yellow coupler residue, a magenta coupler residue, a cyan coupler residue or a coupler residue which forms substantially no image forming chromogenic dye, preferably a coupler residue represented by the formulae (DSR-Ia) through (DSR-Ih) shown below.

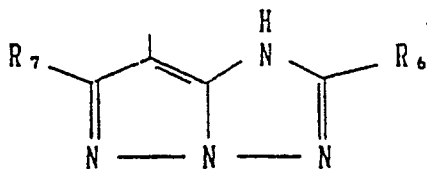
Formula (DSR-Ia)



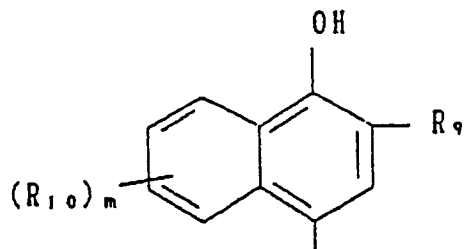
Formula (DSR-Ic)



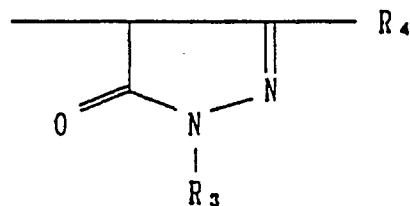
Formula (DSR-Ie)



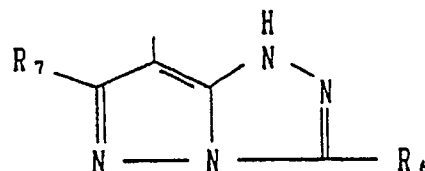
Formula (DSR-Ig)



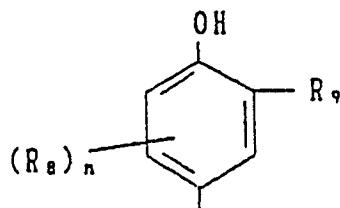
Formula (DSR-Ib)



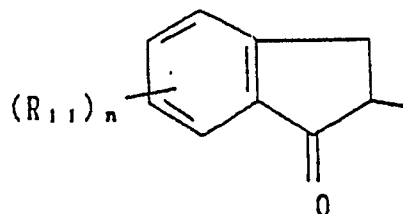
Formula (DSR-Id)



Formula (DSR-If)



Formula (DSR-Ih)



In the above formula (DSR-Ia), R_1 represents an alkyl group, an aryl group or an arylamino group, and R_2 represents an aryl group or an alkyl group.

In the above formula (DSR-Ib), R_3 represents an alkyl group or an aryl group, and R_4 represents an alkyl group, an acylamino group, an arylamino group, an arylureido group or an alkylureido group.

In the above formula (DSR-Ic), R_4 has the same meaning as R_4 in the formula (DSR-Ib), and R_5 represents an acylamino group, a sulfonamide group, an alkyl group, an alkoxy group or a halogen atom.

In the above formulae (DSR-Id) and (DSR-Ie), R_7 represents an alkyl group, an aryl group, an acylamino group, an arylamino group, an alkoxy group, an arylureido group, an alkylureido group, and R_6 represents an alkyl group or an aryl group.

In the above formula (DSR-If), R_9 represents an acylamino group, a carbamoyl group or an arylureido group, and R_8 represents a halogen atom, an alkyl group, an alkoxy group, an acylamino group or a sulfonamide group.

In the above formula (DSR-Ig), R_9 has the same meaning as R_9 in the formula (DSR-If), and R_{10} represents an amino group, an acid amide group, a sulfonamide group or a hydroxyl group.

In the above formula (DSR-Ih), R_{11} represents a nitro group, an acylamino group, a succinimide group, a sulfonamide group, an alkoxy group, an alkyl group, a halogen atom or a cyano group.

In the above formulae, l in (DSR-Ic) represents an integer of 0 to 3, n in the formulae (DSR-If) and

(DSR-Ih) of 0 to 2, m in (DSR-Ig) of 0 or 1, and when l and n are 2 or more, the respective R₅, R₈ and R₁₁ may be either the same or different.

The above respective groups include those having substituents, and preferred substituents may include halogen atoms, nitro group, cyano group, sulfonamide group, hydroxyl group, carboxyl group, alkyl groups, alkoxy groups, carbonyloxy groups, acylamino group, aryl groups, and otherwise those containing the coupler moiety constituting the so-called bis-type coupler or polymer coupler.

The lipophilicity exhibited by R₁ to R₁₁ in the above respective formulae can be chosen as desired depending on the purpose. In the case of an ordinary image forming coupler, the total carbon atoms of R₁ to R₁₀ should be preferably 10 to 60, more preferably 15 to 30. When a dye formed by color developing is made migratable adequately in the light-sensitive material, the total carbon atoms of said R₁ to R₁₀ are preferably 15 or less.

The coupler forming substantially no image forming chromogenic dye means, in addition to those forming no chromogenic dye, those which give no color image remaining after the developing processing such as the so-called flowable dye forming coupler of which the chromogenic dye flows out into the processing solution, the so-called bleachable dye forming coupler which is bleached through the reaction with the component in the processing solution. In the case of the flowable dye forming coupler, the total carbon atoms of R₁ to R₁₀ are preferably 15 or less, and further it is preferred that R₁ to R₁₀ have at least one carboxyl group, arylsulfonamide group or alkylsulfonamide group as substituent.

In the above formula (DSR-I), the timing group represented by Time is represented preferably by the following formula (DSR-II), (DSR-Ij) or (DSR-Ik).

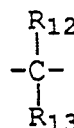


wherein B represents a group of atoms necessary for completion of a benzene ring or a naphthalene ring; Y represents -O-, -S- or

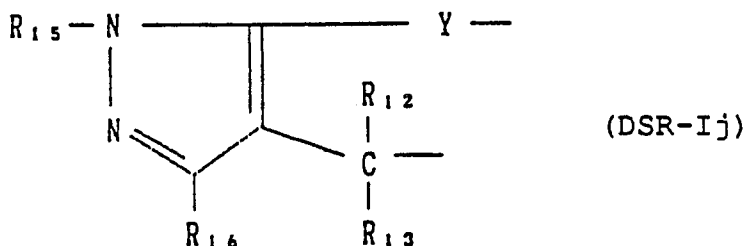


which is bonded to the active site of Coup (coupling component) of the above formula (DSR-I); R₁₂, R₁₃ and R₁₄ each represent hydrogen atom, an alkyl group or an aryl group.

The above group



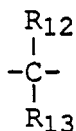
is substituted at the ortho- or para-relative to Y, and the other is bonded to Sc of the above formula (DSR-I).



wherein Y, R₁₂ and R₁₃ have respectively the same meanings as in the above formula (DSR-II); R₁₅ represents hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfonyl group, an alkoxy carbonyl group or a heterocyclic residue; R₁₆ represents hydrogen atom, an alkyl group, an aryl group, a

heterocyclic residue, an alkoxy group, an amino group, an acid amide group, a sulfonamide group, a carboxyl group, an alkoxy carbonyl group, a carbamoyl group or a cyano group.

Also, the timing group represented by the above formula (DSR-Ij) has Y bonded to the active site of Coup (coupling component) and the group



to Sc, similarly as in the above formula (DSR-li).

Next, as the Time group which releases Sc through the intramolecular nucleophilic reaction, there is one represented by the following formula (DSR-lk).

-Nu-D-E- (DSR-lk)

wherein Nu represents a nucleophilic group having oxygen, sulfur or nitrogen atom, which is rich in electrons and bonded to the active site of Coup (coupling component) in the above formula (DSR-l); E represents an electrophilic group having carbonyl group, thiocarbonyl group, phosphinyl group or thiophosphinyl group, which is deficient in electrons, which electrophilic group E is bonded to the hetero atom of Sc; D represents a bonding group which correlates sterically Nu and E, can perform intramolecular nucleophilic substitution through the reaction with accompaniment of formation of a 3- to 7-membered ring after Nu is released from Coup (coupling component), and can also release Sc thereby.

The scavenger of the oxidized product of the color developing agent represented by Sc (in the case when Sc is a precursor, the scavenger formed from said precursor) is inclusive of the redox type and the coupling type.

In the formula (DSR-l), when Sc is one which scavenges the oxidized product of the color developing agent through the redox reaction, said Sc is a group capable of reducing the oxidized product of the color developing agent, including preferably the reducing agents as disclosed in Angew. Chem. Int. Ed., vol. 17, pp 875 - 886 (1978), The Theory of the Photographic Process, The 4th Ed. (Macmillan, 1977) and Japanese Provisional Patent Publication No. 5247/1984, and Sc may be also a precursor capable of releasing those reducing agents during developing. Specifically, aryl groups or heterocyclic groups having at least two of -OH group, -NHSO₂R group,



(wherein R, R' represent hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group or an aryl group) are preferred. Among them, an aryl group is preferred, and further a phenyl group is preferred. The lipophilicity of Sc is chosen as desired depending on the purpose similarly as the coupler represented by the above formulae (DSR-la) to (DSR-lh), but for exhibiting the effect of the present invention to the maximum, the total carbon atoms of Sc may be 6 to 50, preferably 6 to 30, more preferably 6 to 20.

When Sc is one which scavenges the oxidized product of the color developing agent through the coupling reaction, said Sc can be various coupler residues, but preferably a coupler residue which forms substantially no image forming chromogenic dye, and the flowable dye forming couplers, bleachable dye forming couplers as described above, and Weiss couplers having non-eliminatable substituent at the reaction active site and forming no dye, can be utilized.

Specific examples of the compounds represented by the formula (DSR-l):

Coup{Time}-Sc (DSR-l)

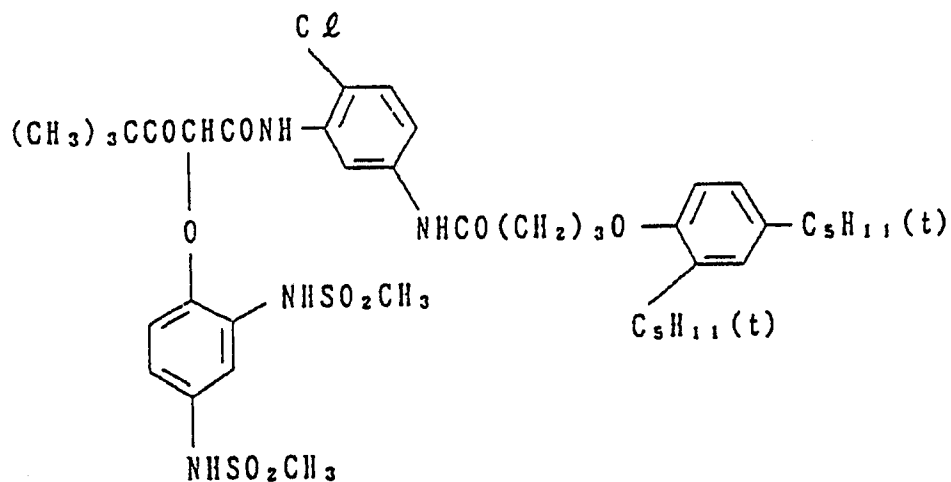
may include those disclosed in U.K. Patent No. 1546837, Japanese Provisional Patent Publications No. 150631/1977, No. 111536/1982, No. 111537/1982, No. 138636/1982, No. 185950/1985, No. 203943/1985, No. 213944/1985, No. 214358/1985, No. 53643/1986, No. 84646/1986, No. 86751/1986, No. 102646/1986, No. 102647/1986, No. 107245/1986, No. 113060/1986, No. 231553/1986, No. 233741/1986, No. 236550/1986, No. 236551/1986, No. 238057/1986, No. 240240/1986, No. 249052/1986, No. 81638/1987, No. 205346/1987, No. 287249/1987, etc.

As Sc, the redox type scavenger can be preferably used, and in this case, the color developing agent

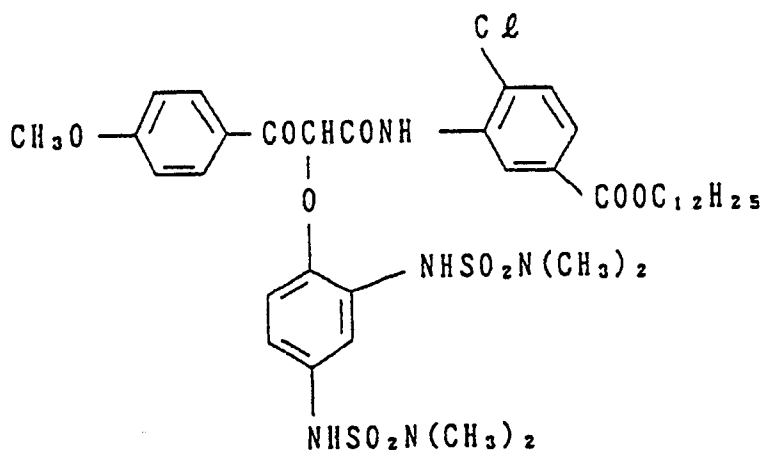
can be utilized again by reducing the oxidized product of the color developing agent.

In the following, examples of DSR compounds represented by the above formula (DSR-I) are shown, but the present invention is not limited to the exemplary compounds set forth below.

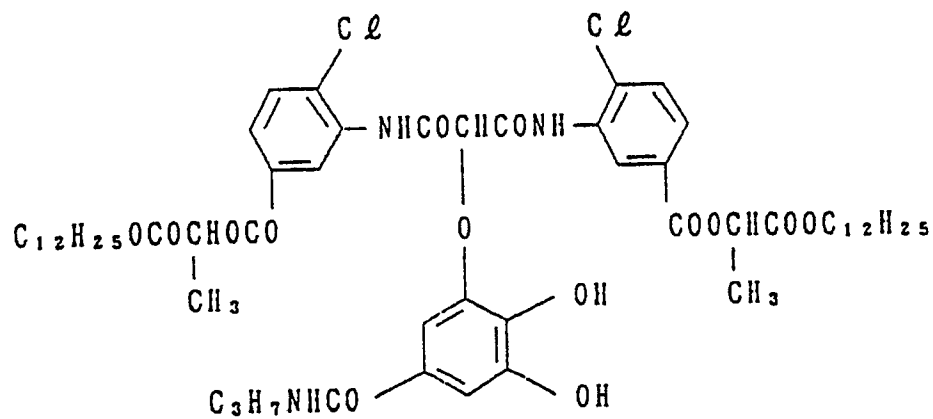
DSR - 1



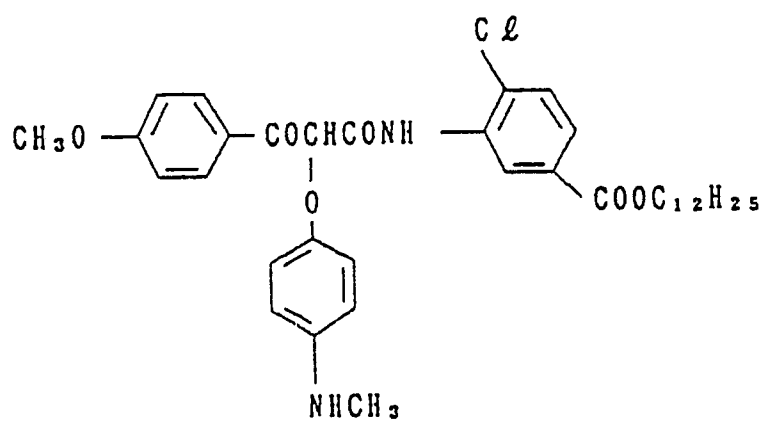
DSR - 2



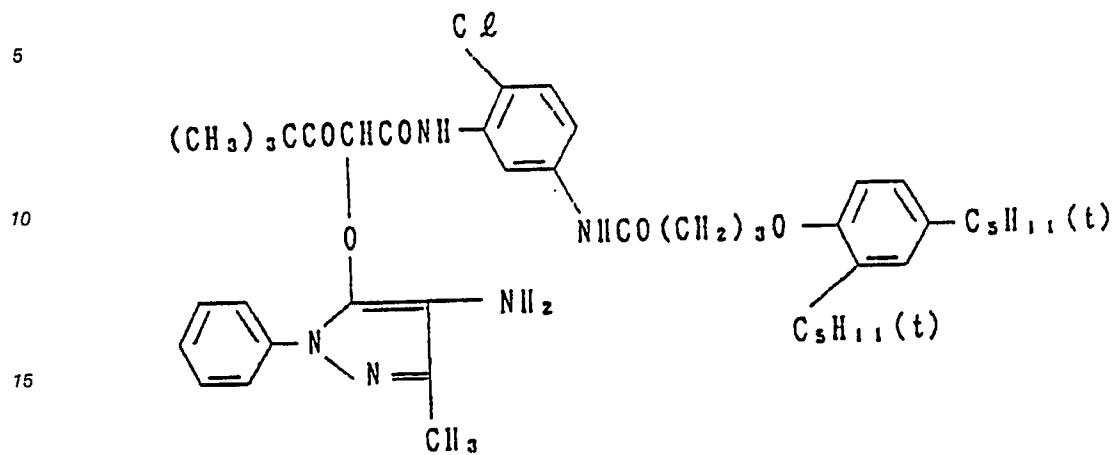
D S R - 3



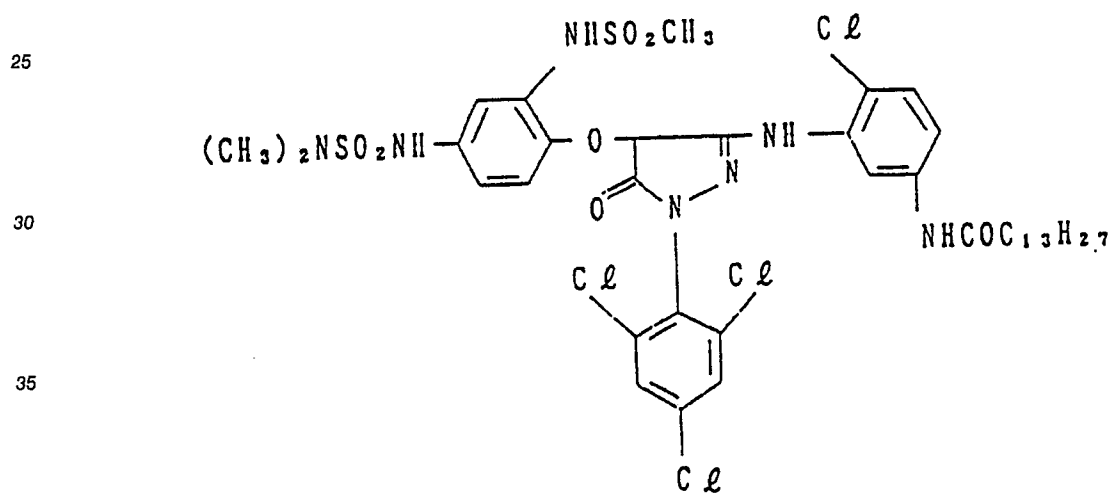
DSR - 4



D S R - 5



D S R - 6



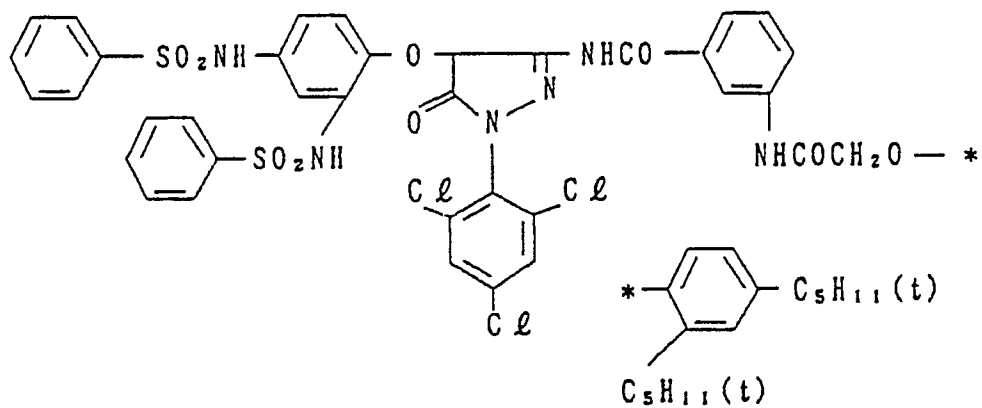
DSR - 7

5

10

15

20



DSR - 8

25

30

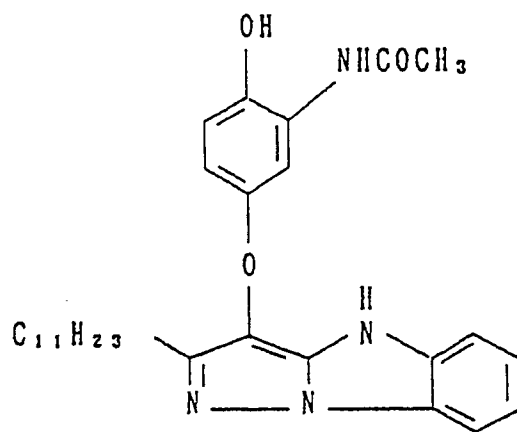
35

40

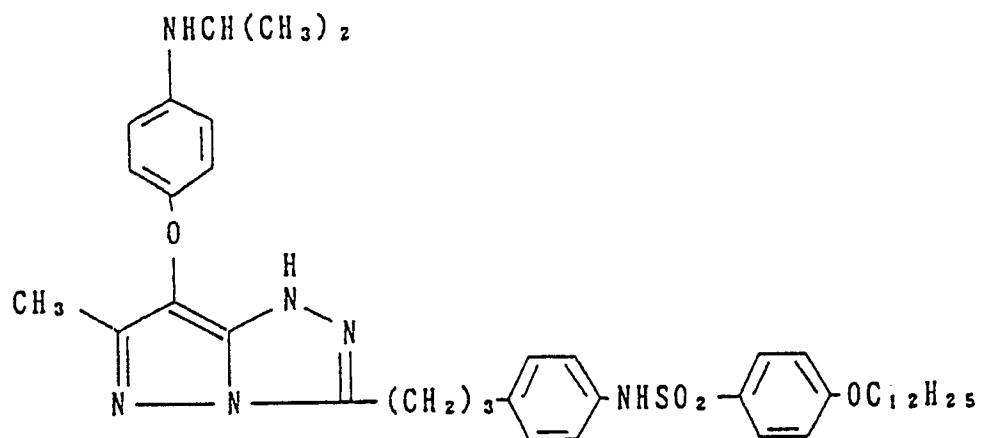
45

50

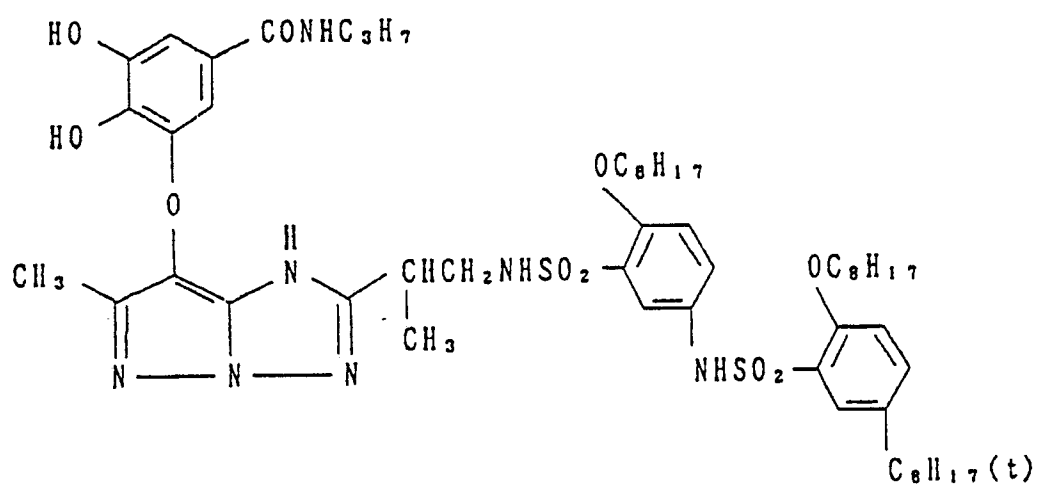
55



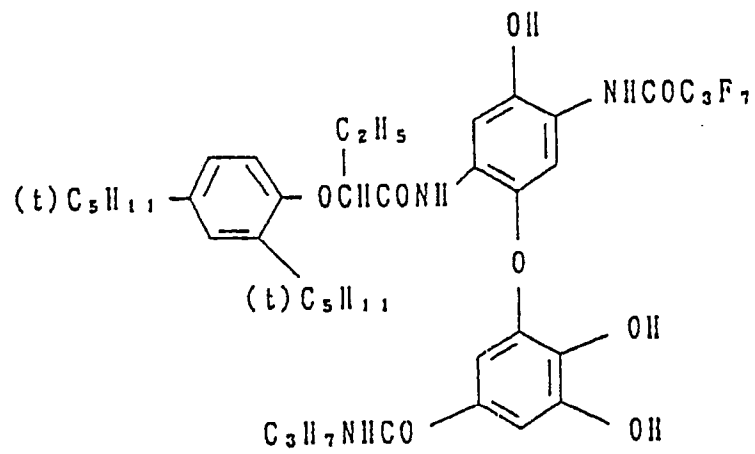
D S R - 9



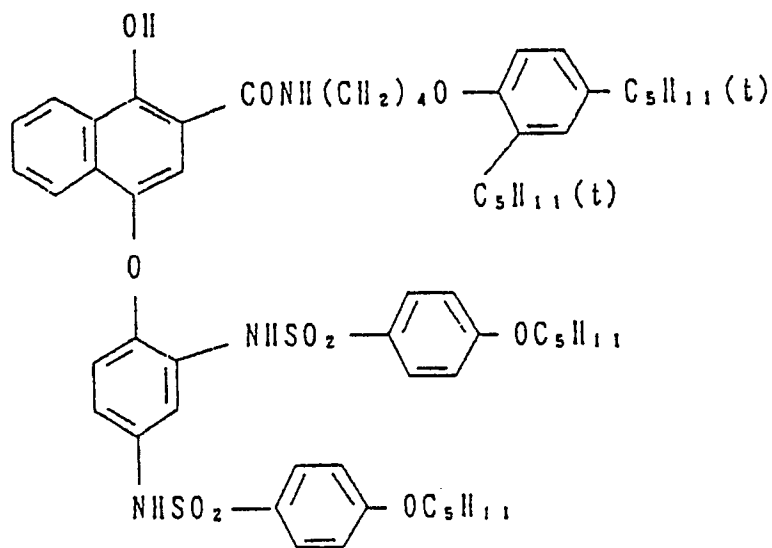
DSR - 10



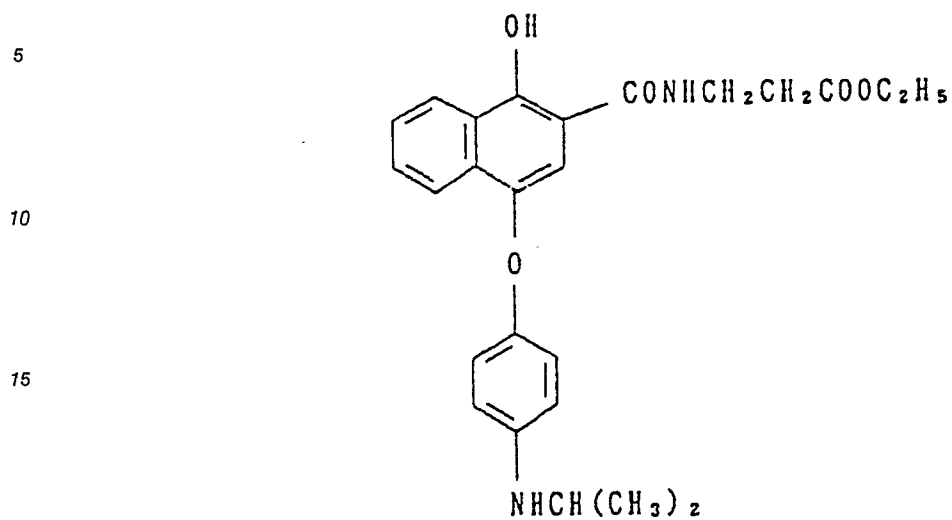
DSR - 1 1



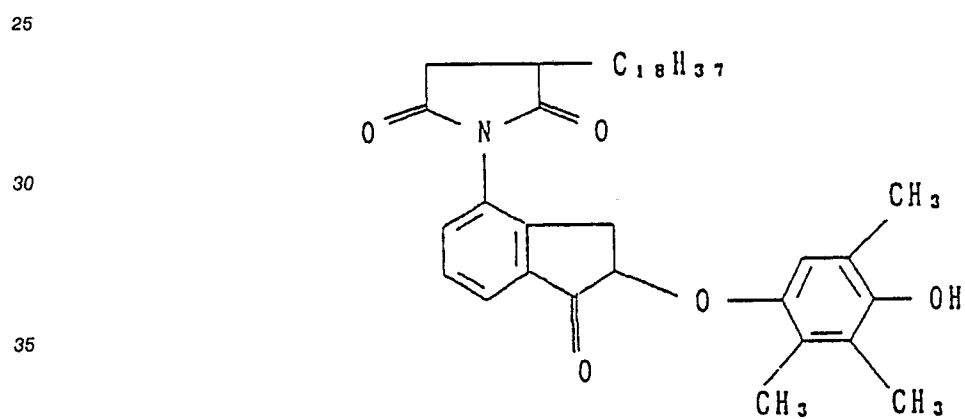
DSR - 1 2



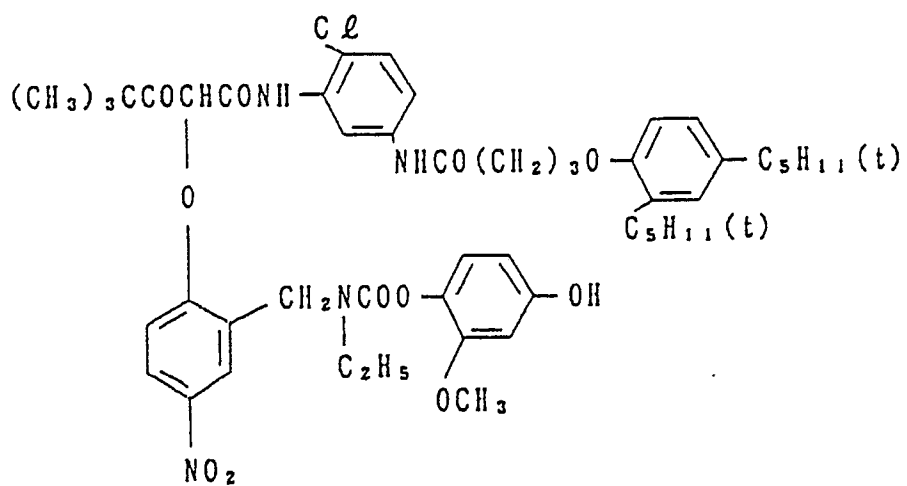
DSR - 1 3



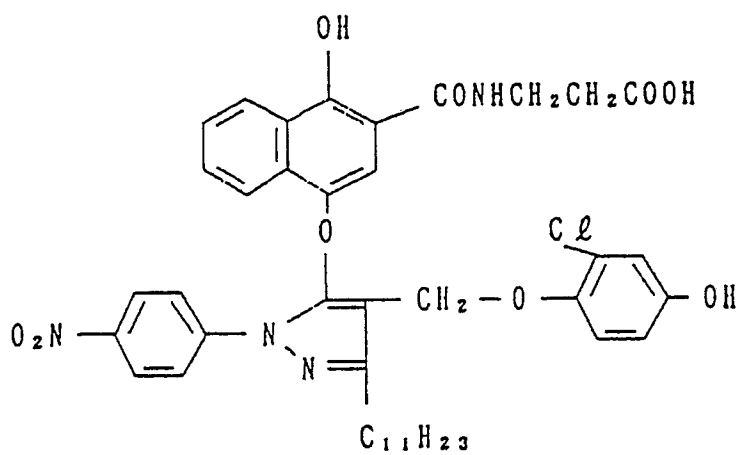
DSR - 1 4



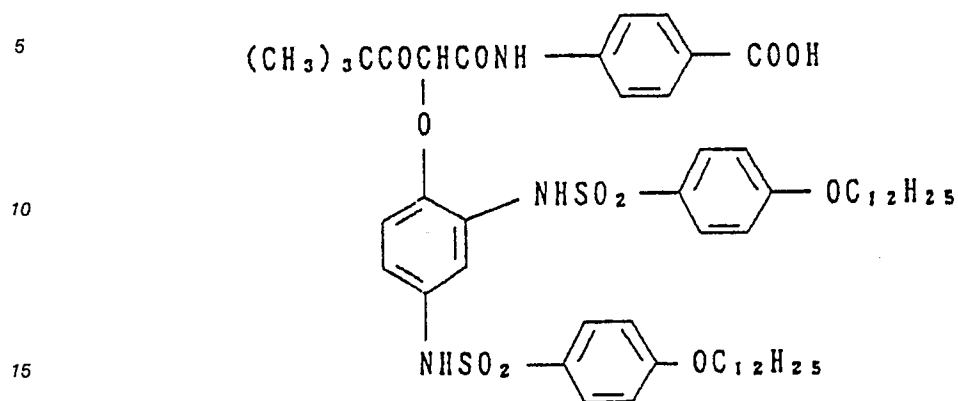
DSR - 15



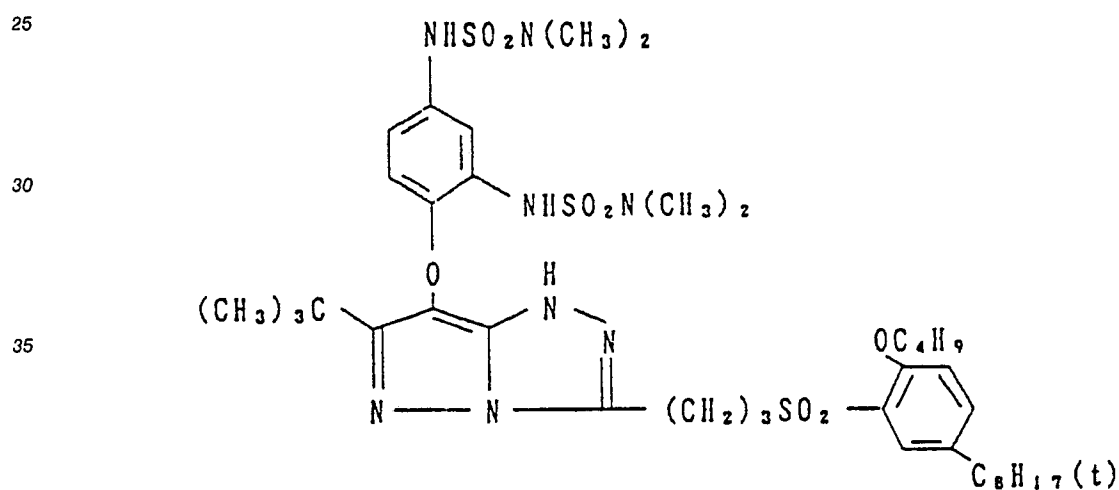
DSR - 16



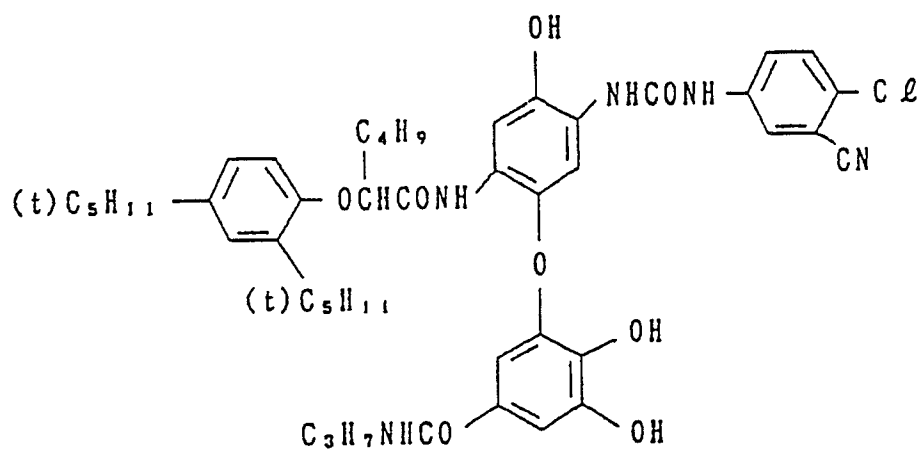
DSR - 17



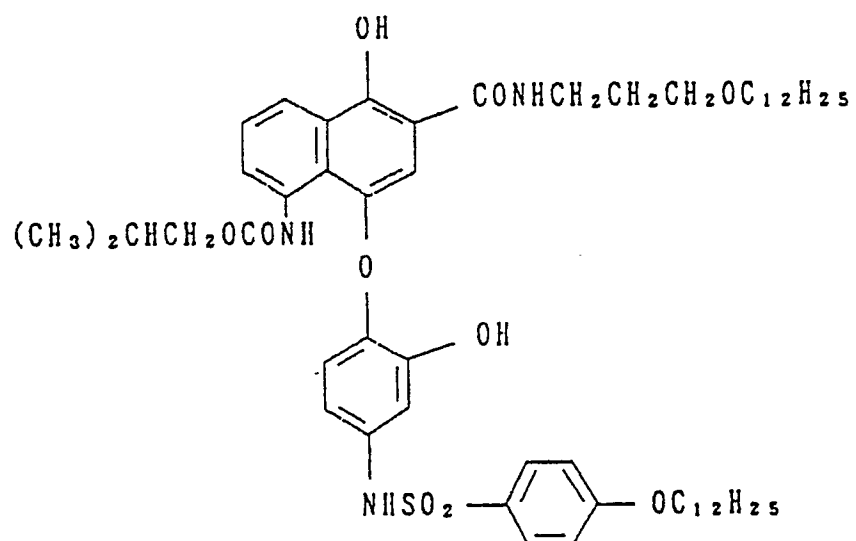
DSR - 18



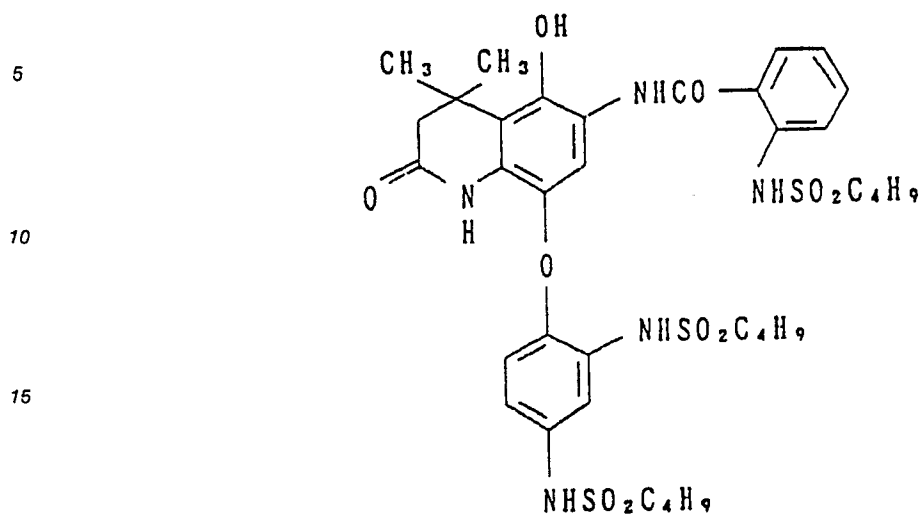
DSR - 19



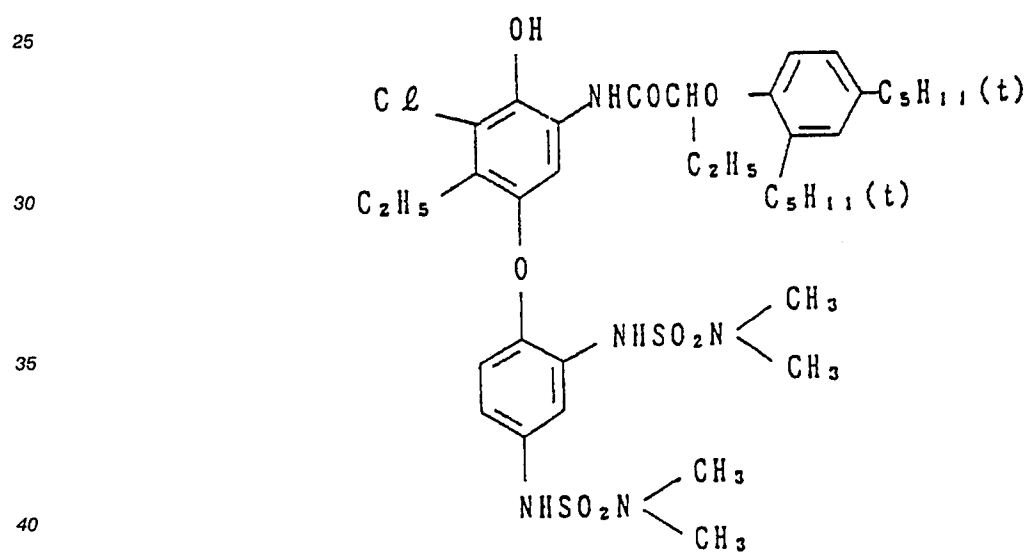
DSR - 20



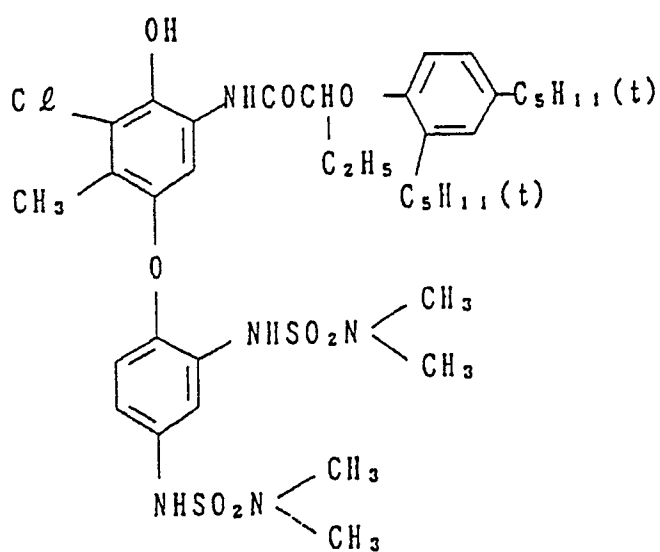
DSR - 2 1



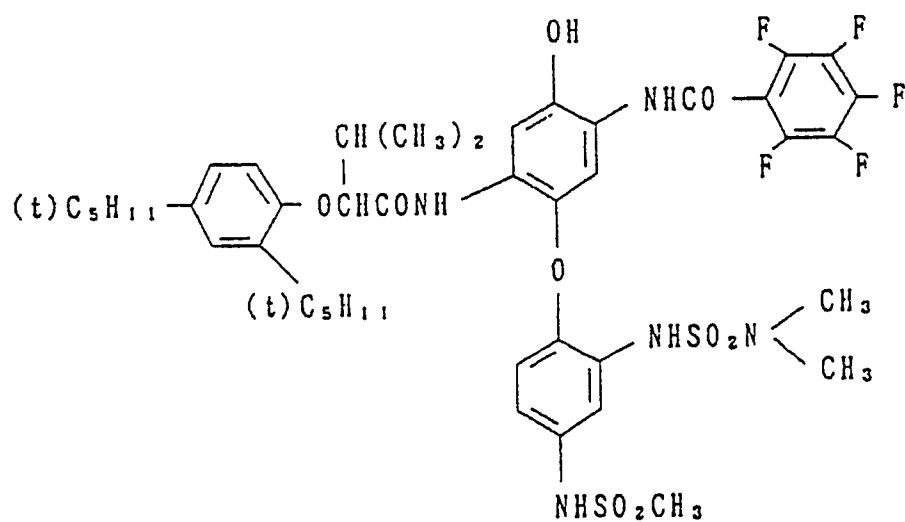
DSR - 2 2



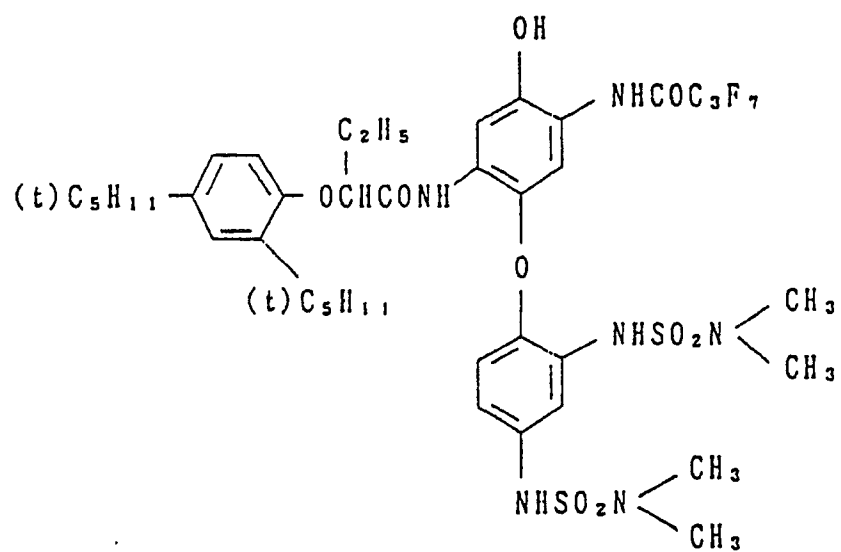
DSR - 2 3



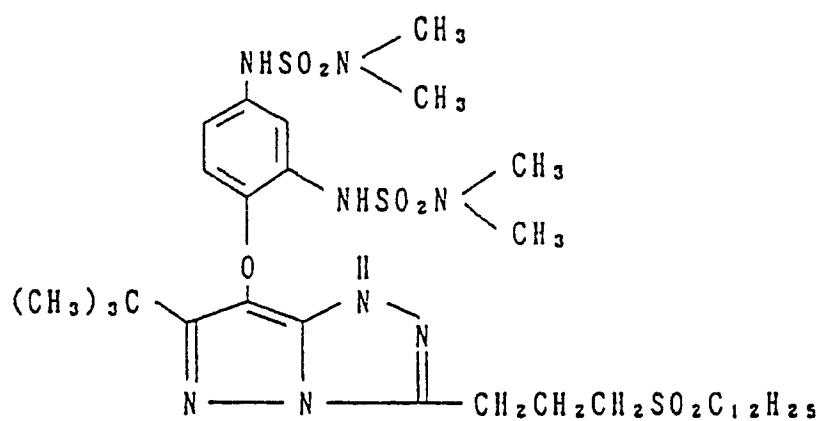
DSR - 2 4



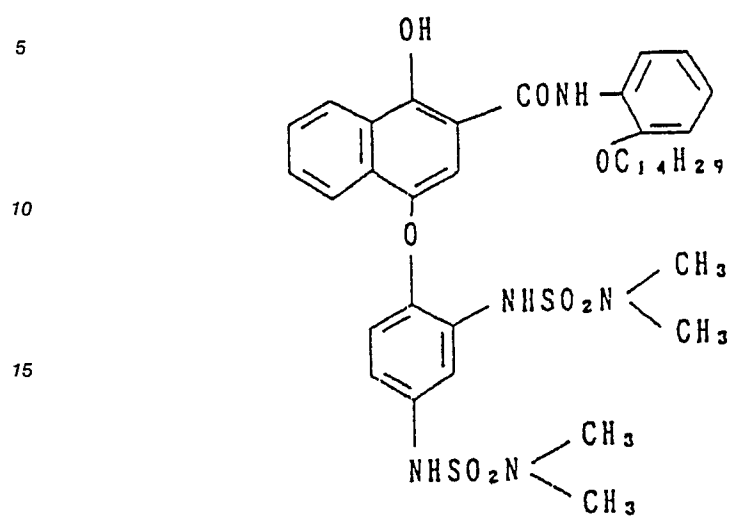
DSR - 25



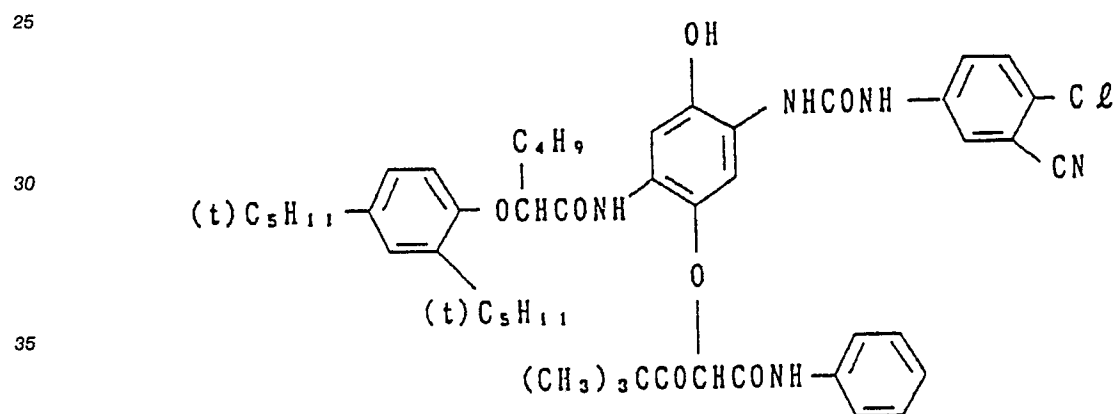
DSR - 26



DSR - 27



DSR - 28



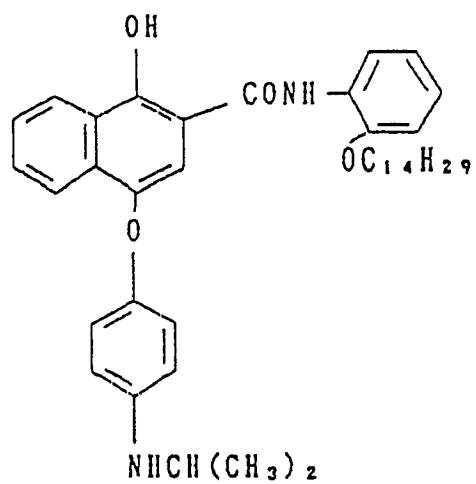
DSR - 29

5

10

15

20



DSR - 30

25

30

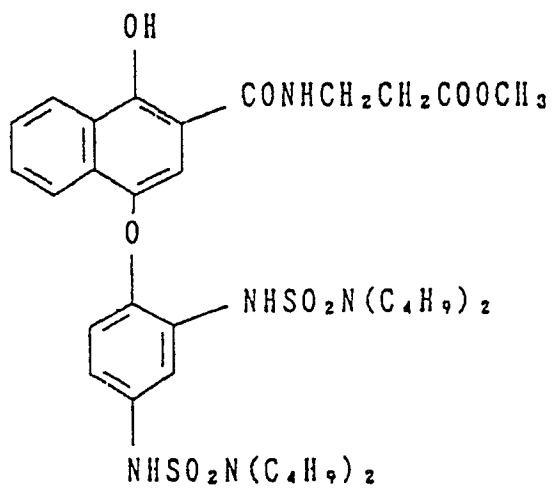
35

40

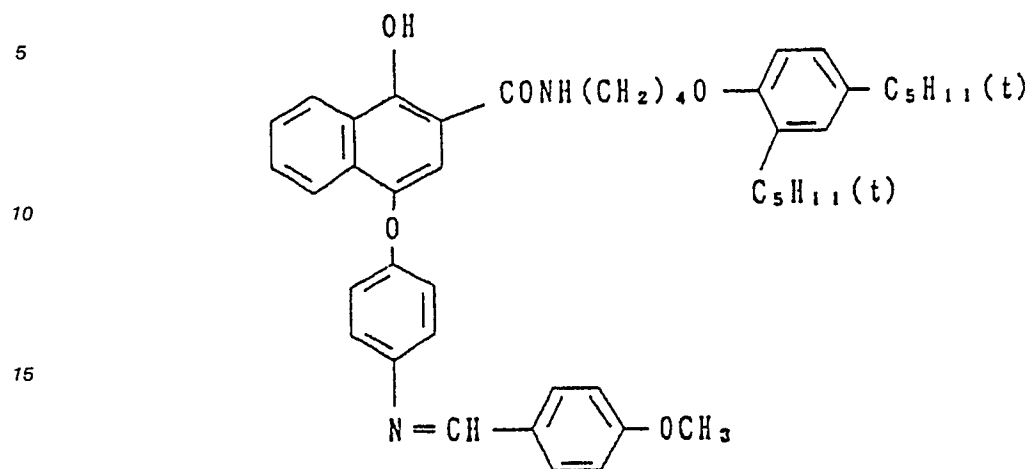
45

50

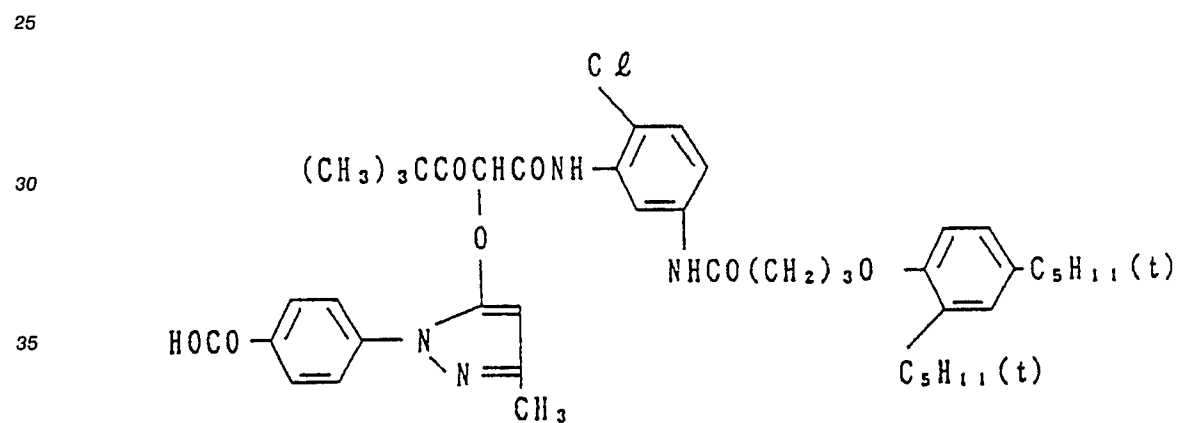
55



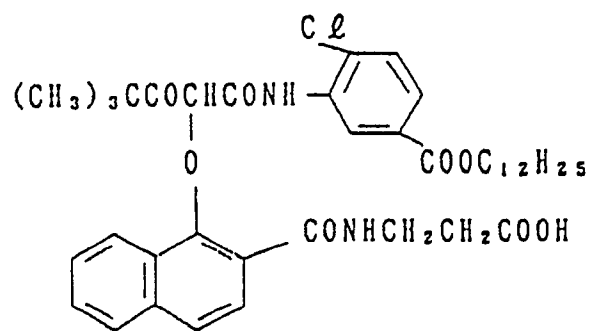
DSR - 3 1



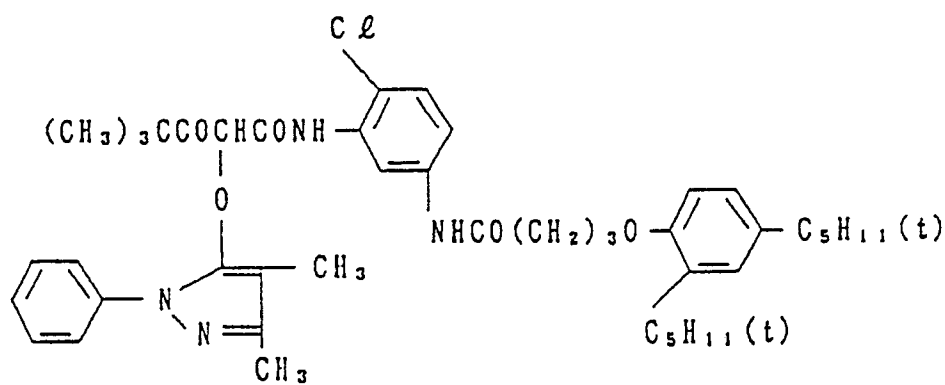
DSR - 3 2



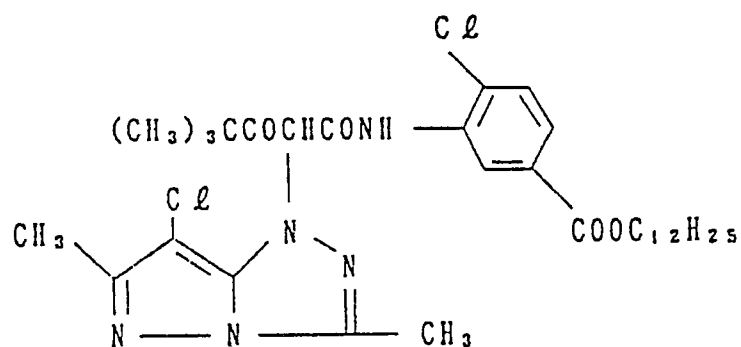
D S R - 3 3



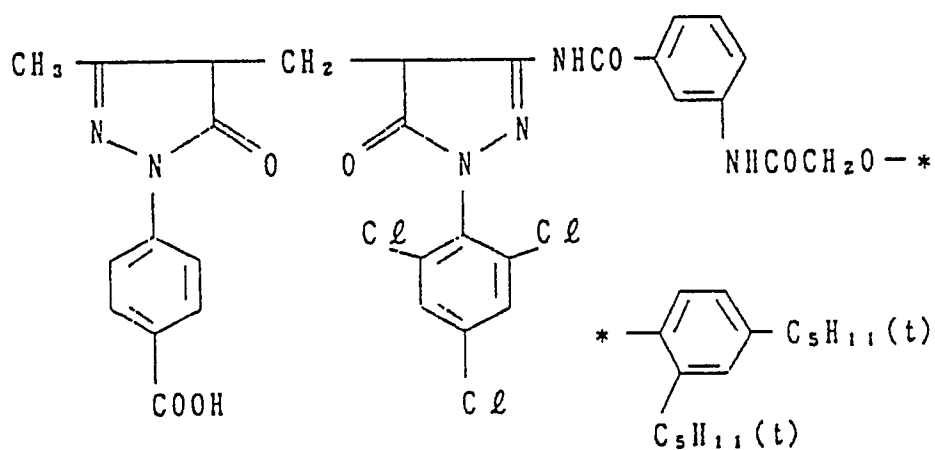
D S R - 3 4



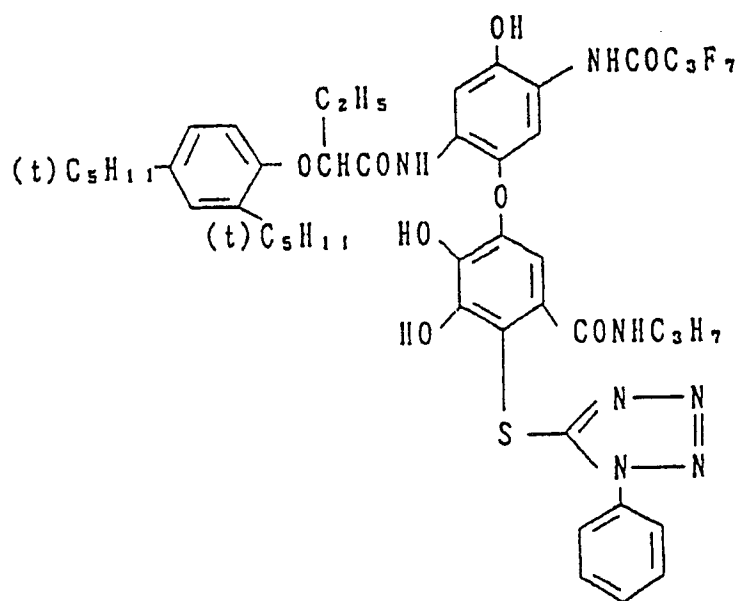
DSR - 3 5



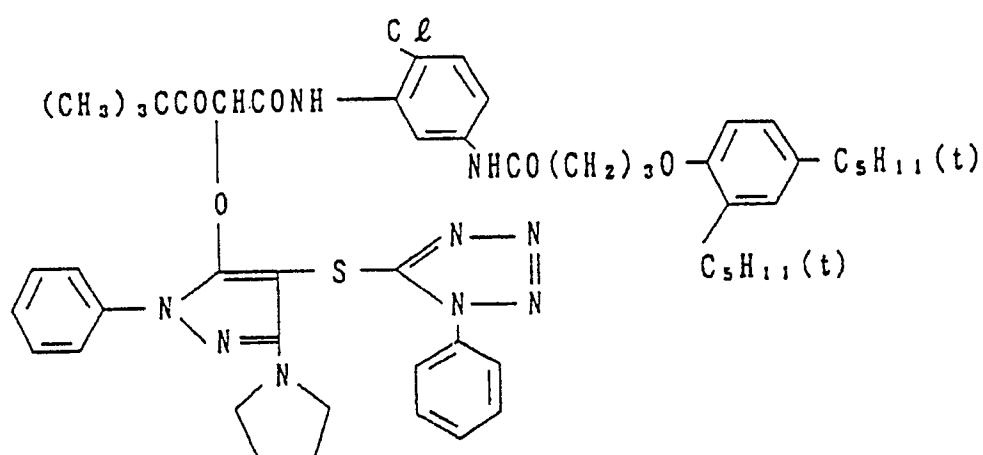
DSR - 3 6



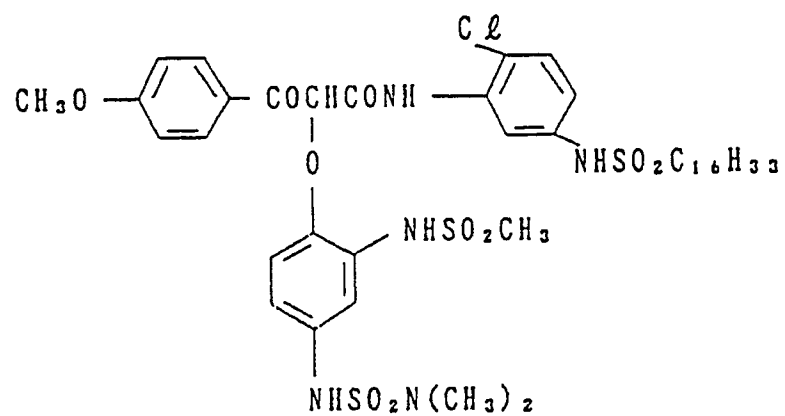
DSR - 37



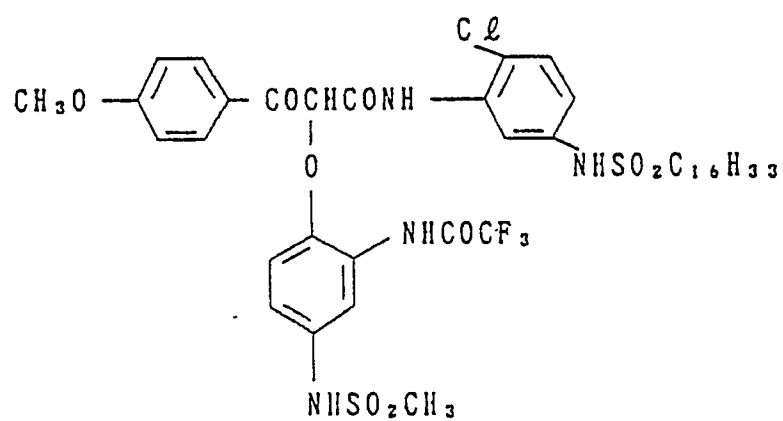
DSR - 38



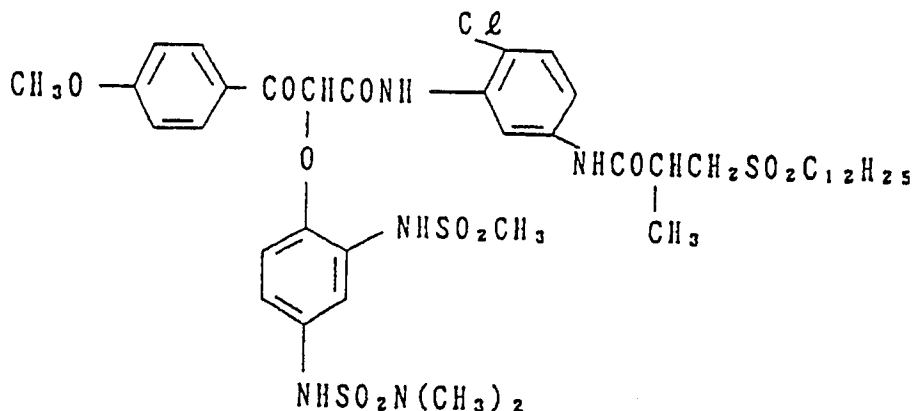
DSR - 39



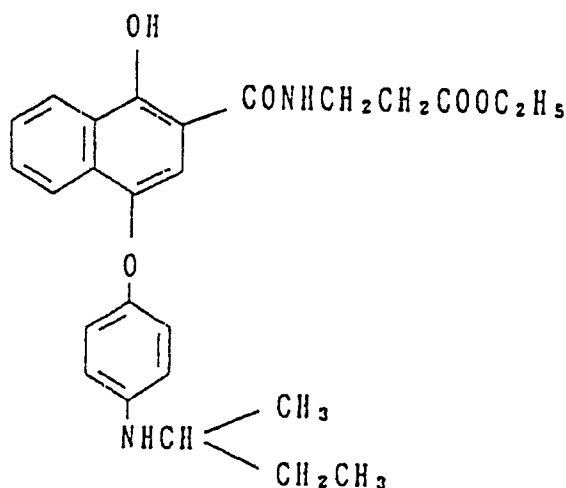
DSR - 40



DSR - 4 1



DSR - 4 2



The DSR compound of the present invention can be added in the light-sensitive silver halide photographic emulsion layer and/or the non-light-sensitive photographic constituent layer, but preferably in the light-sensitive silver halide emulsion layer.

The DSR compound of the present invention can be contained in two or more kinds in the same layer. Also, the same DSR compound can be contained in two or more different layers.

These DSR compounds may be generally used in amounts preferably of 2×10^{-4} to 5×10^{-1} mole, more preferably of 1×10^{-3} to 1×10^{-1} mole, per mole of silver in the emulsion layer.

For incorporating these DSR compounds in the silver halide emulsion according to the present invention or in other photographic constituent layer coating solutions, when said DSR compound is alkali soluble, it may be also added as an alkaline solution, or when it is oil soluble, the DSR compound is preferably dissolved in a high boiling solvent optionally in combination with a low boiling solvent and added as a fine dispersion into the silver halide emulsion, following the methods as disclosed in U.S. Patents No. 2,322,027, No. 2,801,170, No. 2,801,171, No. 2,272,191 and No. 2,304,940.

The DSR compounds as described above can be synthesized according to the methods as disclosed in Japanese Provisional Patent Publications No. 138638/1982, No. 155537/1982, No. 171334/1982, No. 111941/1983, No. 53643/1986, No. 84646/1986, No. 86751/1986, No. 102646/1986, No. 102647/1986, No. 107245/1986, No. 113060/1986, etc.

The compound which undergoes the coupling reaction or the redox reaction with the oxidized developing agent released from the DSR compound of the present invention corresponding to the density of the image during developing or its precursor can obtain two kinds of image effects of inhibiting the dye forming reaction (coupling reaction) corresponding to the image density in the light-sensitive emulsion layer, thereby giving rise to the so-called intra-image effect such as improvement of sharpness of image, etc., while on the other hand, in other layer to which it has been diffused, giving rise to the so-called inter-image effect such as the masking action, etc. by interfering with the dye forming reaction in such layers corresponding to the density of the image in the layer of the diffusion source.

In the present invention, use of a DIR compound is further preferred with respect to 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.

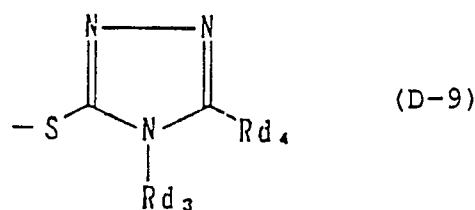
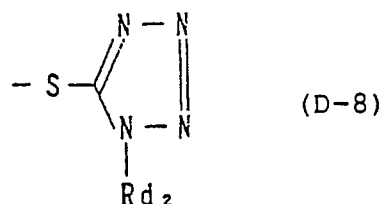
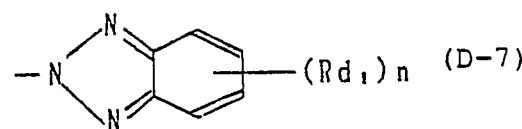
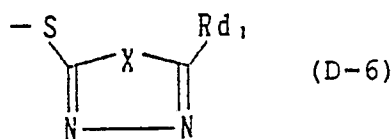
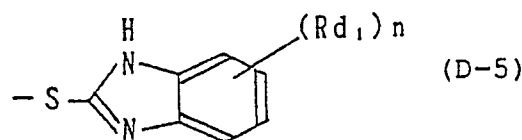
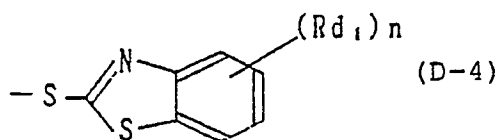
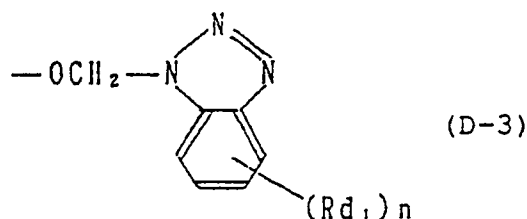
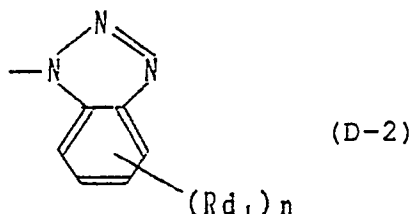
Imagewise release may be effected by, for example, the reaction with the oxidized product of the developing agent, while non-imagewise release by utilizing; for example, the TIME group as described below.

In the following, representative structural formulae are shown.

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

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-20) set forth below.



In the formulae (D-2) to (D-7), Rd_1 represents a hydrogen atom, a halogen atom or an alkyl, alkoxy, acylamino, alkoxy carbonyl, thiazolidinylideneamino, aryloxy carbonyl, acyloxy, carbamoyl, N-alkylcarbamoyl, N,N-dialkylcarbamoyl, nitro, amino, N-arylcarbamoyloxy, sulfamoyl, N-alkylcarbamoyloxy, hydroxy, alkoxy carbonylamino, alkylthio, arylthio, aryl, heterocyclic, cyano, alkylsulfonyl or aryloxy carbonylamino group. n

represents 0, 1 or 2, and when n is 2, the respective Rd₁'s may be either the same or different. The total carbon atoms contained in n Rd₁'s may be 0 to 10. On the other hand, the carbon atoms contained in Rd₁ in the formula (D-6) may be 0 to 15.

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

5 In the formula (D-8), Rd₂ represents an alkyl group, an aryl group or a heterocyclic group.

In the formula (D-9), Rd₃ represents a hydrogen atom, an alkyl, cycloalkyl, aryl or heterocyclic group, Rd₄ represents a hydrogen atom, a halogen atom or an alkyl, cycloalkyl, aryl, acylamino, alkoxy carbonylamino, aryloxy carbonylamino, alkanesulfonamide, cyano, heterocyclic, alkylthio or amino group.

10 When Rd₁, Rd₂, Rd₃ or Rd₄ represents an alkyl group, the alkyl group includes those having substituents, and may be either straight or branched.

When Rd₁, Rd₂, Rd₃ or Rd₄ represents an aryl group, the aryl group includes those having substituents.

15 When Rd₁, Rd₂, Rd₃ or Rd₄ represents a heterocyclic group, the heterocyclic group includes 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, and may be selected from the groups of, for example, pyridyl, quinolyl, furyl, benzothiazolyl, oxazolyl, imidazolyl, thiazolyl, triazolyl, benzotriazolyl, imide or oxazine group.

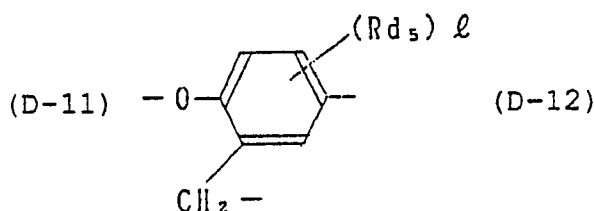
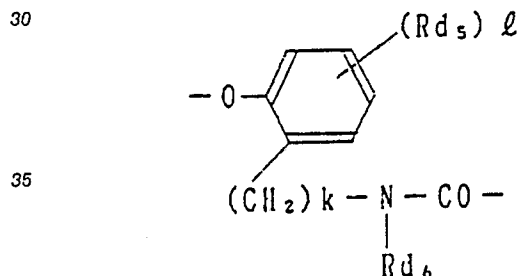
The carbon atoms contained in Rd₂ in the formula (D-8) may be 0 to 15.

In the above formula (D-9), the total carbon atoms contained in Rd₃ and Rd₄ may be 0 to 15.

20 {TIME}_n INHIBIT (D-10)

wherein the TIME group is a group bound to the coupling position of A which cleavable through the reaction with the oxidized product of the color developing agent, which is a group cleaved successively after cleavage from the coupler, 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.

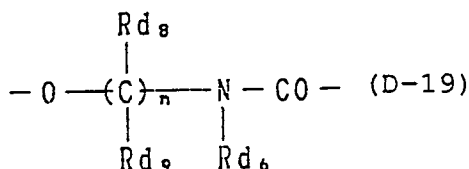
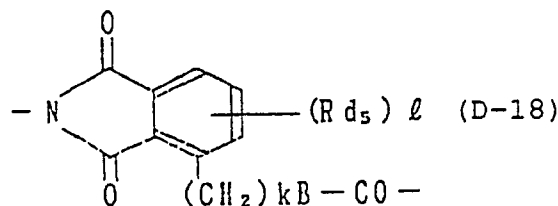
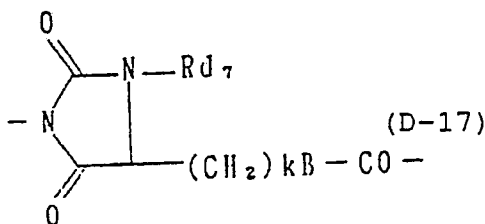
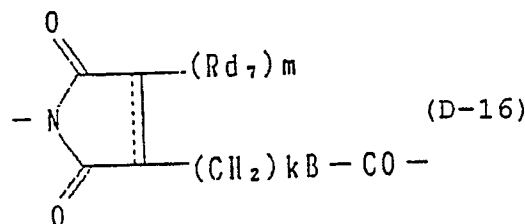
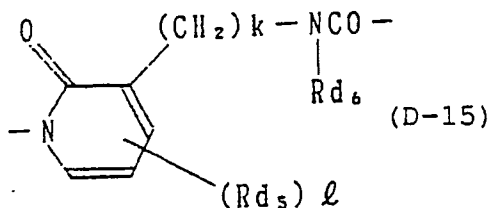
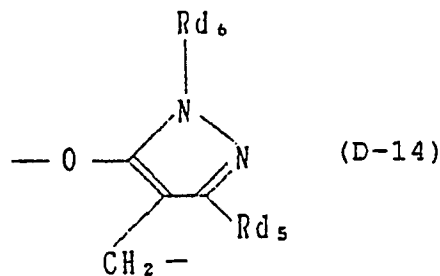
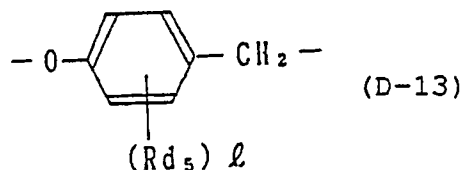


40

45

50

55



In the formulae (D-11) to (D-15) and (D-18), Rd₅ represents a 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), Rd₅'s may be mutually bonded together to form a fused ring. In the formulae (D-11), (D-14), (D-15) and (D-19), Rd₆ represents an aralkyl, alkenyl, alkyl, cycloalkyl, heterocyclic or aryl group. In the formulae (D-16) and (D-17), Rd₇ represents a hydrogen atom or an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. Each of Rd₈ and Rd₉ in the formulae (D-19) represents a hydrogen atom or an alkyl group (preferably an alkyl group having 1 to 4 carbon atoms), k in the formulae (D-11), (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 Rd₅ and Rd₇ may be either the same or different. n in the formula (D-19) represents an integer of 2 to 4, and Rd₈ and Rd₉ in number of n may be each the same or different. B in the formulae (D-16) to (D-18) represents an oxygen atom or



(Rd₆ represents the same meaning as already defined), and — 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 or m is 1 in the case of the double bond.

$(T_1)_T$ SR $(T_2)_m$ INHIBIT (D-20)

wherein T_1 represents a component which cleaves SR $(T_2)_m$ INHIBIT, SR represents 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 represents a component which cleaves INHIBIT after formation of $(T_2)_m$ INHIBIT, INHIBIT represents 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 coupling 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 and cyan couplers such as acylacetanilides, 5-pyrazolones, pyrazoloazoles, phenols, naphthols, acetophenones, indanones, carbamoylacetylides, 2(5H)-imidazolones, 5-isoxazolones, uracils, homophthalimides, oxazolones, 2,5-thiadiazoline-1,1-dioxides, triazolothiadiazines and indoles, and otherwise those which form various dyes or form no dye. The $(T_1)_T$ 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 $(T_1)_T$ and $(T_2)_m$ INHIBIT so as to function for the first time as the coupler after cleavage from $(T_1)_T$.

For example, the oxygen atom of hydroxyl group when the coupler component is phenols or naphthols, the oxygen atom at the 5-position or the nitrogen atom at the 2-position of the enantiomer when it is 5-pyrazolones, and also the oxygen atom of hydroxyl group of the enantiomer when it is acetophenones or indanones, are preferably bonded to $(T_1)_T$, 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 and o-aminophenols), naphthalenediols (e.g. 1,2-naphthalenediols, 1,4-naphthalenediols and 2,6-naphthalenediols) and aminonaphthols (e.g. 1,2-aminonaphthols, 1,4-aminonaphthols and 2,6-aminonaphthols).

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

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

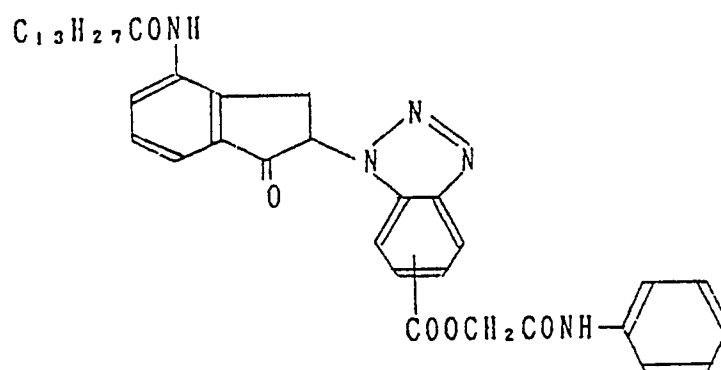
Among the DIR compounds, preferred are those wherein Y is represented by the formula (D-2), (D-3), (D-8), (D-10) or (D-20), and among (D-10) and (D-20), those wherein INHIBIT is represented by the formula (D-2), (D-3), (D-6) (particularly when X of the formula (D-6) is an oxygen atom), or (D-8) are preferred.

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.

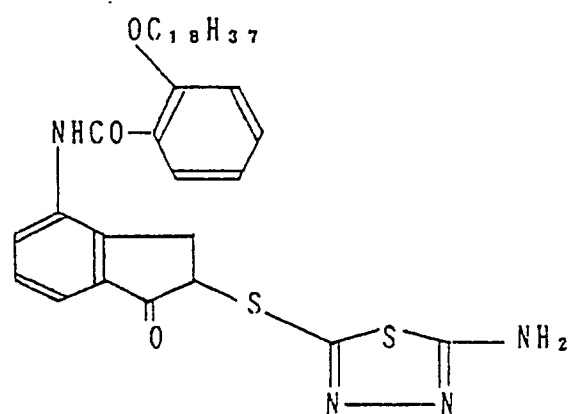
As preferred DIR compounds to be used in the present invention, the compounds as shown below may be included, but these are not limitative of the invention.

Exemplary compounds:

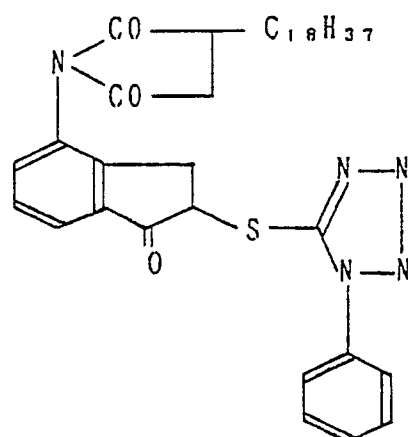
D - 1

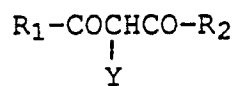


D - 3 6



D - 3 7





5

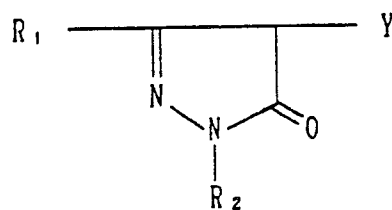
10

15

20

25

30



35

40

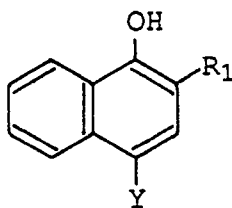
45

50

55

Exemplary compound No.	R ₁	R ₂	Y
D - 2	(1)	(1)	(30)
D - 3	(2)	(3)	(30)
D - 4	(2)	(4)	(30)
D - 5	(5)	(6)	(31)
D - 6	(2)	(4)	(32)
D - 7	(2)	(3)	(32)
D - 8	(7)	(8)	(33)
D - 33	(2)	(4)	(55)
D - 40	(2)	(4)	(56)
D - 43	(2)	(25)	(59)

Exemplary compound No.	R ₁	R ₂	Y
D - 9	(9)	(10)	(30)
D - 10	(11)	(10)	(30)
D - 11	(12)	(7)	(34)
D - 12	(12)	(13)	(35)
D - 13	(9)	(14)	(36)
D - 14	(15)	(16)	(37)
D - 35	(56)	(24)	(23)



5

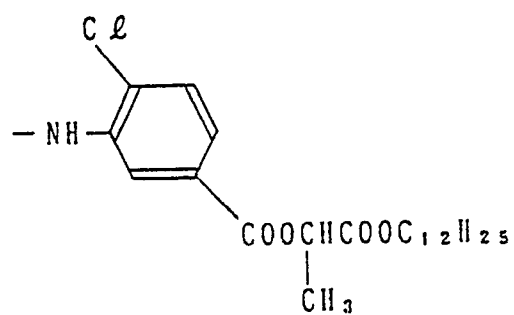
10

Exemplary compound No.	R ₁	Y
D - 15	(17)	(38)
D - 16	(17)	(39)
D - 17	(18)	(40)
D - 18	(19)	(41)
D - 19	(18)	(42)
D - 20	(18)	(43)
D - 21	(18)	(44)
D - 22	(18)	(45)
D - 23	(18)	(46)
D - 24	(20)	(47)
D - 25	(20)	(48)
D - 26	(21)	(49)
D - 27	(21)	(50)
D - 28	(21)	(51)
D - 29	(22)	(52)
D - 30	(18)	(53)
D - 31	(18)	(54)
D - 32	(22)	(49)
D - 34	(18)	(56)
D - 38	(19)	(46)
D - 39	(18)	(57)
D - 41	(18)	(60)
D - 42	(18)	(48)
D - 44	(18)	(58)

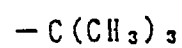
50

55

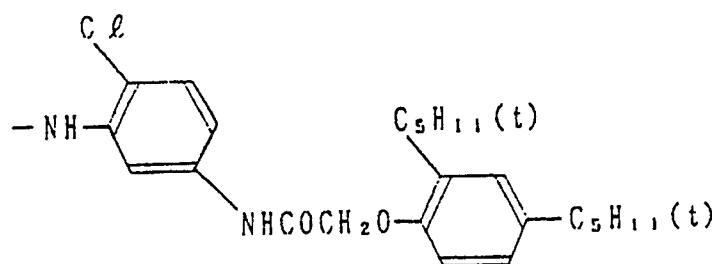
1



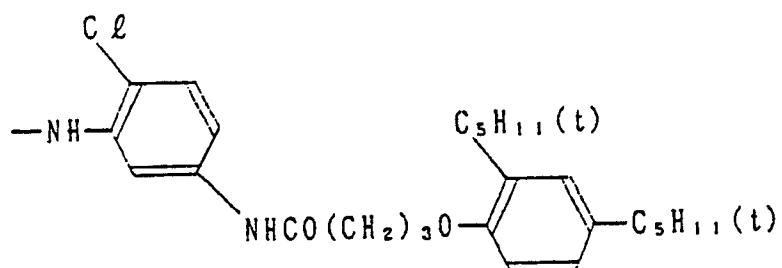
2



3



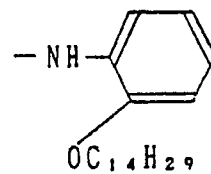
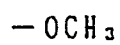
4



5

6

5

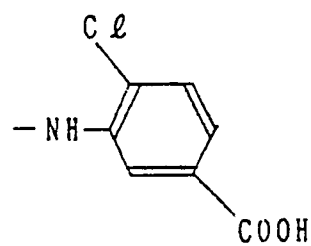
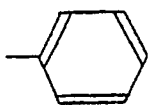


10

7

8

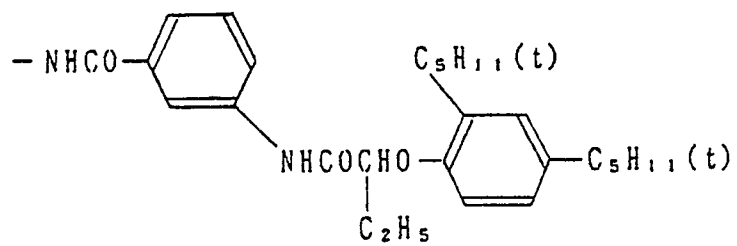
15



20

9

25

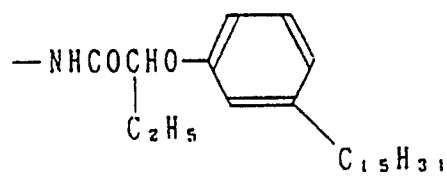
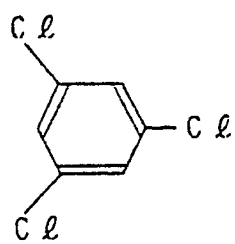


30

35

1 0

1 1



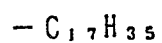
40

45

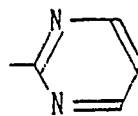
50

55

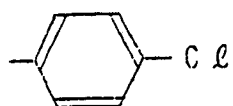
1 2



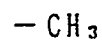
1 3



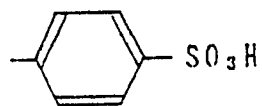
1 4



1 5



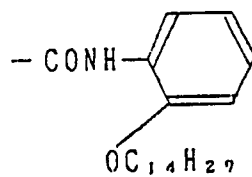
1 6



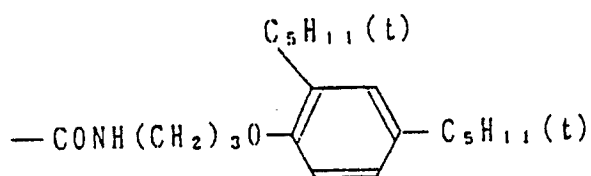
1 7



1 8

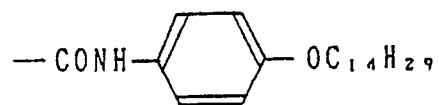


1 9



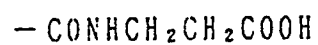
2 0

5



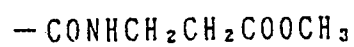
2 1

10



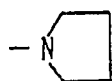
2 2

15



2 3

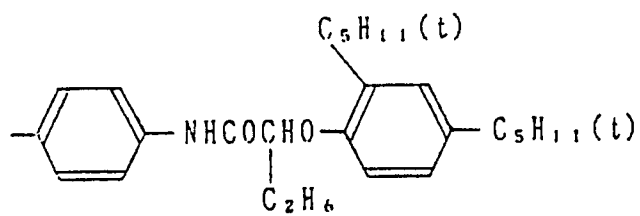
20



25

2 4

30



35

40

45

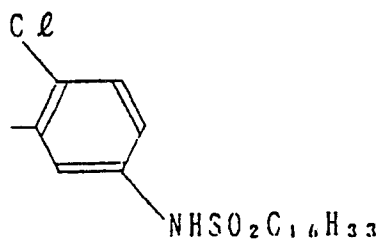
50

55

2 5

5

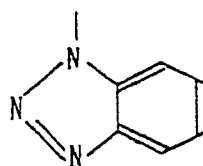
10



3 0

15

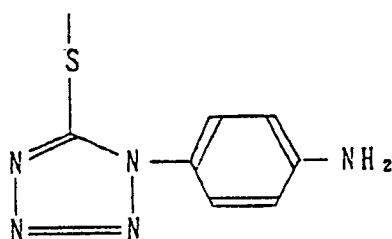
20



3 1

25

30

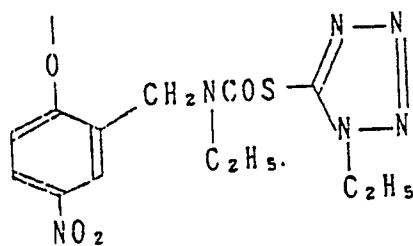


35

3 2

40

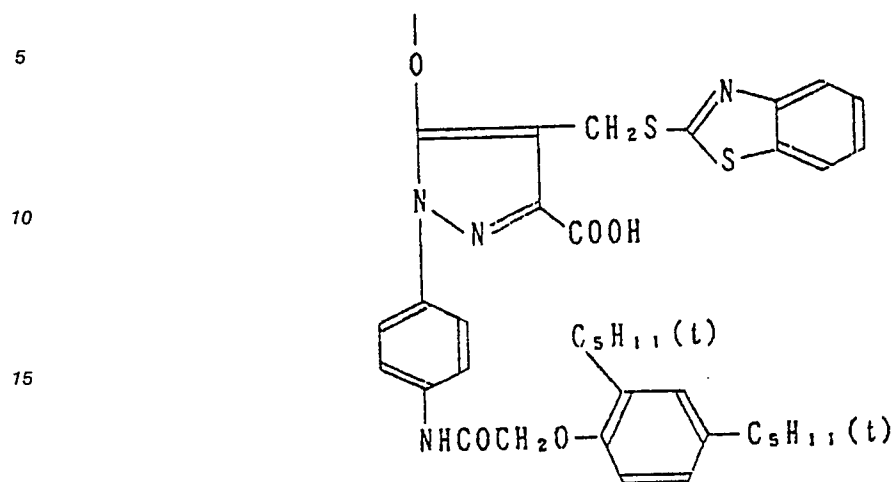
45



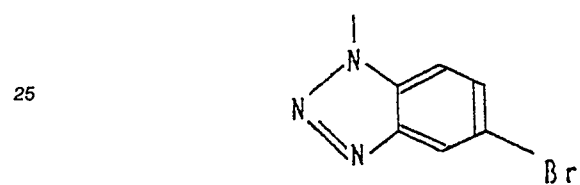
50

55

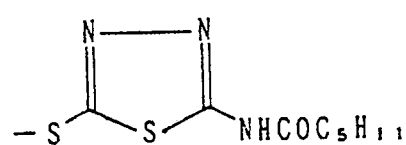
3 3



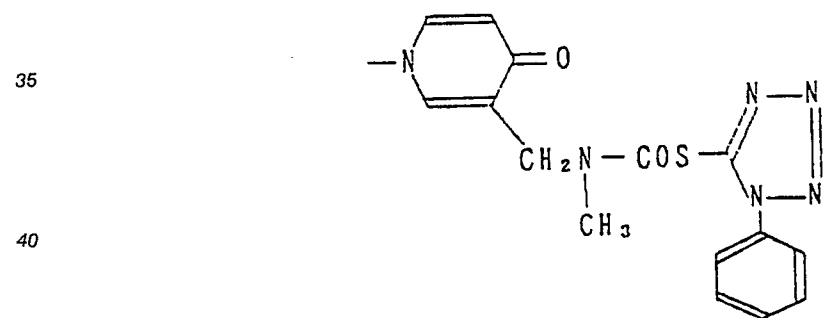
3 4



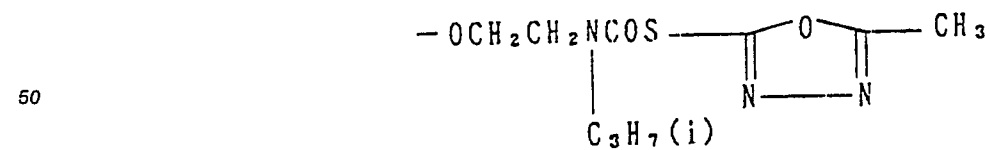
3 5



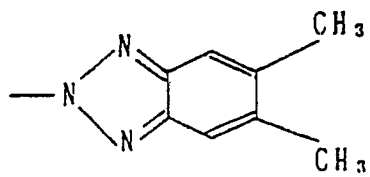
3 6



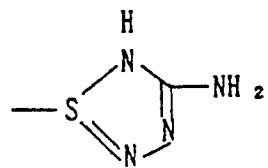
3 7



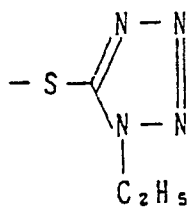
3 8



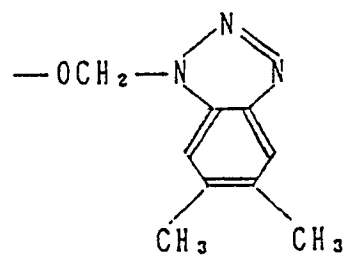
3 9



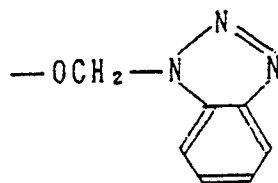
4 0



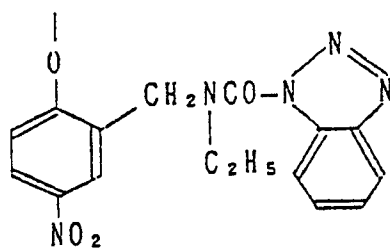
4 1



4 2



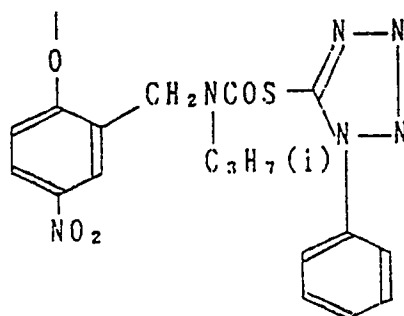
4 3



4 4

5

10

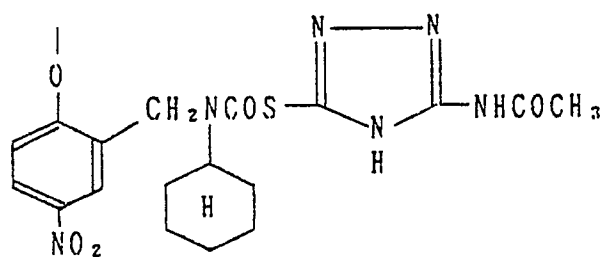


15

4 5

20

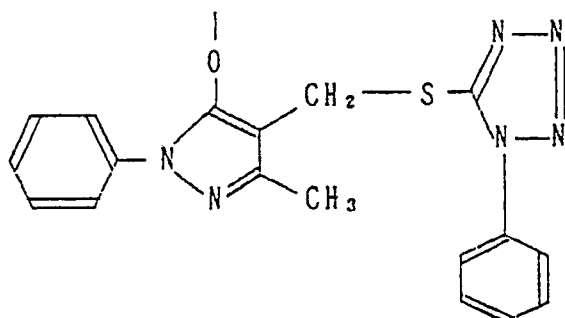
25



30

35

4 6

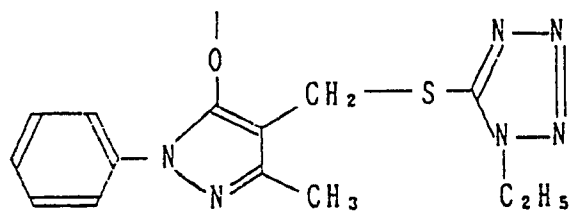


40

4 7

45

50

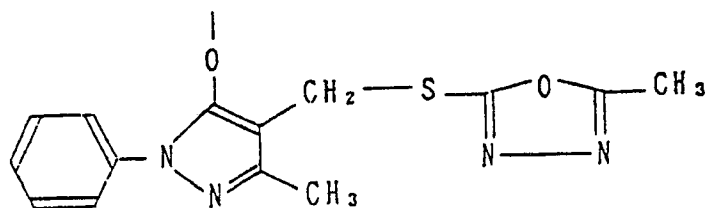


55

4 8

5

10

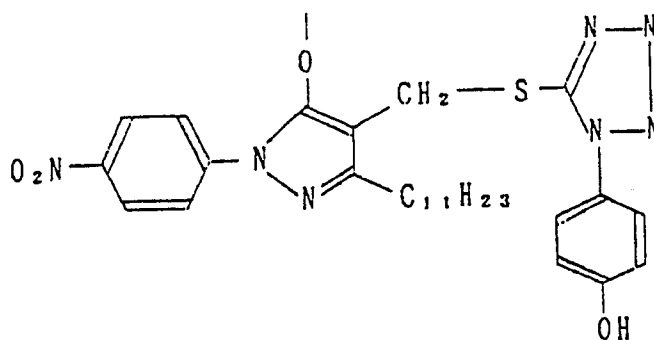


4 9

15

20

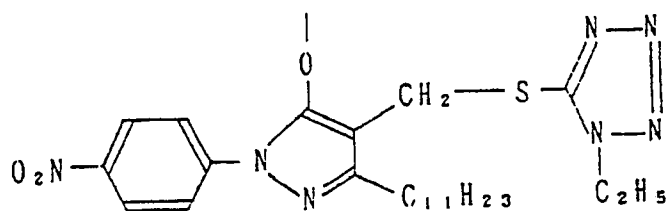
25



5 0

30

35



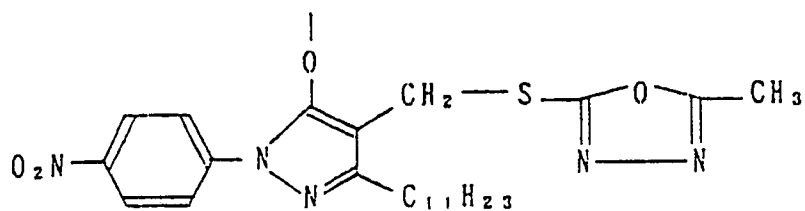
5 1

40

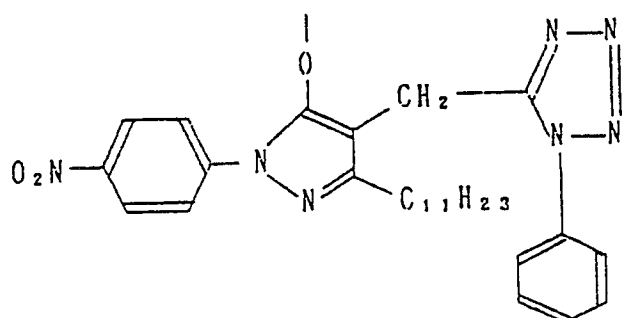
45

50

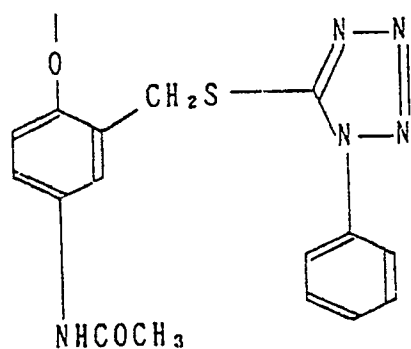
55



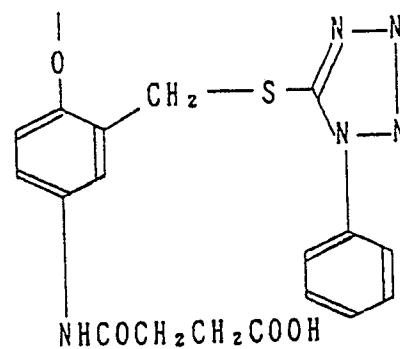
5 2



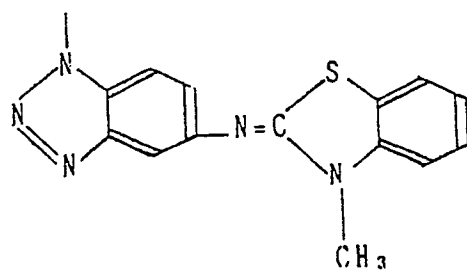
5 3



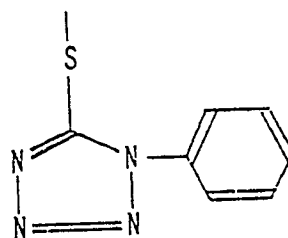
5 4



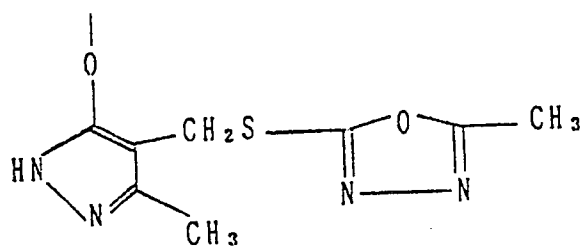
5 5



5 6



5 7





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

In the present invention, the blue light-sensitive layer is preferably a single layer, and further preferably, both the blue light-sensitive layer and the green light-sensitive layer are single layers. Particularly, all of the blue light-sensitive, green light-sensitive and red light-sensitive silver halide emulsion layers are 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 and sharpness are improved, and graininess is also improved. The film thickness is preferably 20 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 (Chemistry of Photography)", p. 393 (published by Shashin Kogyo Shuppansha, Japan, 1982).

More specifically, it is the difference in log H's between the two points where the slope of the tangential line at the leg 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 of the present invention is 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 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.

For obtaining a broad exposure latitude, there is a method in which two kinds of monodispersed grains having different grain sizes and each sensitized are combinedly used. In this case, a mean grain size of the grains having larger grain size is preferably 0.2 to 2.0 μm and that of the grains having smaller grain size is preferably 0.05 to 1.0 μm , and the latter grains have smaller mean grain size than that of the former ones.

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 grains 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 as a mixture.

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 chemically sensitize 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 and sensitizing dyes 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 and VIII in the periodic table of elements. Preferred metal ions may include Au, Zn, Cd, Ti, 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, and the pH of the AgX suspended system during doping is preferably 5 or lower.

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 sensitivities and qualities can be given to the silver halide grains.

With a doping amount of 10^{-2} mole/AgX or less, 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 grains 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. benzthiazolium salt, indazoles, triazoles, benztriazoles and benzimidazoles), heterocyclic mercapto compounds (e.g. mercaptotetrazoles, mercaptothiazoles, mercaptothiadiazoles, mercaptobenzthiazoles, mercaptobenzimidazoles and mercaptopyrimidines), azaindenes (e.g. tetraazaindenes and pentaazaindenes), nucleic acid decomposed products (e.g. adenine and guanine), benzenethiosulfonates and thioketo compounds.

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.

As the position where the desensitizer exists, it is preferably mixed internally of the silver halide grains in the points of preservability of the light-sensitive material and standing stability of the coating solution, and its distribution may be either uniform, localized at the central portion of grain or the intermediate positions, 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 the grain is preferred, 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 desirably has at least one color sensitive layer (e.g. blue light-sensitive layer) containing AgX grains which contain a desensitizer. Preferably, it is the case when the blue light-sensitive layer contains AgX grains which contain a desensitizer, more preferably when the blue light-sensitive layer and the green light-sensitive layer contain them, most preferably when all of the color light-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 ($\bar{r}$) is preferably 0.4 or less, more preferably 0.33 or less, further preferably 0.25 or less, particularly preferably 0.20 or less.

$$S = \sqrt{\frac{\sum (\bar{r} - r_i)^2 n_i}{\sum n_i}}$$

The mean grain size ($\bar{r}$) is defined by the following formula when the number of grains with a grain size r_i (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 n_i :

$$\bar{r} = \frac{\sum n_i \cdot r_i}{\sum n_i}$$

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), pp. 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 preferred, particularly preferably silver iodobromide with respect to sensitivity. The amount of iodine may be preferably 1 mole % to 20 mole %, particularly 3.5 mole % to 12 mole %.

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 40 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 %.

5 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.

10 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.

15 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.

20 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 following Examples, 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.

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

30 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 the conventional manner, and optically sensitized to a desired wavelength region by use of a sensitizing dye.

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

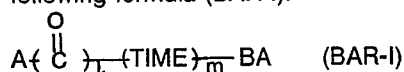
The emulsion layer and other hydrophilic colloid layers can be hardened, and also a plasticizer, a dispersion (latex) of a water-insoluble or difficultly soluble synthetic polymer can be contained therein.

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

40 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, hardeners, antifoggants, chemical sensitizers, spectral sensitizers and desensitizers through the coupling reaction with the oxidized product of the developing agent.

45 Furthermore, by adding a compound which can release a bleaching accelerator or precursor thereof through the reaction with an oxidized product of a color developing agent (hereinafter referred to as "bleaching accelerator releasing compound") in at least one layer of the light-sensitive material of the present invention, bleachability and processing stability can be more improved as compared with the case where it is contained in a light-sensitive material having no single layer.

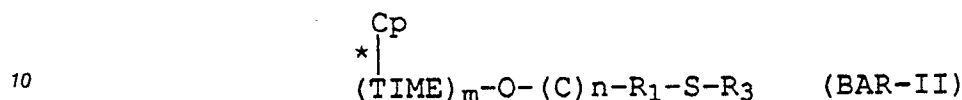
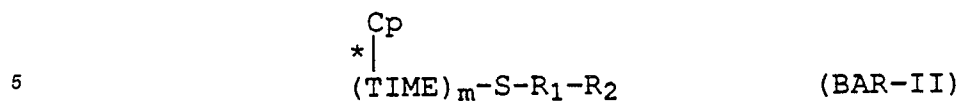
50 The bleaching accelerator releasing compound (BAR compound) may preferably be represented by the following formula (BAR-I).



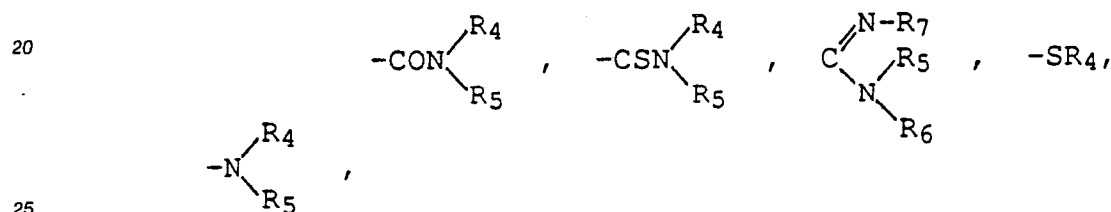
55 wherein A is a coupler residue which can be subjected to a coupling reaction with an oxidized product of a color developing agent, or a residue of an oxidation-reduction nucleus which can be cross-oxidized with an oxidized product of a color developing agent; TIME is a timing group; BA is a bleaching 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).



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; R₁ is an aliphatic group, an aromatic group, a saturated heterocyclic group or a 5- or 6-membered aromatic nitrogen-containing heterocyclic group; R₂ is a water solubilizing substituent or its precursor; R₃ is a hydrogen atom, a cyano group, -COR₄, -CSR₄,



or a heterocyclic group, in which R₄ is an aliphatic group or an aromatic group, R₅, R₆ and R₇ 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 Literaturverisicht 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.

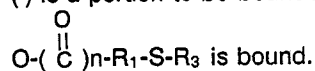
The representative examples of a cyan coupler residue are described in U.S. Patents No. 2,367,531, No. 2,423,730, No. 2,474,293, No. 2,772,162, No. 2,395,826, No. 3,002,836, No. 3,034,892, No. 3,041,236 and No. 4,666,999 and in the above-mentioned Agfa Mitteilung (Band II), pp. 156 to 175 (1961). Of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

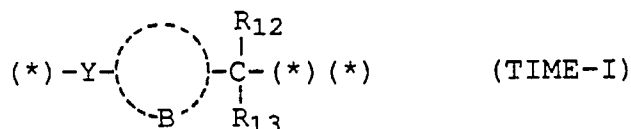
(*) is a portion to be bounded to an active position of Cp; and (**) is a portion to which -S-R₁-R₂ or



(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.

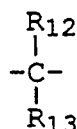
Of these, groups represented by the following formulae (TIME-I) and (TIME-II) are preferred.



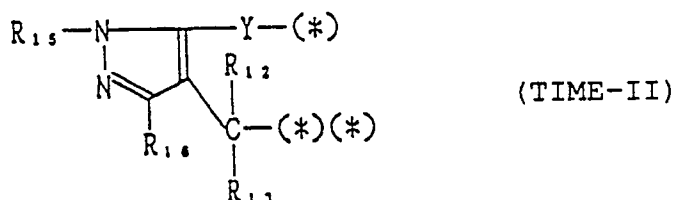
wherein B is a group of atoms necessary for the formation of a benzene ring or a naphthalene ring; Y is -O-, -S- or



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



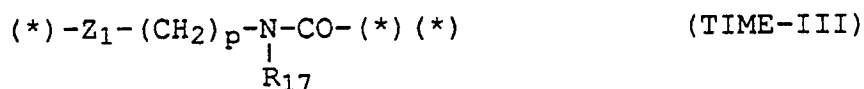
group is substituted at the ortho-or para-position relative to Y.

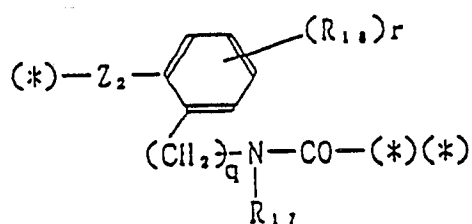


wherein Y, R_{12} and R_{13} are as described above; R_{15} is a hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfon group, an alkoxycarbonyl group or a heterocyclic group; and R_{16} is a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an amino group, an acylamino group, a sulfonamido group, a carboxy group, an alkoxycarbonyl group, a carbamoyl group or a cyano group.

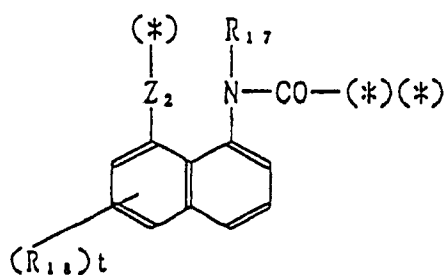
(2) A group which causes a cleavage reaction by using an intramolecular nucleophilic substitution reaction.

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).



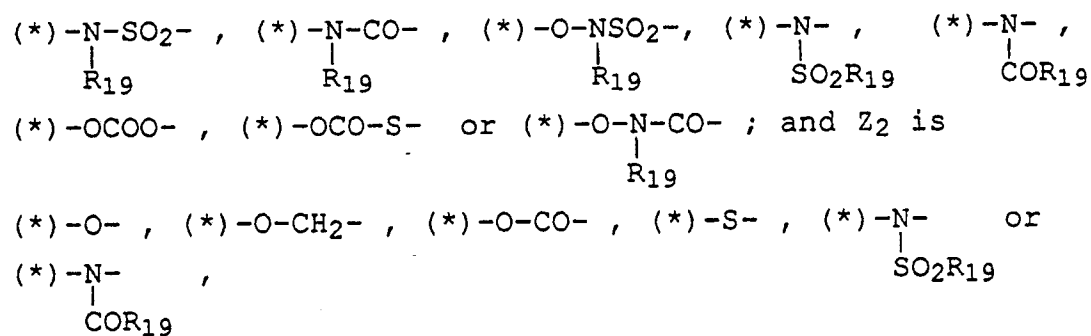


(TIME-IV)

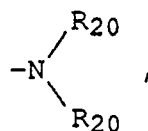


(TIME-V)

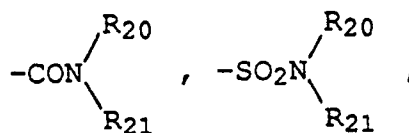
wherein Z_1 is $(*)-O-$, $(*)-O-CO-$, $(*)-O-CON-$, $(*)-S-$, $(*)-N-SO_2-$, $(*)-N-CO-$, $(*)-O-NSO_2-$, $(*)-N-SO_2R_{19}$, $(*)-N-COR_{19}$, $(*)-OCO-$, $(*)-OCO-S-$ or $(*)-O-N-CO-$; and Z_2 is



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, $-O-R_{20}$, $-S-R_{20}$, $-OCO-R_{20}$, $-OSO_2R_{20}$,



$-N-CO-R_{21}$, $-N-SO_2-R_{21}$, $-COOR_{20}$,



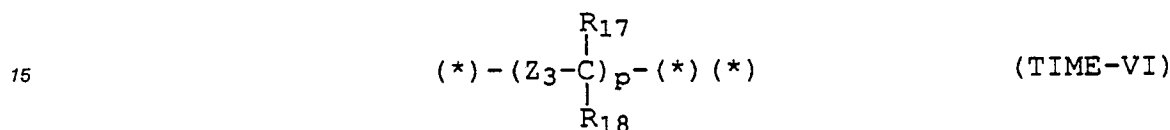
a cyano group, a halogen atom or a nitro group. R_{20} and R_{21} may be either identical or different and each are the same group as that represented by R_{19} ; p is an integer of 1 to 4, q is 0, 1 or 2; r is an integer of 1 to 4; t is an integer of 1 to 3; when r or t is 2 or more, R_{18} may be either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

5

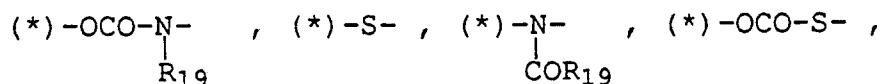
(3) A group which uses a cleavage reaction of hemiacetal

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

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



20 wherein Z_3 represents $(*)-O-$, $(*)-OCO-O-$, $(*)-\overset{\overset{R_{17}}{|}}{\underset{\underset{SO_2 R_{19}}{|}}{N}}-$,

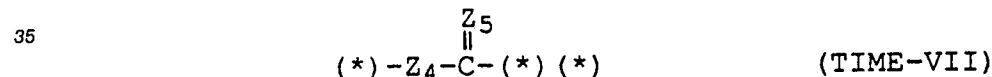


25

$(*)-OCH_2-O-$ 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).

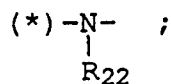
30

(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.



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

40



45

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.

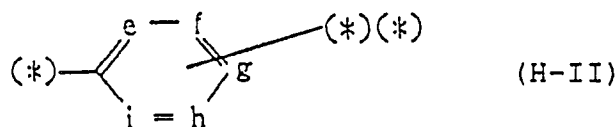
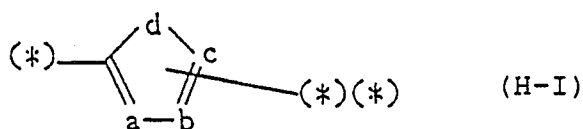
50

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.

55

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).

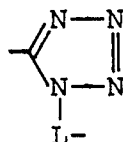


wherein a, b, c, e, f, g, h and i each are a nitrogen atom or a methyn group; d is an oxygen atom, a sulfur atom or an imino group; (*) is a position to which Cp-(TIME)_m-S-

or Cp-(TIME)_m-O-($\text{C} \begin{smallmatrix} \text{O} \\ \parallel \end{smallmatrix} \text{C} \end{smallmatrix})_n$ - is bound; and (*) (*) is a position to which R₃-S- or R₂ is bound.

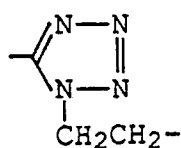
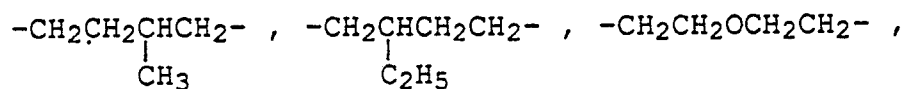
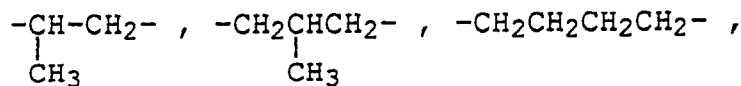
In the above formula, at least one of e, f, g, i and h is a nitrogen atom.

R₁ may more preferably be an aliphatic group or

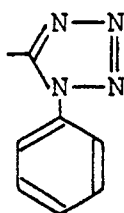


wherein L represents a divalent aliphatic group or a phenylene group having a carbon number of 1 to 8.

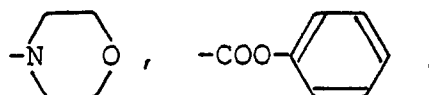
The preferred examples of R₁ include -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-,



and



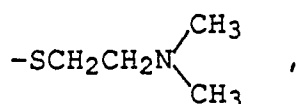
The preferred examples of an water-solubilizing substituent or its precursor represented by R₂ include -COOH, -COONa, -COOCH₃, -COOC₂H₅, -NHSO₂CH₃, -NHCOOCH₃, -NHCOOC₂H₅, -SO₃H, -SO₃K, -OH,



-SO₂NH₂, -NR₁₀R₁₁,

wherein R₁₀ and R₁₁ each are a hydrogen atom or an alkyl group having a carbon number of 1 to 4,

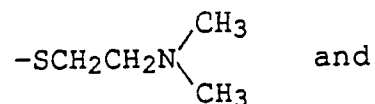
-CONH₂, -COCH₃, -NHCOCH₃, -CH₂CH₂COOH, -CH₂CH₂NH₂, -SCH₂COOH,



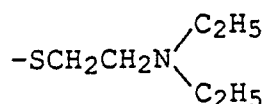
5

$-\text{CH}_2\text{COOH}$, $-\text{SCH}_2\text{CONH}_2$, $-\text{SCH}_2\text{COCH}_3$ and $-\text{SCH}_2\text{CH}_2\text{COOH}$;
and the particularly preferred examples of the bleaching accelerator or precursor thereof represented by $-\text{S}-$
 R_1-R_2 include $-\text{SCH}_2\text{CH}_2\text{COOH}$, $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{COOH}$,

10

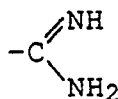


15



20

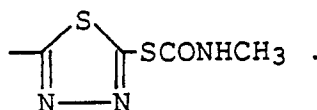
The preferred examples of R_3 include H , $-\text{CN}$, $-\text{COH}$, $-\text{COCH}_3$, $-\text{COCH}_2\text{OCH}_3$, $-\text{COCF}_3$, $-\text{CSCH}_3$,
 $-\text{CON}(\text{CH}_3)_2$, $-\text{CON}(\text{C}_2\text{H}_5)_2$, $-\text{CSN}(\text{CH}_3)_2$,



25

$-\text{SCH}_3$, $-\text{SCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$, $-\text{SCH}_2\text{CH}_2\text{OH}$, $-\text{SCH}_2\text{CH}_2\text{COOH}$, $-\text{NHCH}_3$, $-\text{NHCH}_2\text{CH}_2\text{COOH}$ and

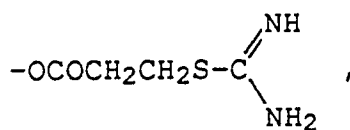
30



35

The particularly preferred examples of a bleaching accelerator or its precursor represented by
 $-\text{O}-\left(\text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \right)_n-\text{R}_1-\text{S}-\text{R}_3$ include $-\text{OCOCH}_2\text{CH}_2\text{SH}$, $-\text{OCH}_2\text{CH}_2\text{SH}$,

40



45

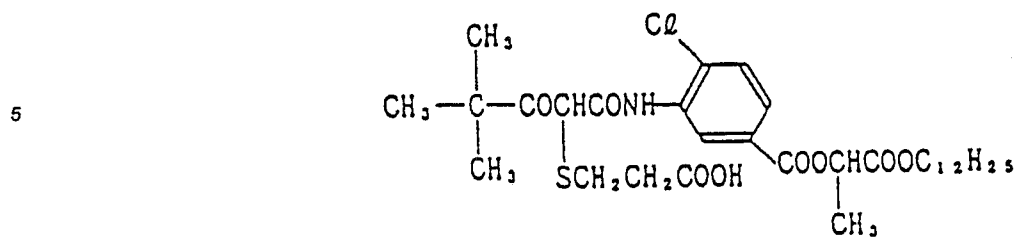
$-\text{OCOCH}_2\text{CH}_2\text{SCOCH}_3$, $-\text{OCOCH}_2\text{CH}_2\text{SCSCH}_3$, $-\text{OCOCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{COOH}$,
 $-\text{OCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{OH}$ and $-\text{OCOCH}_2\text{CH}_2\text{SCN}$.

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.

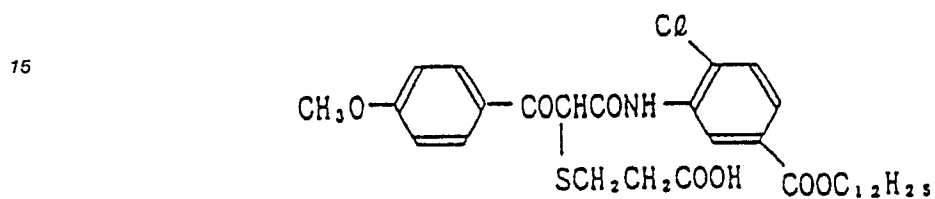
50

55

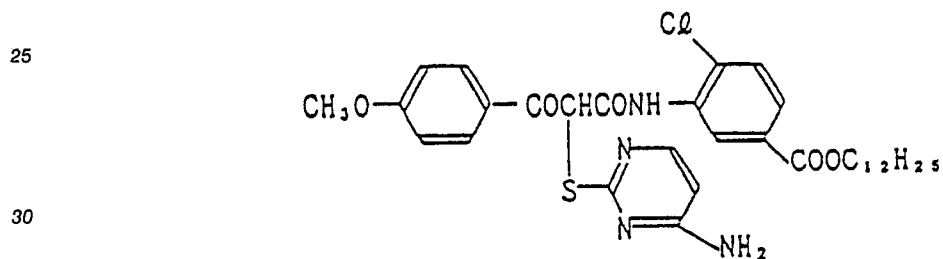
BAR - 1



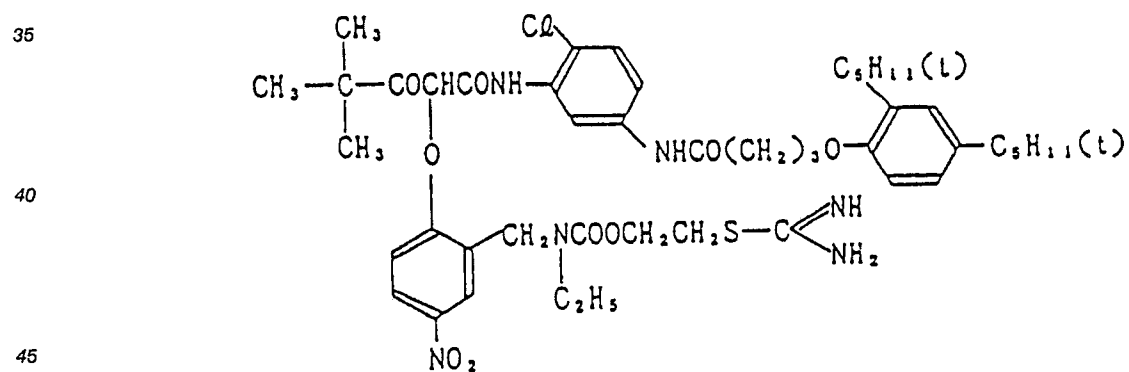
BAR - 2



BAR - 3



BAR - 4

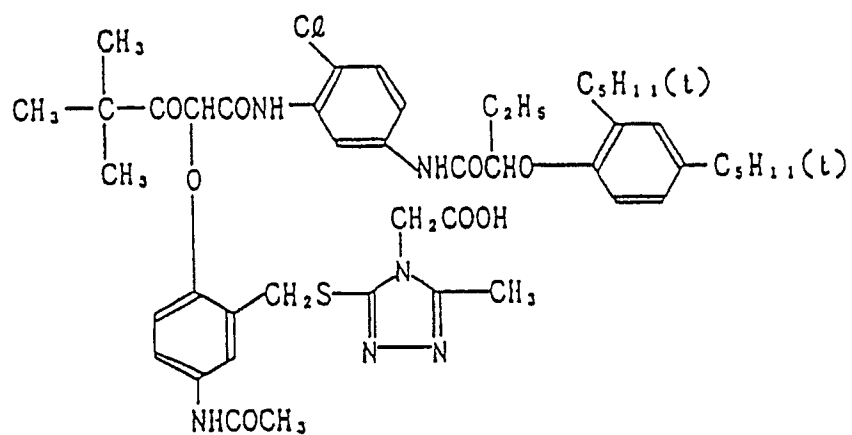


BAR - 5

5

10

15

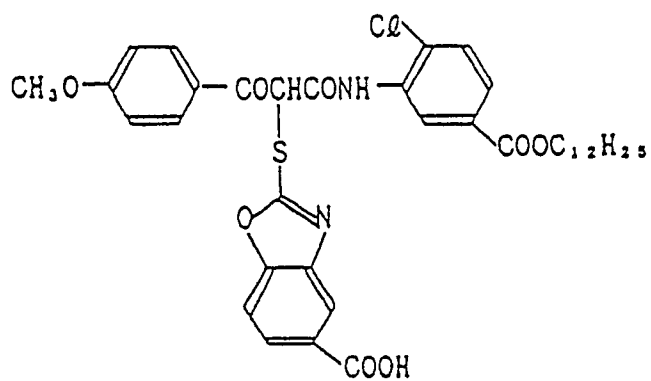


BAR - 6

20

25

30



BAR - 7

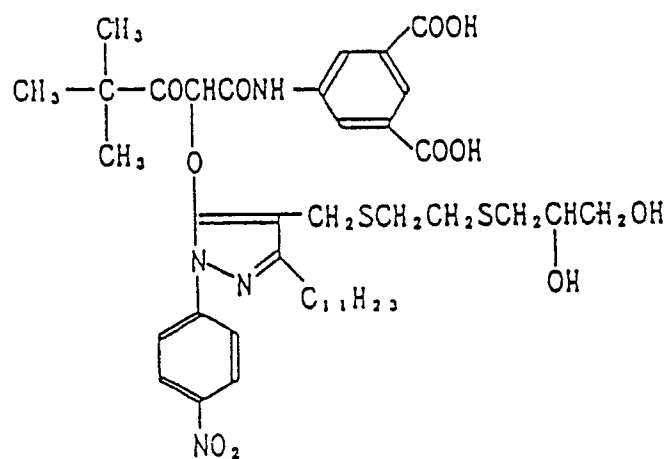
35

40

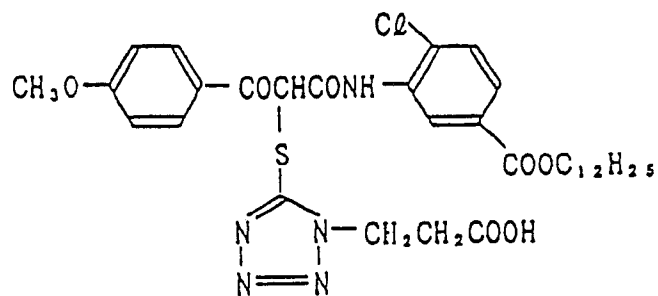
45

50

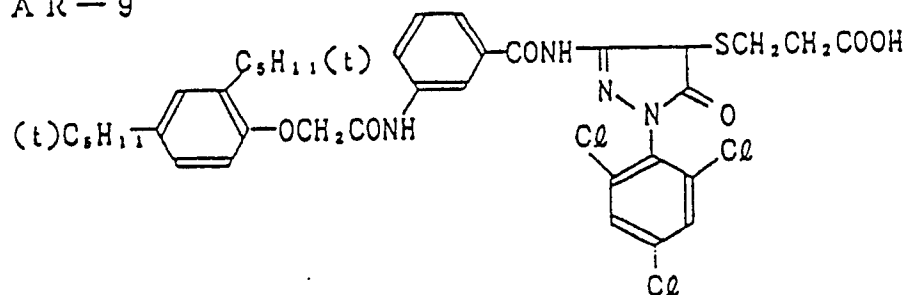
55



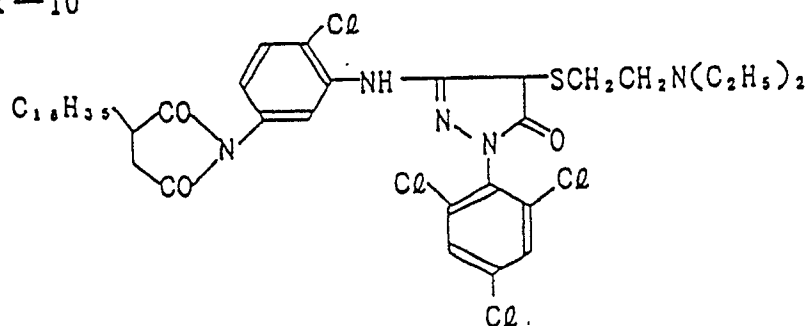
BAR-8



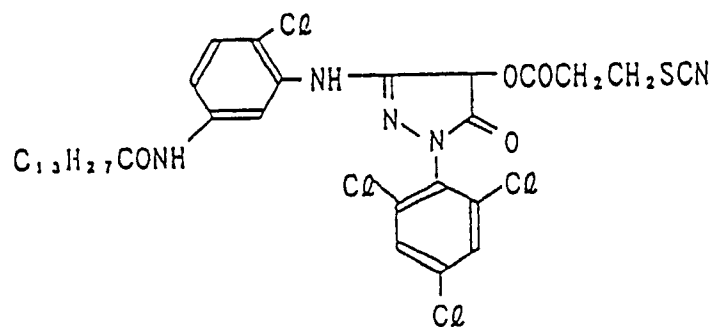
BAR-9



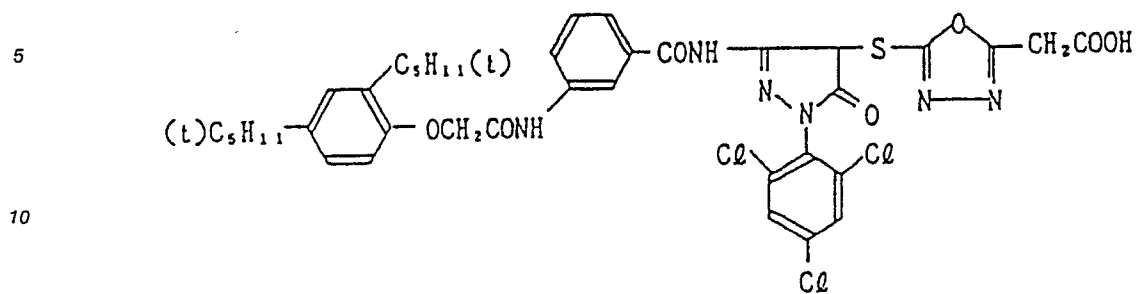
BAR-10



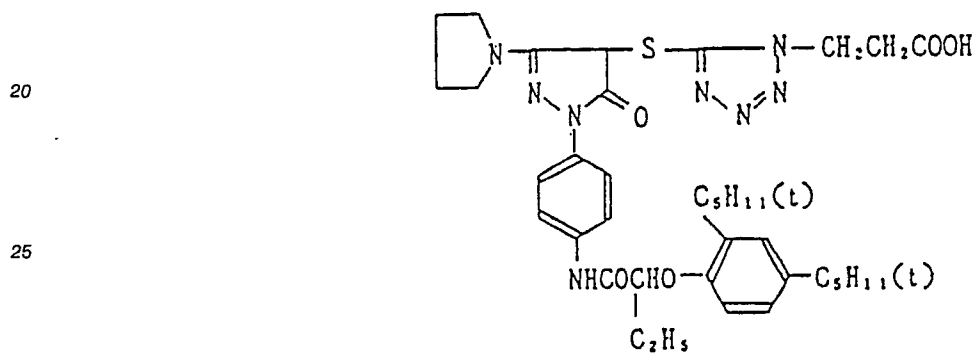
BAR-11



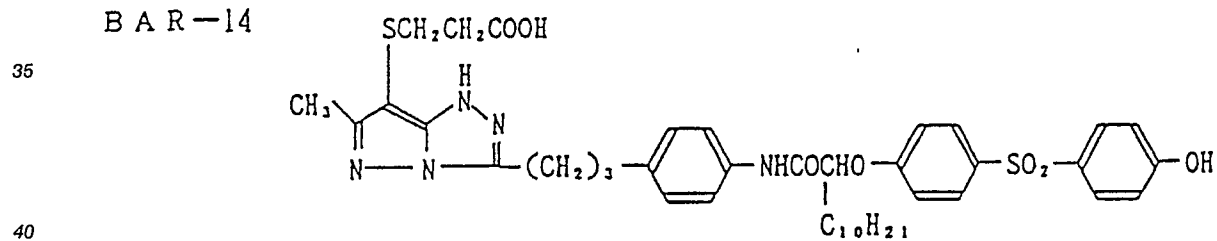
BAR-12



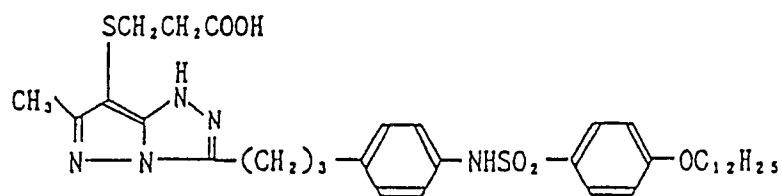
BAR-13



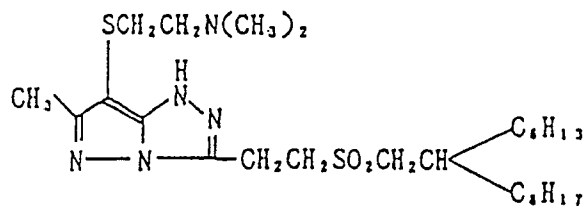
BAR-14



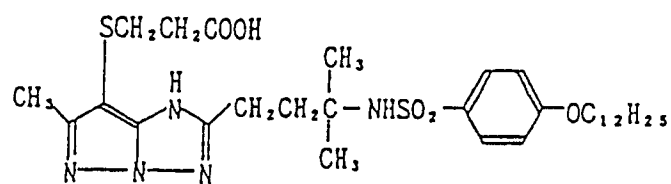
BAR-15



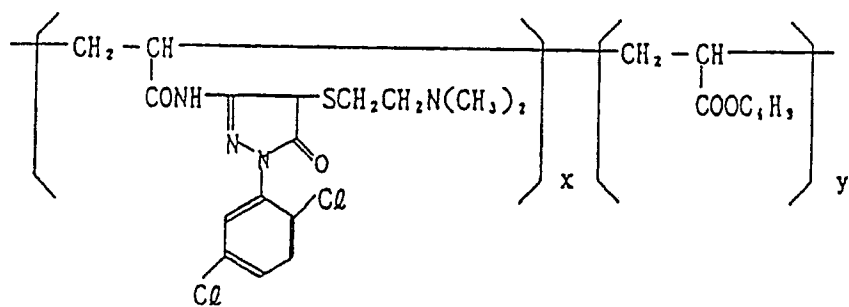
BAR-16



BAR-17

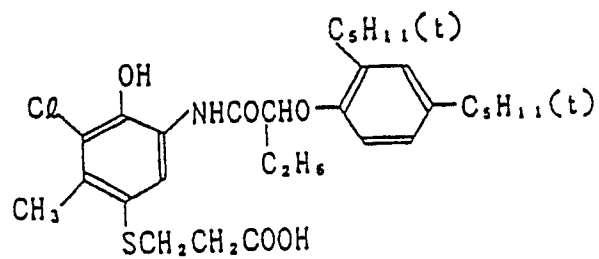


BAR-18

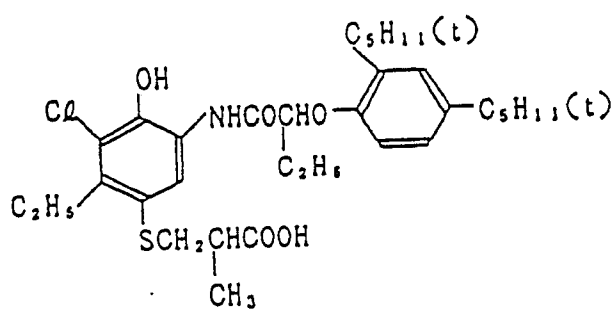


x:y=50:50 (weight ratio)

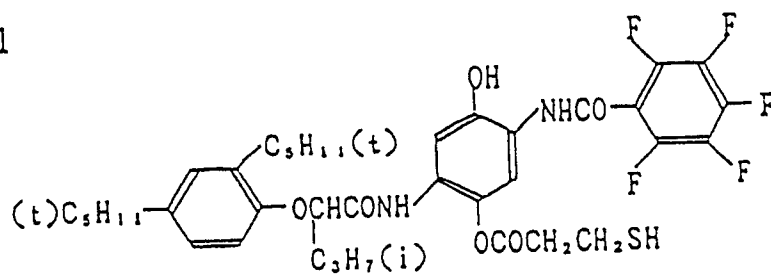
B A R - 19



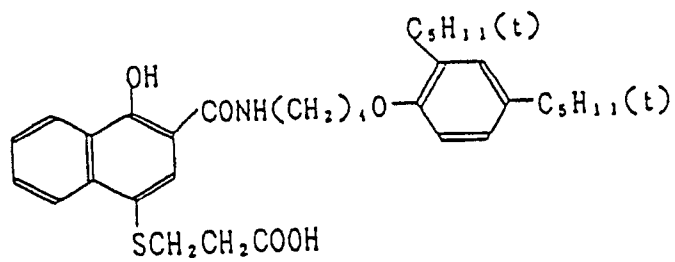
B A R - 20



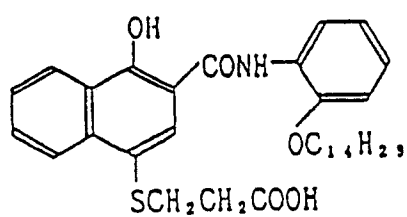
B A R - 21



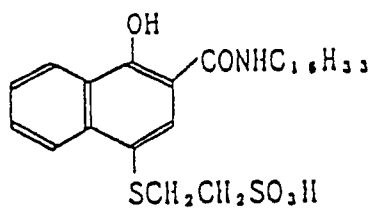
B A R - 22



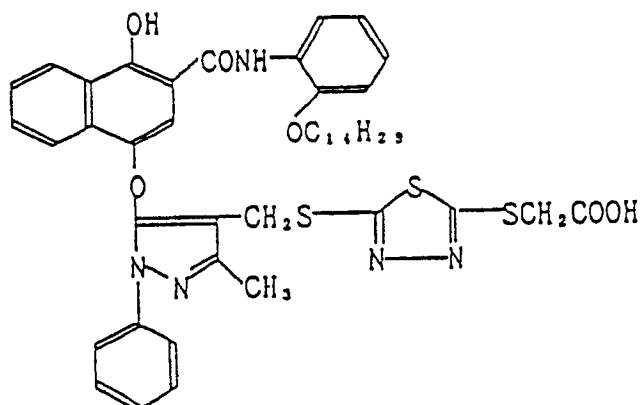
B A R - 23



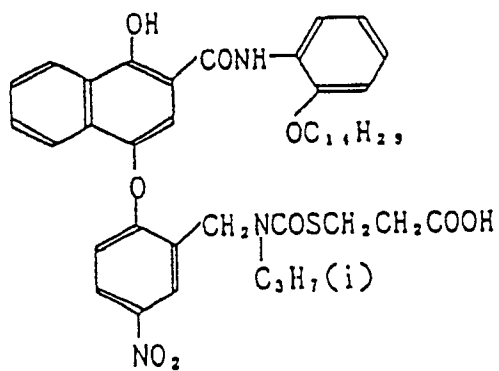
B A R - 24



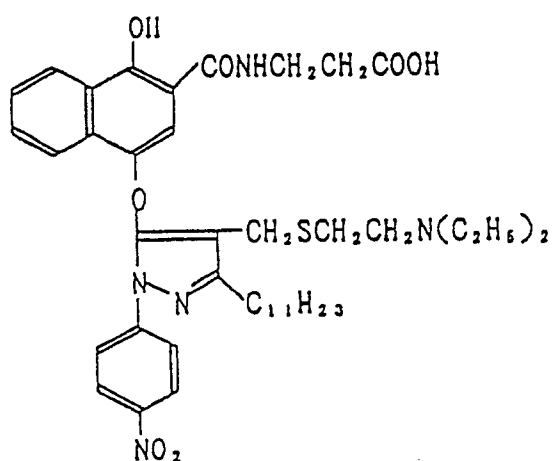
B A R - 25



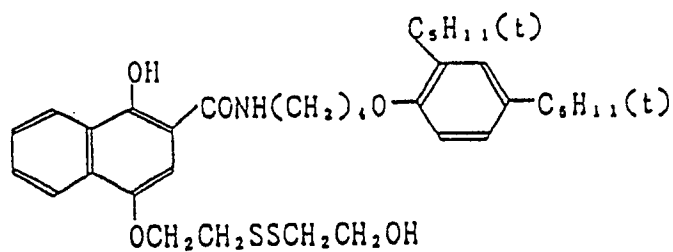
B A R - 26



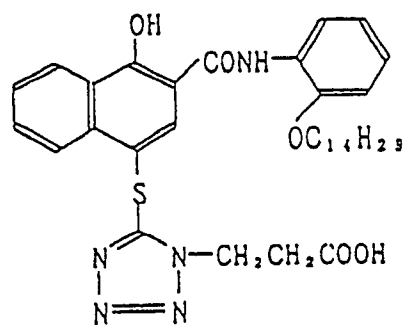
BAR - 27



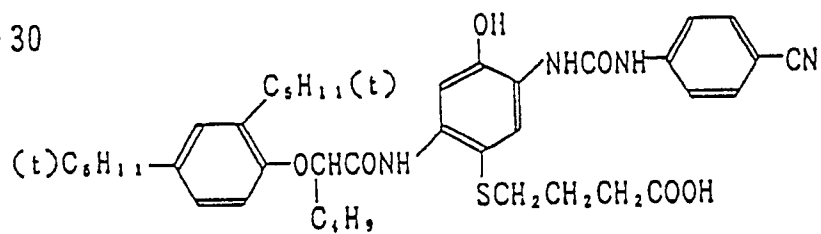
BAR - 28



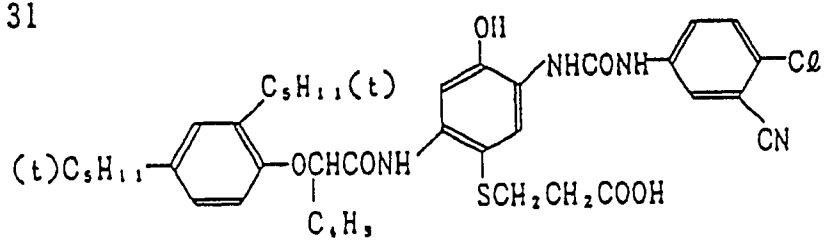
BAR - 29



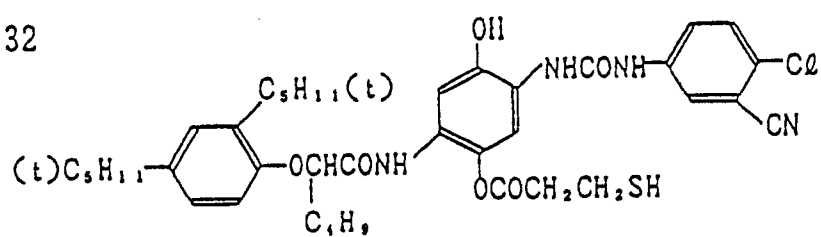
BAR - 30



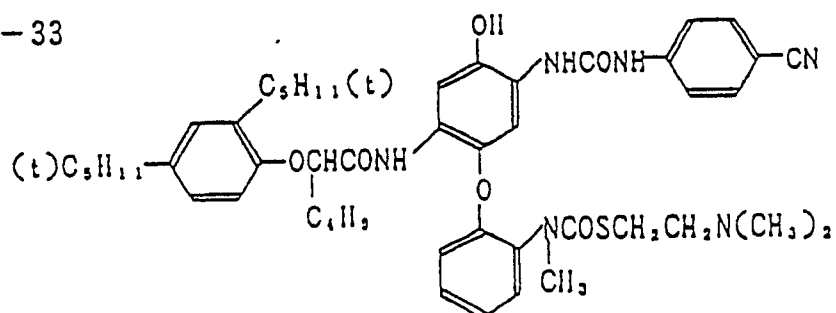
BAR-31



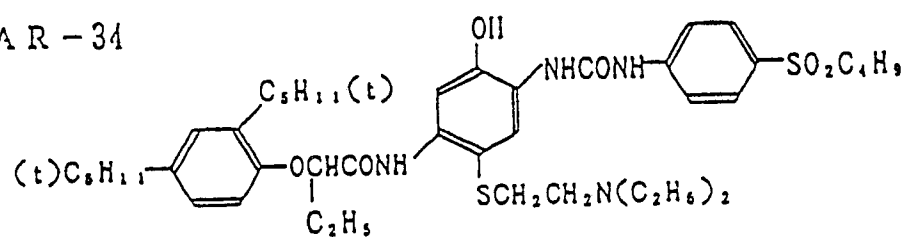
BAR-32



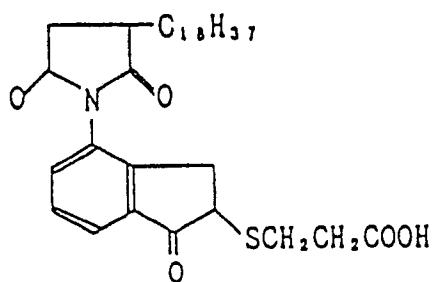
BAR-33



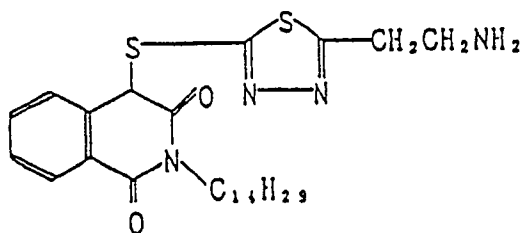
BAR-34



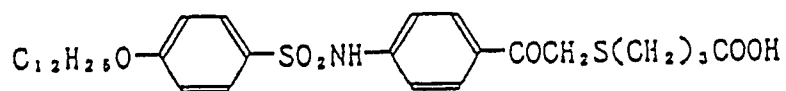
B A R - 35



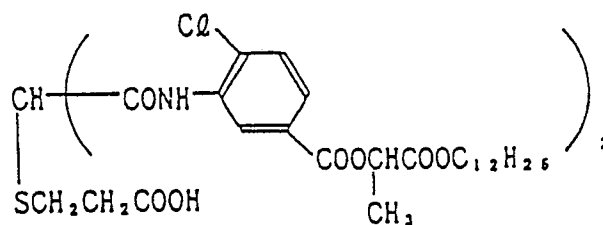
B A R - 36



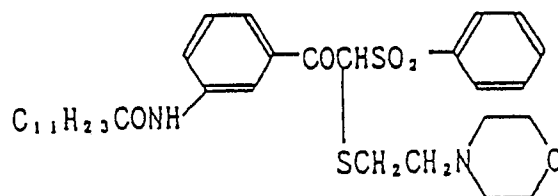
B A R - 37



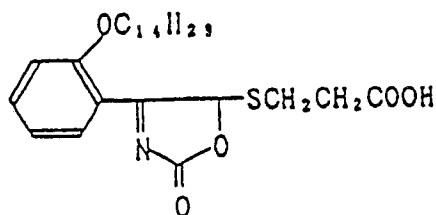
B A R - 38



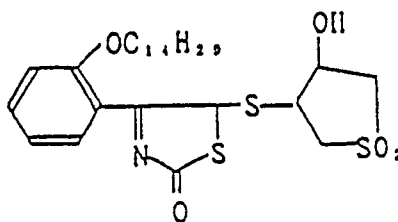
B A R - 39



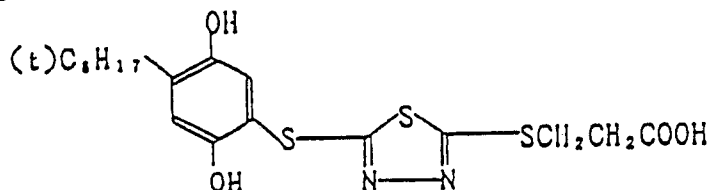
BAR - 40



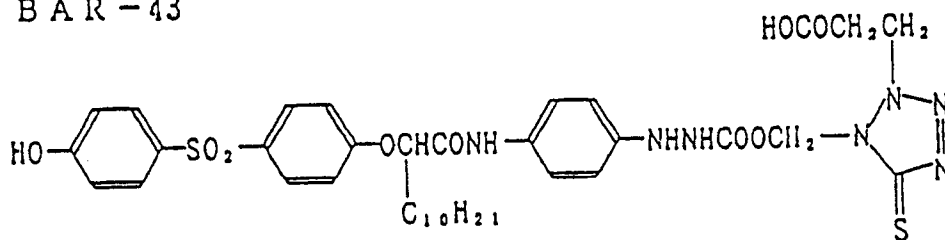
BAR - 41



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 and anti-irradiation layer 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, anti-color foggant, developing accelerator, developing retarder or bleaching accelerator 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 improvement in storage stability has been more 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 is 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 monodispersed emulsion

Into a reaction kettle in which an aqueous gelatin solution had been thrown, while controlling the pAg and the pH in the reaction kettle and also controlling the addition time, were added at the same time an aqueous silver nitrate solution, 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 kettle (NE-2). The emulsions and their contents are shown in Table 1.

Table 1

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

In a reaction kettle in which the above seed emulsion and an aqueous gelatin had been added, while controlling the pAg and the pH in the reaction kettle, 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 the seed emulsion, gelatin was added to effect re-dispersion to give an emulsion having pAg 7.8 and pH 6.0. Thus, silver iodobromide emulsions EM-1 to EM-3 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 (mole %)	Seed emulsion	Variation coefficient
EM - 1	0.65	6.5	NE - 1	0.20
EM - 2	0.38	7.0	NE - 1	0.19
EM - 3	0.38	7.0	NE - 1 ^{*1}	0.19
			NE - 2	

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

Example 1

Preparation of Sample No. 101 (Comparative)

On a cellulose acetate support applied with subbing treatment was prepared a multi-layer color light-sensitive material 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 additives and gelatin, and further in moles per mole of silver halide within the same layer for the 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.

EP 0 383 637 A2

	<u>Layer</u>	<u>Main composition</u>	<u>Amount used</u>
	First layer (HC)	Black colloidal silver	0.20
5	(halation pre-ventive layer)	Gelatin	1.5
		UV-ray absorber UV-1	0.1
		UV-ray absorber UV-2	0.2
10		Dioctyl phthalate (abbreviated as DOP)	0.03
	Second layer(IL-1)	Gelatin	2.0
15	(Intermediate layer)	Antistaining agent (AS-1)	0.1
		DOP	0.1
20	Third layer(R-1)	EM-2	1.2
	(First red-sensitive emulsion layer)	Gelatin	1.1
		Sensitizing dye I	6×10^{-4}
25		Sensitizing dye II	1×10^{-4}
		Coupler (C-1)	0.085
30			
35			
40			
45			
50			
55			

		Coupler (CC-1)	0.005
		DIR compound (D-23)	0.0015
5		DIR compound (D-42)	0.002
		DOP	0.6
10	Fourth layer(R-2)	EM-1	1.3
	(Second red-	Gelatin	1.1
	sensitive emulsion	Sensitizing dye I	3×10^{-4}
15	layer)	Sensitizing dye II	1×10^{-4}
		Coupler (C-2)	0.007
		Coupler (C-3)	0.027
		Coupler (CC-1)	0.0015
20		DIR compound (D-42)	0.001
		DOP	0.2
25	Fifth layer(IL-2)	Gelatin	0.8
	(Intermediate	AS-1	0.03
	layer)	DOP	0.1
30	Sixth layer(G-1)	EM-2	1.3
	(First green-	Gelatin	1.2
	sensitive	Sensitizing dye III	2.5×10^{-4}
35	emulsion layer)	Sensitizing dye IV	1.2×10^{-4}
		Coupler (M-2)	0.09
		Coupler (CM-1)	0.004
40		DIR compound (D-23)	0.001
		DIR compound (D-26)	0.003
		Tricresyl phosphate	0.5
45		(abbreviated as TCP)	
	Seventh layer(G-2)	EM-1	1.4
	(Second green-	Gelatin	0.8
50	sensitive	Sensitizing dye III	1.5×10^{-4}
	emulsion layer)	Sensitizing dye IV	1.0×10^{-4}
		Coupler (M-1)	0.03
55		Coupler (CM-1)	0.002

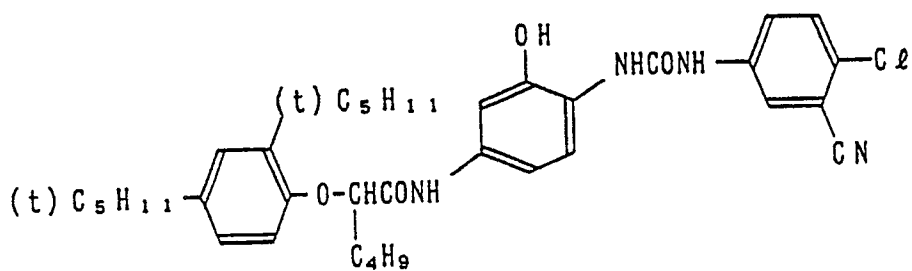
EP 0 383 637 A2

		DIR compound (D-26)	0.001
5		TCP	0.3
	Eighth layer (YC)	Gelatin	0.6
10	(Yellow filter layer)	Yellow colloidal silver	0.08
		AS-1	0.1
		DOP	0.3
15	Ninth layer (B-1)	EM-2	0.5
	(First blue-sensitive emulsion layer)	Gelatin	1.1
		Sensitizing dye V	1.3×10^{-4}
20		Coupler (Y-1)	0.29
		TCP	0.2
25	Tenth layer (B-2)	EM-1	0.5
	(Second blue-sensitive emulsion layer)	Gelatin	1.2
		Sensitizing dye V	1×10^{-4}
30		Coupler (Y-1)	0.08
		DIR compound (D-42)	0.003
		TCP	0.1
35	Eleventh layer	Gelatin	0.55
	(Pro-1)	UV-ray absorber UV-1	0.1
	(First protective layer)	UV-ray absorber UV-2	0.2
40		DOP	0.03
		Silver iodobromide AgI 1 mol%	0.5
		mean grain size 0.07 μm	
45	Twelfth layer	Gelatin	0.5
	(Pro-2) (Second protective layer)	Polymethyl methacrylate grains (diameter 1.5 μm)	0.2
50		Formalin scavenger (HS-1)	3.0
		Hardener (H-1)	0.4

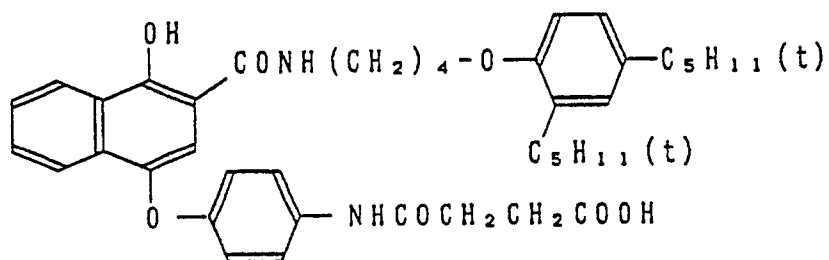
55

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

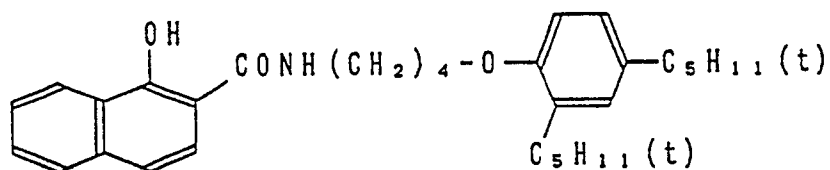
C - 1



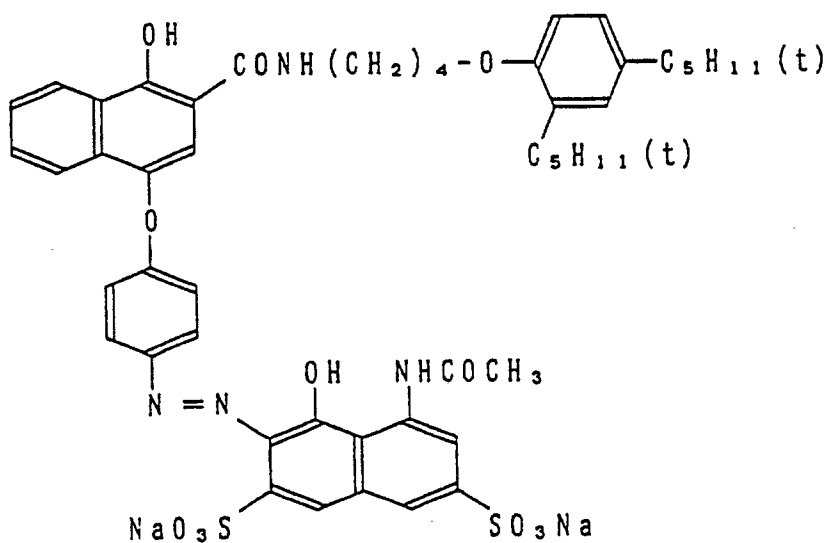
C - 2



C - 3



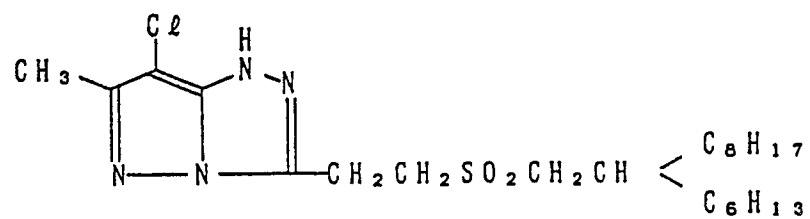
CC - 1



M - 1

5

10



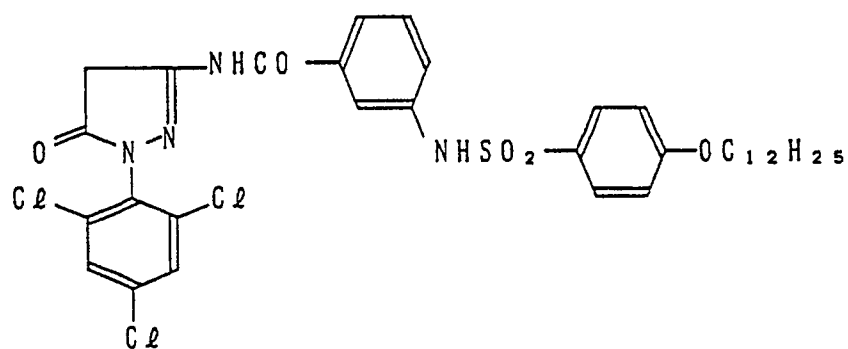
15

M - 2

20

25

30



Y - 1

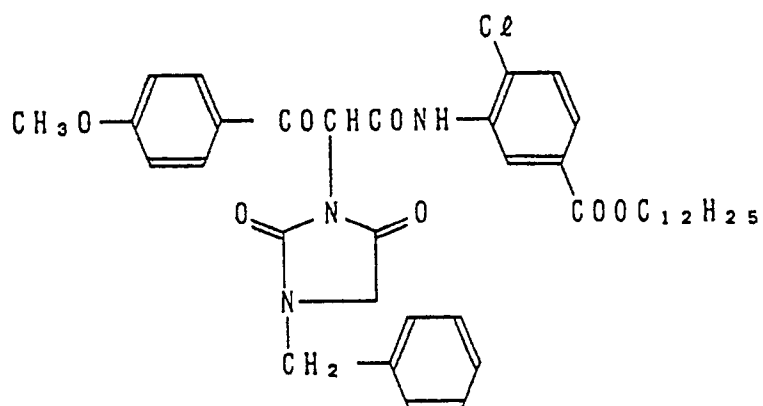
35

40

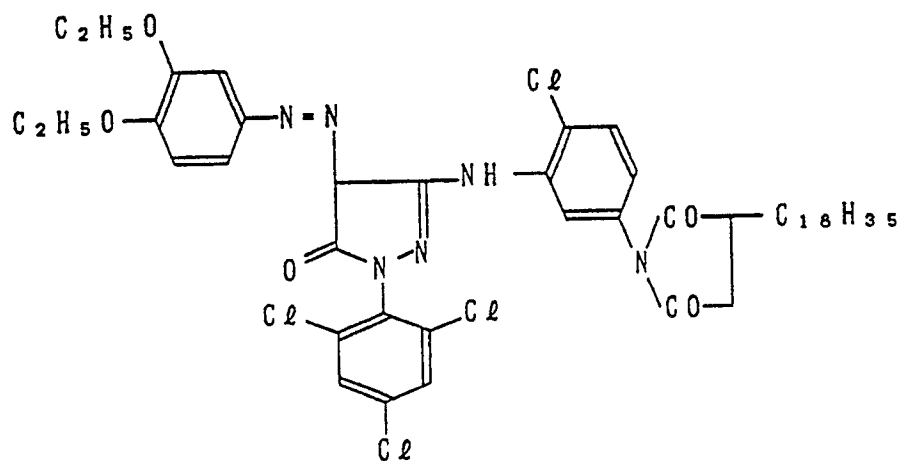
45

50

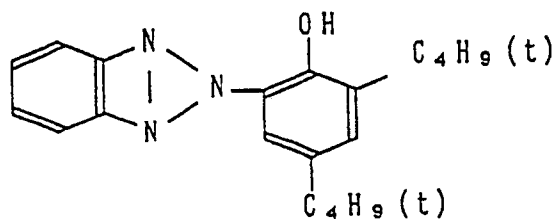
55



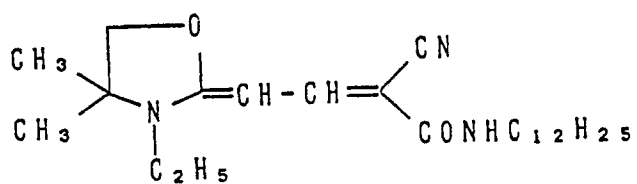
CM - 1



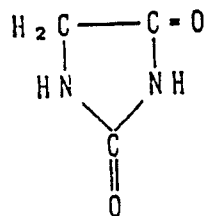
UV - 1



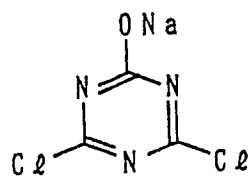
UV - 2



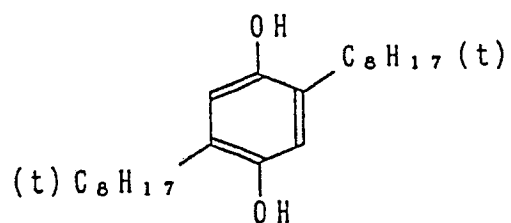
HS - 1



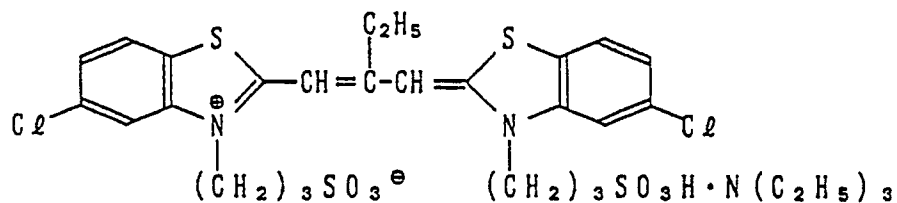
H - 1



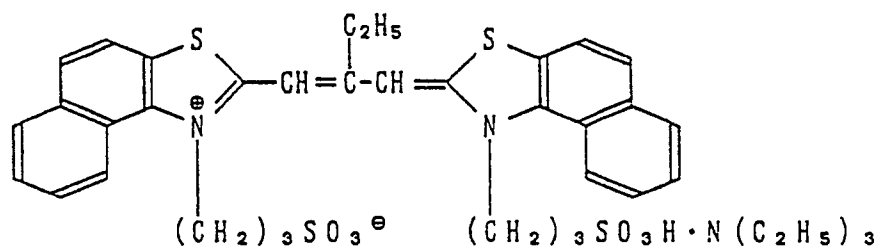
AS - 1



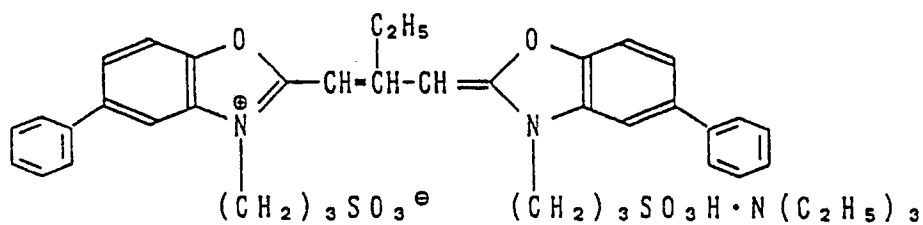
Sensitizing dye I



Sensitizing dye II



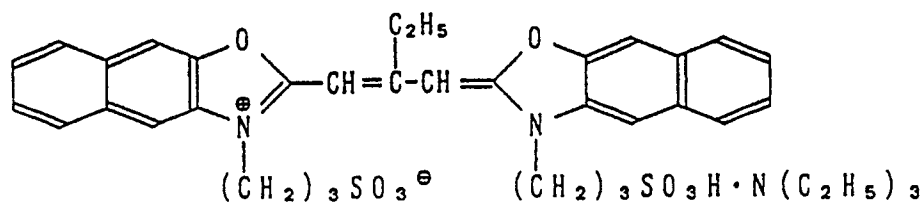
Sensitizing dye III



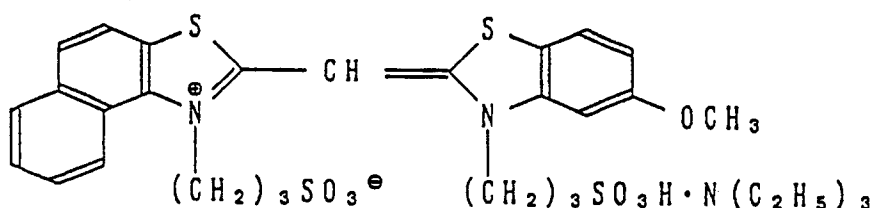
50

55

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 and Pro-2.

Next, Samples No. 102 to No. 108 were prepared.

Samples No. 102 and No. 103 were prepared in the same manner as Sample No. 101 except for changing the amount of the coupler Y-1 contained in B-2 of Sample No. 101 to 0.06 mole/mole AgX, and adding 0.02 mole/mole AgX of the DSR compound indicated in Table 3 in place of D-42.

Sample No. 104 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 %, and further adding 0.011 mole/mole AgX of the DIR compound D-42 (the amounts of the sensitizing dye and the coupler of B-1 per mole of silver halide are the same as in Sample No. 101).

Samples No. 105 and No. 106 were prepared in the same manner as Sample No. 104 except for changing the coupler Y-1 contained in B-1 of Sample No. 104 to 0.22 mole/mole AgX, and adding 0.07 mole/mole AgX of the DSR compound indicated in Table 3 in place of D-42.

Samples No. 107 and No. 108 were prepared in the same manner as Sample No. 105 except for adding 0.011 mole/mole AgX of the DIR compound indicated in Table 3 in B-1 of Sample No. 105.

For the samples thus obtained, sensitivity and gradation stability to processing fluctuations were evaluated. Each sample was subjected to wedge exposure in conventional manner and processed with the following processing steps as the standard.

The results are shown in Table 3.

Sensitivity is shown in terms of the reciprocal number of the exposure dose necessary for imparting a density of the minimum density + 0.1 as a relative value to that of Sample No. 101 which is made 100, and the results of the green-sensitive layers are shown in Table 3.

Gradation stability to processing fluctuations was evaluated when developed at the color developer with a pH of 9.8 with the gradation when processed according to the processing steps shown below as the standard.

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 a density of the minimum density + 1 in Fig. 1 to the exposure point of $\Delta \log H = +3.0$ ($\Delta \log H = 0.15$ between the respective exposure points).

Here from Fig. 2, the absolute values $\Delta \gamma$ of the difference of the point gamma value 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 1000 ($\Delta \bar{\gamma}$) and value of Σ of the standard deviation σ of $\Delta \gamma$ multiplied by 1000. Thus, the difference in

point gamma between the both characteristics 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.

5

10

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

15

Compositions of the processing solutions used in the respective processing steps are shown below.

20

25

(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.	

30

35

40

(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 aqueous ammonia.	

45

50

55

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

EP 0 383 637 A2

(Stabilizing solution)	
Formalin (37 % aqueous solution)	1.5 ml
Konidax (manufactured by Konica Corp.)	7.5 ml
Made up to one liter with addition of water.	

5

10

15

20

25

30

35

40

45

50

55

Table 3

	Sample No.	Constitution of light-sensitive layer			DIR compound and DSR compound added in blue-sensitive emulsion layer	Sensitivity	Gradation stability to processing fluctuations	
		B*1	G*2	R*1			$\Delta\bar{y}$	Σ
Comparative	101	Double layer	Double layer	Double layer	D-42	100	105	77
	102	Double layer	Double layer	Double layer	DSR-2	109	99	72
	103	Double layer	Double layer	Double layer	DSR-39	113	98	73
	104	Single layer	Double layer	Double layer	D-42	101	95	71
This invention	105	Single layer	Double layer	Double layer	DSR-2	111	81	65
	106	Single layer	Double layer	Double layer	DSR-39	112	83	66
	107	Single layer	Double layer	Double layer	DSR-2 D-42	110	83	65
	108	Single layer	Double layer	Double layer	DSR-2 D-29	112	80	64

*1 Blue-sensitive emulsion layer,

*2 Green-sensitive emulsion layer,

*3 Red-sensitive emulsion layer.

As is apparent from Table 3, the samples of the present invention were found to have high sensitivity and also good gradation stability to processing fluctuations. Also, when graininess by printing was evaluated, the samples by using in combination the DSR compound and the DIR compound in a single layer (No. 107 and No. 108) were found to have better graininess.

Also, in the respective samples by use of DSR-15, DSR-32 and DSR-38 in place of DSR-39 of B-1 in Sample No. 106, the effects of the present invention could be recognized.

Further, Sample No. 102 and Sample No. 105 in which a blue-sensitive emulsion layer is a single layer constitution were cut to 35 mm size with a length which corresponds to 24 sheets photographing. These samples were wound so as to become the color sensitivity layers inside, contained directly in a film container of a package unit attached with a lens as disclosed in Fig. 1 of U.S. Patent No. 4,827,298, and an outer end thereof was provided to patron for 35 mm size and contained in a patron room to obtain a light-sensitive photographic material package unit provided to photographing function (fixed focus F : 8, shutter speed 1/100 sec).

One unit contained each light-sensitive photographic material was stored in a refrigerator (5 °C) (standard) and the other was stored in the conditions of 37 °C and a relative humidity of 80 % for each one month.

An object of continuous wedge was photographed and then processed with the processing steps as mentioned above.

The results are shown in the following table.

Sample No.	Gradation stability Σ
102 (Comparative)	85
105 (This invention)	65

As seen from the above table, Sample No. 105 of this invention shows small change in gradation from high light portion to shadow portion of the characteristic curve even when contained in a package unit and stored with a lapse of time and shows good tone reproducibility. Further, exposure latitude is 3 or higher in $\Delta \log H$ and thus it can be understood that it has wide exposure latitude.

Example 2

For Sample No. 201, the same one as Sample No. 104 was used.

Sample No. 202 was prepared in the same manner as Sample No. 201 except for adding D-29 in place of the DIR compound D-42 contained in B-1 of Sample No. 201.

For Sample No. 203, the same one as Sample No. 105 was used.

Samples No. 204 and 205 were prepared in the same manner as Sample No. 203 except for adding the DSR compound shown in Table 4 in place of DSR-2 contained in B-1 of Sample No. 203.

Sample No. 206 was prepared in the same manner as Sample No. 201 except for omitting D-42 from B-1 of Sample No. 201, and adding 0.07 mole/mole AgX of DSR-30.

Sample No. 207 and No. 208 were prepared in the same manner as Sample No. 204 except for adding 0.03 mole/mole AgX of DIR compound in B-1 of Sample No. 204 as shown in Table 4.

Sample No. 209 was prepared in the same manner as Sample No. 207 except for omitting G-2, changing the emulsions contained in G-1 to a mixture of equal moles of EM-1 and EM-2, further increasing the amounts used of the emulsion, gelatin and TCP contained in G-1 by 30 %, also 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 G-1 and R-1 are the same as in Sample No. 207).

Sample No. 210 was prepared in the same manner as Sample No. 201 except for adding BAR compound as shown in Table 4 in the layer of R-1 of Sample No. 201, Samples No. 211 and No. 212 were prepared in the same manner as Sample No. 203 except for adding BAR compound as shown in Table 4 in the layer of R-1 of Sample No. 203, and Samples No. 213 and No. 214 were prepared in the same manner

as Samples No. 207 and No. 209 except for adding BAR compound as shown in Table 4 in the layer of R-1s of Samples No. 207 and No. 209, respectively.

The samples thus prepared and their contents are shown in Table 4.

For the samples obtained as described above, sensitivity of the blue-sensitive layer, gradation stability to external conditions, gradation stability to processing fluctuations and bleachability were examined.

The respective samples were subjected to the same processing as in Example 1.

The results are shown in Table 4.

Sensitivity is shown in the reciprocal number of the exposure dose necessary to imparting the density of the minimum density of the blue-sensitive layer + 0.1 as relative value to that of Sample No. 201 which is made as 100.

For gradation stability to external conditions, stability of gradation (to be evaluated) when stored under compulsory deterioration conditions of 40 °C, relative humidity of 80 % for 7 days, relative to the gradation (the standard) when stored in a refrigerator (5 °C), was evaluated.

Bleachability was shown in the bleachability of Sample No. 201 as standard (100). For measurement, fluorescent X ray analyzer is used and the results mean that a larger value shows excellent in improved effect of bleachability.

20

25

30

35

40

45

50

55

Table 4

	Sample No.	Constitution of light-sensitive layer			DIR compound and DSR compound added in blue-sensitive emulsion layer	BAR compound in R-1	Sensitivity	Gradation stability to processing fluctuations				Bleachability
		B	G	R				To external conditions	To processing fluctuations			
									$\Delta\bar{y}$	Σ	$\Delta\bar{y}$	
Comparative	201	Single layer	Double layer	Double layer	D-42	None	100	92	81	98	73	100
	202	Single layer	Double layer	Double layer	D-29	None	97	91	79	96	74	100
This invention	203	Single layer	Double layer	Double layer	DSR-2	None	117	69	70	73	65	100
	204	Single layer	Double layer	Double layer	DSR-39	None	119	72	71	82	65	100
	205	Single layer	Double layer	Double layer	DSR-41	None	114	68	70	78	64	100
	206	Single layer	Double layer	Double layer	DSR-30	None	118	71	70	79	66	100
	207	Single layer	Double layer	Double layer	D-42, DSR-39	None	118	68	71	79	65	100
	208	Single layer	Double layer	Double layer	D-29, DSR-39	None	117	70	71	80	63	100
209	Single layer	Single layer	Single layer	D-42, DSR-39	None	118	62	63	65	58	105	
Comparative	210	Single layer	Double layer	Double layer	D-42	BAR-22	98	92	81	98	73	110
This invention	211	Single layer	Double layer	Double layer	DSR-2	BAR-22	117	69	70	63	60	120
	212	Single layer	Double layer	Double layer	DSR-2	BAR-23	117	69	70	60	55	115
	213	Single layer	Double layer	Double layer	D-42, DSR-39	BAR-22	118	68	71	69	60	120
	214	Single layer	Single layer	Single layer	D-42, DSR-39	BAR-22	118	62	63	55	53	130

As is apparent from Table 4, it can be understood that the samples of the present invention have high sensitivity as well as good gradation stability to external conditions and processing fluctuations.

Further, when all the color sensitive emulsion layers are made single layers, it has been found that the improvement effect of gradation stability becomes greater, thus providing a preferred embodiment of the present invention.

Moreover, in the samples (Samples No. 211 to No. 214) wherein the DSR compound and the BAR compound are combinedly used in the single layer constitution, it can be understood that gradation stability to processing fluctuations and bleachability are excellent.

Also, when graininess by print was evaluated, the samples by using in combination the DSR compound and the DIR compound in a single layer (No. 207, No. 208 and No. 209) were found to have better graininess.

Furthermore, the samples of this invention show small change in gradation from high light portion to shadow portion of the characteristic curve and show good tone reproducibility. Further, exposure latitude is 3 or higher in $\Delta \log H$ and thus it can be understood that they have wide exposure latitude.

In this Example, an emulsion with a fluctuation coefficient of 19 to 20 % was used, but also the effects of the present invention could be recognized when an emulsion with a fluctuation coefficient of 30 % was used.

Example 3

For Sample No. 301, the same one as Sample No. 101 was used.

Sample No. 302 was prepared in the same manner as Sample No. 101 except for changing the couplers and the DIR compounds contained in the respective light-sensitive emulsion layers to those indicated in Table 5.

Table 5

Layer	Additive	Amount added
R-1	C-1	0.064
	CC-1	0.005
	DSR-19	0.021
R-2	C-2	0.005
	C-3	0.020
	CC-1	0.0015
G-1	DSR-19	0.009
	M-2	0.09
	CM-1	0.004
G-2	DSR-30	0.023
	M-1	0.03
	CM-1	0.002
B-1	DSR-30	0.008
	Y-1	0.29
	Y-1	0.06
B-2	DSR-39	0.02

For Sample No. 303, the same one as Sample No. 106 was used.

Sample No. 304 was prepared in the same manner as Sample No. 303 except for using EM-3 in place of the emulsion contained in B-1 of Sample No. 303.

Sample No. 305 was prepared in the same manner as Sample No. 302 except for omitting B-2, changing the emulsion contained in B-1 to a mixture of equal moles of EM-1 and EM-2, further increasing the amounts used of the emulsion, gelatin and TCP contained in B-1 by 15 %, further changing 1/4 of mole numbers of the coupler (Y-1) contained in B-1 to DSR-39, also omitting G-2, changing the emulsion contained in G-1 to a mixture of equal moles of EM-1 and EM-2, further increasing the amounts used of the

emulsion, gelatin and TCP contained in G-1 by 30 %, further 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 B-1, G-1 and R-1 are the same as in Sample No. 302).

5 Sample No. 306 was prepared in the same manner as in Sample No. 305 except for using EM-3 in place of the emulsion contained in Sample No. 305.

Sample No. 307 was prepared in the same manner as in Example No. 306 except for changing DSR-19 contained in R-1 of Sample No. 306 to DSR-27.

10 Sample No. 308 was prepared in the same manner as in Example 306 except for adding the DIR compounds indicated in Table 6 in the respective light-sensitive emulsion layers of Sample No. 306.

Table 6

Emulsion layer	DIR compound	Amount added
R-1	D-42	0.002
G-1	D-26	0.003
B-1	D-42	0.003

The samples thus prepared and their contents are shown in Table 7.

Table 7

Sample No.	Constitution of light-sensitive layer			DIR compound and DSR compound added	Emulsion used in blue-sensitive emulsion layer
	B	G	R		
301	Double layer	Double layer	Double layer	D-23 (R-1, G-1), D-26 (G-1, G-2)	EM-1 (B-2)
				D-42 (R-1, R-2, B-2)	EM-2 (B-1)
302	Double layer	Double layer	Double layer	DSR-19 (R-1, R-2)	EM-1 (B-2)
				DSR-30 (G-1, G-2), DSR-39 (B-2)	EM-2 (B-1)
303	Single layer	Double layer	Double layer	D-23 (R-1, G-1), D-26 (G-1, G-2)	EM-1,
				D-42 (R-1, R-2), DSR-39 (B-1)	EM-2
304	Single layer	Double layer	Double layer	D-23 (R-1, G-1), D-26 (G-1, G-2)	EM-3
				D-42 (R-1, R-2), DSR-39 (B-1)	
305	Single layer	Single layer	Single layer	DSR-19 (R-1), DSR-30 (G-1)	EM-1,
				DSR-39 (B-1)	EM-2
306	Single layer	Single layer	Single layer	DSR-19 (R-1), DSR-30 (G-1)	EM-3
				DSR-39 (B-1)	
307	Single layer	Single layer	Single layer	DSR-27 (R-1), DSR-30 (G-1)	EM-3
				DSR-39 (B-1)	
308	Single layer	Single layer	Single layer	DSR-19 (R-1), DSR-30 (G-1)	EM-3
				DSR-39 (B-1)	
				D-42 (R-1, B-1), D-26 (G-1)	

For the samples obtained as described above, gradation stability of the blue-sensitive layer was examined.

The respective samples were processed as described in Example 1.

The results are shown in Table 8.

Table 8

	Gradation stability to external conditions		Gradation stability to processing fluctuations	
	$\Delta\bar{y}$	Σ	$\Delta\bar{y}$	Σ
301 (Comparative)	92	79	103	77
302 (Comparative)	86	80	102	76
303 (This invention)	72	71	77	67
304 (This invention)	70	71	70	62
305 (This invention)	61	63	69	58
306 (This invention)	55	60	61	52
307 (This invention)	54	58	60	53
308 (This invention)	53	57	60	51

As is apparent from Table 8, it can be understood that the samples of the present have good gradation stability.

When comparison is made among the samples of the present invention, those having all the color sensitive emulsion layers respectively of single layers (Samples No. 305 to No. 308) are preferred with greater improvement effect for gradation stability.

Also, in the respective samples by use of D-2 or D-4 in place of D-42 in B-1 of Sample No. 308, also D-6 or D-10 in place of D-26 in G-1, and further D-17, D-19 or D-21 in place of D-42 in R-1, the effects of the present invention could be recognized.

It has also been found that the samples No. 304 and No. 306 to No. 308 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.

Also, the samples containing EM-3 are preferred with respect to production efficiency as compared with other samples, because physical ripening and chemical ripening can be practiced at one time in preparation of the emulsion.

Also, in the respective samples by use of seed emulsions prepared by addition of RuCl_3 , OsCl_3 or $\text{Pb}(\text{NO}_3)_2$ in place of K_3RhCl_6 in place of NE-2, the effects of the present invention could be recognized.

When graininess by print was evaluated, the sample using in combination of the DSR compound and the DIR compound in a single layer (No. 308) was found to have better graininess.

The light-sensitive photographic material obtained by the present invention is not only high in sensitivity, but also excellent in storability before photographing, and also excellent in stability to fluctuations in processing conditions.

Claims

1. A light-sensitive silver halide color photographic material, comprising on a support material at least silver halide emulsion layers which are respectively blue-sensitive, green-sensitive and red-sensitive, wherein a compound which can react with an oxidized product of a developing agent to scavenge said oxidized product or a compound which can release a precursor thereof is contained, and also at least one of said blue-, green- and red-sensitive layers has a single layer constitution.

2. A light-sensitive silver halide color photographic material according to Claim 1, wherein said single

layer constitution means 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 the ratio of the coupler to the silver halide, are arranged as continuous layers.

5 3. A light-sensitive silver halide color photographic material according to Claim 1, wherein said blue-sensitive layer is a single layer.

4. A light-sensitive silver halide color photographic material according to Claim 1, wherein said blue-sensitive layer and said green-sensitive layer are single layers.

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

6. A light-sensitive silver halide color photographic material according to Claim 1, wherein said compound which can react with an oxidized product of a developing agent to scavenge said oxidized product or said compound which can release a precursor thereof is a compound represented by the formula (DSR-I):

15 $\text{Coup} \{ \text{Time} \} \text{---} \text{Sc} \quad (\text{DSR-I})$

wherein Coup represents the coupler residue which can release the $(\text{Time}) \text{---} \text{Sc}$ through the reaction with the oxidized product of the color developing agent, Time represents a timing group which can release Sc after Time-Sc is released from Coup, Sc represents the scavenger of the oxidized product of the color developing agent which can scavenge the oxidized product of the color developing agent through redox
20 reaction or coupling reaction after released from Coup or Time-Sc or a precursor thereof, and --- represents 0 or 1.

7. A light-sensitive silver halide color photographic material according to Claim 6, wherein said coupler residue represented by Coup is a yellow coupler residue, a magenta coupler residue, a cyan coupler residue or a coupler residue which forms substantially no image forming chromogenic dye.

25 8. A light-sensitive silver halide color photographic material according to Claim 7, wherein said coupler residue is those represented by the following formulae (DSR-Ia) to (DSR-Ih):

30

35

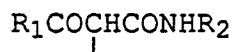
40

45

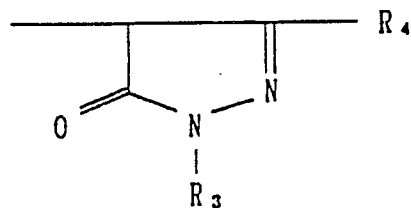
50

55

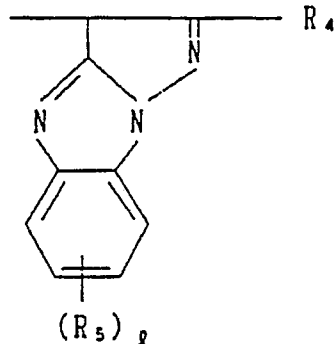
Formula (DSR-Ia)



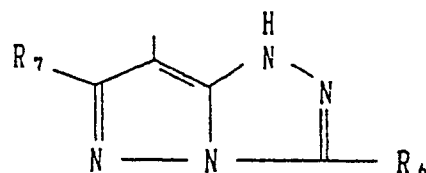
Formula (DSR-Ib)



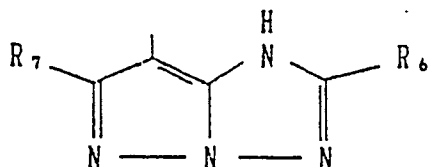
Formula (DSR-Ic)



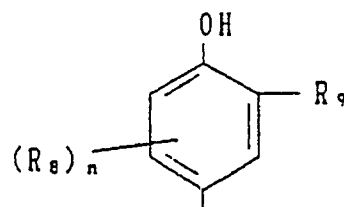
Formula (DSR-Id)



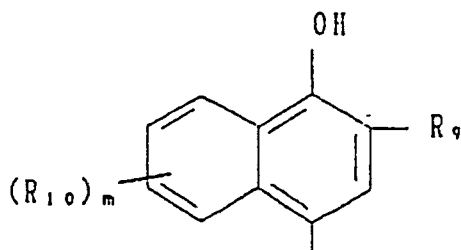
Formula (DSR-Ie)



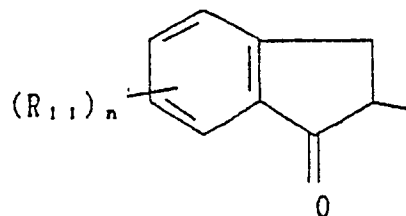
Formula (DSR-If)



Formula (DSR-Ig)

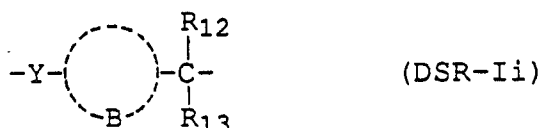


Formula (DSR-Ih)



wherein R_1 represents an alkyl group, an aryl group or an arylamino group, R_2 represents an aryl group or an alkyl group, R_3 represents an alkyl group or an aryl group, R_4 represents an alkyl group, an acylamino group, an arylamino group, an arylureido group or an alkylureido group, R_5 represents an acylamino group, a sulfonamide group, an alkyl group, an alkoxy group or a halogen atom, R_7 represents an alkyl group, an aryl group, an acylamino group, an arylamino group, an alkoxy group, an arylureido group or an alkylureido group, and R_6 represents an alkyl group or an aryl group, R_8 represents an acylamino group, a carbamoyl group or an arylureido group, R_8 represents a halogen atom, an alkyl group, an alkoxy group, an acylamino group or a sulfonamide group, R_{10} represents an amino group, an acid amide group, a sulfonamide group or a hydroxyl group, R_{11} represents a nitro group, an acylamino group, a succinimide group, a sulfonamide group, an alkoxy group, an alkyl group, a halogen atom or a cyano group, l represents an integer of 0 to 3, n is 0 to 2, m is 0 or 1, and when l and n are 2 or more, the respective R_5 , R_8 and R_{11} may be either the same or different.

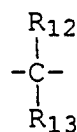
9. A light-sensitive silver halide color photographic material according to Claim 1, wherein the timing group represented by Time is represented by the following formula (DSR-li), (DSR-lj) or (DSR-lk).



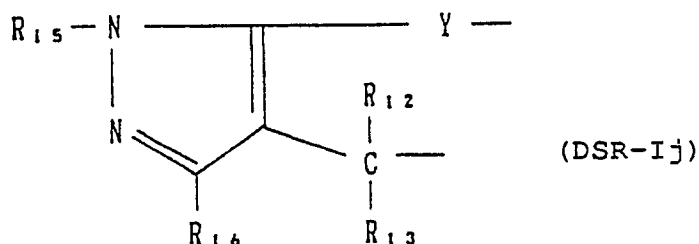
wherein B represents a group of atoms necessary for completion of a benzene ring or a naphthalene ring; Y represents -O-, -S- or



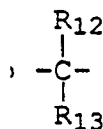
which is bonded to the active site of Coup (coupling component) of the above formula (DSR-I); R_{12} , R_{13} and R_{14} each represent a hydrogen atom, an alkyl group or an aryl group, the above group



is substituted at the ortho- or para-relative to Y, and the other is bonded to Sc of the above formula (DSR-I),



wherein Y, R_{12} and R_{13} have respectively the same meanings as in the above formula (DSR-II); R_{15} represents a hydrogen atom, an alkyl group, an aryl group, an acyl group, a sulfonyl group, an alkoxy carbonyl group or a heterocyclic residue; R_{16} represents hydrogen atom, an alkyl group, an aryl group, a heterocyclic residue, an alkoxy group, an amino group, an acid amide group, a sulfonamide group, a carboxyl group, an alkoxy carbonyl group, a carbamoyl group or a cyano group, also, the timing group represented by the above formula (DSR-Ij) has Y bonded to the active site of Coup (coupling component) and the group



to Sc, similarly as in the above formula (DSR-II),

-Nu-D-E- (DSR-Ik)

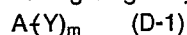
wherein Nu represents a nucleophilic group having oxygen, sulfur or nitrogen atom, which is rich in electrons and bonded to the active site of Coup (coupling component) in the above formula (DSR-I); E represents an electrophilic group having carbonyl group, thiocarbonyl group, phosphinyl group or thiophosphinyl group, which is deficient in electrons, which electrophilic group E is bonded to the hetero atom of Sc; D represents a bonding group which correlates sterically Nu and E, can perform intramolecular nucleophilic substitution through the reaction with accompaniment of formation of a 3- to 7-membered ring after Nu is released from Coup (coupling component), and can also release Sc thereby.

10. A light-sensitive silver halide color photographic material according to Claim 6, wherein said compound is used in an amount of 2×10^{-4} to 5×10^{-1} mole per mole of silver in the emulsion layer.

11. A light-sensitive silver halide color photographic material according to Claim 10, wherein said compound is used in an amount of 1×10^{-3} to 1×10^{-1} mole per mole of silver in the emulsion layer.

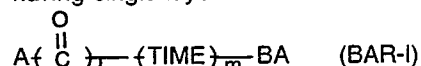
12. A light-sensitive silver halide color photographic material according to Claim 1, wherein said layer having single layer constitution contains at least two kinds of silver halide grains having different mean grain sizes.

13. A light-sensitive silver halide color photographic material according to Claim 1, wherein said layer having single layer constitution contains a DIR compound represented by the formula:



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.

14. A light-sensitive silver halide color photographic material according to Claim 1, wherein said layer having single layer constitution contains a BAR compound represented by the formula:



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.

15. A light-sensitive silver halide color photographic material according to Claim 1, wherein said layer having single layer constitution contains a core/shell type silver halide emulsion.

16. A light-sensitive silver halide color photographic material according to Claim 1, wherein said layer having single layer constitution contains silver halide grains containing desensitizer and silver halide grains not containing desensitizer.

FIG. 1

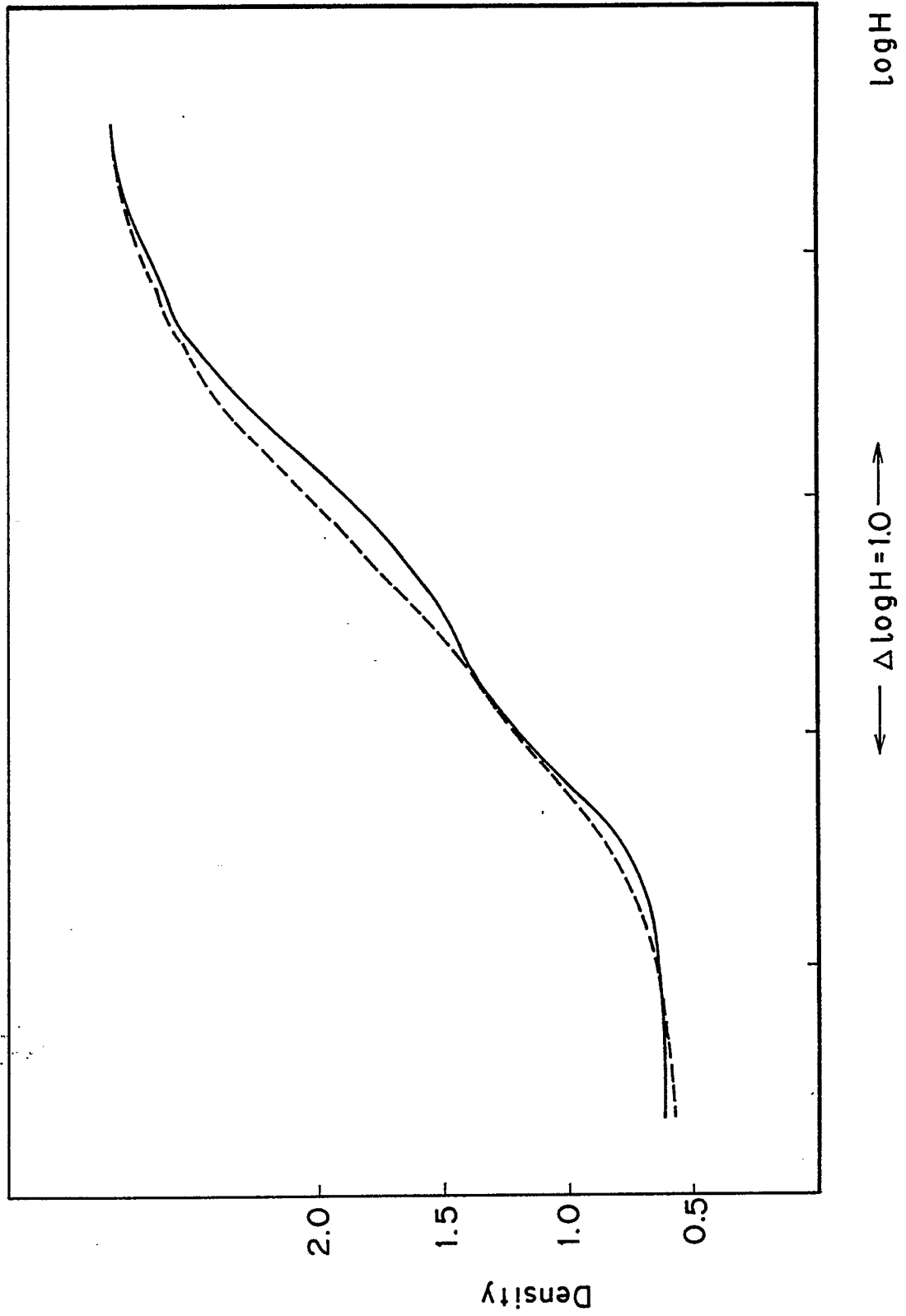


FIG. 2

