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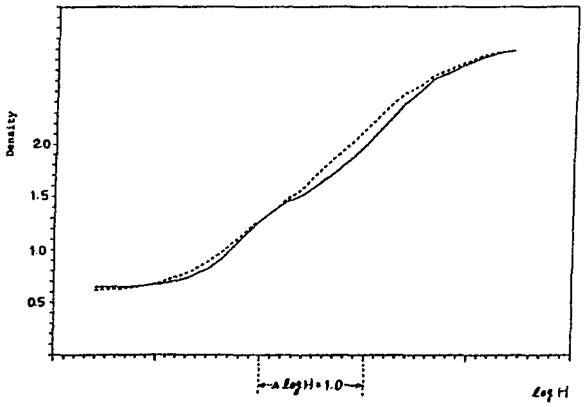
(54) Light-sensitive silver halide color photographic material.

(57) Disclosed is a light-sensitive silver halide color photographic material, comprising a support and silver halide emulsion layers which are respectively blue-sensitive, green-sensitive or red-sensitive and are provided on the support, wherein the material contains a DIR compound and at least one selected from the group consisting of a film hardner which acts through activation of carboxyl groups, a chlorotriazine type film hardener, a bis-(vinylsulfonyl-alkyl)ether type film hardener and at least two of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers have single layer constitutions. According to the present invention, a light-sensitive color photographic material suitable for full color photographing can be obtained.

FIG. 1



Light-sensitive silver halide color photographic material

BACKGROUND OF THE INVENTION

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

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

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

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

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

However, in a color negative film having a multi-layer constitution by use of a plurality of emulsion layers containing silver halide grains with different grain sizes, which further controls strictly the gradation by use of a DIR compound, when a film hardner which acts through activation of carboxyl groups or a chlorotriazine type film hardener is used, there have been involved the drawbacks that the density of the dye image obtained is unstable, and that the storage stability of the light-sensitive material to external conditions such as temperature, humidity, etc. when stored after preparation of the light-sensitive material (hereinafter called light-sensitive material stability) is deteriorated to deteriorate gradation, color reproducibility, tone reproducibility, etc.

As the technique for improving such gradation stability, there has been known the method in which after chemical sensitization of the silver halide emulsion with equal mean grain sizes, sensitizing dyes with various molar ratios are added into the respective emulsions to remix them (Japanese Unexamined Patent Publication No. 244944/1985), but the remixed emulsion will cause undesirably adsorption equilibrium between grains during the stagnation period before coating.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive silver halide color photographic material having high color formed density stable to storage after preparation of the light-sensitive material and excellent in gradation, color reproduction and tone reproducibility.

Further, in the photographic layers of these light-sensitive materials, hydrophilic colloid such as gelatin, etc. is used as the binder, and recently in order to stand damages of the film which are liable to be generated by the rapid processing by means of an automatic developing machine at high temperature and high pH, or based on the demands from aspect of productivity, film hardening treatment is generally applied.

Whether such film hardener treatment is good or not is indispensable for ensuring the quality from aspect of physical properties except for special cases, and investigations have been made, including primitive inorganic film hardeners such as potassium alum, chromium alum, etc. to organic film hardeners adapted more highly to photographic characteristics.

For example, a large number of film hardeners such as chlorotriazine type film hardeners disclosed in U.S. Patents 3,325,287 and 3,645,743 and Japanese Unexamined Patent Publication No. 40244/1982 and vinyl sulfone type film hardeners disclosed in U.S. Patent 3,490,911 and German Patent (OLS) No. 2,749,260, other aldehyde type, epoxy type, etc. may be included.

As the characteristics demanded for film hardener, with a premise that it has the film hardening effect, it is desired that the film as the result of film hardening should have luster, film attachment should be good, film hardening should proceed rapidly, scratching strength should be great, it should be harmless to photographic characteristics, and there should be otherwise no problem in labour hygiene, no fear of environmental pollution, etc.

In response to such demands, for example, the s-triazine type has the drawback of lacking rapid film hardenability, the vinyl sulfone type various drawbacks such as lacking luster, film attachment, scratching strength, etc. Whereas, among them, the film hardener which acts through activation of carboxyl groups and the chlorotriazine type film hardener have characteristics at least satisfactory for the above-mentioned items of physical properties, and are described in Japanese Patent Publication No. 6151/1972 and Japanese Unexamined Patent Publications Nos. 19220/1973, 78788/1976, 128130/1977, 130326/1977 and 1043/1981.

The object of the present invention is accomplished by a light-sensitive silver halide color photographic material, comprising a support, and silver halide emulsion layers which are respectively blue-sensitive, green-sensitive or red-sensitive and provided on the support, wherein said material contains a DIR compound and at least one selected from the group consisting of a film hardner which acts through activation of carboxyl groups, a chlorotriazine type film hardener and a bis(vinylsulfonylalkyl)ether type film hardener, and at least two of said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers have single layer constitutions.

BRIEF DESCRIPTION OF THE DRAWINGS

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

Hereinafter, the present invention will be described in more detail.

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

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

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

In the following, representative structural formulae are shown.

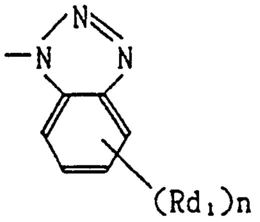
Formula (D-1)

$A - (Y)m$

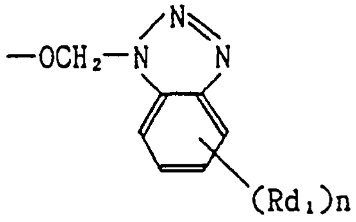
wherein A represents a coupler residue, m represents 1 or 2, Y represents a group bonded to the coupling position of the coupler residue A and eliminatable through the reaction with the oxidized product of the color developing agent, which is a developing inhibitor group or a group capable of releasing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

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

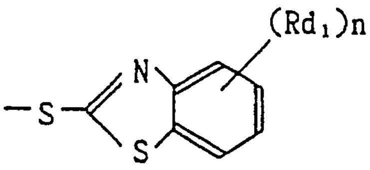
Formula (D-2)



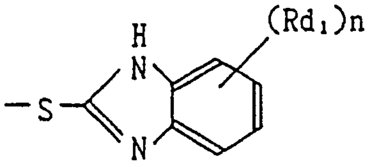
Formula (D-3)



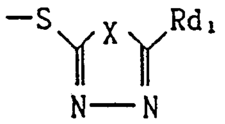
Formula (D-4)



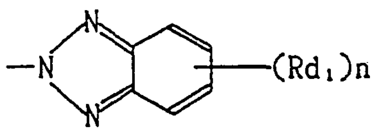
Formula (D-5)



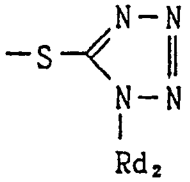
Formula (D-6)



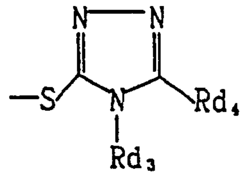
Formula (D-7)



Formula (D-8)



Formula (D-9)



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

n represents 0, 1 or 2, and when n is 2, the respective Rd_1's may be either the same or different. The total carbon atoms contained in n Rd_1's may be 0 to 10.

On the other hand, the total number of the carbon atoms contained in Rd_1 in the formula (D-6) may be 0 to 15.

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

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

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

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

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

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

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

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

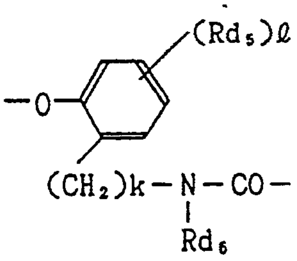
Formula (D-10)

$-(\mathrm{TIME})_n-\mathrm{INHIBIT}$

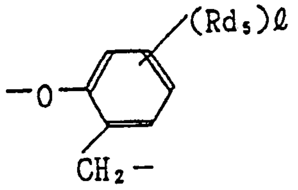
wherein the TIME group is a group, bound to the coupling position of A and being cleavable through the reaction with the oxidized product of the color developing agent, which is a group cleaved successively after cleavage from the coupler and until finally can release the INHIBIT groups with adequate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

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

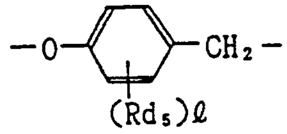
Formula (D-11)



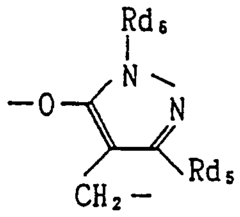
Formula (D-12)



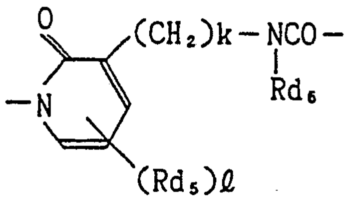
Formula (D-13)



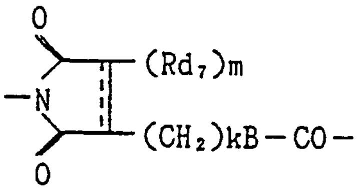
Formula (D-14)



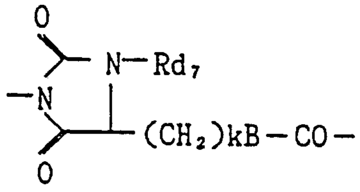
Formula (D-15)



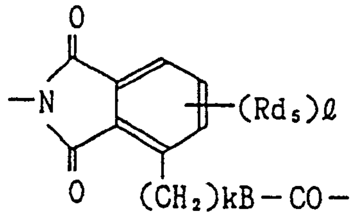
Formula (D-16)



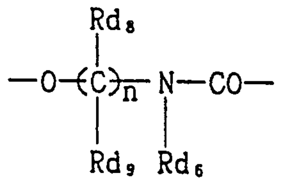
Formula (D-17)



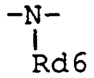
Formula (D-18)



Formula (D-19)



In the formulae (D-11) to (D-15) and (D-18), Rd_5 represents hydrogen atom, a halogen atom or an alkyl, cycloalkyl, alkenyl, aralkyl, alkoxy, alkoxycarbonyl, anilino, acylamino, ureido, cyano, nitro, sulfonamide, sulfamoyl, carbamoyl, aryl, carboxy, sulfo, hydroxy or alkanesulfonyl group. In the formulae (D-11) to (D-13), (D-15) and (D-18), Rd_5's may be mutually bonded together to form a fused ring. In the formulae (D-11), (D-14), (D-15) and (D-19), Rd_6 represents an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. In the formulae (D-16) and (D-17), Rd_7 represents a hydrogen atom or an alkyl, alkenyl, aralkyl, cycloalkyl, heterocyclic or aryl group. Each of Rd_8 and Rd_9 in the formulae (D-19) represents hydrogen atom or an alkyl group (preferably an alkyl group having 1 to 4 carbon atoms), k in the formulae (D-11) and (D-15) to (D-18) represents an integer of 0, 1 or 2, ℓ in the formulae (D-11) to (D-13). (D-15) and (D-18) represents an integer of 1 to 4, m in the formula (D-16) represents an integer of 1 or 2. When ℓ and m are 2 or more, the respective Rd_5 and Rd_7 may be either the same or different. n in the formula (D-19) represents an integer of 2 to 4, and Rd_8 and Rd_9 in number of n may be each the same or different. B in the formulae (D-16) to (D-18) represents oxygen atom or



$$-\underset{\displaystyle Rd6}{\underset{|}{N}}-$$

(Rd_6 represents the same meaning as already defined), and $\overline{\cdots\cdots}$ in the formula (D-16) may be either a single bond or a double bond, and m is 2 in the case of the single bond and m is 1 in the case of the double bond.

Formula (D-20)

$\{T_1\}_{\ell}$ SR$\{T_2\}_{m}$INHIBIT

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

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

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

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

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

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

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

In the case when SR is a redox component, SR is bonded to $\{T_1\}_{\ell}$ and $\{T_2\}_{m}$ INHIBIT so as to function for the first time as the redox component after cleavage from $\{T_1\}_{\ell}$. Examples of the group represented by T_1 and T_2 may include those represented by the formulae (D-11) to (D-19) as described above.

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

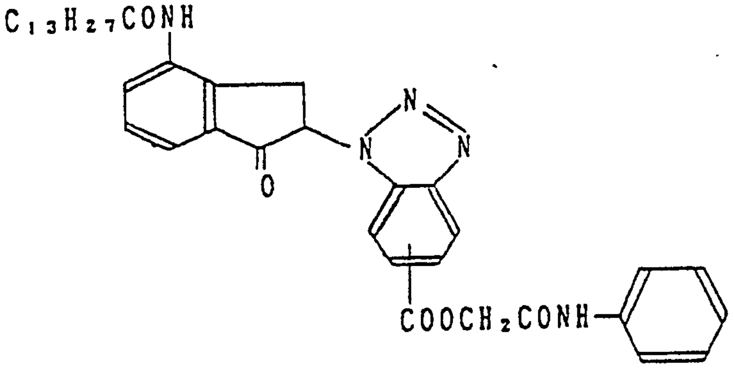
Among the DIR compounds, preferable are those wherein Y is represented by the formula (D-2), (D-3), (D-8), (D-10) or (D-20), and among (D-10) and (D-20), those wherein INHIBIT is represented by the formula (D-2), (D-3), (D-6) (particularly when X of (D-6) is oxygen atom), or (D-8) are preferred.

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

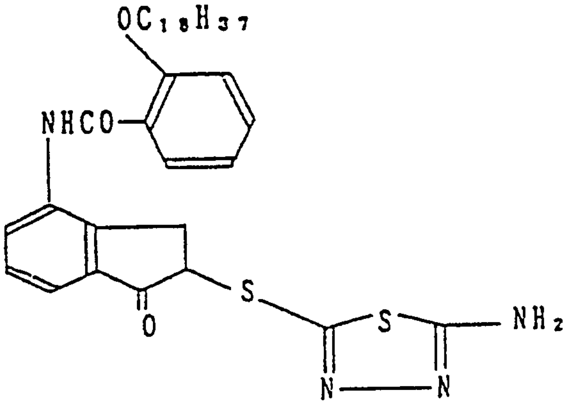
As preferable DIR compounds to be used in the present invention, the compounds as shown below may be included, but these are not limitative of the invention.

Exemplary compounds

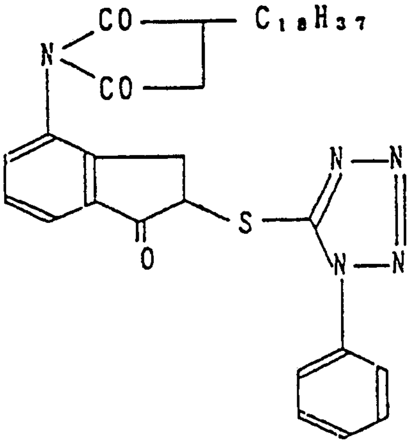
E − 1

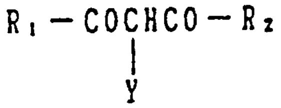


E − 36



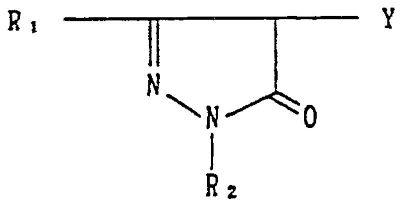
E − 37



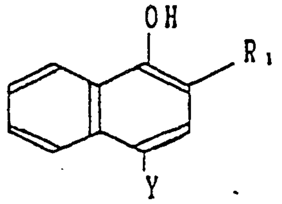


$$R_1-\underset{\displaystyle Y}{\underset{|}{COCHCO}}-R_2$$

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



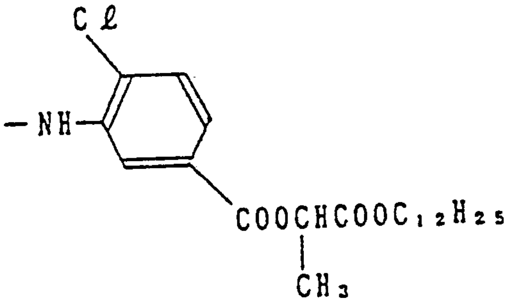
Exemplary compound No.	R_1	R_2	Y
E - 9	(9)	(10)	(30)
E -10	(11)	(10)	(30)
E -11	(12)	(7)	(34)
E -12	(12)	(13)	(35)
E -13	(9)	(14)	(36)
E -14	(15)	(16)	(37)
E -35	(56)	(24)	(23)



Exemplary compound No.	R_1	Y
E－15	(17)	(38)
E－16	(17)	(39)
E－17	(18)	(40)
E－18	(19)	(41)
E－19	(18)	(42)
E－20	(18)	(43)
E－21	(18)	(44)
E－22	(18)	(45)
E－23	(18)	(46)
E－24	(20)	(47)
E－25	(20)	(48)
E－26	(21)	(49)
E－27	(21)	(50)
E－28	(21)	(51)
E－29	(22)	(52)
E－30	(18)	(53)
E－31	(18)	(54)
E－32	(22)	(49)
E－34	(18)	(56)
E－38	(19)	(46)

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

1



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$-C(CH_3)_3$

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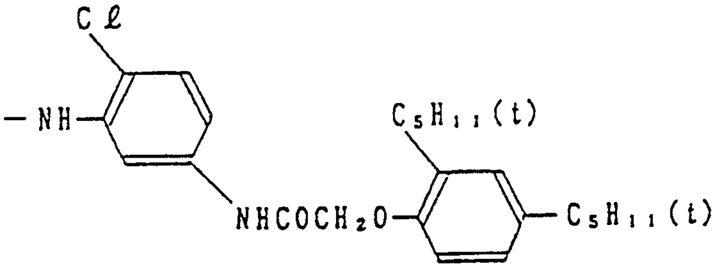

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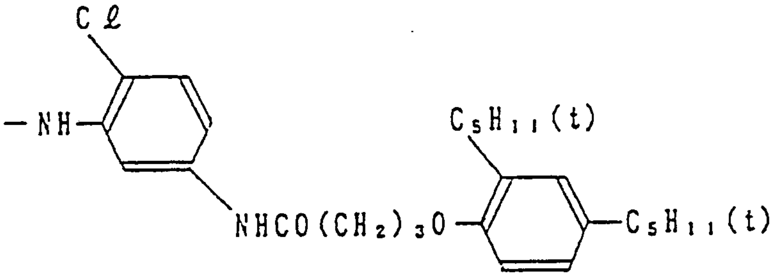

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$-OCH_3$

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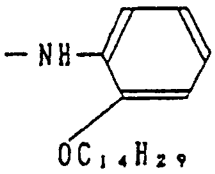

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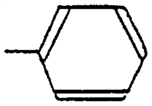

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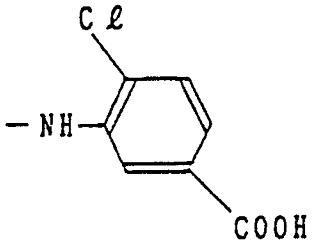

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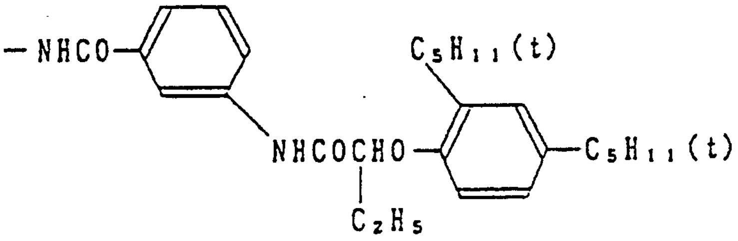

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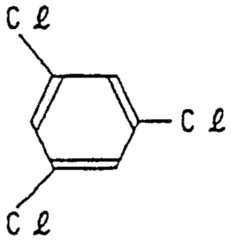

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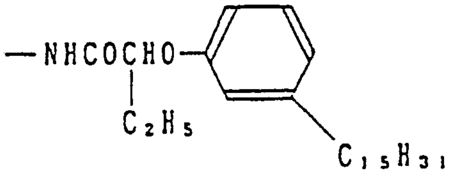

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$-C_{17}H_{35}$

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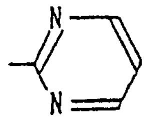

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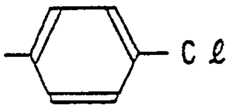

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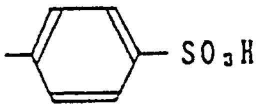
$-CH_3$

16



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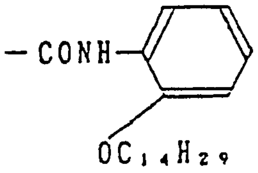
$-CONHC_{18}H_{37}$

18



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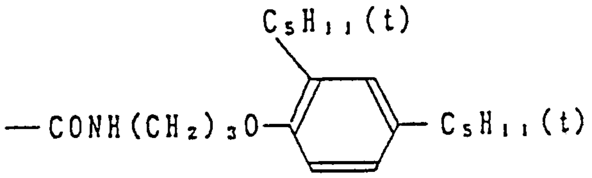

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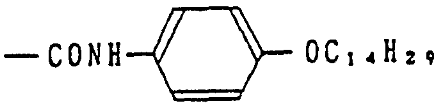

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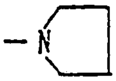
$-CONHCH_2CH_2COOH$

22

$-CONHCH_2CH_2COOCH_3$

23



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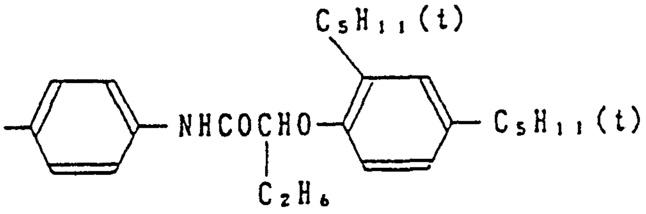

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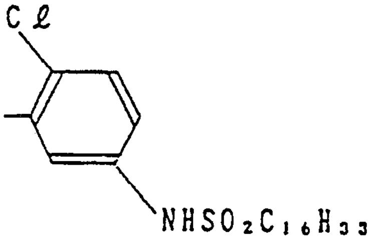

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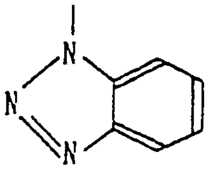

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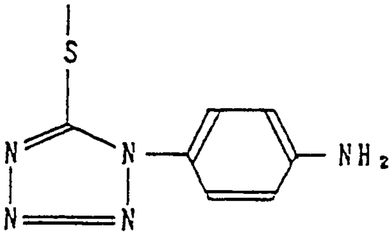

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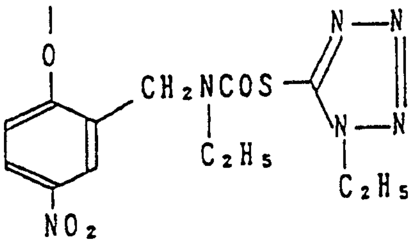

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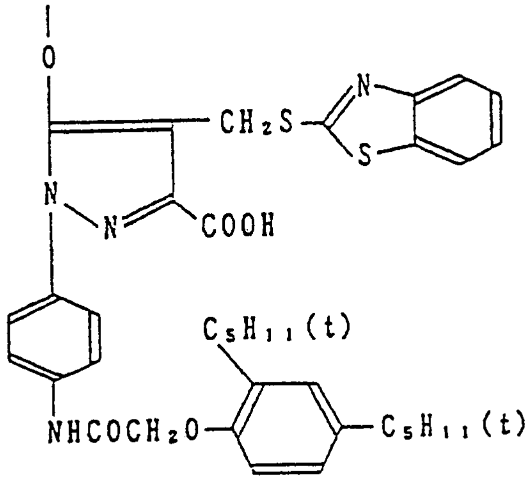

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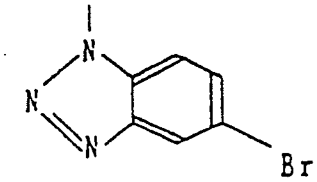

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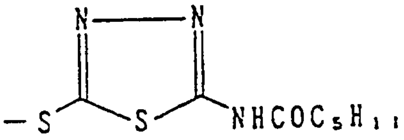

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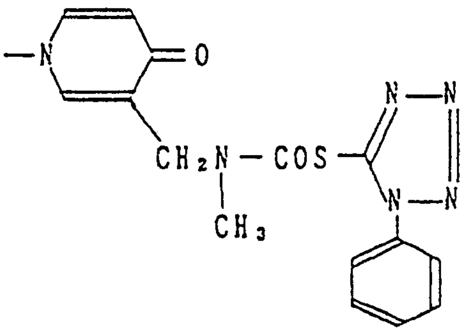

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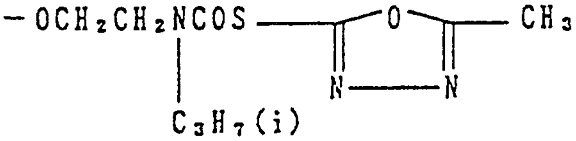

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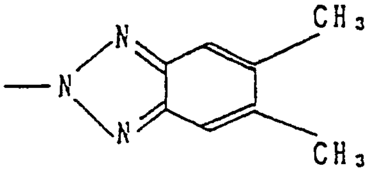

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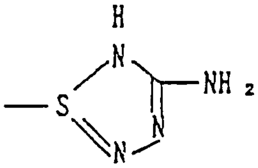

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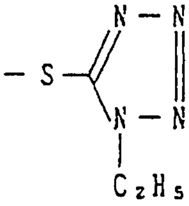

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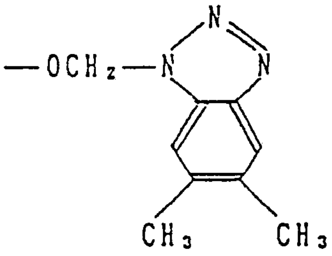

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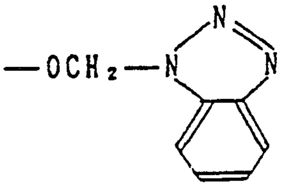

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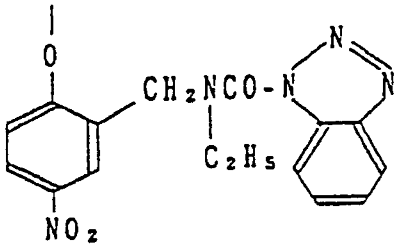

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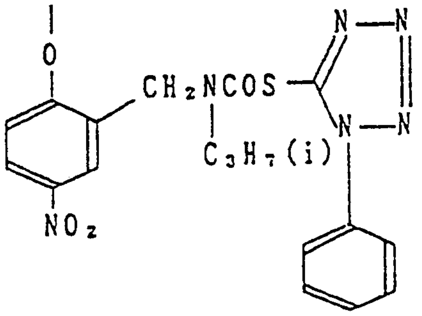

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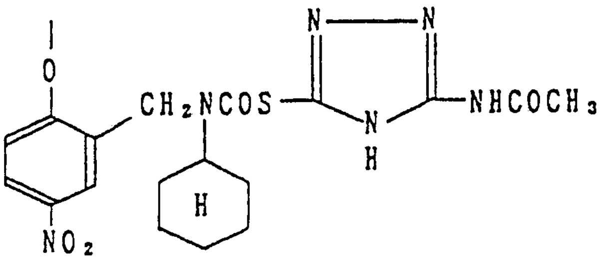
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N
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N
H
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H
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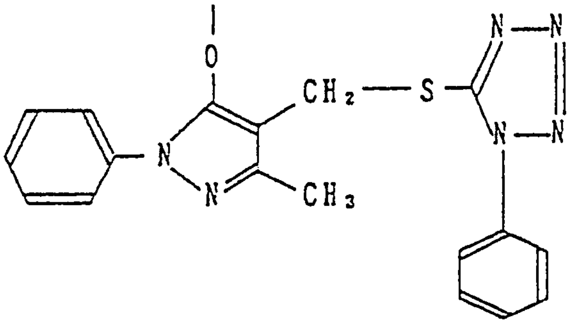
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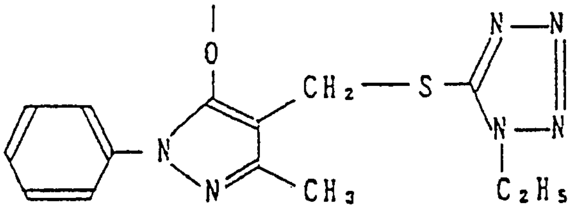
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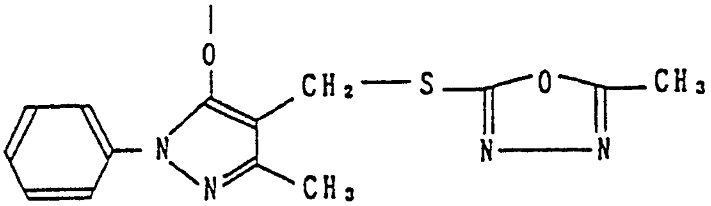

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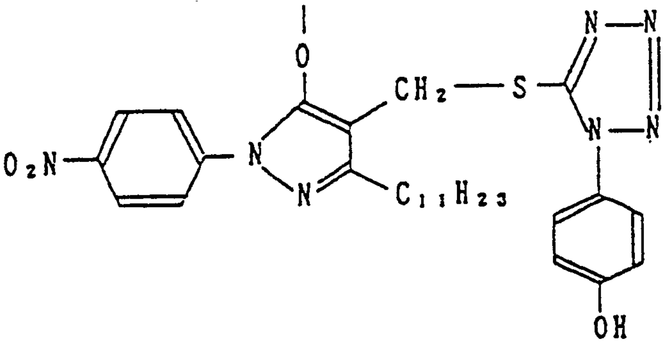

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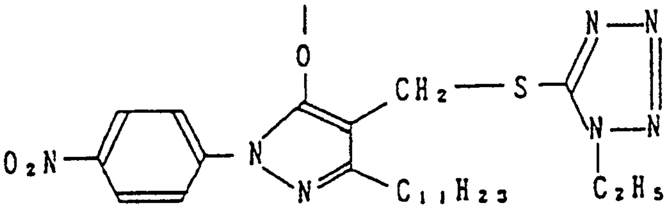

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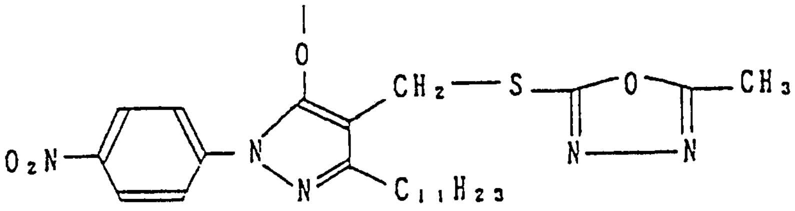

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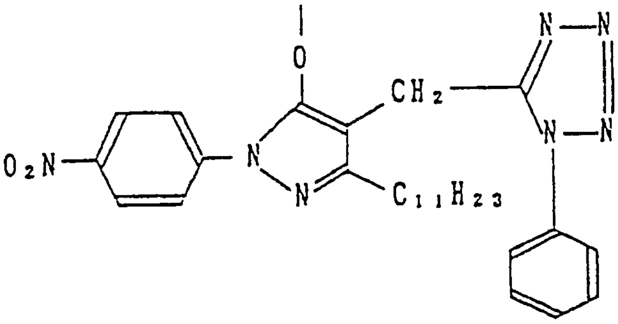

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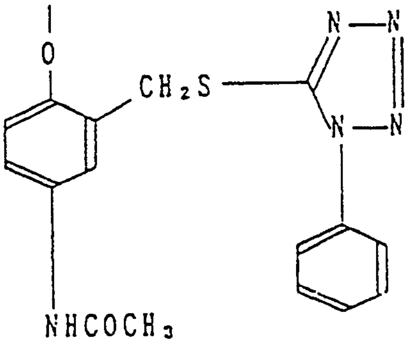

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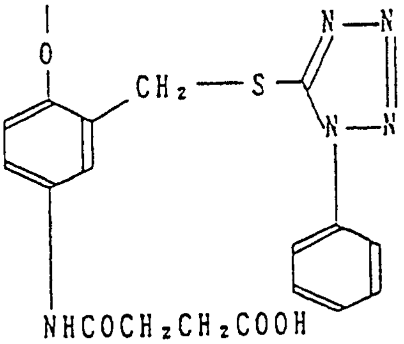

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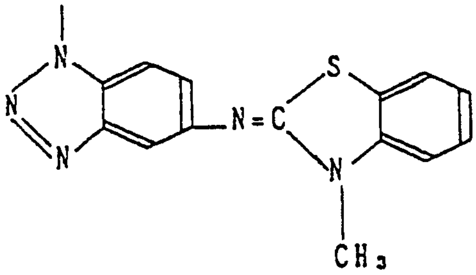

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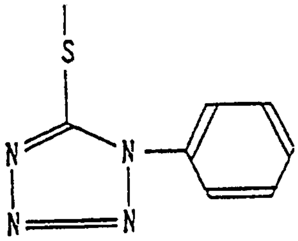

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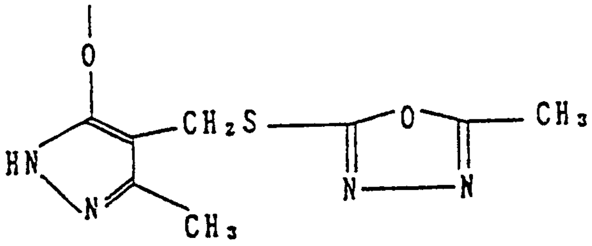

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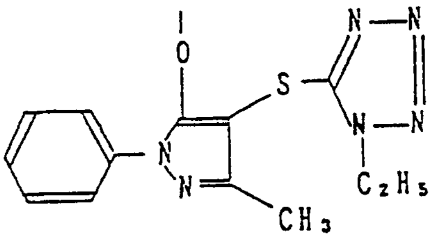

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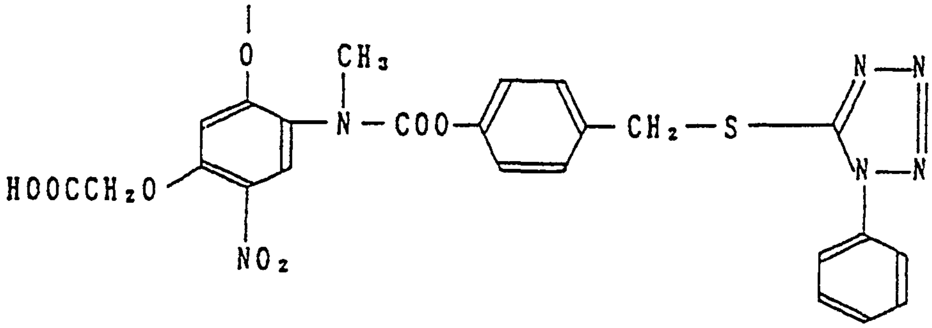

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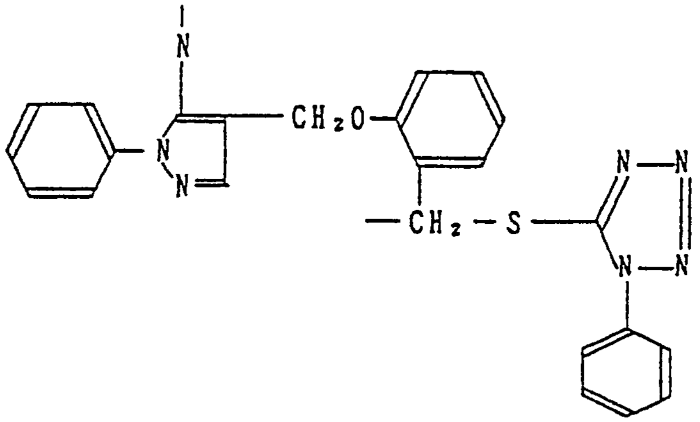


Specific examples of the DIR compounds which can be used in the present invention, including these are described in U.S. Patents 4,234,678, 3,227,554, 3,617,291, 3,958,993, 4,i49,886, 3,933,500, Japanese Unexamined Patent Publications Nos. 56837/1982 and 13239/1976, U.S. Patents 2,072,363 and 2,070,266, Research Disclosure (hereinafter abbreviated to RD) No. 21228, December, 1981, etc.

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

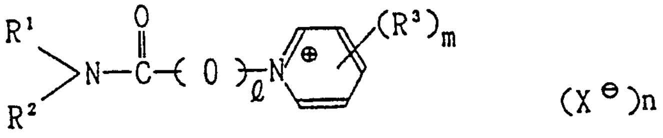
The place in which the DIR compound to be used in the present invention is added may be any place which can affect developing of the silver halide in the emulsion layer of single layer constitution, preferably in a silver halide emulsion layer, more preferably in an emulsion layer having a single layer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

Next, the hardener which acts through activation of carboxyl groups is to be described in detail.

The hardener which acts through activation of carboxyl groups (hereinafter referred to as carboxyl group activation type film hardener) in the present invention refers to a hardener which reacts with the carboxyl groups in the binder.

As the above-mentioned hardener in the present invention, the compounds represented by the following formulae (H-1) to (H-VIII) can be included.

Formula (H-I)



In the formula, R^1 and R^2 each represent an alkyl group (e.g. methyl, ethyl, benzyl, phenethyl, 2-ethylhexyl group, etc.) or an aryl group (e.g. phenyl, naphthyl group, etc.), and it is also preferable that the both are bonded to form a heterocyclic ring together with nitrogen atom. As examples of said ring, pyrrolidine ring, piperazine ring, morpholine ring, etc. may be included.

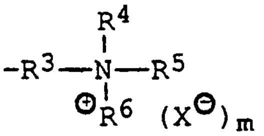
R^3 represents, for example, $-NR^4R^5$ (R^4 and R^5 have the same meanings as R^1 and R^2), a halogen atom, a carbamoyl group, a sulfo group, a ureido group, an alkoxy group, an alkyl group, etc. R^3 is inclusive of those having substituents, and examples of substituents may include halogen atoms, an alkyl group, a carbamoyl group, a sulfo group, a sulfooxy group, a ureido group, etc.

m represents 0 to 5, and when $m \geqq 2$, the plural number of R^3's may be either the same or different from each other.

$X^{\ominus}$ represents an anion, and preferable examples may include halide ions, sulfate ion, sulfonate ion, $ClO_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, etc. ℓ represents 0 or 1, n represents 0 to 2, and when an intramolecular salt is formed, n is 0.

Formula (H-II) $R^1-N=C=N-R^2$

In the formula, R^1 and R^2 each represent a cycloalkyl group (e.g. cyclohexyl group, etc.) or an alkyl group (e.g. methyl, ethyl, 2-ethylhexyl, etc.), or otherwise an alkoxy alkyl group such as methoxyethyl group, an aralkyl group such as benzyl group, phenethyl group, etc. or an group represented by the formula:

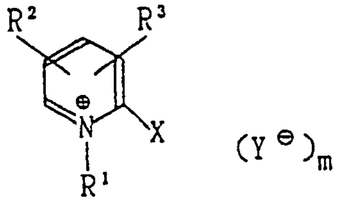


$$-R^3-\underset{\oplus R^6}{\overset{R^4}{N}}-R^5 \quad (X^{\ominus})_m$$

Here, R^3 represents an alkylene group (e.g. ethylene, propylene and trimethylene group, etc.), R^4, R^5 and R^6 each represent an alkyl group (e.g. methyl and ethyl group, etc.), including the case wherein two of the R^4 to R^6 are bonded to form a heterocyclic ring (e.g. pyrrolidine ring, piperazine ring, morpholine ring, etc.) together with nitrogen atom and the case of having substituents.

Examples of substituents may be preferably carbamoyl groups such as diethylcarbamoyl, piperidinocarbonyl, etc., sulfo group, etc. m represents 0 or 1, $X^{\ominus}$ represents an anion, preferably a halide ion, sulfonate ion, sulfate ion, $ClO_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, etc. When an intramolecular salt is formed, m is 0.

Formula (H-III)



In the formula, R^1 represents an alkyl group (e.g. methyl, ethyl, butyl group, etc. or otherwise, an aralkyl group such as benzyl, and phenethyl group, etc.) or an aryl group (e.g. phenyl group, naphthyl group, etc.). These groups further include those having substituents, and examples of substituents may include carbamoyl, sulfamoyl, sulfo groups, etc. R^2 and R^3 represent, for example, hydrogen atom or substituents such as halogen atoms, acylamido, nitro, carbamoyl, ureido, alkoxy, alkyl, alkenyl, aryl, aralkyl groups, etc., and it is also preferable that R^2 and R^3 may be bonded to form a fused ring together with the pyridinium ring skelton.

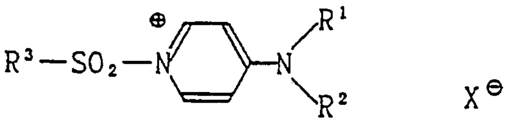
X represents a group eliminable when the compound represented by the formula (H-III) reacts with a nucleophilic reagent. Preferable examples may include halogen atoms, sulfonyloxy group, sulfoalkyl group or a group represented by $-O\underset{\underset{O}{\|}}{P}(OR^4)_2$ (R^4 represents an alkyl group or an aryl group).

When X represents a sulfonyloxy group, it is also preferable that X and R^1 may be bonded to each other.

$Y^{\ominus}$ represents an anion, preferably a halide ion, sulfonate ion, sulfate ion, $ClO_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, etc.

m represents 0 or 1, and when an intramolecular salt is formed, m is 0.

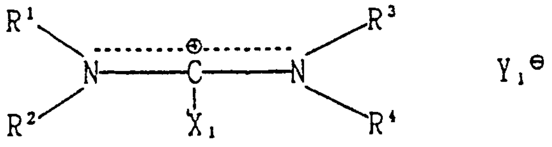
Formula (H-IV)



In the formula, the definitions of R^1 and R^2 are entirely the same as R^1 and R^2 in the formula (H-I), and R^3 represents an alkyl group (e.g. methyl, ethyl, butyl group, or otherwise an aralkyl group such as benzyl and phenethyl group, etc.), or an aryl group (e.g. phenyl and naphthyl group, etc.).

$X^{\ominus}$ represents an anion, preferably a halide ion, sulfonate ion, sulfate ion, $ClO_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, etc.

Formula (H-V)

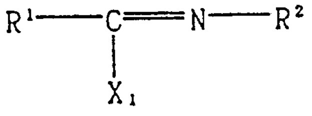


In the formula, the definitions of R^1, R^2, and R^3, R^4 are entirely the same as R^1, R^2 in the formula (H-I), and further R^1 and R^3 may form a ring.

X_1 represents a group eliminable during the reaction with a nucleophilic reagent, preferably a halogen atom, a sulfonyloxy group (preferably alkylsulfonyloxy and arylsulfonyloxy), 1-pyridium group, an imidyloxy group (e.g. phthalimidyloxy, succinimidyloxy and glutarimidyloxy), an azoyloxy group and an ammonio group.

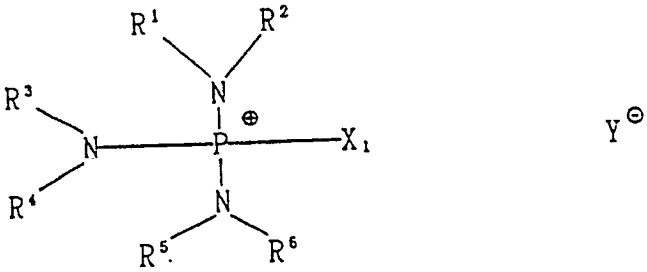
The anion represented by $Y_1^{\ominus}$ may include, for example, a halide ion, sulofnate ion, sulfate ion, $ClO_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, phosphonate ion, phosphate ion.

Formula (H-VI)



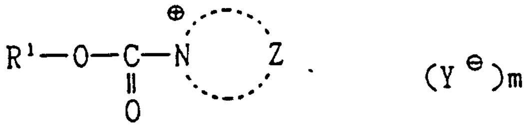
In the formula, R^1 and R^2 each represent an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aromatic heterocyclic group or $-NR^3R^4$ (R^3 and R^4 each represent an alkyl, alkenyl, cycloalkyl, aryl or aromatic heterocyclic group, and also include one having a ring formed through bonding of R^3 and R^4). X_1 is the same as the definition of X_1 in the formula (H-V).

Formula (H-VII)



In the formula, R^1, R^2, and R^3, R^4, and R^5, R^6 are the same as the definitions of R^1, R^2 in the formula (H-I), X_1 is the same as the definition of X_1 in the formula (H-V), and $Y_1^{\ominus}$ the same as the definition as $Y_1^{\ominus}$ in the formula (H-V).

Formula (H-VIII)



In the formula, R^1 represents an aryl group, Z represents a group of non-metallic atoms necessary for formation of an aromatic heterocyclic ring, and the ring formed by R^1 and Z is inclusive of those having substituents.

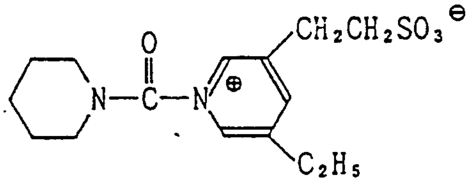
$Y^{\ominus}$ represents an anion, m represents 0 or 1, and when an intramolecular salt is formed, m is 0.

As the carboxyl activation type hardener to be used in the present invention, other than the compounds represented by the above formulae (H-I) through (H-VIII), the compounds described in Japanese Unexamined Patent Publications Nos. 38540/1975, 93470/1977, 43353/1981, 113929/1983, U.S. Patent 3,321,313, etc. are also preferable. In the following, specific examples of the compounds to be used in the present invention are set forth as classified, but the present invention is not limited at all to these.

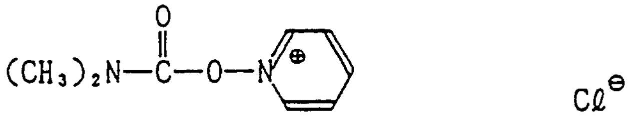
Compounds of the formula (H-I)

(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publications Nos. 51945/1974, 59625/1976, 9641/1986, 262854/1987, 264044/1987)

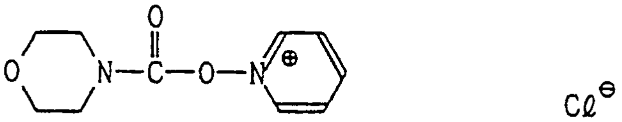
H－I－1



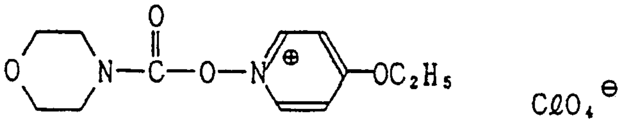
H－I－2



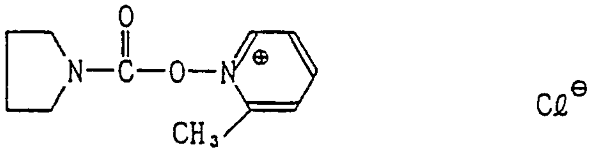
H－I－3



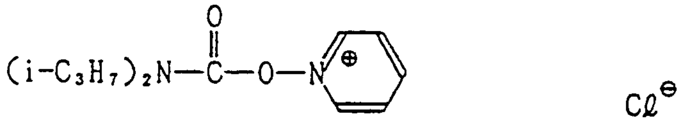
H－I－4



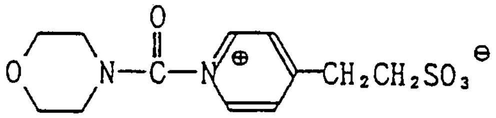
H－I－5



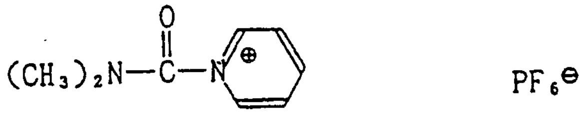
H－I－6



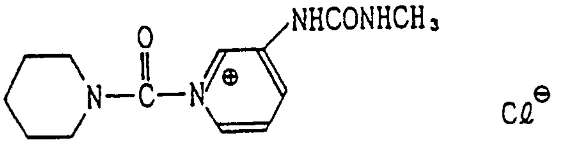
H－I－7



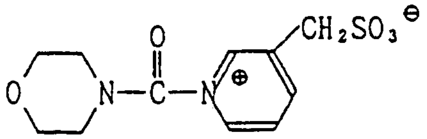
H－I－8



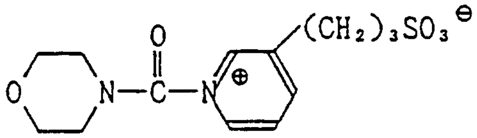
H－I－9



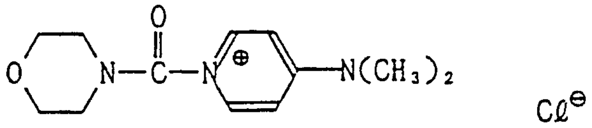
H－I－10



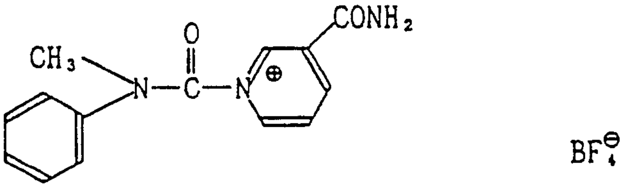
H－I－11



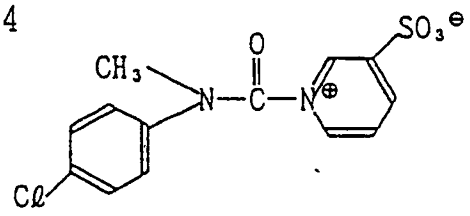
H－I－12



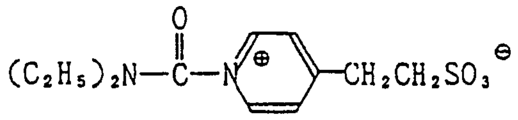
H－I－13



H－I－14

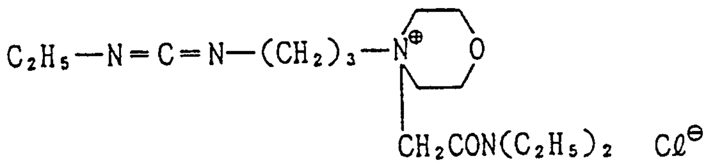


H－I－15

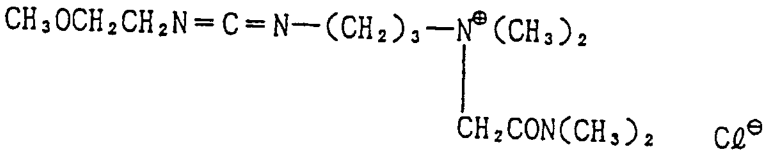


Compounds of the formula (H-II)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined patent Publications Nos. 126125/1976 and 48311/1977)

H－II－1

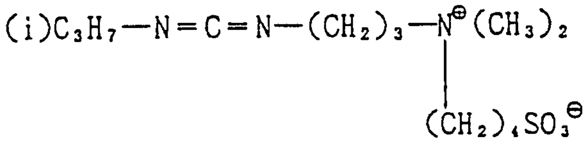


H－II－2



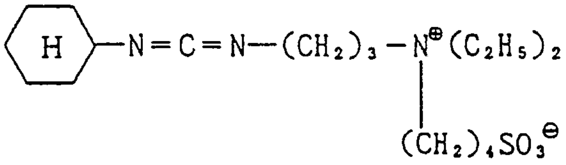
$$CH_3OCH_2CH_2N=C=N-(CH_2)_3-\underset{\displaystyle CH_2CON(CH_3)_2}{\underset{|}{N^{\oplus}}}(CH_3)_2 \qquad Cl^{\ominus}$$

H－II－3

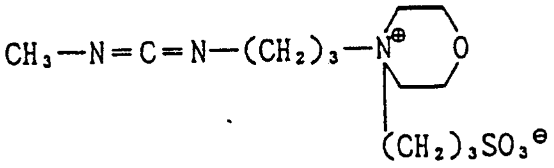


$$(i)C_3H_7-N=C=N-(CH_2)_3-\underset{\displaystyle (CH_2)_4SO_3^{\ominus}}{\underset{|}{N^{\oplus}}}(CH_3)_2$$

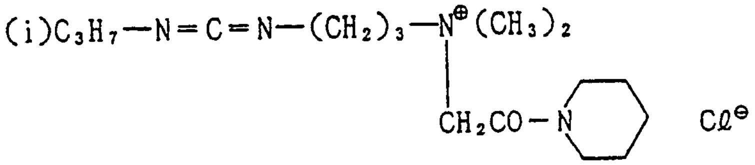
H－II－4



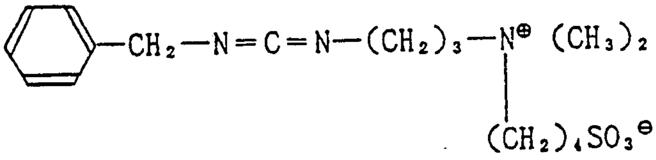
H−II−5



H−II−6

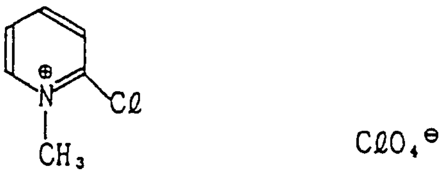


H−II−7

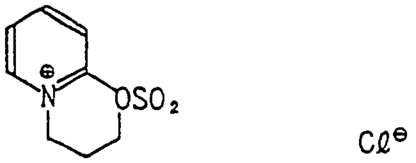


Compounds of the formula (H-III)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publication No. 44140/1982 and Japanese Patent Publications Nos. 46538/1982 and 50669/1983)

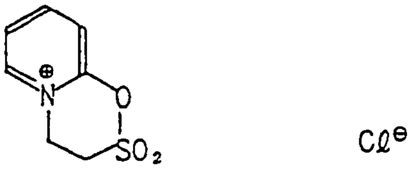
H−III−1



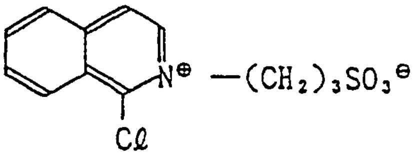
H—Ⅲ—2



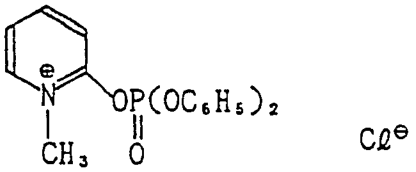
H—Ⅲ—3



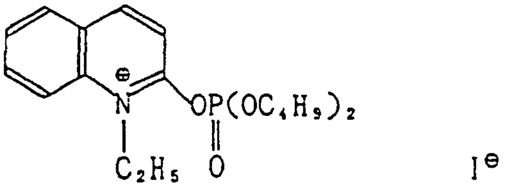
H—Ⅲ—4



H—Ⅲ—5

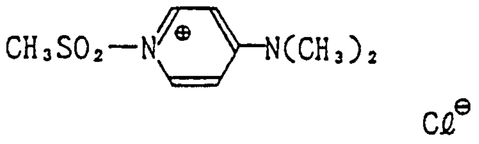


H—Ⅲ—6

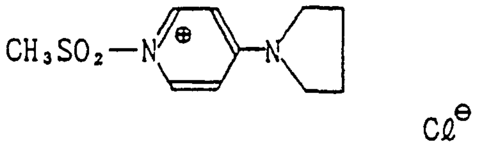


Compounds of the formula (H-IV)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publications No. 54427/1977)

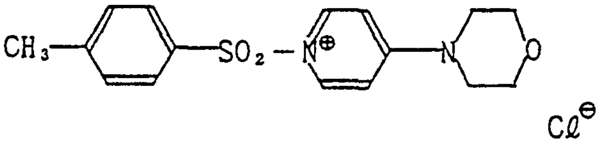
H — IV — 1



H — IV — 2

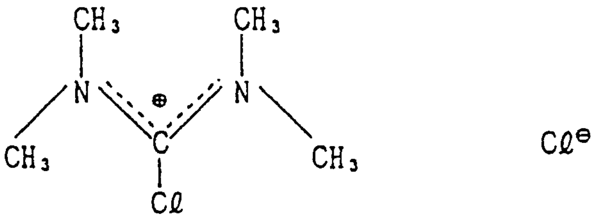


H — IV — 3

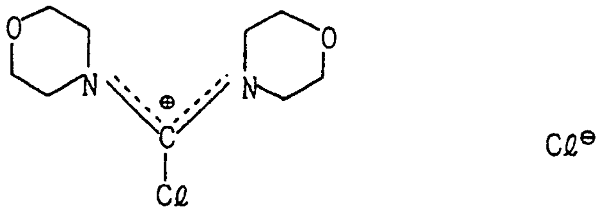


Compounds of the formula (H-V)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publications Nos. 225148/1985 and 240236/1986)

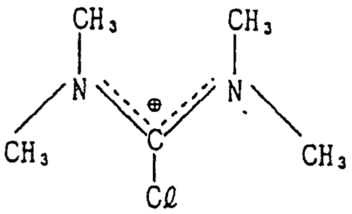
H — V — 1



H — V — 2

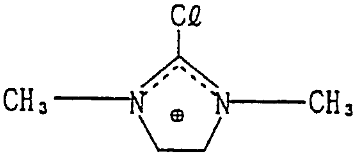


H — V — 3



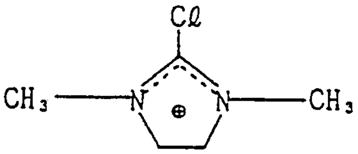
$PF_6^{\ominus}$

H — V — 4



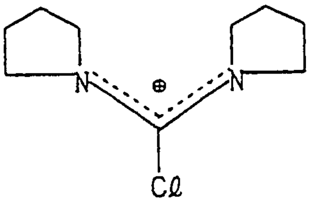
$PF_6^{\ominus}$

H — V — 5



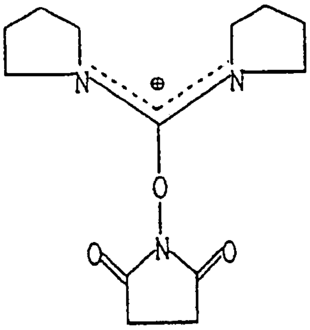
$Cl^{\ominus}$

H — V — 6



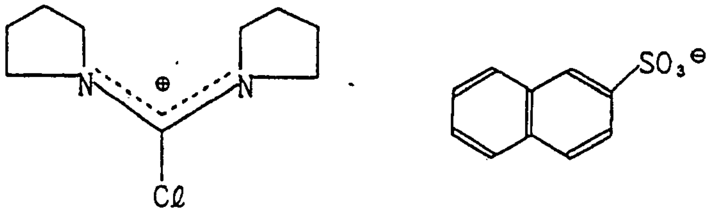
$Cl^{\ominus}$

H — V — 7

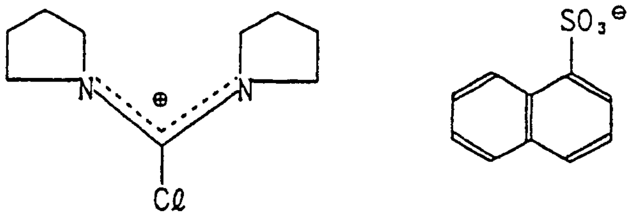


$BF_4^{\ominus}$

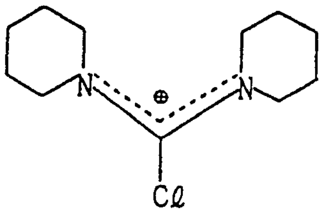
H — V — 8



H — V — 9

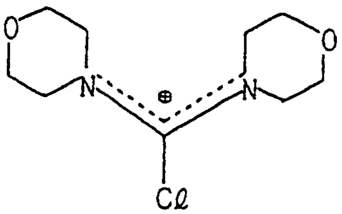


H — V — 10



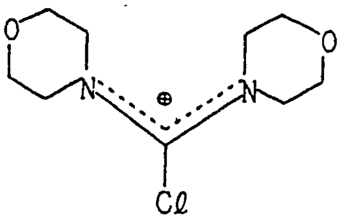
$Cl^{\ominus}$

H — V — 11



$Cl^{\ominus}$

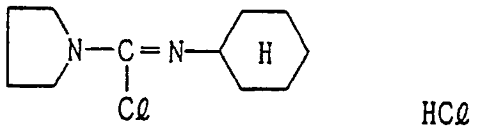
H — V — 12



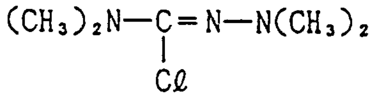
$BF_4^{\ominus}$

Compounds of the formula (H-VI)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publications Nos. 68866/1987 and 68867/1987)

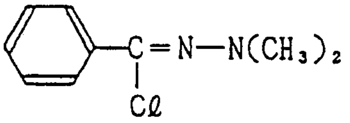
H—VI—1



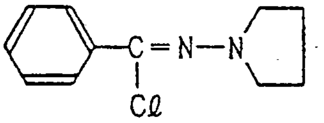
H—VI—2


$(CH_3)_2N\text{—}\underset{\displaystyle Cl}{\underset{|}{C}}\text{=}N\text{—}N(CH_3)_2$

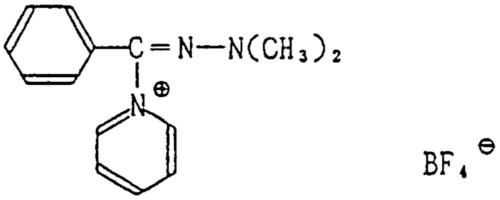
H—VI—3



H—VI—4



H—VI—5



Compounds of the formula (H-VII)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publication No. 128241/1986)

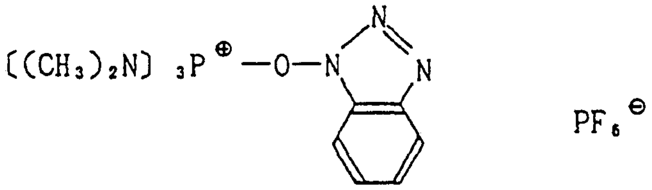
H—VII—1

$$[(CH_3)_2N]_3P^{\oplus}—Cl \qquad Cl^{\ominus}$$

H—VII—2

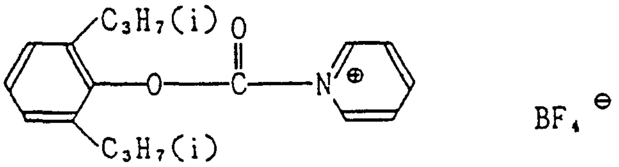
$$[(CH_3)_2N]_3P^{\oplus}—Cl \qquad BF_4^{\ominus}$$

H—VII—3

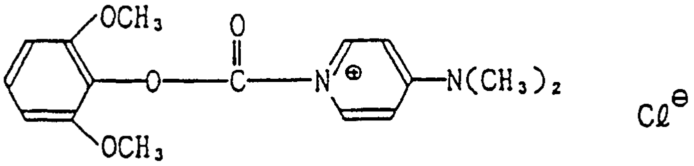


Compounds of the formula (H-VIII)
(these compounds and their synthetic methods are described in detail in Japanese Unexamined Patent Publication No. 234152/1987)

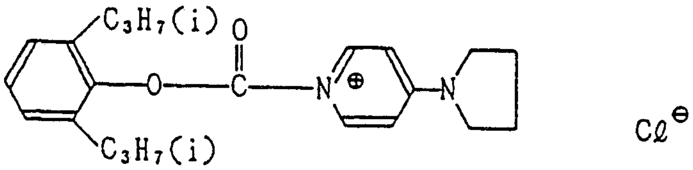
H—VIII—1



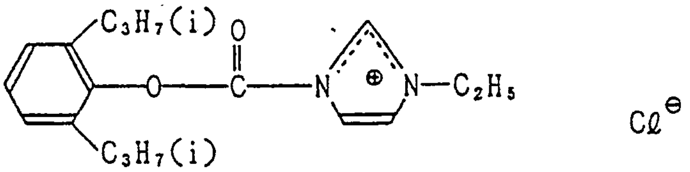
H—VIII—2



H—VIII—3

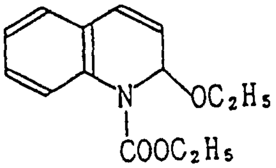


H—VIII—4

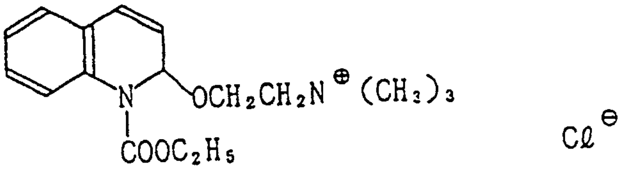


Compounds disclosed in Japanese Unexamined Patent Publication No. 38540/1975

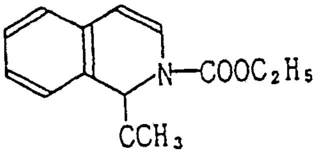
H—O—1



H—O—2

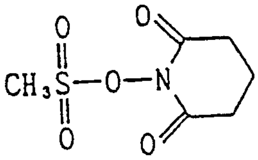


H—O—3

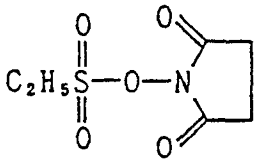


Compounds disclosed in Japanese Unexamined Patent Publication No. 93470/1977.

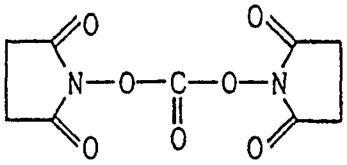
H—O—4



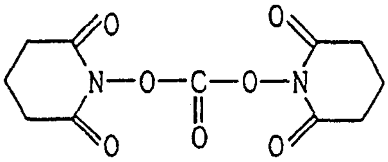
H—O—5



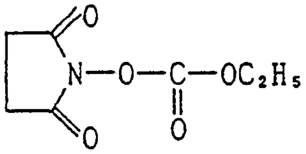
H—O—6



H—O—7

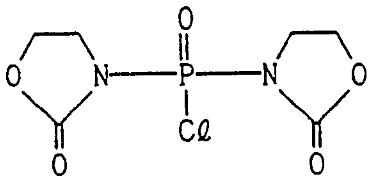


H—O—8

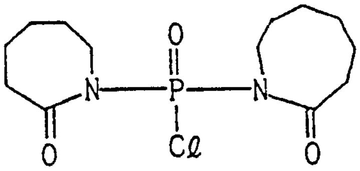


Compounds disclosed in Japanese Unexamined Patent Publication No. 113929/1983

H—O—9

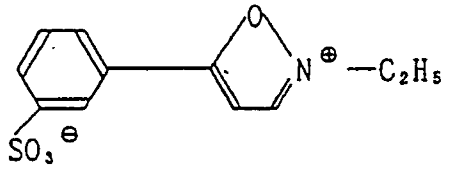


H—O—10

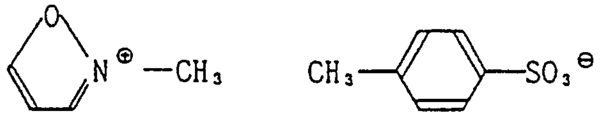


Compounds disclosed in U.S. Patent 3,321,313

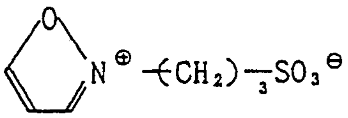
H—O—11



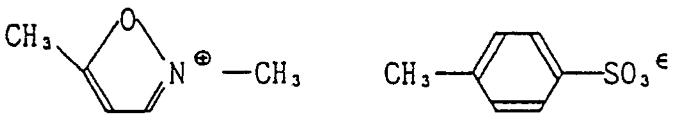
H—O—12



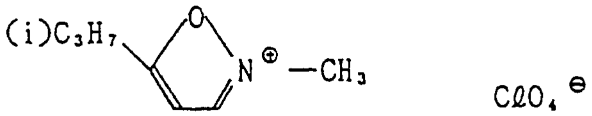
H—O—13



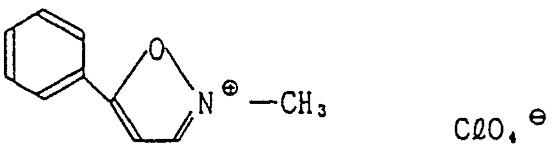
H—O—14



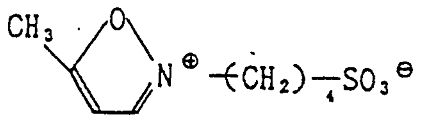
H—O—15



H—O—16



H-O-17



The amount of the carboxyl group activation type hardener to be used in the present invention can be selected as desired depending on the purpose. Generally, it can be used at a ratio of 0.01 to 10 % by weight based on dry gelatin. Particularly, preferable ratio is 0.05 to 5 % by weight.

The carboxyl group activation type hardener and other hardeners can be also used at any desired ratio, but when the carboxyl group activation type hardener is made 1, other hardeners may be used preferably within the range from 0.01 to 1 by weight ratio.

Next, the hydrophilic colloidal layer is to be described.

The hydrophilic colloidal layer in the present invention may be preferably a binder having amino groups and carboxyl groups, and may be a binder which undergoes hardening reaction with the carboxyl group activation type hardening agent, but generally gelatin may be advantageously used.

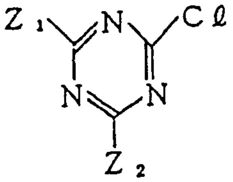
Gelatin may include, in addition to lime-treated gelatin, acid-treated gelatin, the enzyme-treated gelatin as described in Bull. Soc. Sci. Phot, Japan, No. 16, p. 30 (1966), gelatin derivatives (those obtained by reacting various compounds such as acid halide, acid anhydride, isocyanates, bromoacetic acid, alkanesultones, vinylsulfonamides, maleimide compounds, polyalkylene oxides, epoxy compounds, etc. with gelatin).

The emulsion layer and other hydrophilic colloid layers can incorporate plasticizers, dispersions of synthetic polymers insoluble or difficultly soluble in water (latices).

In the following, the chlorotriazine type film hardener according to the present invention is to be described

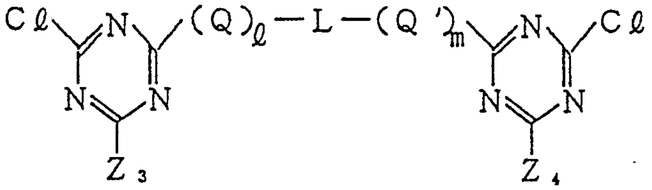
Preferable as the chlorotriazine type film hardner are those represented by the formula (H-1) or (H-2) shown below.

Formula (H-1)



In the formula, Z_1 represents chlorine atom, a hydroxy group, an alkyl group, an alkoxy group, an alkylthio group, -OM group (M represents a monovalent metal atom) or $-NR'R''$, $-NHCOR'''$ (R', R'', R''' each represent hydrogen atom, an alkyl group or an aryl group), and Z_2 has the same meaning as Z_1 excluding chlorine atom.

Formula (H-2)



In the formula, Z_3 and Z_4 each represent chlorine atom, hydroxy group, an alkyl group, an alkoxy group or -OM group (M represents a monovalent metal atom).

Q and Q′ are each linking group representing -O-, -S-, -NH-, L represents an alkylene group or an arylene group. ℓ and m each represent 0 or 1.

The alkyl group represented by Z_1 and Z_2 in the above formula (H-1) may be exemplified by a methyl,

ethyl and butyl groups, etc., the alkylthio group by a methylthio, ethylthio and butylthio groups, etc., and alkoxy group by a methoxy, ethoxy and butoxy groups, etc. Further, M of the -OM group represented by Z_1 or Z_2 may be, for example, sodium atom or potassium atom.

The chlorotriazine type film hardener shown by the above formula (H-2) is described in U.S. Patents 3,645,743, Japanese Patent Publications Nos. 6151/1972, 33380/1972 and 9607/1976, and Japanese Unexamined Patent Publications Nos. 19220/1973, 78788/1976, 60612/1977, 128130/1977, 130326/1977 and 1043/1981.

Next, the alkyl group represented by R_3 and R_4 may be, for example, a methyl, ethyl or butyl groups, etc., the alkoxy group may be, for example, a methoxy, ethoxy or butoxy groups, etc., and the M of -OM group, for example, sodium atom or potassium atom.

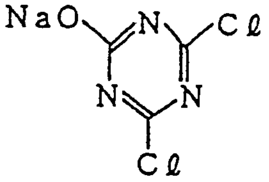
The alkylene group represented by L in the formula (H-2) may be the group of ,for example, $-CH_2-$, $--(CH_2)_2-$, $-(CH_2)_3-$, etc., the arylene group, for example, p-, o- or m-phenylene group, etc.

The chlorotriazine type film hardener represented by the above formula (H-2) is described in Canadian Patent 895,808, Japanese Patent Publication No. 33542/1983 and Japanese Unexamined Patent Publication No. 40244/1982.

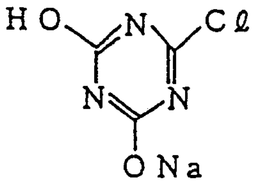
The compound represented by the above formula (H-1) or (H-2) is generally diffused into all the layers provided by coating, and therefore it may be added in at least one layer or a plurality of layers selected from among the emulsion layers according to the present invention or the auxiliary layers. Said addition may be performed by dissolving the compound in water or an alcohol (e.g. methyl alcohol, ethyl alcohol, etc.) and adding the solution in an amount of 1 to 100 mg, preferably 5 to 50 mg per 1 g of gelatin. The addition method may be either the batch system or the inline system.

In the following, representative examples of the chlorotriazine type film hardeners are set forth, but the present invention is not limited at all to these.

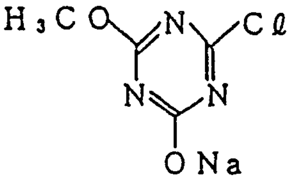
(H —1 - 1)



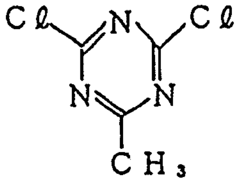
(H —1 - 2)



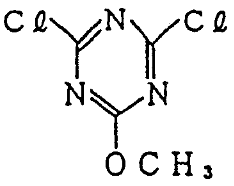
(H —1 - 3)



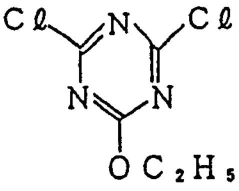
(H —1 - 4)



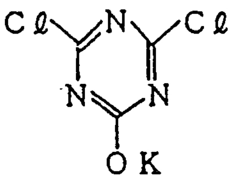
(H — 1 - 5)



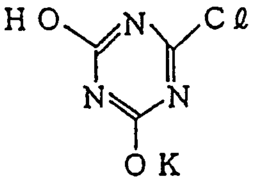
(H —1 - 6)



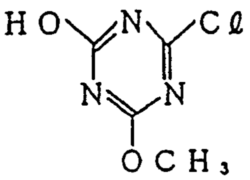
(H —1 - 7)



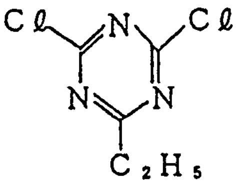
(H —1 - 8)



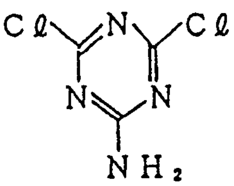
(H — 1 - 9)



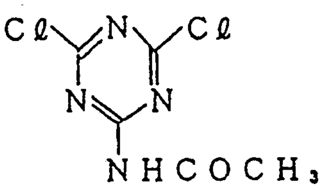
(H — 1 - 10)



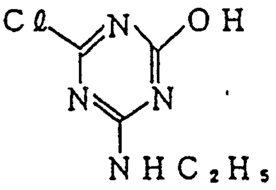
(H - 1 - 11)



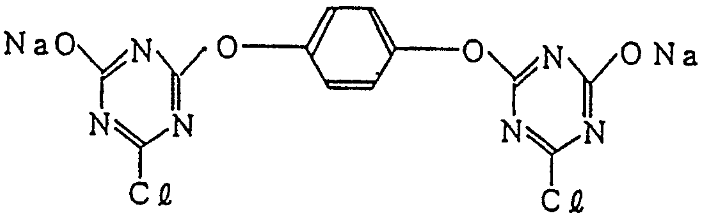
(H - 1 - 12)



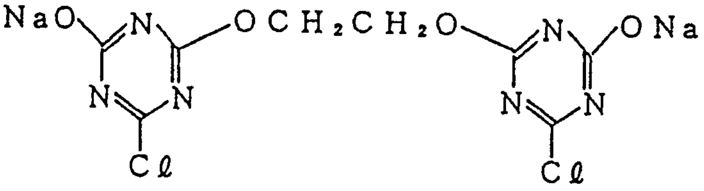
(H - 1 - 13)



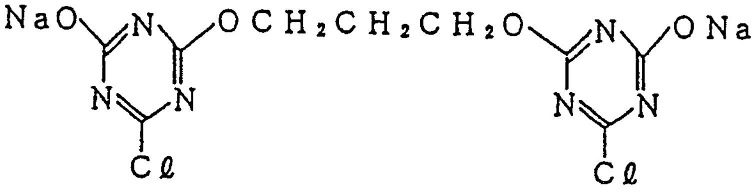
(H — 2 -1)



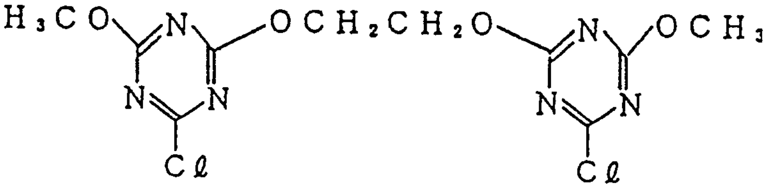
(H — 2 - 2)



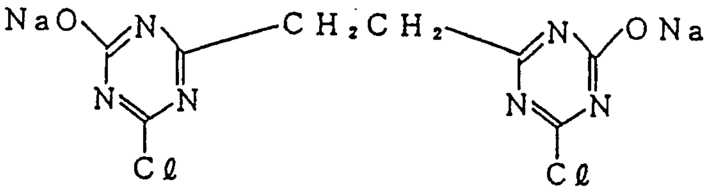
(H — 2 - 3)



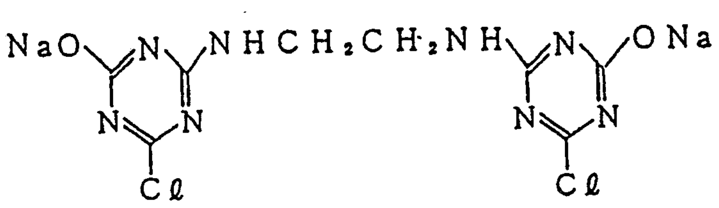
(H — 2 - 4)



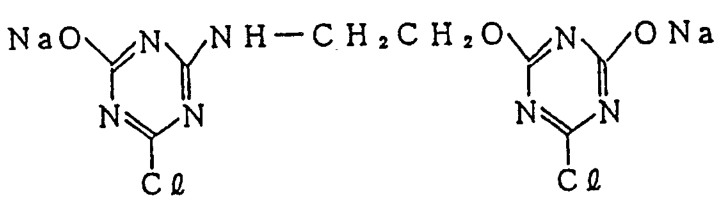
(H —2 - 5)



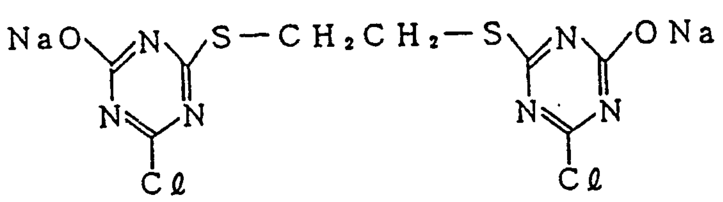
(H-2-6)



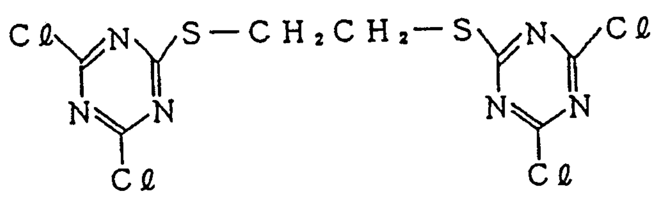
(H-2-7)



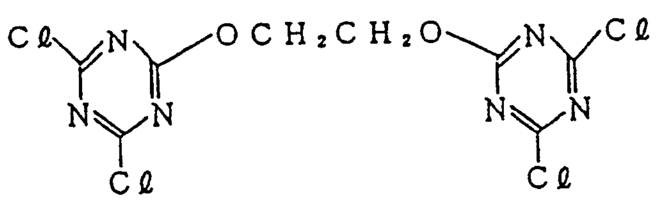
(H-2-8)



(H-2-9)



(H-2-10)



The bis(vinylsulfonylalkyl)ether type hardners to be used in the present invention will be described bellow.

Preferred Bis(vinylsulfonylalkyl)ether type hardner is represented by the following formula (H-a):

$CH_2=CHSO_2(CH_2)_mO\text{-}(L\text{-}O)_p\text{-}(CH_2)_nSO_2CH=CH_2$

In the formula; L denotes a divalent organic group, m and n denote positive integers, and p denotes 0 or 1.

More detail explanation on the hardener represented by the formula (H-a) will be made bellow. As the divalent organic group represented by L in the formula (H-a), preferred is an alkylene group having 1 to 10 carbon atoms, an arylene group having 6 to 10 carbon atoms, a divalent heterocyclic group, a divalent group represented by -O-, -S-, -SO-, -SO₂- or $-\underset{\underset{O}{\|}}{C}-$, or a divalent groups prepared by combining plural number of these divalent groups. The both ends of the divalent groups represented by L (portions to be bonded with oxygen atoms) should preferably be carbon atoms. n and m should preferably be an integer of 1 to 6, particularly preferably 1.

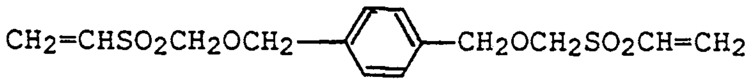
Methods for preparing the bis(vinylsulfonylalkyl)ether type hardners are described in Japanese Patent Publications No. 29622/1969, No. 24259/1972 and No. 25373/1972.

The amount of the bis(vinylsulfonylalkyl)ether type hardners can be selected depending on the purpose. It may be generally used in the rage of 0.01 to 20 % by weight, particularly preferably, in the range of 0.05 to 15 % by weight based on a dry gelatin.

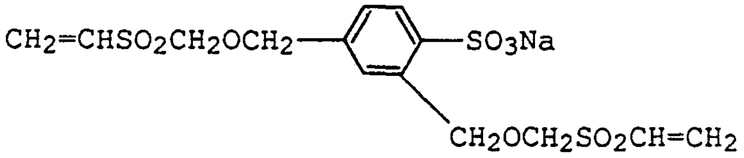
Representative specific examples of the bis(vinylsulfonylalkyl)ether type hardners will be enumerated bellow. However, it is not limitative thereto.

H-a-1 $CH_2=CHSO_2CH_2OCH_2SO_2CH=CH_2$
H-a-2 $CH_2=CHSO_2CH_2CH_2OCH_2CH_2SO_2CH=CH_2$
H-a-3 $CH_2=CHSO_2(CH_2)_4-O-(CH_2)_4-SO_2CH=CH_2$
H-a-4 $CH_2=CHSO_2CH_2OCH_2CH_2OCH_2SO_2CH=CH_2$
H-a-5 $CH_2=CHSO_2CH_2OCH_2CH_2CH_2OCH_2SO_2CH=CH_2$
H-a-6 $CH_2=CHSO_2CH_2OCH_2CH_2OCH_2CH_2OCH_2SO_2CH=CH_2$
H-a-7 $CH_2=CHSO_2CH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH=CH_2$

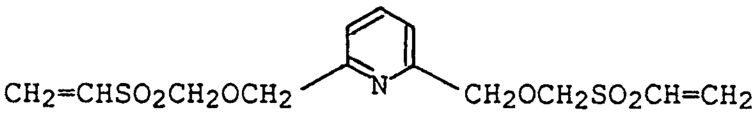
H-a-8



H-a-9



H-a-10



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

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

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

When the same color sensitive layer has a single layer constitution, the number of the layers coated of the light-sensitive layer can be reduced as compared with the overlaid constitution of the prior art, whereby the film can be made thinner. Therefore, production efficiency, sharpness are improved, and graininess is also improved.

The film thickness should be 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 (Shashin Kogyo Shuppansha, 1982).

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

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

As the means for making the exposure latitude of the silver halide emulsion layer which is a single layer wide, e.g. 3.0 or more, it is possible to use the method in which silver halide grains with different sensitivities are used as a mixture.

Specifically, there may be included, for example, the method in which silver halide grains with different grain sizes are used as a mixture, and the method in which the desensitizer is contained in at least a part of the silver halide grains.

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

As the silver halide grains with different grain sizes used in a mixture for obtaining a broad exposure latitude, the combination of silver halide grains having a maximum mean grain size of 0.2 to 2.0 µm and silver halide grains having a minimum mean grain size of 0.05 to 1.0 µm may be preferable, and further one or more of silver halide grains having an intermediate mean grain size may be also combined.

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

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

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

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

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

In the present invention, the metal ion doping method is preferred. As the metal ion to be used for doping, there may be included the metal ions of the groups Ib, IIb, IIIa, IIIb, IVb, Va, VIII in the periodic table of elements. Preferable metal ions may include Au, Zn, Cd, Tl, Sc, Y, Bi, Fe, Ru, Os, Rh, Ir, Pd, Pr, Sm and Yb. Particularly, Rh, Ru, Os and Ir are preferred.

These metal ions can be used as, for example, halogeno complexes, etc., and the pH of the AgX system during doping should be preferably 5 or less.

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

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

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

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

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

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

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

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

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

Also, the fluctuation coefficient defined by the ratio $S/\bar{r}$ of the standard deviation of grain size (S) as the silver halide grains contained in the respective silver halide emulsion layers and the mean grain size ($\bar{r}$) should be preferably 0.4 or less, more preferably 0.33 or less, further preferably 0.25 or less, particularly preferably 0.20 or less.

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

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

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

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

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

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

The content of silver iodide in an inner phase (core) having the maximum silver iodide content is preferably 6 to 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 %.

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

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

% based on the whole grains.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 mono-dispersed emulsion

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

Table 1

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

In a reaction vessel in which the above seed emulsion and an aqueous gelatin solution had been added, while controlling the pAg and the pH in the reaction vessel, were added an aqueous ammoniacal silver nitrate solution, an aqueous potassium iodide solution and an aqueous potassium bromide solution in proportion to the surface area during the grain growth, followed by subsequent addition in place of the aqueous potassium bromide solution at an adequate grain size.

After precipitation and desalting were practiced similarly as in the case of the seed emulsion, gelatin was added to effect re-dispersion to give an emulsion of pAg 7.8, pH 6.0.

Thus, silver iodobromide emulsions EM-1 and EM-2 with high iodine contents internally of grains were prepared.

The emulsions and their contents are shown in Table 2.

Table 2

EM No.	Mean grain size (μm)	Mean Ag content (mol %)	Seed emulsion	Fluctuation coefficient
EM-1	0.65	6.5	NE-1	0.17
EM-2	0.35	8.5	NE-1	0.18
EM-3	0.65	6.5	NE-1 and NE-2 (*1)	0.17

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

Example 1

Preparation of Sample No. 101 (Control)

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

The amounts coated are indicated in the amount represented in g/m^2 unit calculated on silver for silver halide and colloidal silver, the amount represented in g/m^2 unit for the additive and gelatin, and further in moles per mole of silver within the same layer for sensitizing dye, coupler and DIR compound.

The emulsion contained in each color sensitive emulsion layer was applied with optimum sensitization with sodium thiosulfate and chloroauric acid.

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

	Dioctyl phthalate (abbreviated as DOP)	0.03
Second layer(IL-1)	Gelatin	2.0
(Intermediate	Antistaining agent (AS-1)	0.1
layer)	DOP	0.1
Third layer(R-1)	EM-2	1.2
(First red-	Gelatin	1.1
sensitive	Sensitizing dye I	6×10^{-4}
emulsion layer)	Sensitizing dye II	1×10^{-4}
	Coupler (C-1)	0.085
	Coupler (CC-1)	0.005
	DIR compound (E-23)	0.0015
	DIR compound (E-42)	0.002
	DOP	0.6
Fourth layer(R-2)	EM-1	1.3
(Second red-	Gelatin	1.1
sensitive	Sensitizing dye I	3×10^{-4}
emulsion layer)	Sensitizing dye II	1×10^{-4}
	Coupler (C-2)	0.007
	Coupler (C-3)	0.027
	Coupler (CC-1)	0.0015
	DIR compound (E-42)	0.001
	DOP	0.2
Fifth layer(IL-2)	Gelatin	0.8
(Intermediate	AS-1	0.03
layer)	DOP	0.1
Sixth layer(G-1)	EM-2	1.3
(First green-	Gelatin	1.2
sensitive	Sensitizing dye III	2.5×10^{-4}
emulsion layer)	Sensitizing dye IV	1.2×10^{-4}
	Coupler (M-2)	0.09
	Coupler (CM-1)	0.004

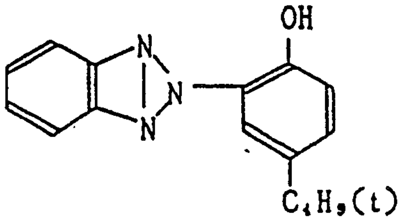
	DIR compound (E-23)	0.001
	DIR compound (E-26)	0.003
	Tricresyl phosphate (abbreviated as TCP)	0.5
Seventh layer(G-2) (Second green-sensitive emulsion layer)	EM-1	1.4
	Gelatin	0.8
	Sensitizing dye III	1.5 x 10^{-4}
	Sensitizing dye IV	1.0 x 10^{-4}
	Coupler (M-1)	0.03
	Coupler (CM-1)	0.002
	DIR compound (E-26)	0.001
	TCP	0.3
Eighth layer (YC) (Yellow filter layer)	Gelatin	0.6
	Yellow colloidal silver	0.08
	AS-1	0.1
	DOP	0.3
Ninth layer (B-1) (First blue-sensitive emulsion layer)	EM-2	0.5
	Gelatin	1.1
	Sensitizing dye V	1.3 x 10^{-4}
	Coupler (Y-1)	0.29
	TCP	0.2
Tenth layer (B-2) (Second blue-sensitive emulsion layer)	EM-1	0.5
	Gelatin	1.2
	Sensitizing dye V	1 x 10-4
	Coupler (Y-1)	0.08
	DIR compound (E-42)	0.003
	TCP	0.1
Eleventh layer (Pro-1) (First protective layer)	Gelatin	0.55
	UV-ray absorber UV-1	0.1
	UV-ray absorber UV-2	0.2
	DOP	0.03
	Silver iodobromide AgI 1 mol%	0.5

mean grain size 0.07 μm

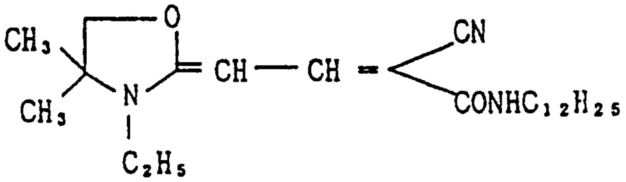
Twelfth layer (Pro-2) (Second protective layer)	Gelatin	0.5
	Polymethyl methacrylate grains (diameter 1.5 μm)	0.2
	Formalin scavenger (HS-1)	3.2
	Film hardener (HH-1)	0.4

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

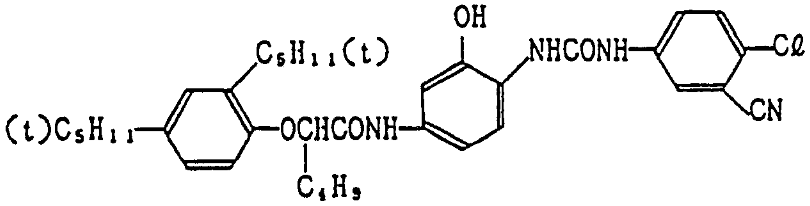
UV-1



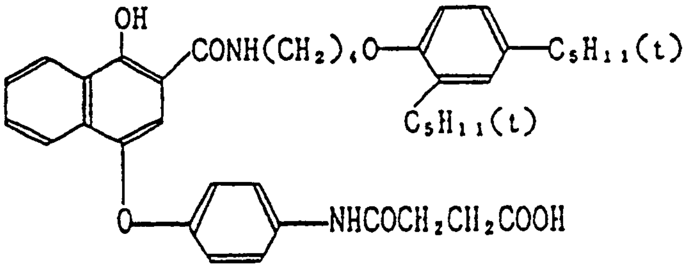
UV-2



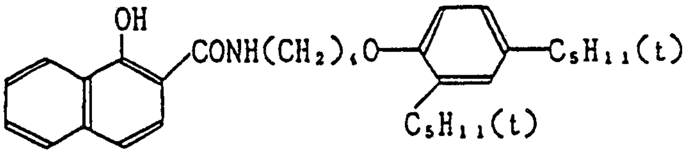
C-1



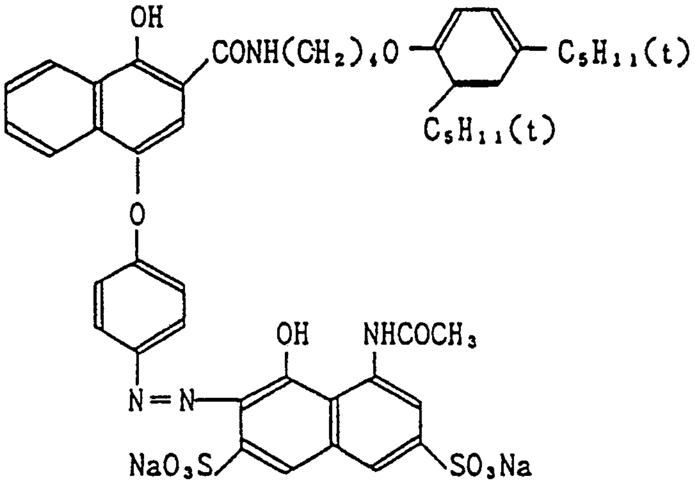
C-2



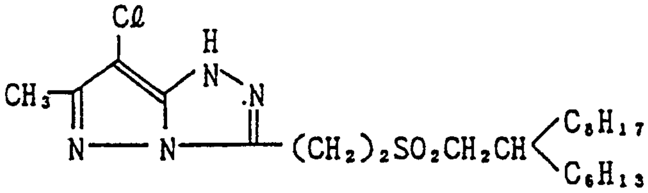
C-3



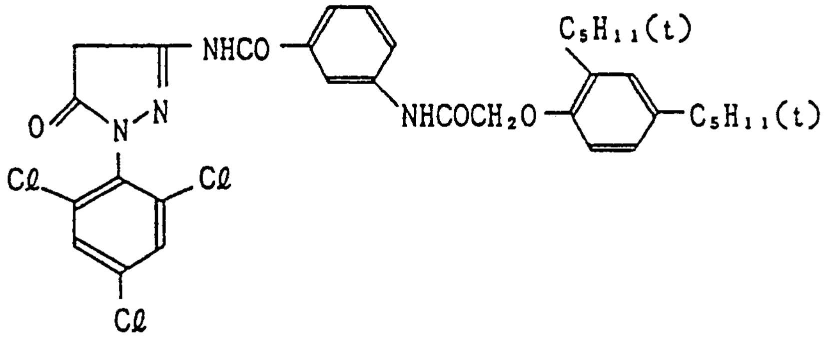
CC－1


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

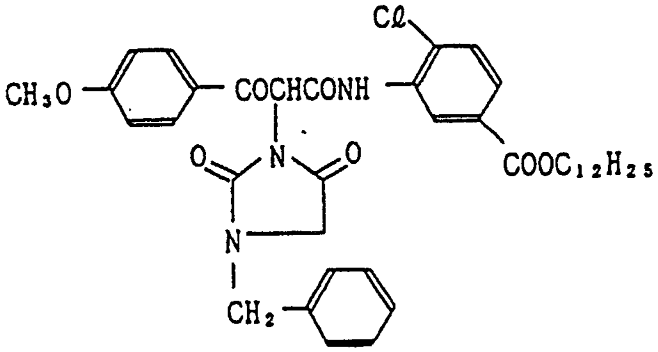
M－1


Cℓ
H
N
N
CH₃
N
N
(CH₂)₂SO₂CH₂CH
C₈H₁₇
C₆H₁₃

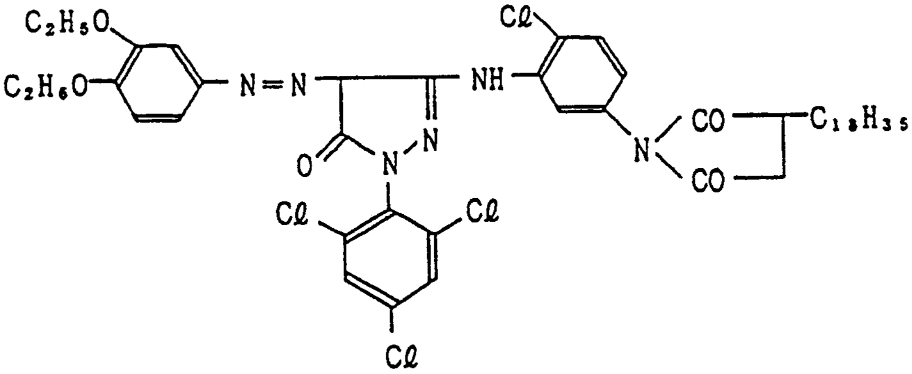
M－2


NHCO
C₅H₁₁(t)
O
N
N
NHCOCH₂O
C₅H₁₁(t)
Cℓ
Cℓ
Cℓ

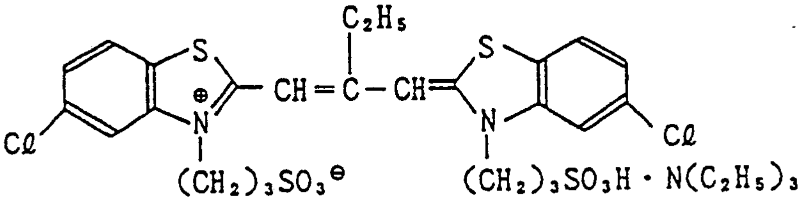
Y－1



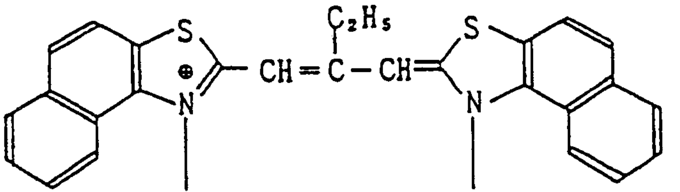
CM－1



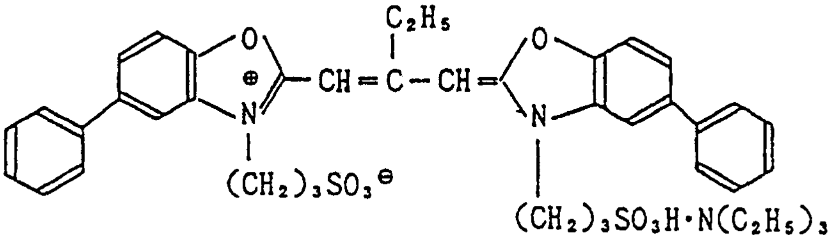
Sensitizing dye I



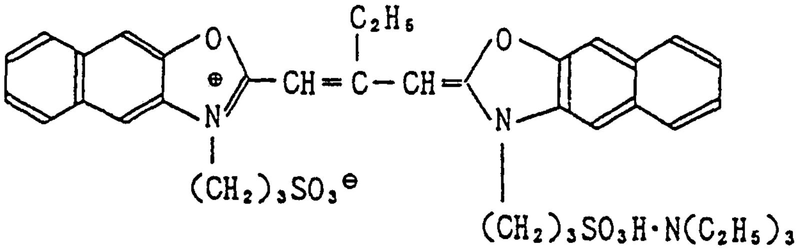
Sensitizing dye II



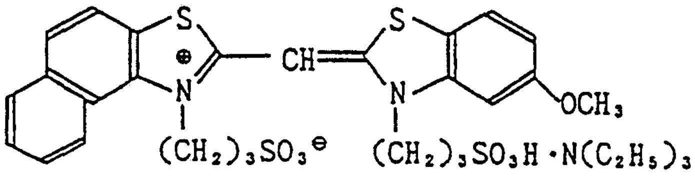
Sensitizing dye III



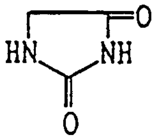
Sensitizing dye IV



Sensitizing dye V



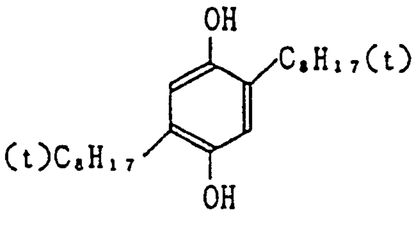
H S — 1



H H — 1

$CH_2=CHSO_2CH_2SO_2CH=CH_2$

A S — 1



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. 112 were prepared.

Samples No. 102 to 106 were prepared in the same manner as Sample No. 101 except for adding those indicated in Table 3 in place of the film hardener HH-1 contained in Pro-2.

Sample No 107 was prepared in the same manner as Sample No. 101 except for omitting G-2 and B-2 in Sample No. 101, changing the emulsion contained in G-1 and B-1 to a mixture of equal moles of EM-1 and EM-2.

Samples No. 108 to No. 112 were prepared in the same manner as Sample No. 107 except for adding those shown in Table 3 in place of the film hardener HH-1 contained in Pro-2.

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

Table 3

Sample No.	Constitution of light-sensitive layer			Film hardener of the presents invention added in Pro-2	
	B *1	G *2	R *3	Kind	Amount added
Control					
101	Double	Double	Double	HH-1	0.4
102	Double	Double	Double	HH-2	0.4
103	Double	Double	Double	H-I-7	0.4
104	Double	Double	Double	H-I-10	0.4
105	Double	Double	Double	H-1-1	0.4
106	Double	Double	Double	H-1-2	0.4
107	Single	Single	Double	HH-1	0.4
108	Single	Single	Double	HH-2	0.4
Invention:					
109	Single	Single	Double	H-I-7	0.4
110	Single	Single	Double	H-I-10	0.4
111	Single	Single	Double	H-1-1	0.4
112	Single	Single	Double	H-1-2	0.4

*1 B : blue-sensitive emulsion layer,
*2 G : green-sensitive emulsion layer,
*3 R : red-sensitive emulsion layer
HH-2 $CH_2=CHSO_2CH_2CH_2SO_2CH=CH_2$

The samples Nos. 101 to 112 thus obtained were divided into two, one of which was provided as the standard sample, while the other subjected to storage stability test of the light-sensitive material by leaving it to stand under the conditions of 25 °C, RH of 80 % for 15 days.

Subsequently, wedge exposure was effected in conventional manner, and then color developing was performed with the processing liquors and processing steps shown below.

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

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

Color developing solution	
4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	4.75 g
Anhydrous sodium sulfite	4.25 g
Hydroxylamine 1/2 sulfate	2.0 g
Anhydrous potassium carbonate	37.5 g
Potassium bromide	1.3 g
Nitrilotriacetic acid•trisodium salt (monohydrate)	2.5 g
Potassium hydroxide	1.0 g
(made up to one liter with addition of water)	
Bleaching solution	
Iron (III) ammonium ethylenediaminetetraacetate	100.0 g
Diammonium ethylenediaminetetraacetate	10.0 g
Ammonium bromide	150.0 g
Glacial acetic acid	10.0 g
(made up to one liter with addition of water, and adjusted to pH 6.0 with ammonia water)	
Fixing solution	
Ammonium thiosulfate	175.0 g
Anhydrous ammonium thiosulfite	8.6 g
Sodium metasulfite	2.3 g
(made up to one liter with additon of water, and adjusted to pH 6.0 with acetic acid)	
Stabilizing solution	
Formalin (37 % aqueous solution)	1.5 ml
Konidax (manufactured by Konica K.K.)	7.5 ml
(made up to one lither with addition of water)	

For observing the storage stability of the light-sensitive material of each sample thus processed, the results of the green-sensitive layer evaluated as a storage stability of the gradation according to the evaluation method as described below by comparison of the characteristic curves are shown in Table 4.

The evaluation method of the storage stability of the gradation is to be described by use of drawings as the attached sheet.

Fig. 1 is the characteristic curve, the broken line shows the characteristic of the standard sample and the solid line that of the sample to be evaluated.

Fig. 2 shows the point gamma values of the respective exposure points from the exposure point which gives + 1 to a density of the minimum density in Fig. 1 to the exposure point of $\Delta \log H = +3.0$ ($\Delta \log H = 0.15$ between the respective exposure points).

From Fig. 2, storage stability of gradation is represented by the value Σ which is a product of 1,000 with the standard deviation σ of the absolute value $\Delta\gamma$ of the difference between the point gamma values at the respective exposure points of the characteristic curve which is the standard and the characteristic curve to be evaluated.

The gradation change is not uniform, and the storage stability of the gradation is not excellent as the value of Σ is greater.

Table 4

Sample No.	Storage stability of gradation
Control:	
101	81
102	85
103	78
104	79
105	74
106	75
107	75
108	76
Present invention:	
109	55
110	63
111	60
112	59

As is apparent from Table 4, the samples of the present invention were found to have excellent storage stability of gradation with little fluctuation of gradation from the highlight to the shadow of the characteristic curve in storage of light-sensitive material.

When the film hardener as a control is used, as can be seen from comparison between Samples No. 101 and No. 107 and comparison between No. 102 and No. 108, even if the two color-sensitive layers may be made single layer constitutions, only slight improvement can be effected. In contrast, when the film hardener of the present invention is used, as is apparent from comparison between Samples No. 103 and No. 109, comparison between No. 104 and No. 110, comparison between No. 105 and No. 111, and comparison between No. 106 and No. 112, it can be understood that great extent of improvements can be effected. Also, the samples of the present invention were found to have higher color forming densities as compared with the control.

Also, the effects of the present invention are not limited to the film hardeners used in the examples, but could be observed in all the compounds in the film hardeners shown by the exemplary compounds.

Also, the effects were observed most greatly when all the three layers of the blue-sensitive, green-sensitive and red-sensitive layers were made single layer constitutions.

Also, the effects of the present invention could be recognized in the respective samples by use of E-2, E-4 or E-29 in place of the DIR compound E-42 in B-2 of Sample No. 109, the respective samples by use of E-2, E-6 or E-10 in place of the DIR compound E-26 in G-2 of Sample No. 111, and the respective samples by use of E-17, E-19 or E-21 in place of the DIR compound E-23 in R-1 of Sample No. 112.

Also, in the respective samples by use of seed emulsions prepared by addition of $RuCl_3$, $OsCl_3$ or $Pb(NO_3)_2$ in place of K_3RhCl_6 in place of NE-2 as substitute for EM-3 in Samples No. 107 to No. 112, the effects of the present invention could be recognized.

Example 2

Sample No. 201 was prepared in the same manner as in Sample No. 101 of Example 1.

35 Next, Samples Nos. 202 to 206 were prepared. In Samples Nos. 202 and 203, H-a-1 was added in place of the hardner HH-1 contained in the Pro-2 layer of Sample No. 201.

Sample No. 204 was a multi-layer light-sensitive color material entirely the same as Sample No. 201. Sample Nos. 202 and 205 were prepared in the same manner as in Sample No. 201 excepting for removing the G-2 and B-2 layers in Sample No. 201, changing the emulsions contained in the G-1 and B-1 layers in Sample No. 201 to Em-3 in an equimolar amount with Em-2 and changing the hardner contained in the Pro-2 layer of Sample No. 201 as described above.

Sample Nos. 203 and 206 were prepared in the same manner as in Sample No. 202 excepting for removing the R-2 layer in Sample No. 202, changing the emulsions contained in the R-2 layer in Sample No. 202 to Em-3 in an equimolar amount with Em-2 and changing the hardner contained in the Pro-2 layer of Sample No. 202 as described above.

The content of samples thus prepared are shown in Table 5. The evaluations of gradation and storability and the exposure and developing processings were conducted in the same manner as in Example 1.

Table 5

Sample No.	Constitution of light-sensitive layer			Film hardner of the present invention added in Pro-2		Storage stability of gradation
	B *1	G *2	R *3	Kind	Amount	
Control:						
201	Double	Double	Double	HH-1	0.4	81
202	Single	Single	Double	HH-1	0.4	75
203	Single	Single	Single	HH-1	0.4	63
204	Double	Double	Double	H-a-1	0.4	65
Present invention:						
205	Single	Single	Double	H-a-1	0.4	48
206	Single	Single	Single	H-a-1	0.4	40

As is apparent from Table 5, it is realized that the samples of the present invention show small variation in gradation from the highlight thorough the shadow of the characteristic curve and good storability of gradation. It is also realized that the samples of the present invention has a wide exposure latitude as the exposure latitude represented by log H was 3.0 or more. Further, when the blue-sensitive and red-sensitive layers comprise a single layer constitution and when the green-sensitive and red-sensitive layers comprise a single layer constitution in place of Sample No. 205, the same effect as in Sample No. 205 could be recognized.

Further, it was recognized that the effect of the present invention was shown with good gradation storability when EM-3 used for the blue-sensitive and green-sensitive layers of Sample No. 205 were replaced with a mixed emulsion of EM-1 and EM-2 in the equimoler amount in terms of a total Ag amount.

Also, the effect of the present invention was mostly shown when the hardner of the present invention was used and all of the three color sensitive layers were composed of a single layer constitution.

Claims

1. A light-sensitive silver halide color photographic material, comprising a support and silver halide emulsion layers which are respectively blue-sensitive, green-sensitive or red-sensitive and are provided on the support, wherein said material contains a DIR compound and at least one selected from the group consisting of a film hardner which acts through activation of carboxyl groups, a chlorotriazine type film hardener, a bis(vinylsulfonylalkyl)ether type film hardener and at least two of said blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers have single layer constitutions.

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

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

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

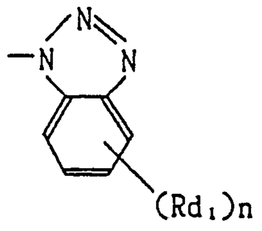
A - (Y)m

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

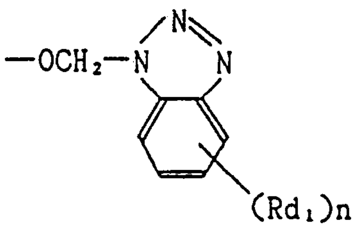
5. The light-sensitive silver halide color photographic material according to Claim 4, wherein the group

represented by Y is represented by Formulae (D-2) to (D-9) set forth below:

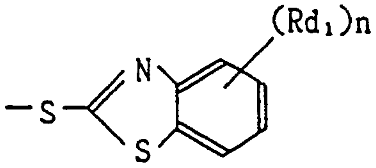
Formula (D-2)



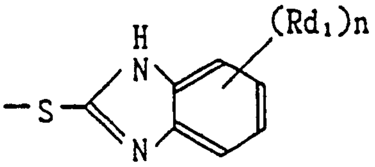
Formula (D-3)



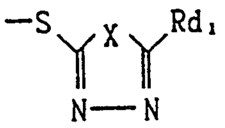
Formula (D-4)



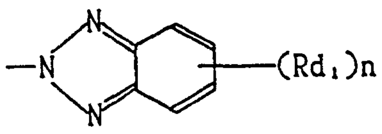
Formula (D-5)



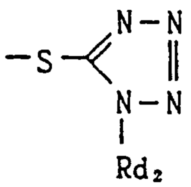
Formula (D-6)



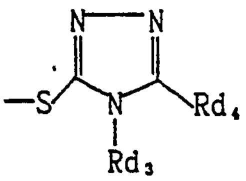
Formula (D-7)



Formula (D-8)



Formula (D-9)



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

in Formula (D-6), X represents oxygen atom or sulfur atom;

in Formula (D-8), Rd_2 represents at least one selected from the group consisting of an alkyl group, an aryl group and a heterocyclic group;

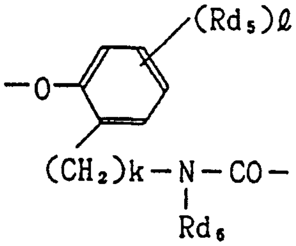
in Formula (D-9), Rd_3 represents selected from the group consisting of hydrogen atom and an alkyl, cycloalkyl, aryl and heterocyclic group, Rd_4 represents at least one selected from the group consisting of

hydrogen atom, a halogen atom and an alkyl, cycloalkyl, aryl, acylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkanesulfonamide, cyano, heterocyclic, alkylthio and amino group;
when at least one of Rd_1, Rd_2, Rd_3 and Rd_4 represents an alkyl group, the alkyl group may include those having substituents, and may be either straight or branched;
when at least one of Rd_1, Rd_2, Rd_3 and Rd_4 represents an aryl group, the aryl group may include those having substituents;
when at least one of Rd_1, Rd_2, Rd_3 and Rd_4 represents a heterocyclic group, the heterocyclic group may include those having substituents;
the carbon atoms contained in Rd_2 in Formula (D-8) is 0 to 15; and
in Formula (D-9), the total carbon atoms contained in Rd_3 and Rd_4 is 0 to 15.

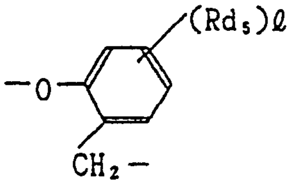
6. The light-sensitive silver halide color photographic material according to Claim 4, wherein the group represented by Y is a compound represented by Formula (D-10) set forth below:
$-(TIME)_n-INHIBIT$
wherein the TIME group is a group, bound to the coupling position of A and being cleavable through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

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

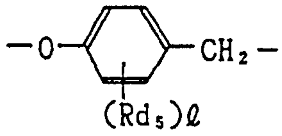
Formula (D-11)



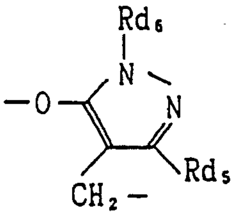
Formula (D-12)



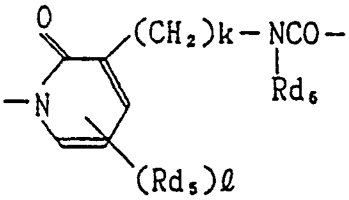
Formula (D-13)



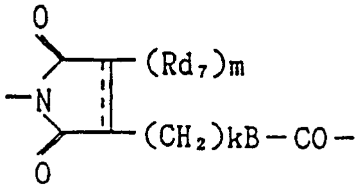
Formula (D-14)



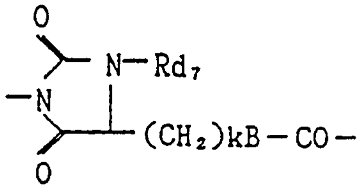
Formula (D-15)



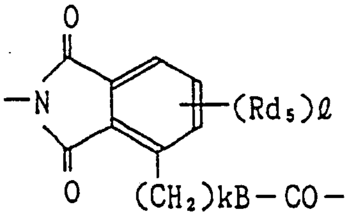
Formula (D-16)



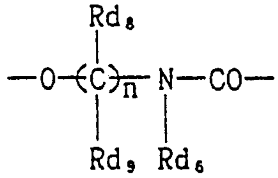
Formula (D-17)



Formula (D-18)



Formula (D-19)



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

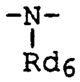
in Formulae (D-11) to (D-13), (D-15) and (D-18), Rd_5's may be mutually bonded together to form a fused ring;

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

each of Rd_8 and Rd_9 in Formulae (D-19) represents at least one of hydrogen atom and an alkyl group, k in Formulae (D-11) and (D-15) to (D-18) represents an integer of 0, 1 or 2, ℓ in the formulae (D-11) to (D-13), (D-15) and (D-18) represents an integer of 1 to 4, m in Formula (D-16) represents an integer of 1 or 2;

when ℓ and m are 2 or more, the respective Rd_5 and Rd_7 may be either the same or different; n in Formula (D-19) represents an integer of 2 to 4, and Rd_8 and Rd_9 in number of n may be each the same or different;

B in Formulae (D-16) to (D-18) represents oxygen atom or



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

(Rd_6 represents the same meaning as already defined); and -------- in Formula (D-16) may be either a single bond or a double bond, and m is 2 in the case of the single bond and m is 1 in the case of the double bond.

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

$\{T_1\}_{\ell}SR\{T_2\}_{m}\text{INHIBIT}$

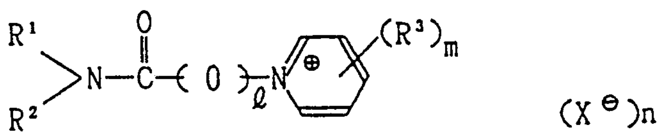
wherein T_1 represents a component which cleaves $SR\{T_2\}_{m}\text{INHIBIT}$, SR a component which forms $(T_2)_{m}\text{ INHIBIT}$ through the reaction with the oxidized product of a developing agent after formation of

$SR{(T_2)}_m$ INHIBIT, T_2 a component which cleaves INHIBIT after formation of ${(T_2)}_m$ INHIBIT, INHIBIT a developing inhibitor and ℓ and m are each 0 or 1.

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

10. The light-sensitive silver halide color photographic material according to Claim 1, wherein the hardener which acts through activation of carboxyl groups is at least one of compounds represented by Formulae (H-1) to (H-VIII):

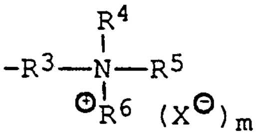
Formula (H-I)



in the formula, R^1 and R^2 each represent an alkyl group or an aryl group, R^3 represents at least one selected from the group consisting of $-NR^4R^5$ (R^4 and R^5 have the same meanings as R^1 and R^2), a halogen atom, a carbamoyl group, a sulfo group, a ureido group, an alkoxy group and an alkyl group, m represents 0 to 5, and when m ≧ 2, the plural number of R^3's may be either the same or different from each other, $X^\ominus$ represents an anion, ℓ represents 0 or 1, n represents 0 to 2, and when an intramolecular salt is formed, n is 0;

Formula (H-II) $R^1-N=C=N-R^2$

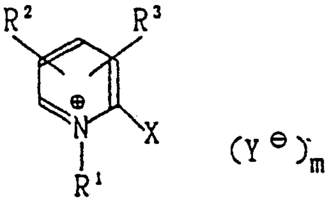
in the formula, R^1 and R^2 each represent at least one selected from the group consisting of a cycloalkyl group, an alkyl group, an alkoxy, alkyl group, an aralkyl group, phenethyl group and a group represented by the formula:



$$-R^3-\overset{R^4}{\underset{\oplus R^6}{N}}-R^5 \quad (X^\ominus)_m$$

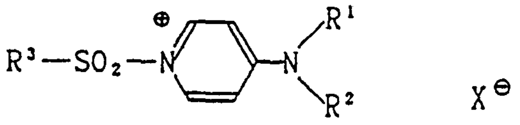
in the formula, R^3 represents an alkylene group, R^4, R^5 and R^6 each represent an alkyl group, m represents 0 or 1, $X^\ominus$ represents an anion;

Formula (H-III)



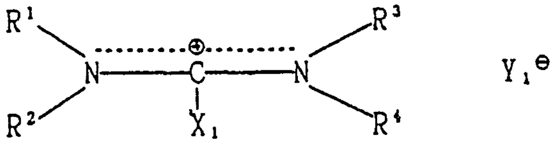
in the formula, R^1 represents an alkyl group or an aryl group, R^2 and R^3 each represent hydrogen atom or substituents, X represents a group eliminable when the compound represented by the formula (H-III) reacts with a nucleophilic reagent, $Y^\ominus$ represents an anion, m represents 0 or 1;

Formula (H-IV)



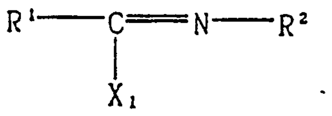
in the formula, the definitions of R^1 and R^2 are entirely the same as R^1 and R^2 in Formula (H-I), and R^3 represents at least one of an alkyl group and an aryl group, $X^{\ominus}$ represents an anion;

Formula (H-V)



in the formula, the definitions of R^1, R^2, and R^3, R^4 are entirely the same as R^1, R^2 in Formula (H-I), X_1 represents a group eliminable during the reaction with a nucleophilic reagent, the anion represented by $Y_1^{\ominus}$ represents at least one selected from the group consisting of a halide ion, sulofnate ion, sulfate ion, $ClO_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, phosphonate ion and phosphate ion;

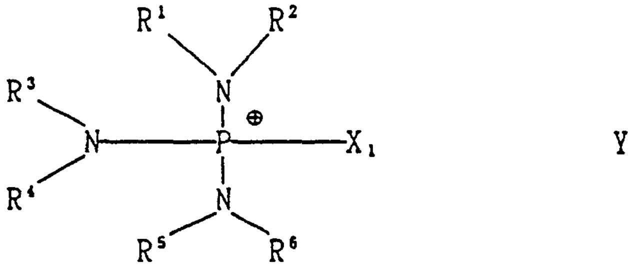
Formula (H-VI)



$$R^1-\underset{\displaystyle X_1}{\underset{|}{C}}=N-R^2$$

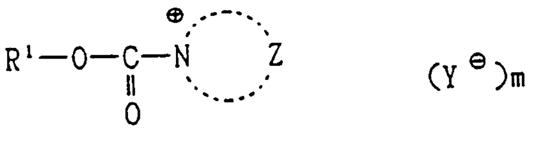
in the formula, R^1 and R^2 each represent at least one selected from the group consisting of an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aromatic heterocyclic group and $-NR^3R^4$, where R^3 and R^4 each represent at least one selected from the group consisting of an alkyl, alkenyl, cycloalkyl, aryl and aromatic heterocyclic group and also include one having a ring formed through bonding of R^3 and R^4, X_1 is the same as the definition of X_1 in Formula (H-V);

Formula (H-VII)



in the formula, R^1, R^2, and R^3, R^4, and R^5, R^6 are the same as the definitions of R^1, R^2 in Formula (H-I), X_1 is the same as the definition of X_1 in Formula (H-V), and $Y_1^{\ominus}$ is the same as the definition as $Y_1^{\ominus}$ in Formula (H-V);

Formula (H-VIII)



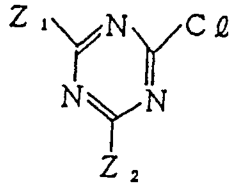
in the formula, R^1 represents an aryl group, Z represents a group of non-metallic atoms necessary for formation of an aromatic heterocyclic ring, and the ring formed by R^1 and Z is inclusive of those having substituents, $Y^{\ominus}$ represents an anion, m represents 0 or 1.

11. The light-sensitive silver halide color photographic material according to Claim 1, wherein the hardener which acts through activation of carboxyl groups is contained at a ratio of 0.01 to 10 % by weight based on a dry gelatin.

12. The light-sensitive silver halide color photographic material according to Claim 11, wherein the hardener which acts through activation of carboxyl groups is contained at a ratio of 0.05 to 5 % by weight on the dry gelatin.

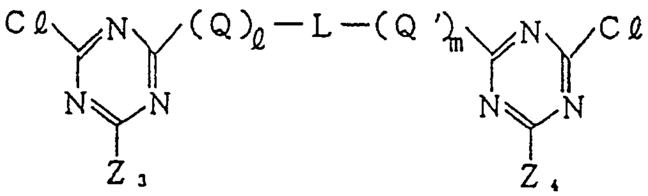
13. The light-sensitive silver halide color photographic material according to Claim 1, wherein the chlorotriazine type film hardener is at least one of the compounds represented by Formulae (H-1) anf (H-2) shown below:

Formula (H-1)



in the formula, Z_1 represents at least one selected from the group consisting of chlorine atom, a hydroxy group, an alkyl group, an alkoxy group, an alkylthio group, -OM group (M represents a monovalent metal atom) and $-NR'R''$, $-NHCOR'''$ (R', R'', R''' each represent at least one of hydrogen atom, an alkyl group and an aryl group), and Z_2 has the same meaning as Z_1 excluding chlorine atom;

Formula (H-2)



in the formula, Z_3 and Z_4 each represent at least one selected from the group consisting of chlorine atom, hydroxy group, an alkyl group, an alkoxy group and -OM group (M represents a monovalent metal atom), Q and Q' are each linking group representing at least one of -O-, -S-and -NH-, L represents at least one of an alkylene group and an arylene group, ℓ and m each represent 0 or 1.

14. The light-sensitive silver halide color photographic material according to Claim 13, wherein the alkyl group represented by Z_1 and Z_2 in Formula (H-1) is at least one of a methyl, ethyl and butyl groups; the alkylthio group represented by Z_1 and Z_2 in Formula (H-1) is at least one of a methylthio, ethylthio and butylthio groups; and alkoxy group represented by Z_1 and Z_2 in Formula (H-1) is at least one of a methoxy, ethoxy and butoxy groups; M of the -OM group represented by Z_1 or Z_2 is at least one of sodium atom and potassium atom.

15. The light-sensitive silver halide color photographic material according to Claim 13, wherein the the alkyl group represented by R_3 and R_3 of Formula (H-2) is at least one of a methyl, ethyl and butyl groups; the alkoxy group represented by R_3 and R_4 of Formula (H-2) is at least one of a methoxy, ethoxy and butoxy groups; the M of -OM group is at least one of sodium atom and potassium atom; the alkylene group represented by L in Formula (H-2) is at least one of the groups of $-CH_2-$, $-(CH_2)_2-$ and $-(CH_2)_3-$; and the arylene group represented by L in Formula (H-2) is at least one of the groups of p-, o- and m-phenylene group.

16. The light-sensitive silver halide color photographic material according to Claim 1, wherein the compound represented by Formulae (H-1) and (H-2) is added in an amount of 1 to 100 mg of a gelatin.

17. The light-sensitive silver halide color photographic material according to Claim 16, wherein the

compound represented by Formulae (H-1) and (H-2) is added in an amount of 5 to 50 mg per 1 g of gelatin.

18. The light-sensitive silver halide color photographic material according to Claim 1, wherein the blue-sensitive layer and the green-sensitive layer is single layers.

19. The light-sensitive silver halide color photographic material according to Claim 18, wherein the all of the blue-sensitive, green-sensitive and red-sensitive silver halide emulsion layers are single layers.

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

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

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

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

24. The light-sensitive silver halide color photographic material according to Claim 1, wherein the bis-(vinylsulfonylalkyl)ether type hardner is represented by the formula (H-a).

$CH_2=CHSO_2(CH_2)_mO(L\text{-}O)_p(CH_2)_nSO_2CH=CH_2$

in the formula, L denotes a divalent organic group, m and n denote positive integers, and p denotes 0 or 1.

25. The light-sensitive silver halide color photographic material according to Claim 24, wherein the divalent organic group represented by L in the formula (H-a) is at least one selected from the group consisting of an alkylene group having 1 to 10 carbon atoms, an arylene group having 6 to 10 carbon atoms, a divalent heterocyclic group, a divalent group represented by -O-, -S-, -SO-, $-SO_2-$ or $-\underset{\underset{O}{\|}}{C}-$, or a divalent groups prepared by combining plural number of these divalent groups; and the both ends of the divalent groups represented by L (portions to be bonded with oxygen atoms) are carbon atoms. n and m are an integer of 1 to 6.

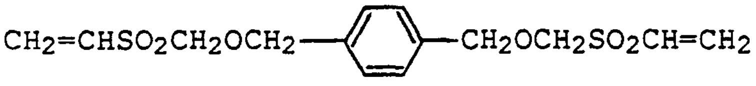
26. The light-sensitive silver halide color photographic material according to Claim 1, wherein the bis-(vinylsulfonylalkyl)ether type hardner is used in the rage of 0.01 to 20 % by weight.

27. The light-sensitive silver halide color photographic material according to Claim 26, wherein the bis-(vinylsulfonylalkyl)ether type hardner is used in the range of 0.05 to 15 % by weight based on a dry gelatin.

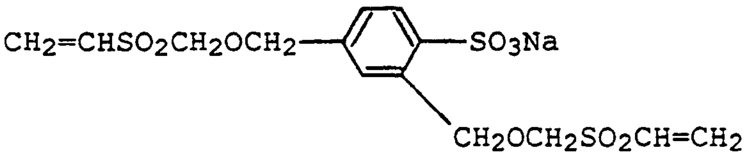
28. The light-sensitive silver halide color photographic material according to Claim 24, wherein the bis-(vinylsulfonylalkyl)ether type hardner is at least one selected from the group consisting of

H-a-1 $CH_2=CHSO_2CH_2OCH_2SO_2CH=CH_2$
H-a-2 $CH_2=CHSO_2CH_2CH_2OCH_2CH_2SO_2CH=CH_2$
H-a-3 $CH_2=CHSO_2(CH_2)_4\text{-}O\text{-}(CH_2)_4\text{-}SO_2CH=CH_2$
H-a-4 $CH_2=CHSO_2CH_2OCH_2CH_2OCH_2SO_2CH=CH_2$
H-a-5 $CH_2=CHSO_2CH_2OCH_2CH_2CH_2OCH_2SO_2CH=CH_2$
H-a-6 $CH_2=CHSO_2CH_2OCH_2CH_2OCH_2CH_2OCH_2SO_2CH=CH_2$
H-a-7 $CH_2=CHSO_2CH_2CH_2OCH_2CH_2OCH_2CH_2SO_2CH=CH_2$

H-a-8



H-a-9



H-a-10

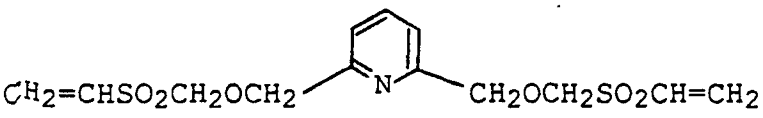


FIG. 1

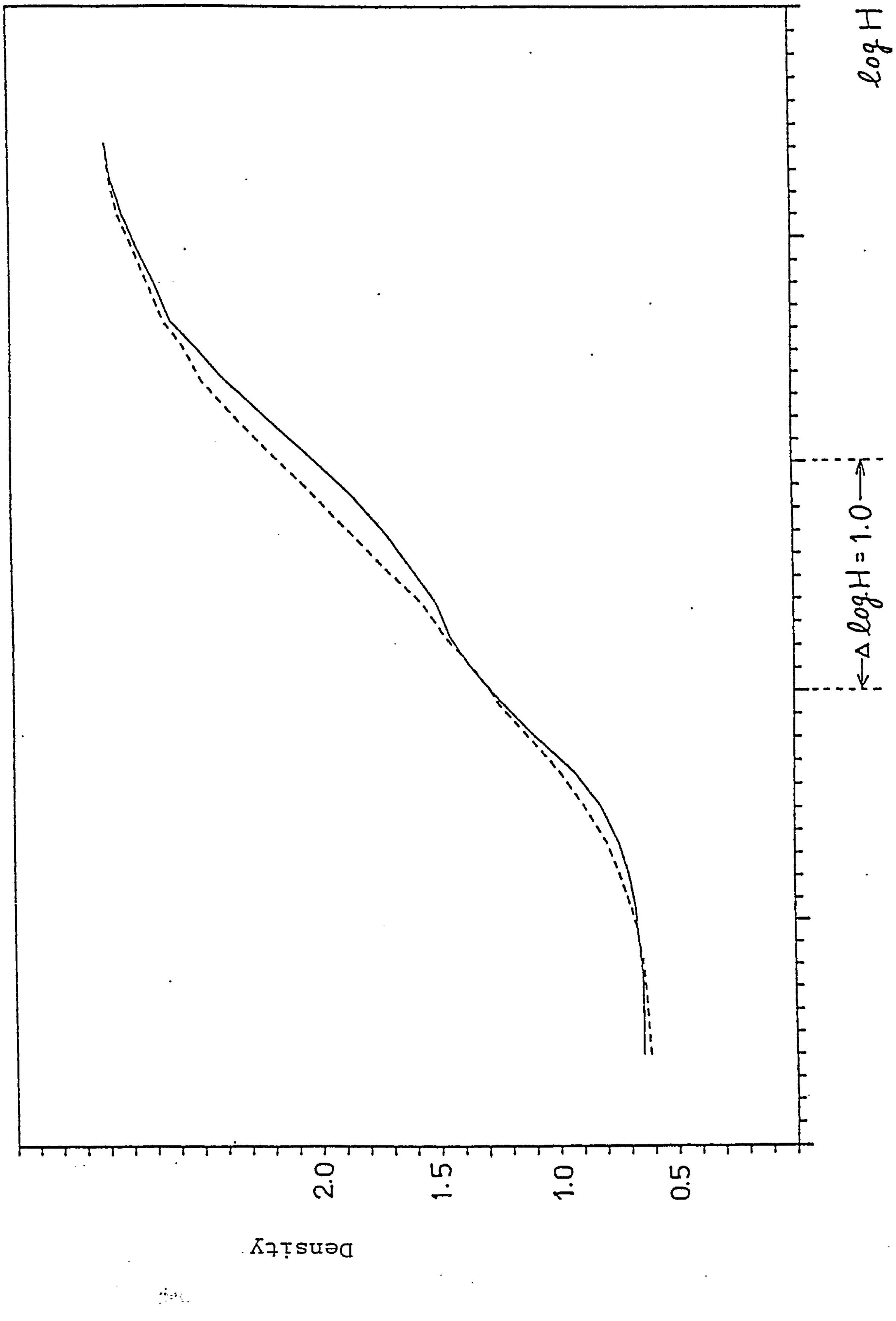


FIG. 2