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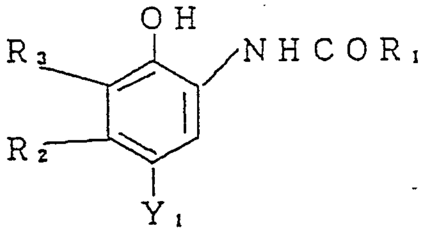
㊿ Direct positive color photosensitive material.

(57) A direct positive color photosensitive material comprised of a support having thereon at least one photographic emulsion layer containing nonprefogged internal latent image silver halide grains and at least one nondiffusible cyan coupler represented by formula (C-I):



(C-I)

in which R_1 represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R_2 represents an aliphatic group containing 2 to 20 carbon atoms; R_3 represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group; and Y_1 represents a hydrogen atom or a coupling-off group. The material provides images having high maximum cyan image density and low minimum cyan density, despite fluctuations in processing conditions.

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DIRECT POSITIVE COLOR PHOTOSENSITIVE MATERIAL

FIELD OF THE INVENTION

The present invention relates to a direct positive color photographic material, and more particularly to a direct positive silver halide photographic material containing a non-prefogged internal latent image silver halide emulsion.

BACKGROUND OF THE INVENTION

Photographic processes for obtaining a direct positive image without requiring a reversal process or a negative film are well known.

Known methods which have been used for obtaining a positive image using a direct positive silver halide photographic material can be classified, except for certain special methods, into two major types.

In the first type, a direct positive image is obtained by employing a previously fogged silver halide emulsion, and destroying a latent fog (a latent image) in the exposed areas by solarization, Herschel effect, etc., followed by development.

In the second type, a direct positive image is obtained by employing an unfogged internal latent image type silver halide emulsion, and carrying out imagewise exposure followed by surface development, either after a fogging treatment or along with a fogging treatment.

The term "internal latent image silver halide photographic emulsion" as used herein refers to a silver halide photographic emulsion of the type in which photosensitive nuclei are mainly present in the interior of silver halide grains and a latent image is formed mainly in the interior of the grains by exposure.

In comparison to the first material, the second material is generally high in sensitivity and is suitable where high sensitivity is required. The present invention is directed to the latent type.

In this field, various conventional techniques include those disclosed in U.S. Patents 2,592,250, 2,466,957, 2,497,875, 3,317,322, 2,588,982, 3,761,266, 3,761,276 and 3,796,577 and British Patents 1,151,363, 1,150,553 and 1,011,062.

If these known methods are used, direct positive photographic materials relatively high in sensitivity can be obtained.

Details of the mechanism of forming direct positive images are described, for example, by T.H. James in The Theory of the Photographic Process, Chapter 7, pages 182 to 193 (4th ed.) and in U.S. Patent 3,761,276.

Without being limited by theory, it is believed that latent fog is selectively formed only on the surface of silver halide grains in the unexposed areas by the surface desensitizing action due to the internal latent image produced in the inside of silver halide grains by the initial imagewise exposure, and a photographic image (a direct positive image) is formed in the unexposed areas by carrying out conventional surface development treatment.

Techniques of selectively forming latent fog, include a "light fogging method" in which a second exposure is effected throughout a photosensitive layer, for example, as described in British Patent 1,151,363; and a "chemical fogging method" that uses a nucleating agent. The latter method is described, for example, in Research Disclosure, Vol. 151, No. 15162 (November, 1976), pages 72 to 87.

In order to form a direct positive color image, either after an internal latent image type silver halide photosensitive material is subjected to a fogging treatment or while an internal latent image type silver halide photosensitive material is being subjected to a fogging treatment, surface color development is carried out, followed by bleaching and fixing (or bleach-fixing). Generally, after bleaching and fixing, washing and/or stabilizing are performed.

In the presence of a nucleating agent there is a problem that the maximum image density is not constant and the color reproduction is unstable because the internal latent image type silver halide photosensitive material is influenced by changes in the temperature and pH of the developing solution during continuous processing.

On the other hand, although the light fogging method does not require high pH conditions in comparison with the chemical fogging method, and is relatively advantageous in practice, the light fogging method is also influenced by changes in the temperature and the pH of the developing solution, and it is difficult to obtain consistent performance.

In particular, the minimum density areas of a direct positive emulsion photosensitive material, which corresponds to the fogged part of a usual negative emulsion, is influenced, for example, by changes in the temperature and the pH of the developing solution and the wavelength and the amount of light used for light fogging, and it is difficult to obtain a constant low minimum density.

Particularly, when an internal latent image type direct positive emulsion photosensitive material is processed using an automatic developing processing machine, the change in the liquid composition due to the processed amount of the photosensitive material can be calculated to a certain extent in the case of continuous processing, and the liquid composition of the replenisher can be adjusted based thereon. However, air oxidation of the processing liquid is also caused when the processing liquid is allowed to stand with the automatic developing processing machine in operation, i.e., at an elevated temperature in contact with air. For this reason, the oxidation resistance fo the liquid must be improved, by designing the photosensitive material and the processing liquid in such a way that if a certain degree of oxidation occurs the photographic performance does not change. Often an automatic developing processing machine is left in operation, for example, one day to save the time required for warm-up for restarting the operation, in a lab where the frequency of use of the automatic developing processing machine is decreased.

However, in a photosensitive material containing an internal latent image type direct positive emulsion, it has been impossible to eliminate undesirable changes in the photographic performance (particularly the increase in the minimum density of a cyan image).

SUMMARY OF THE INVENTION

An object of the invention is to provide a nonprefogged internal latent image type silver halide photosensitive material that can form quickly and stably a direct positive color image with high maximum density, particularly of the cyan color image formed, and low minimum image density thereof, when processed with a low-pH color developing solution.

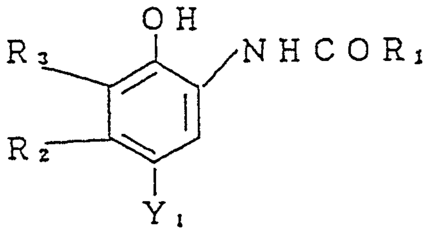
Another object of the present invention is to provide a photosensitive material that can form a direct positive color image with consistent color reproduction, in which the minimum image density and the maximum image density, particularly of the cyan color formed, scarcely deviate from the optimum values even if the temperature and the pH of the color developing solution change.

Still another object of the present invention is to provide a photosensitive material that can form a direct positive color image, in which the color reproduction scarcely changes and the minimum density and the maximum image density of the cyan color formed hardly deviate from the optimum values, even if the color development period deviates from the standard period.

Still another object of the present invention is to provide a photosensitive material that can form a direct positive color image in which the minimum image density scarcely increases and the maximum image density scarcely decreases when the photosensitive material is stored for a long period of time.

A still further object of the present invention is to provide a photosensitive material that can form a direct positive color image having reduced negative image rereversal in the case of high illumination exposure.

After long study, it has now been found that these and other objects can be attained by a direct positive color photosensitive material composed of a support having thereon at least one photographic emulsion layer containing nonprefogged internal latent image silver halide grains and at least one non diffusible cyan coupler repersented by formula (C-I):

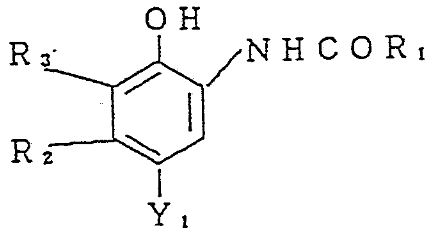


(C-I)

in which R_1 represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R_2 represents an aliphatic group containing 2 to 20 carbon atoms; R_3 represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group; and Y_1 represents a hydrogen atom or a coupling off group. A plurality of such non-diffusible couplers may be linked through R_1, R_2, R_3 or Y_1 to form a dimer or higher polymer.

DETAILED DESCRIPTION OF THE INVENTION

The present cyan couplers are disclosed in Japanese Patent Application (OPI) No. 232550/85 (the term "OPI" as used herein refers to a "published unexamined Japanese pat ent "application") and U.S. patenat 3,772,002, and are represented by the following general formula (C-1):



(C-I)

in which R_1 represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R_2 represents an aliphatic group having 2 to 20 carbon atoms; R_3 represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group; and Y_1 represents a hydrogen atom or a coupling-off group. A dimer or higher polymer thereof may be formed through R_1, R_2, R_3 or Y_1.

R_1 to R_3 and Y_1 in general formula (C-I) are described in greater detail as follows:

In general formula (C-I), when Y_1 represents a coupling-off group, i.e., a group capable of being cleaved upon a coupling reaction with the oxidized product of a color developing agent, this group includes an aliphatic group, an aromatic group, a heterocyclic group, an aliphatic, aromatic or heterocyclic sulfonyl group and an aliphatic, aromatic or heterocyclic carbonyl group, each linked to the coupling active carbon via an oxygen, nitrogen, sulfur or carbon atom; a halogen atom or an aromatic azo group. The aliphatic group, the aromatic group and the heterocyclic group included in the coupling-off group may be substituted with the substituents for R_1 described below. If there are two or more such substituents, they may be the same or different, and the substituents may be further substituted by substituents for R_1.

Specific examples of the coupling-off groups include halogen atoms (e.g., a fluorine atom, a chlorine atom and a bromine atom), alkoxy groups (e.g., an ethoxy group, a dodecyloxy group, a methoxyethylcarbamoylmethoxy group, a carboxypropyloxy group and a methylsulfonylethoxy group), aryloxy groups (e.g., a 4-chlorophenoxy group, a 4-methoxyphenoxy group and a 4-carboxyphenoxy group), acyloxy groups (e.g., an acetoxy group, a tetradecanoyloxy group and a benzoyloxy group), aliphatic or aromatic sulfonyloxy groups (e.g., a methanesulfonyloxy group and a toluenesulfonyloxy group), acylamino groups (e.g., a dichloroacetylamino group and a heptafluorobutyrylamino group), aliphatic or aromatic sulfonamido groups (e.g., a methanesulfonamide group and a p-toluenesulfonylamido group), alkoxycarbonyloxy groups (e.g., an ethoxycarbonyloxy group and a benzyloxycarbonyloxy group), aryloxycarbonyloxy groups (e.g., a phenoxycarbonyloxy group), aliphatic, aromatic or heterocyclic thio groups (e.g., an ethylthio group, a phenylthio group and a tetrazolylthio group), carbamoylamino groups (e.g., an N-methylcarbamoylamino group and an N-phenylcarbamoylamino group), 5-or 6-membered nitrogen-containing heterocyclic groups (e.g., an imidazolyl group, a pyrazolyl group, a triazolyl group, a tetrazolyl group and a 1,2-dihydro-2-oxo-1-pyridyl group), imido groups (e.g., a succinimido group and a hydantoinyl group), aromatic azo groups (e.g., a phenylazo group), etc. Coupling off groups linked via the carbon atom include bis type couplers obtained by condensing four-equivalent couplers with aldehydes or ketones. In the present invention, the coupling off group may contain a photographically useful group such as a development inhibitor and a development accelerator.

The aliphatic group represented by R_1, R_2 or R_3 includes linear, branched or cyclic alkyl, alkenyl or alkynyl groups that may be unsubstituted or substituted.

In general formula (C-I), R_1 represents an aliphatic group preferably having 1 to 36 carbon atoms, an aromatic group preferably having 6 to 36 carbon atoms (e.g., a phenyl group and a naphthyl group), a heterocyclic group (e.g, a 3-pyridyl group and a 2-furyl group), an aromatic or heterocyclic amino group (e.g., an anilino group, a naphthylamino group or a 2-benzothiazolylamino group and a 2-pyridylamino group), each of which may be substituted by substituents selected from an alkyl group, an aryl group, a heterocyclic group, an alkoxy group (e.g., a methoxy group and a 2-methoxyethoxy group), an aryloxy group (e.g., a 2,4-di-tert-amylphenoxy group, a 2-chlorophenoxy group and a 4-cyanophenoxy group), an alkenyloxy group (e.g., a 2-propenyloxy group), an acyl group (e.g., an acetyl group and a benzoyl group), an ester group (e.g., a butoxycarbonyl group, a phenoxycarbonyl group, an acetoxy group, a benzoyloxy group, a butoxysulfonyl group and a toluenesulfonyloxy group), an amido group (e.g., an acetylamino group, an ethylcarbamoyl group, a dimethylcarbamoyl group, a methanesulfonamido group and a butylsulfamoyl group), a sulfamido group (e.g., a dipropylsulfamoylamino group), an imido group (e.g., a succinimido group and a hydantoinyl group), a ureido group (e.g., a phenylureido group and a dimethylureido group), an aliphatic or aromatic sulfonyl group (e.g., a methanesulfonyl group, a phenylsulfonyl group), an aliphatic or aromatic thio group (e.g., an ethylthio group and a phenylthio group), a hydroxyl group, a cyano group, a carboxyl group, a nitro group, a sulfo group and a halogen atom.

Typical examples of the aliphatic group represented by R_1 and R_{12} and a methyl group, an ethyl group, a butyl group, a dodecyl group, an octadecyl group, an eicosenyl group, an isopropyl group, a tert-butyl group, a tert-octyl group, a tert-dodecyl group, a cyclohexyl group, a cyclopentyl group, an allyl group, a vinyl group, a 2-hexadecenyl group and a propargyl group, which may be substituted by the substituents for R_1.

In general formula (C-I), R_3 represents a hydrogen atom, a halogen atom (e.g., a fluorine atom, a chlorine atom and a bromine atom), an aliphatic group preferably having 1 to 20 carbon atoms, an aliphatic oxy group preferably having 1 to 20 carbon atoms or an acylamino group having 1 to 20 carbon atoms (e.g., an acetamido group, a benzamide group and a tetradecaneamide group), and these aliphatic groups, aliphatic oxy groups and acylamino groups may be substituted by the substituents for R_1.

One or two of R_1, R_2, R_3 and Y_1 in general formula (C-I) may be linked to form a dimer or higher polymer. In the case of a dimer, these groups can represent a single bond or a divalent linking group (e.g., an alkylene group, an arylene group, an ether group, an ester group and an amide group and a combination of these), and if they form an oligomer or a polymer, it is preferable that these groups constitute the polymer main chain or link with the polymer main chain via such a divalent group as mentioned for a dimer. When a polymer is formed, the polymer may be a homopolymer of a coupler derivative or a copolymer with one or more of other non-color forming ethylenic monomers (e.g., acrylic acid, methacrylic acid, methyl acrylate, n-butyl acrylamide, β-hydroxymethacrylate, vinyl acetate, acrylonitrile, styrene, crotonic acid, maleic anhydride and N-vinyl pyrrolidone).

In general formula (C-I), R_1 preferably represents a substituted or unsubstituted alkyl group or aryl group; the substituent for the alkyl group is particularly preferably an optionally substituted phenoxy group or a halogen atom (the substituent for the phenoxy group is preferably an alkyl group, an alkoxy group, a halogen atom, a sulfonamido group or a sulfamico group); and the aryl group is particularly preferably a phenyl group substituted with at least one of a halogen atom, an alkyl group, a sulfonamido group and an acylamino group.

In general formula (C-I), R_2 preferably represents an optionally substituted alkyl group having 2 to 20 carbon atoms. The substituent for R_2 is preferably an alkyloxy group, an aryloxy group, an acylamino group, an alkylthio group, an arylthio group, an imdo group, a ureido group, an alkylsulfonyl group or an arylsulfonyl group. In general formula (C-I), more preferably R_2 represents an alkyl group having 2 to 4 carbon atoms.

In general formula (C-I), R_3 preferably represents a hydrogen atom, a halogen atom (particularly preferably a fluorine atom or a chlorine atom) or an acylamino group, with a halogen atom more preferred.

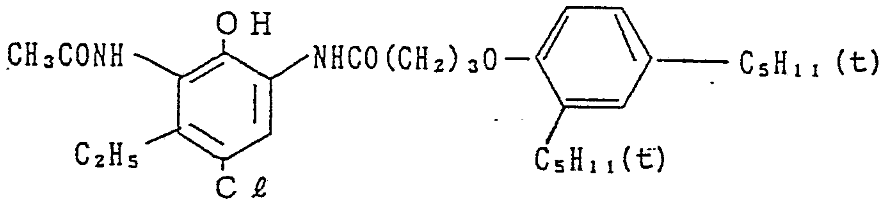
In general formula (C-I), Y_1 preferably represents a halogen atom, and moer preferably a chlorine atom.

The couplers represented by general formula (C-I) may be used alone or in the form of a mixture thereof, and also may be used in combination with cyan couplers other than cyan couplers represented by general formula (C-I).

The present cyan coupler is used in an amount of from about 0.01 to 1.0 mol, preferably of about 0.02 to 0.5 mol, more preferably 0.01 to 0.4 mol per mol of silver in the layer containing the coupler.

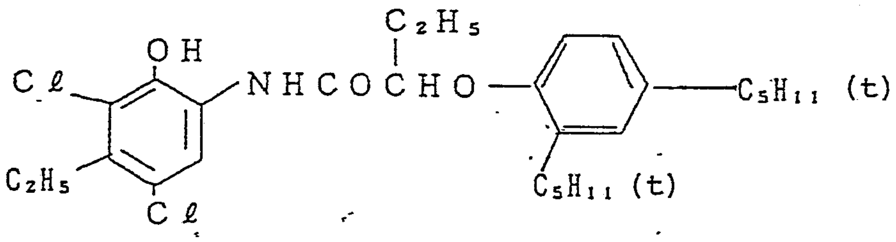
Specific examples of the present non-diffusible cyan couplers represented by general formula (C-I) are given below, but the present invention is not to be construed as being limted to them.

(C-I-1)



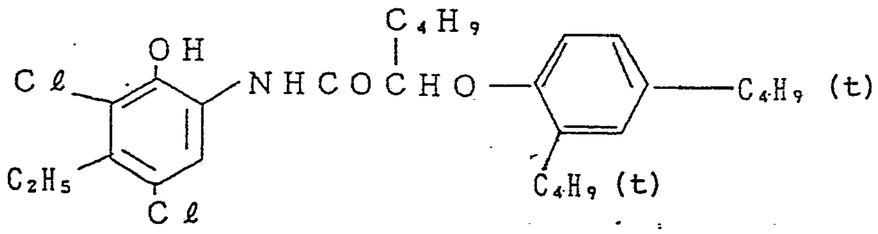
OH
CH3CONH
NHCO(CH2)3O
C5H11(t)
C2H5
Cl
C5H11(t)

(C-I-2)



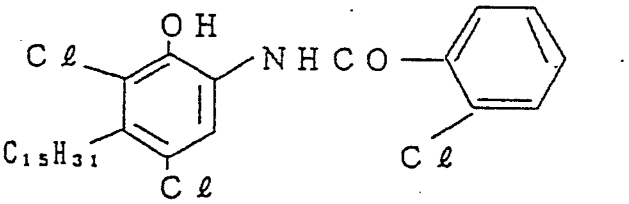
C2H5
OH
Cl
NHCOCHO
C5H11 (t)
C2H5
Cl
C5H11 (t)

(C-I-3)

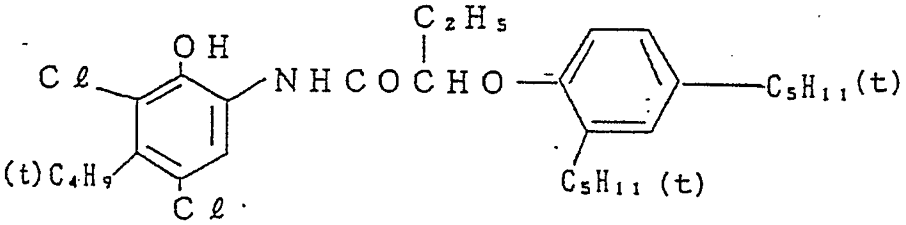


C4H9
OH
Cl
NHCOCHO
C4H9 (t)
C2H5
Cl
C4H9 (t)

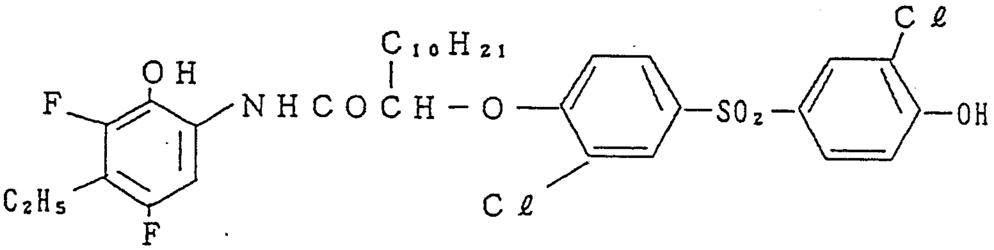
(C－I－4)



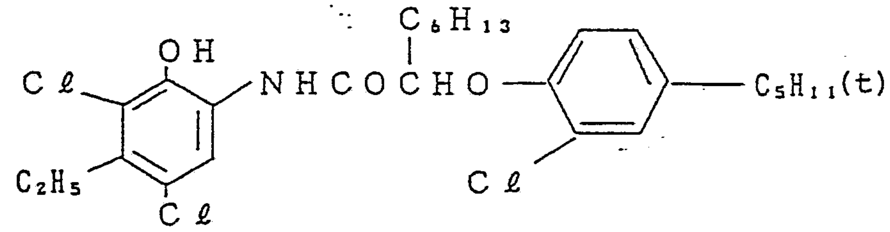
(C－I－5)



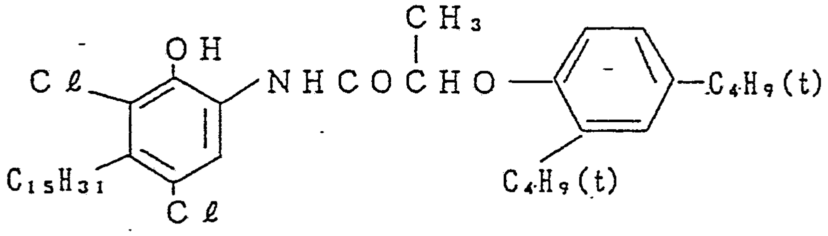
(C－I－6)



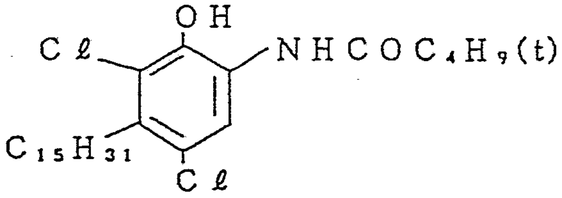
(C－I－7)


C₆H₁₃
OH
Cℓ
NHCOCHO
C₅H₁₁(t)
C₂H₅
Cℓ
Cℓ

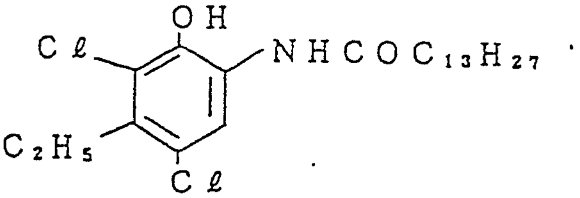
(C－I－8)


CH₃
OH
Cℓ
NHCOCHO
C₄H₉(t)
C₁₅H₃₁
Cℓ
C₄H₉(t)

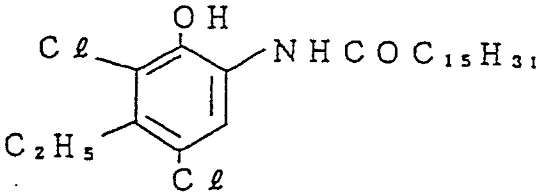
(C－I－9)


OH
Cℓ
NHCOC₄H₉(t)
C₁₅H₃₁
Cℓ

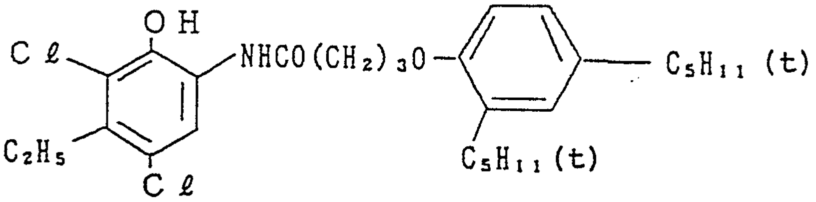
(C-I-10)



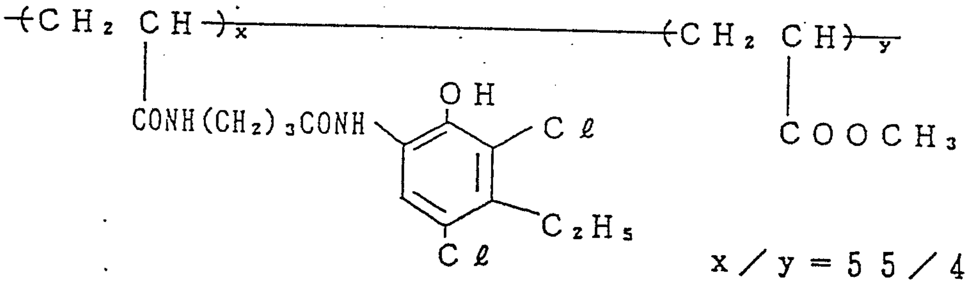
(C-I-11)



(C-I-12)



(C-I-13)

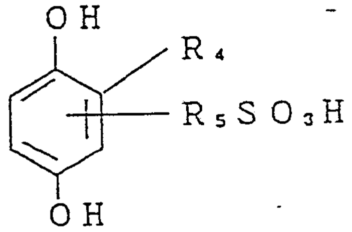


x/y = 55/45

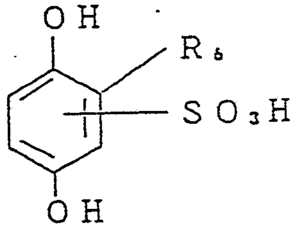
wherein the ratio of x to y is by weight.

It has been bound that the objects of the present invention, in particular, the restraint of the increase in minimum image density of the formed cyan color due to deterioration by air oxidation of a developing solution, can be enhanced by including in the photosensitive material a hydroquinone compound having a sulfonic acid group.

Hydroquinone compounds having a sulfonic acid group that can additionally be used effeectively in the present invention include compounds represented by formulae (HQ-1) and (HQ-II) and their ammonium and alkali metal salts:



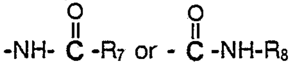
(HQ-I)



(HQ-II)

in which R_4 represents an alkyl group, an acylamino group, a hydrogen atom or a sulfonic acid group; R_5 represents an alkylene group or an acylamino group; and R_6 represents an alkyl group or an acylamino group. These compounds are described, for example, in U.S. patent 3,227,552.

The acylamino group represented by R_4, R_5 and R_6 may be unsubstituted or substituted, and for example include



$-NH-\overset{O}{\overset{\|}{C}}-R_7$ or $-\overset{O}{\overset{\|}{C}}-NH-R_8$ wherein R_7 and R_8 each represents an aryl group (e.g., a phenyl group), an alkyl group, a hydrogen atom or a sulfonic acid group.

The alkyl group represented by R_4 and R_6 may be unsubstituted or substituted, and includes an aralkyl group.

The length or the size of the alkyl group, the alkylene group and the acylamino group may be varied widely depending on the desired degree of diffusibility, and those skilled in the art can easily determine the amount of the required "ballast" according to the purpose. An alkyl group and an alkylene group having 1 to 22 carbon atoms are suitably used and preferably an alkyl group having 8 to 22 carbon atoms and an alkylene group having 1 to 8 carbon atoms are used, for this purpose.

Specific examples of the hydroquinone compounds having a sulfonic acid group that can be used in the present invention are given below, but the present invention is not to be construed as being limited thereto:

(HQ-1): 2-[β-{3-[3-(4-amyl-x-sulfophenoxy)benzamido]-benzamido}ethyl]hydroquinone (sodium salt)

(HQ-2): 2,5-bis[N-{3-[2,4-(diamylphenoxy)-5-(2-sulfobenzamido)benzamido]phenyl}carbamylmethyl]-hydroquinone (sodium salt)

(HQ-3): 5-octadecyl-2-(2-sulfo-tert-butyl)hydroquinone (sodium salt)

(HQ-4): 5-sec-octadecyl-2-(2-sulfo-tert-butyl)hydroquinone (sodium salt)

(HQ-5): 2,5-bis{β-[3-(p-tert-amylphenoxy)-x-sulfo]benzamidoethylhydroquinone (sodium salt)

(HQ-6): 2-[2′-(2″,4″-di-tert-amylphenoxy)-5′-(3″,5″-disulfobenzamido)benzamido]hydroquinone (sodium salt)

(HQ-7): potassium sec-undecyl-hydroquinone-x-sulfonate

(HQ-8): potassium n-hexadecyl-hydroquinone-x-sulfonate

(HQ-9): potassium n-octadecyl-hydroquinone-x-sulfonate

(HQ-10): potassium 2-methyl-5-sec-octadecyl-hydroquinone-x-sulfonate

(HQ-11): potassium 3-benzyl-x-sulfonate

(HQ-12): potassium 3-ethylbenzyl-x-sulfonate

(HQ-13): potassium 3-(p-benzyl)-benzyl-x-sulfonate

The above sulfonated hydroquinones can be directly coated in a silver halide emulsion layer, an intermediate layer or a protective layer. Although a suitable concentration of the compound can be determined by those skilled in the art, generally the compound is used in an amount of about 1 to 100 mg, preferably about 10 to 200 mg, per m^2 of the photosensitive material. However an amount greater or smaller than that can be used.

The nonprefogged internal latent image silver halide emulsion that is used in the present invention is an emulsion containing a silver halide wherein the surface of the silver halide grains has not been previously fogged in the manufacturing process, such that a latent image will be formed mainly in the inside of the grain. More specifically, when such a silver halide emulsion is applied on a transparent base in an amount of 0.5 to 3 g/m^2 in terms of silver, and then the emulsions is exposed to light of a fixed period of 0.01 to 10 seconds, and is developed for a period of 5 minutes at 18°C in a developing solution A (an internal type developing solution) shown below, the maximum density measured by a conventional photographic density measuring method is preferably at least about 5 times, more preferably at least about 10 times, as high as the maximum density obtained when the silver halide emulsion is applied and exposed to light in the same amount as above, and is developed for a period of 6 minutes at 20°C in a developing solution B (a surface type developing solution) shown below.

An internal developing solution A Metol	2 g
Sodium sulfite (anhydride)	90 g
Hydroquinone	8 g
Sodium carbonate (monhydrate)	52.5 g
KBr	5 g
KI	0.5 g
Water to make	1 liter

A surface developing solution B Metol	2.5 g
ℓ-ascorbic acid	10 g
$NaBO_2 \cdot 4H_2O$	35 g
KBr	1 g
Water to make	1 liter

Specific examples of internal latent type emulsions include conversion type silver halide emulsions and emulsions having shells over a core of such conversion type silver halide emulsions described, for example, in U.S. Patent 2,592,250, Japanese Patent Publication Nos. 54379/83, 3536/83 and 5582/85, and Japanese Patent Application (OPI) Nos. 156614/77, 79940/82 and 70221/83; and core/shell type silver halide emulsions the core of which is doped with a metal described in U.S. Patents 3,761,276, 3,850,637, 3,923,513, 4,035,185, 4,395,478, 4,431,730 and 4,504,570, Japanese Patent Application (OPI) Nos. 60222/78, 22681/81, 208540/84, 107641/85 and 3137/86, Japanese Patent Application No. 3642/86 and the patents cited in Research Disclosure, No. 23510 (November, 1983), page 236, and No. 18155 (May, 1979), pages 265 to 268.

The silver halide grains used in the present invention may be regular crystals such as cubic, octahedral, dodecahedral and tetradecahedral crystals or irregular crystals such as spherical crystals or tabular grains whose length/thickness ratio is 5 or more. A composite form of these crystal forms may be used, and an emulsion made up of a mixture of these crystals may also be used.

The composition of the silver halide includes silver chloride, silver bromide or a mixed silver halide, and the silver halide preferably used in the present invention is either free from silver iodide, or if it contains silver iodide, it is silver bromo(iodo)chloride, silver (iodo)chloride or silver (iodo)bromide containing about 3 mol% or less of silver iodide.

The average grain size of the silver halide grains is preferably up to 2 µm from about 0.1 µm, more preferably from about 0.15 µm to 1 µm. Although the distribution of the grain size may be wide or narrow, in order to improve graininess, sharpness, etc. it is preferred in the present invention to use a "monodisperse" silver halide emulsion having a narrow grain size distribution such that about 90% or more of all the grains fall within ± about 40%, preferably ± about 20%, of the average grain size, in terms of grain number or weight.

In order to satisfy the gradation required for the photosensitive material, in emulsion layers having substantially the same color sensitivity, two or more monodisperse silver halide emulsions different in grain size or a plurality of grains of the same size but different in sensitivity are mixed in the same layer or are applied as different layers that are superposed. Two or more polydisperse silver halide emulsions or a monodisperse silver halide emulsion and a polydisperse silver halide emulsion can be used in the form of a mixture or in superposed layers.

In the silver halide emulsion used in the present invention, the interior or the surface of the grains may be chemically sensitized by sulfur sensitization, selenium sensitization, reduction sensitization or noble metal sensitization, that can be used alone or in combination. Particular examples of chemical sensitization are described, for example, in the patents cited in Research Disclosure, No. 17643-III (December, 1978), page 23.

The photographic emulsion used in the present invention is spectrally sensitized with a photographic sensitizing dye in a conventional manner. Particularly useful dyes are cyanine dyes, merocyanine dyes and compositie merocyanine dyes, which may be used alone or in combination, and also can be used in combination with supersensitizers. Particular examples are described, for example, in the patents cited in Reserach Disclosure , No. 17643-III (December, 1978), pages 3 to 24.

The photographic emulsion used in the present invention can contain an antifoggant or a stabilizer for the purpose of stabilizing the photographic performance, or of preventing fogging durig photographic treatment, storage or the production of the photographic material. Particular examples of antifoggants and stabilizers are described, for example, in Research Disclosure, No. 17643-VI (December, 1978), pages 24 to 25, and by E.J. Birr in Stabilization of Photographic Silver Halide Emulsions, 1974 (Focal Press).

To form a direct positive color image according to the invention, in addition to the cyan coupler of the present invention, a magenta coupler and a yellow coupler can be used. Useful couplers are compounds that can couple with the oxidized product of an aromatic primary amine type color developer to produce or release a non-diffusible dye and that themselves are substantially non-diffusible. Typical examples of useful color couplers include pyrazolone or pyrazoloneazole compounds or open chain or heterocyclic ketomethylene compounds. Specific examples of these magenta and yellow couplers are compounds described in Research Disclosure, No. 17643 (December, 1978), page 25, section VII-D; No. 18717 (November, 1979); Japanese Patent Application (OPI) No. 215272/87 (pages 298 to 373); and compounds described in the patents cited in them.

Among others, typical yellow couplers that can be used in the present invention include yellow two-equivalent couplers of oxygen atom releasing or nitrogen atom releasing type. Particularly, α-pivaloylacetanilide type couplers are excellent in fastness, in particular light-fastness, of the colored dyes, while α-benzoylacetanilide type couplers are preferred because a high color density can be obtained.

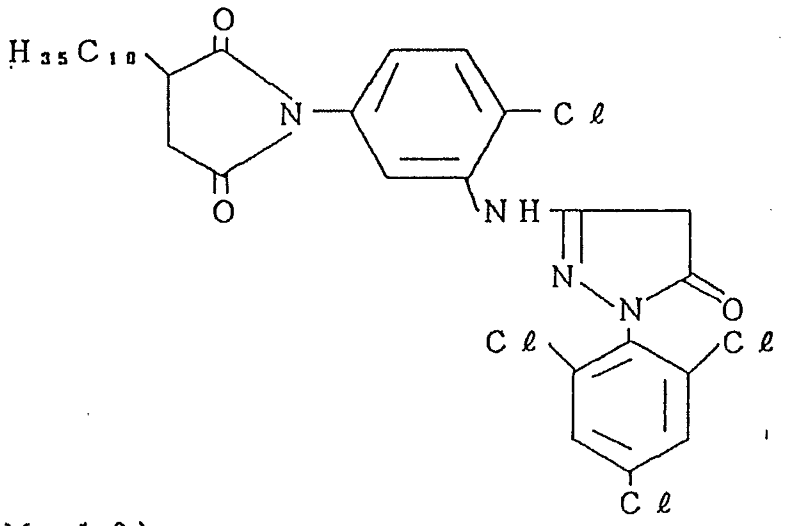
5-Pyrazolone type magenta couplers preferably used in the present invention are 5-pyrazolone type couplers (particularly sulfur atom releasing two-equivalent couplers), substituted at the 3-position by an arylamino group or an acylamino group.

Pyrazoloazole couplers are further preferred pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067 are particularly preferred, imidazo[1,2,-b]pyrazoles described in U.S. Patent 4,500,630 are more preferred in view of the fastness to light and the low yellow subsidary absorption of the colored dye, and pyrazolo[1,5-b][1,2,4]triazoles described in U.S. Patent 4,540,654 are most preferred.

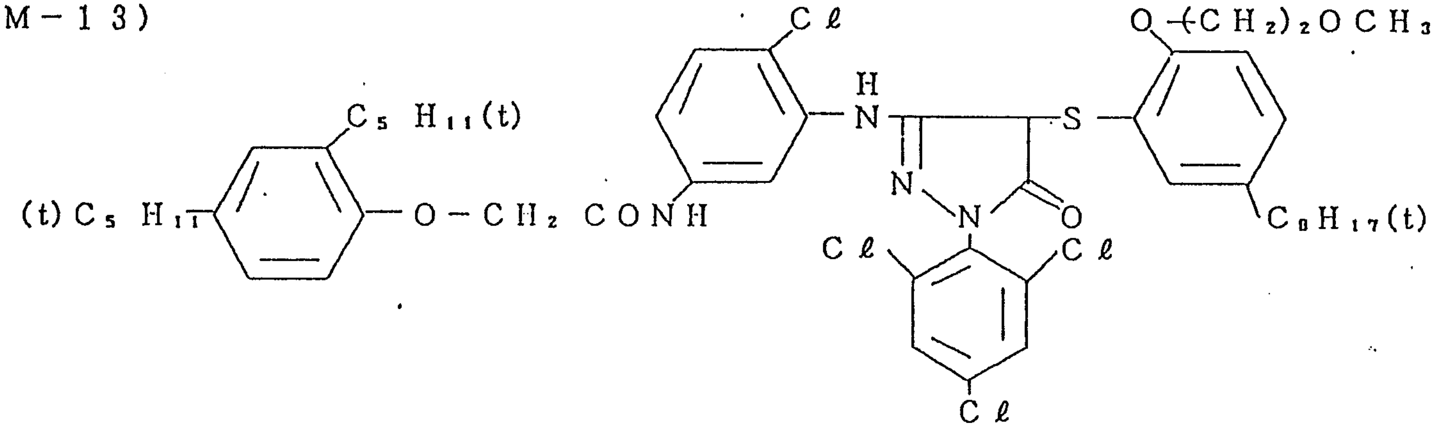
Specific examples of particularly preferred yellow and magenta couplers are compounds listed in Japanese Patent Application (OPI) No. 169523/86 (filed by Fuji Photo Film Co., Ltd. on June 8, 1986), and the compounds listed below are also preferred examples.

Magenta Couplers:

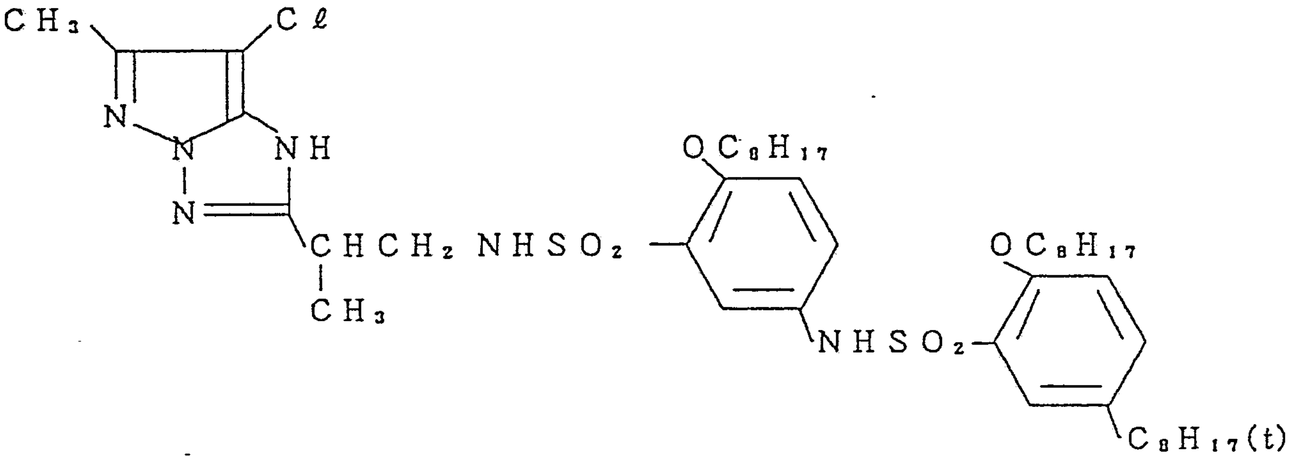
(M－1 2)



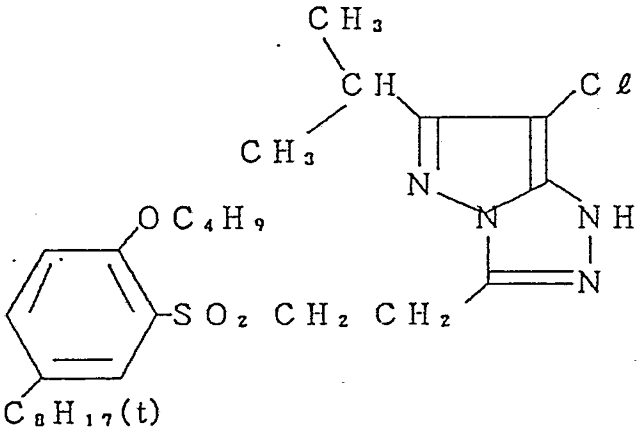
(M－1 3)



(M－１４)

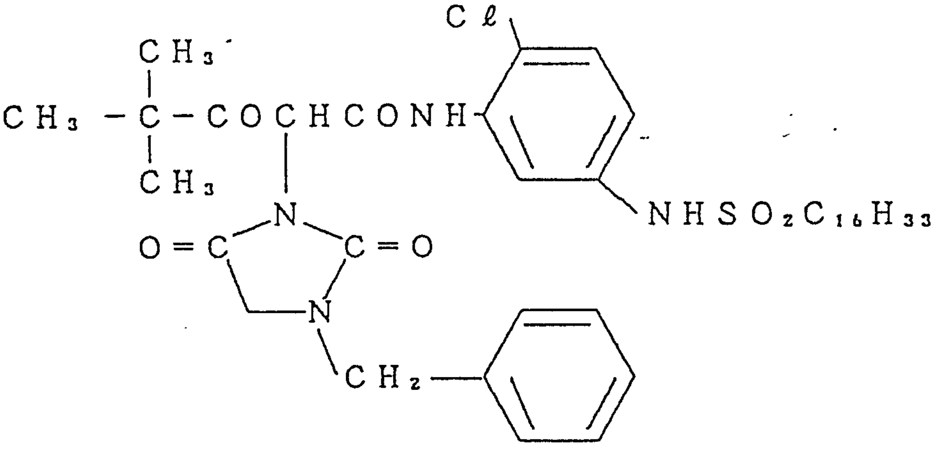


(M－１５)

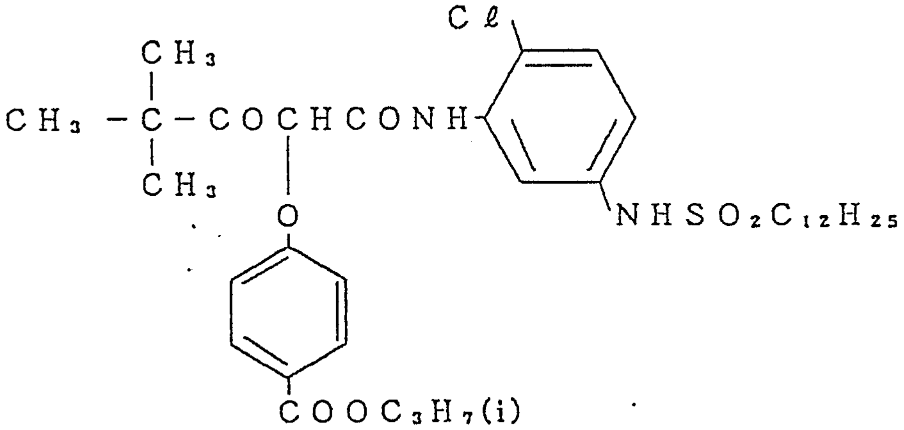


Yellow Couplers:

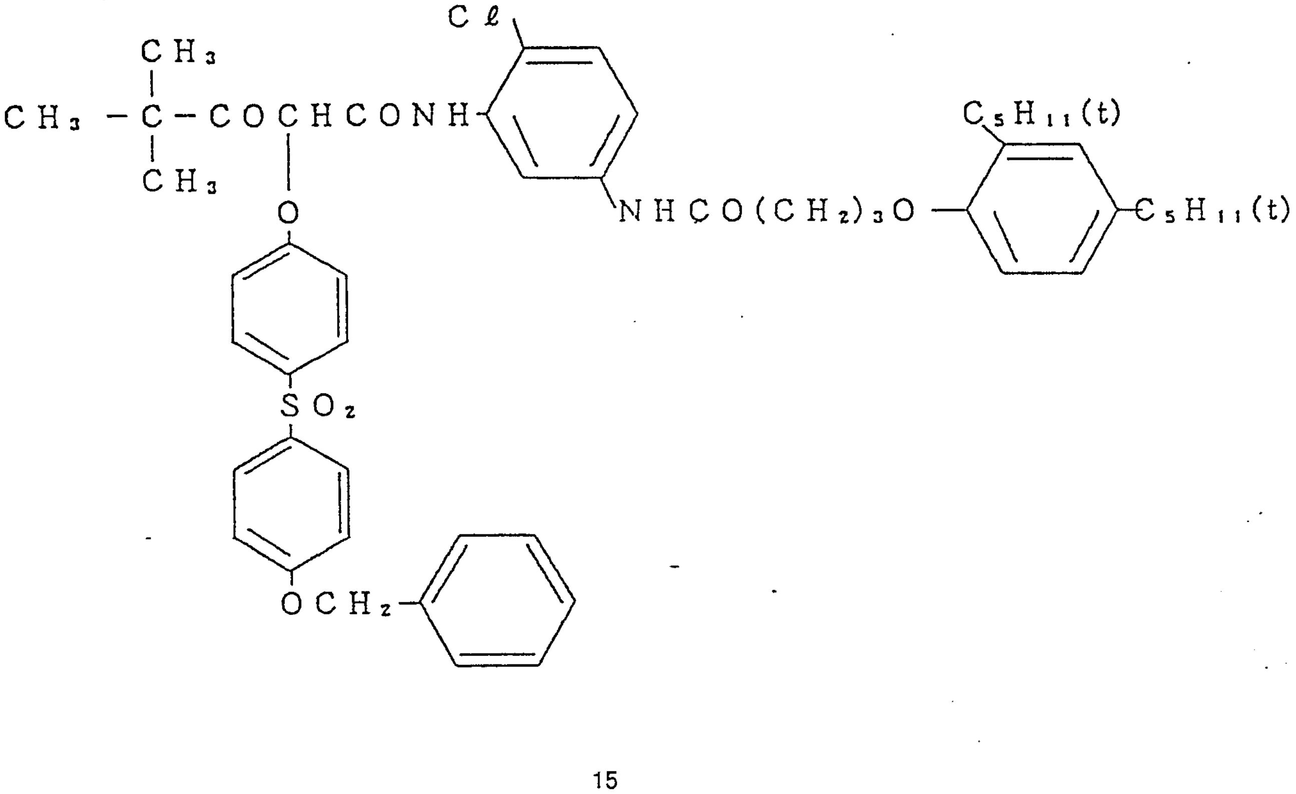
(Y - 9)



(Y - 10)



(Y - 11)



Colored couplers for correcting undesired absorption in the short wavelength range of produced dyes; couplers producing colored dyes with a suitable diffusibility; colorless couplers; DIR couplers that release a development restrainer as a result of the coupling reaction; couplers that can release a development accelerator; and polymerized couplers can also be used.

Generally, the amount of a color-dye forming coupler used is in the range of about 0.001 to 1 mol per mol of a photosensitive silver halide, and preferably in the case of a yellow coupler the amount is about 0.01 to 0.5 mol per mol of a photosensitive silver halide and in the case of a magenta coupler the amount is about 0.003 to 0.5 mol per mol of a photosensitive silver halide in silver halide layers containing these couplers.

Cyan couplers that are outside the scope of the present invention and are generally used can be used in addition to the present cyan coupler.

Photosensitive materials prepared in accordance with the present invention may contain, as a color fogging preventive agent or color mixing preventing agent, hydroquinone derivatives, aminophenol derivatives, amines, gallic acid derivatives, catechol derivatives, ascorbic acid derivatives, colorless couplers, sulfonamidephenol derivatives, etc. Typical examples of color fogging preventive agents and color mixing preventive agents are described in Japanese Patent Application (OPI) No. 215272/87, pages 600 to 630.

In the present photosensitive materials, various discoloration preventing agents can be used. Organic discoloration preventing agents include hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirchromans, p-alkoxyphenols, hindered phenols including bisphenols, gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines and ether or ester derivatives obtained by the silylation or alkylation of the phenolic hydroxyl group of these compounds. Further, metal complexes such as (bissalicylaldoxymato)nickel complex and (bis-N,N-dialkyldithiocarbamato)nickel complexes can be used.

For the purpose of preventing yellow dye images from being deteriorated by heat, humidity and light, compounds having both a hindered amine and a hindered phenol in a single molecule, as described in U.S. Patent 4,268,593, give good results. For the purpose of preventing magenta dye images from being deteriorated, particularly by heat, spiroindanes described in Japanese Patent Application (OPI) No. 159644/81 and chromans substituted by hydroquinone diethers or monoethers described in Japanese Patent Application (OPI) No. 89835/80 give good results.

Typical examples of these discoloration preventing agents are described in Japanese Patent Application (OPI) No. 215272/87, pages 401 to 440. The desired aim can be attained when these compounds are added to photosensitive layers generally in amounts of about 5 to 100 wt% based on the respective color couplers by co-emulsifying them with the couplers. For the purpose of preventing cyan dye images from being deteriorated by heat and, particularly, light, it is effective to introduce an ultraviolet absorbing agent into both layers adjacent to a cyan color forming layer. An ultraviolet absorbing agent can also be added to a hydrophilic colloid layer such as protective layer. Typical examples of such compounds as desribed in Japanese Patent Application (OPI) No. 215272/87, pages 391-400.

As binding agents or protective colloids that can be used in emulsion layers and intermediate layers of the present photosensitive material, it is advantageous to use gelatin, but other hydrophilic colloids other than that can also be used.

The present photosensitive materials can contain dyes for preventing irradiation or halation, ultraviolet absorbing agents, plasticizers, brightening agents, matting agents, air fogging preventing agents, coating assistants. hardening agents, antistatic agents, slipperiness improvers, etc. Typical examples of these additives are described in Research Disclosure, No. 17643, sections VIII to XIII (December, 1978), pages 25 to 27, and No. 18716 (November, 1979), pages 647 to 651.

The present invention can be applied to multilayer multicolor photographic materials having at least two different spectral sensitivities on a base. Generally a multilayer color photographic material has at least one red sensitive emulsion layer, at least one green sensitive emulsion layer and at least one blue sensitive emulsion layer on a base. The order of these layers is arbitrarily selected as desired. In a preferred order of the layers, a red-sensitive emulsion layer, a green-sensitive emulsion layer and a blue-sensitive emulsion layer are coated in that order on a support or a green-sensitive emulsion layer, a red-sensitive emulsion layer and a blue-sensitive emulsion layer are coated in that order on a support. Each of these emulsion layers may consist of two or more emulsion layers different in sensitivity, or may consist of two or more emulsion layers having the same sensitivity with a non-photosensitive layer between them. Generally, the red-sensitive emulsion layer contains a cyan forming coupler, the green-sensitive emulsion layer contains a magenta forming coupler and the blue-sensitive emulsion layer contains a yellow forming coupler, but in some cases the combination can be changed.

It is preferable that the photosensitive material according to the invention is provided with suitable auxiliary layers such as a protective layer, an intermediate layer, a filter layer, a halation preventive layer, a backing layer and a white reflective layer.

In the present photographic materials, the photographic emulsion layers and other layers are applied on supports described in Research Disclosure, No. 17643, section XVII (December, 1978), page 28, European Patent No. 0,182,253, and Japanese Patent Application (OPI) No. 97655/86. The coating methods described in Research Disclosure, No. 17643, section XV, pages 28 to 29 can be employed.

The present invention can be applied to various color photosensitive materials.

For example, color reversal papers and color reversal films for slides and television are typical examples. The present invention can also be applied to color hard copies for storing CRT images or full color copying machines. The present invention can be applied also to black and white photographic materials using a mixture of three color couplers described in Research Disclosure, No. 17123 (June, 1978).

The present photosensitive material can provide a direct positive color image by exposing it to light imagewise, and then by subjecting it to a fogging process using light or a nucleating agent, either before or at the same time as developing it with a surface developing solution containing an aromatic primary amine type color developer, followed by bleaching and fixing.

The fogging process in the present invention can use either a "light fogging method" mentioned above, by which the whole surface of the photosensitive layer is subjected to a second exposure, or the "chemical fogging method" in which development is carried out in the presence of a nucleating agent. The development may be carried out in the presence of a nucleating agent and fogging light. A photosensitive material containing a nucleating agent may be subjected to fogging exposure. The fogging exposure in the light fogging method in the present invention is carried out after the imagewise exposure, and before and/or during the development treatment. While the photosensitive material that has been exposed to light imagewise is dipped in a developing solution or a bath prior to the developing solution, it is subjected to fogging exposure, or after the material is taken out from the solution or the bath, it is subjected to fogging exposure while it is still wet. The fogging exposure during immersion in the developing solution is preferred.

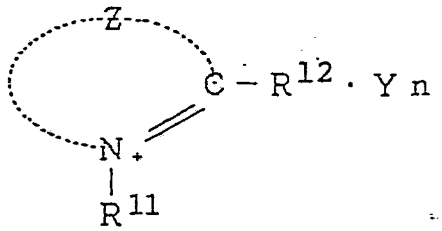
As a light source for the fogging exposure, any light source having wavelengths in the range of the photosensitive wavelength of the photosensitive material can be used. Generally, a fluorescent lamp, a tungsten lamp, a xenon lamp, sunlight, etc. can be used. Specific methods for the fogging exposure are described, for example, in British Patent 1,151,363, Japanese Patent Publication Nos. 12710/70, 12709/70 and 6936/83, and Japanese Patent Application (OPI) Nos. 9727/73, 137350/81, 129438/82, 62652/83, 60739/83, 70223/3 (corresponding to U.S. Patent 4,440,851) and 120248/83 (corresponding to European Patent 89101A2). In the case of a photosensitive material having a sensitivity to the visible length range, such as a color photosensitive material, a light source high in color rendition (a light source nearer white) as described in Japanese Patent Application (OPI) Nos. 137350/81 and 70223/83 is preferred. It is suitable that the illumination of light be about 0.01 to 2000 lux, preferably about 0.05 to 30 lux, and more preferably abou 0.05 to 5 lux. The higher the sensitivity of the emulsion used in a photosensitive material, the more preferred is exposure with a lower illumination. The adjustment of the illumination may be effected by varying the intensity of the light source, reducing the amount of light by filters, or varying the distance or the angel between the photosensitive material and the light source. The exposure time can be shortened by using a weak light at the initial stage of the exposure and then a stronger light.

It is preferred that fogging exposure be performed after the photosensitive material is dipped in a developing solution or a bath prior to the developing solution so that the solution thoroughly penetrates into the emulsion layer. Generally, the time between complete penetration of the solution and light fogging exposure is about 2 seconds to 2 minutes, preferably about 5 seconds to 1 minute, and more preferably about 10 seconds to 30 seconds.

The exposure time for fogging is generally about 0.01 second to 2 minutes, preferably about 0.1 second to 1 minute, and more preferably about 1 second to 40 seconds.

The nucleating agent that can be used in the present invention includes any compound that is capable of nucleating an internal latent type silver halide. Two or moer nucleating agents can be used in combination. Nucleating agents include those described, for example, in Research Disclosure, No. 22534 (January, 1983), pages 50 to 54; No. 15162 (November, 1976), pages 76 to 77; and No. 23510 (November, 1983), pages 346 to 352. These can be classified roughly into three types: quaternary heterocyclic compounds (compounds represented by general formula (N-I)), hydrazine type compounds (compounds represented by general formula (N-II)) and other compounds.

General formula (N-I):


(N-I)

wherein Z represents a substituted or unsubstituted nonmetallic atomic group necessary for forming a 5-membered or 6-membered heterocyclic ring; R^{11} represents a substituted or unsubstituted aliphatic group, R^{12} represents a hydrogen atom, a substituted or unsubstituted aliphatic group or a substituted or unsubstituted aromatic group; provided that at least one of R^{11}, R^{12} and Z contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^{11} and R^{12} together form a 6-membered ring to complete a dihydropyridinium skeleton; Y represents a counter ion necessary for charge balance and n is 0 or 1. At least one of the substituents of R^{11}, R^{12} and Z may contain the group $X^1 \leftarrow\!\!\!\!(L^1)_m$, in which X^1 represents a group capable of accelerating adsorption onto a silver halide grain, L^1 represents a divalent linking group and m is 0 or 1.

More particularly, the heterocyclic ring formed by Z includes a quinolinium nucleus, a benzothiazolium nucleus, a benzimidazolium nucleus, a pyridinium nucleus, a thiazolini um nucleus, a thiazolium nucleus, a naphthothiazolium nucleus, a selenazolium nucleus, a benzoselenazolium nucleus, an imidazolium nucleus, a tetrazolium nucleus, an indolenium nucleus, a pyrrolinium nucleus, an acridinium nucleus, a phenanthridinium nucleus, an isoquinolium nucleus, an oxazolium nucleus, a naphthooxazolium nucleus, a naphthopyridinium nucleus, and a benzoxazolium nucleus. The substituents for Z include an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkynyl group, a hydroxy group, an alkoxy group, an aryloxy group, a halogen atom, an amino group, an alkylthio group, an arylthio group, an acyloxy group, an acylamino group, a sulfonyl group, a sulfonyloxy group, a sulfonylamino group, a carboxyl group, an acyl group, a carbamoyl group, a sulfamoyl group, a sulfo group, a cyano group, a ureido group, a urethane group, a carbonic acid ester group, a hydrazine group, a hydrazone group and an imino group. Preferably, at least one of the above substituents is present as a substituent for Z, and if there are two or moe substituents on Z, they may be the same or different. The above substituents may be further substituted by the substituents mentioned above.

Further, the substituent for Z may have a heterocyclic ring quaternary ammonium group formed by Z via a suitable linking group L. In this case, it forms a dimer structure.

The heterocyclic ring formed by Z is preferably a quinolium nucleus, a benzothiazolium nucleus, a benzimidazolium nucleus, a pyridinium nucleus, an acridinium nucleus, a phenanthridinium nucleus, a naphthopyridinium nucleus or an isoquinolinium nucleus, with a quinolinium nucleus, a benzothiazolium nucleus and a naphthopyridinium nucleus more preferred and a quinolium nucleus most preferred.

The aliphatic group represented by R^{11} and R^{12} is an unsubstituted alkyl group having 1 to 18 carbon atoms or a substituted alkyl group having 1 to 18 carbon atoms in the alkyl moiety. The substituents may be the same as those for Z.

The aromatic group represented by R^{12} is one having 6 to 20 carbon atoms, such as a phenyl group and a naphthyl group. The substituents are the same as those for Z. Preferably R^{12} represents an aliphatic group, most preferably a methyl group or a substituted methyl group.

Of the groups represented by R^{11}, R^{12} and Z, at least one contains an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^{11} and R^{12} are linked to form a 6-membered ring to complete a dihydropyridinium skeleton; and these groups may be substituted with the substituents for Z mentioned above. Preferably the hydrazine group is substituted, particularly with an acyl group or a sulfonyl group. For example, a formyl group, an aliphatic group or an aromatic ketone is preferred as the acyl group. Preferably, the hydrazone group is substituted with an aliphatic group or an aromatic group.

It is preferred that at least one of the substituents on the ring or the group represented by R^{11}, R^{12} and Z is an alkynyl group or an acyl-group, or that R^{11}, R^{12} and Z is an alkynyl group or an acyl-group, or that R^{11} and R^{12} together form a dihydropyridinium skeleton, and it is most preferred that at least one alkynyl group is present.

Preferred examples of a group capable of accelerating adsorption onto a silver halide represnets by X^1 include a thioamido group, a mercapto group and a 5-or 6-membered nitrogen-containing heterocyclic ring group. These groups may be substituted by the substituents for Z. Preferably the thioamido group is a non-cyclic thioamido group (e.g. a thiourethane group and a thioureide group).

The mercapto group represented by X^1 is particularly preferably a heterocyclic mercapto group (e.g., 5-mercaptotetrazole, 3-mercapto-1,2,4-triazole, and 2-mercapto-1,3,4-thiadiazole).

The 5-or 6-membered nitrogen-containing heterocyclic ring represented by X^1 contain a combination of nitrogen, oxygen, sulfur and carbon and preferably is one that will form an imino silver such as benzotriazole.

The 5-to 6-membered nitrogen-containing heterocyclic ring represented by X^1 includes a 5-to 6-membered nitrogen-containing heterocyclic ring made up of a combination of nitrogen, oxygen, sulfur and carbon. Of these, preferable ones are benzotriazole, triazole, tetrazole, indazole, benzimidazole, imidazole, benzothiazole, thiazole, benzoxazole, oxazole, thiadiazole, oxadiazole, triazine, etc., which may have a suitable substituent, for example, the substituents mentioned for Z. More preferably nitrogen-containing heterocyclic rings are benzotriazole, triazole, tetrazole, and indazole, with benzotriazole most preferable.

The divalent linking group represented by L^1 is an atomic group containing at least one of C, N, S and O and more specifically contains, for example, one or a combination of an alkylene group, an alkenylene group, an alkynyl. ene group, an arylene group, -O-, -S-, -NH-, -N-, -CO-and $-SO_2-$which may be substituted.

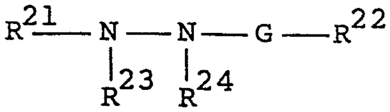
The counter ion for charge balance represented by Y includes a bromide ion, a chloride ion, an iodine ion, a p-toluenesulfonate ion, an ethylsulfonate ion, a perchlorate ion, a trifluoromethanesulfonate ion and a thiocyanate ion.

Examples of these compounds and synthetic methods therefor are described, for example, in the patents cited in Research Disclosure, No. 22524 (January, 1983), pages 50 to 54; and No. 23213 (August, 1983), pages 267 to 270; Japanese Patent Publication Nos. 38164/74, 19452/77 and47326/77; Japanese Patent Application (OPI) Nos. 69613/77, 3426/77; 138742/80 and 11837/85 and U.S. Patents 4,306,016 and 4,417,044.

Specific examples of the compounds represented by general formula (N-1) are given below, but the invention is not to be construed as being limited to these compounds.

(N-I-1): 6-ethoxy-2-methyl-1-propargylquinolinium bromide
(N-I-2): 2,4-dimethyl-1-propargylquinolinium bromide
(N-I-3): 2-methyl-1-{3-[2-(4-methylphenyl)hydrazono]-butyl}quinolinium iodide
(N-I-4): 3,4-dimethyl-dihydropyrido[2,1-b]benzothiazolium bromide
(N-I-5): 6-ethoxythiocarbonylamino-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-6): 2-methyl-6-(3-phenylthioureido)-1-propargylquinolium bromide
(N-I-7): 6-(5-benzotriazolocarboxyamido)-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-8): 6-[3-(2-mercaptoethyl)ureido]-2-methyl-1-propargylquinolinium trifluoromethanesulfonate
(N-I-9): 6-{3-[3-(5-mercapto-thiadiazolo-2-ylthio)propyl]-ureido -2-methyl-1-propargylquinolinium)-trifluoromethanesulfonate
(N-I-10): 6-(5-mercaptotetrazolo-1-yl)-2-methyl-1-propargylquinolinium iodide

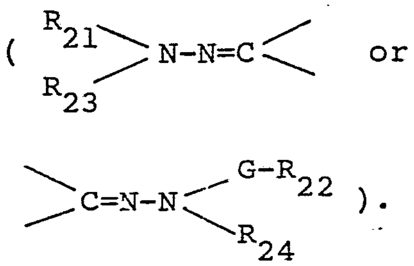
General formula (N-II):



$$R^{21}-\underset{\displaystyle R^{23}}{\underset{|}{N}}-\underset{\displaystyle R^{24}}{\underset{|}{N}}-G-R^{22}$$

(N-II)

wherein R^{21} represents an aliphatic group, an aromatic group or a heterocyclic group; R^{22} represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group or an amino group; G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group ($HN=C<$); and R^{23} and R^{24} both represent a hydrogen atom, or one of R^{23} and R^{24} represents a hydrogen atom and the other represents an alkylsulfonyl group, an arylsulfonyl group or an acyl group. G, R^{23} and R^{24} together with the hydrazine nitrogens may form a hydrazone structure



These groups may, if possible, be substituted by a substituent.

More particularly, R^{21} may be substituted by a substituent, which in turn may be further substituted, such as an alkyl group, an aralkyl group, an alkoxy group, an amino group substituted by an alkyl or aryl group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamoyl group, an aryl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxy group, a halogen atom, a cyano group, a sulfo group and a carboxyl group, with a ureido group or sulfonamido group preferred, which groups may link together to form a ring if possible.

Preferably, R^{21} represents an aromatic group, an aromatic heterocyclic ring group or an aryl-substituted methyl group, with an aryl group (e.g., a phenyl group and a naphthyl group) more preferred.

Preferably, R^{22} represents a hydrogen atom, an alkyl group (e.g., a methyl group) or an aralkyl group (e.g., an o-hydroxybenzyl group), with a hydrogen atom particularly preferred.

The substituents for R^{22} include those for R^{21} as well as an acyl group, an acyloxy group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an alkenyl group, an alkynyl group and a nitro group, which may be further substituted any of those substituents, and, if possible, may link together to form a ring.

R^{21} or R^{22}, in particular R^{21}, may contain a diffusion-resistant group such as a coupler, ballast group (preferably linked through a ureido gorup) and may contain a group $X^2 \!-\!\!\left(L^2 \right)_{m^2}$ capable of accelerating adsorption onto the surface of silver halide grains, where X^2 has the same meaning as X^1 in general formula (N-I) and preferably represents a thioamide group (excluding a thiosemicarbazide and its substitution product), a mercapto group or a 5-or 6-membered nitrogen-containing heterocyclic ring group, L^2 represents a divalent linking group and has the same meaning as L^1 in general formula (N-I), and m^2 is 0 or 1.

Preferably, X^2 represents a non-cyclic thioamido group (e.g., a thioureido group and a thiourethane group), a cyclic thioamido group (i.e., a mercapto-substituted nitrogen-containing heterocyclic ring, e.g., a 2-mercaptothiadiazole group, a 3-mercapto-1,2,4-triazole group, a 5-mercaptotetrazole group, a 2-mercapto-1,3,4-oxadiazole group and a 2-mercaptobenzoxazole group) or a nitrogen-containing heterocyclic ring group (e.g., a benzotriazole group, a benzimidazole group and an indazole group).

Most preferably, X^2 is determined based on the photosensitive material. For example, in the case of a color photosensitive material that uses a coloring material (a so-called coupler) that forms a dye when coupled with the oxidation product of a p-phenylenediamine type developing agent, X^2 peferably represents a mercapto-substituted nitrogen-containing heterocyclic ring or a nitrogen-containing heterocyclic ring that will form an imino silver. In the case of a color photosensitive material that uses a coloring material (a so-called DRR compound) that forms a diffusion-resistant dye by cross-oxidizing the oxidation product of a developing agent, X^2 preferably represents a non-cyclic thiamido group or a mercapto-substituted nitrogen-containing heterocyclic ring. In the case of a black-and-white photosensitive material, X^2 preferably represents a mercapto-substituted nitrogen-containing heterocyclic ring or a nitrogen-containing heterocyclic ring that will form an imino silver.

Most preferably, R^{23} and R^{24} represent a hydrogen atom.

Most preferably, G in general formula (N-II) represents a carbonyl group.

Preferably, the compound represnets by general formula (N-II) contains a group capable of being adsorbed onto a silver halide or a group having a ureido group.

Particularly, examples of hydrazine type nucleating agents having a group capable of being adsorbed onto a silver halide, and synthetic methods therefor are described, for example, in U.S. Patents 4,030,925, 4,080,207, 4,031,127, 3,718,470, 4,269,929, 4,276,364, 4,278,748, 4,385,108, 4,459,347, 4,478,928 and 4,560,638, British Patent 2,011,391B and Japanese Patent Application (OPI) Nos. 74729/79, 163533/80, 74536/80 and 179734/85.

Examples of other hydrazine type nucleating agents and synthetic methods therefor are described, for example, in Japanese Patent Application (OPI) No. 86829/82, U.S. Patents 4,560,638, 4,478,528, 2,563,785 and 2,588,982.

Specific examples of the compounds represented by general formula (N-II) are given below, but the invention is not to be construed as being limited to them.

(N-II-1): 1-formyl-2-{4-[3-(2-methoxyphenyl)ureido]-phenyl}hydrazine

(N-II-2): 1-formyl-2-{4-[3-{3-[3-(2,4-di-tert-pentylphenoxy)propyl]ureido}phenylsulfonylamino]-phenyl}hydrazine

(N-II-3): 1-formyl-2-{4-[3-(5-mercaptotetrazolo-1-yl)benzamido]phenyl}hydrazine

(N-II-4): 1-formyl-2-[4-{3-[3-(5-mercaptotetrazolo-1-yl)phenyl]ureido}phenyl]hydrazine

(N-II-5): 1-formyl-2-[4-{3-[N-(5-mercapto-4-methyl-1,2,4-triazolo-3-yl)carbamoyl]-propaneamido}-phenyl]hydrazine

(N-II-6): 1-formyl-2-{4-[3-{N-[4-(3-mercapto-1,2,4-triazolo-4-yl)phenyl]carbamoyl}propaneamido]-phenyl}-hydrazine

(N-II-7): 1-formyl-2-[4-{3-[N-(5-mercapto-1,3,4-thiadiazolo-2-yl)carbamoyl]propaneamido}-phenyl]-hydrazine

(N-II-8): 2-[4-(benzotriazolo-5-carboxamido)phenyl]-1-formylhydrazine

(N-II-9): 2-[4-{3-[N-benzotriazolo-5-carboxamido)carbamoyl]propaneamido}phenyl]-1-formylhydrazine

(N-II-10): 1-formyl-2-{4-[1-(N-phenylcarbamoyl)thiosemicarbazido]phenyl}hydrazine

(N-II-11): 1-formyl-2-{4-[3-(phenylthioureido)benzamido]phenyl}hydrazine

(N-II-12): 1-formyl-2-[4-{3-hexylureido)phenyl]hydrazine

The nucleating agent used in the present invention can be contained in the photosensitive material or in a processing liquid for the photosensitive material, and preferably is contained in the photosensitive material.

When the nucleating agent used in the present invention is contained in the photosensitive material, although it is preferable that it is added to an internal latent image silver halide emulsion layer, it can be added to other layers such as an intermediate layer, an undercoat layer or a backing layer so long as the nucleating agent diffuses during application or processing to be adsorbed onto a silver halide. When the nucleating agent is added to a processing liquid, it can be added to a developing solution or a prior bath having a low pH as described in Japanese Patent Application (OPI) No. 178350/83.

When the nucleating agent is contained in the photosensitive material, preferably the amount is about 10^{-8} to 10^{-2} mol, more preferably about 10^{-7} to 10^{-3}, per mol of silver halide contained in an emulsion layer.

When the nucleating agent is added to the processing liquid, preferably the amount of the nucleating agent is about 10^{-5} to 10^{-1} mol, more preferably about 10^{-4} to 10^{-2} mol, per liter thereof.

For the purpose of increasing the maximum image density, of lowering the minimum image density, of improving the shelf life of the photosensitive material, and of quickening the development, and for other purposes, the following compounds can be added: hydroquinones (e.g., compounds described in U.S. Patents 3,227,552 and 4,279,987), chromans (e.g., compounds described in U.S. Patent 4,268,621, Japanese Patent Application (OPI) No. 103031/79 and Research Disclosure, No. 18264 (June, 1979), pages 33 to 334); quinones (e.g., compounds described in Research Disclosure, No. 21206 (December, 1981), pages 433 to 434); amines (e.g., compounds described in U.S. Patent 4,150,993 and Japanese Patent Application (OPI) No. 174757/83); oxidizing agents (e.g., compounds described in Japanese Patent Application (OPI) No. 260039/85 and Research Disclosure, No. 16936 (May, 1978), pages 10 to 11); catechols (e.g., compounds described in Japanese Patent Application (OPI) Nos. 21013/80 and 65944/80); compounds that will release a nucleating agent at the time of development (e.g., compounds described in Japanese Patent Application (OPI) No. 107029/85); thioureas (e.g., compounds described in Japanese Patent Application (OPI) No. 95533/85) and spirobisindanes (e.g., compounds described in Japanese Patent Application (OPI) No. 65944/80).

Nucleation accelerators that can be used in the present invention include pentaazaindenes, triazaindenes and tetraazaindenes having at least one mercapto group that is optionally substituted by an alkali metal atom or ammonium group, and compounds described in Japanese Patent Application (OPI) No. 136948/86 (pages 2 to 6 and 16 to 43), Japanese Patent Application Nos. 136949/86 (pages 12 to 43) and 15348/86 (pages 10 to 29).

Specific examples of the nucleation accelerators are given below, but the present invention is not to be construed as being limited to those compounds.

(A-1): 3-mercapto-1,2,4-triazolo[4,5-a]pyridine

(A-2): 3-mercapto-1,2,4-traizolo[4,5-a]pyrimidine

(A-3): 5-mercapto-1,2,4-triazolo[1,5-a]pyrimidine

(A-4): 7-(2-dimethylaminoethyl)-5-mercapto-1,2,4-triazolo[1,5-a]pyrimidine

(A-5): 3-mercapto-7-methyl-1,2,4-triazolo[4,5-a]pyrimidine
(A-6): 3,6-dimercapto-1,2,4-triazolo[4,5-b]pyridadine
(A-7): 2-mercapto-5-methylthio-1,3,4-thiadiazole
(A-8): 3-mercapto-4-methyl-1,2,4-triazole
(A-9): 2-(3-dimethylaminopropylthio)-5-mercapto-1,3,4-thiadiazole hydrochloride
(A-10): 2-(2-morpholinoethylthio)-5-mercapto-1,3,4-thiadiazole hydrochloride
(A-11): 2-mercapto-5-methylthiomethylthio-1,3,4-thiadiazole sodium salt
(A-12): 4-(2-morpholinoethyl)-3-mercapto-1,2,4-triazole
(A-13): 2-[2-(2-dimethylaminoethylthio)ethylthio]-5-mercapto-1,3,4-thiadiazole hydrochloride

It is preferred that the nucleation accelerator is added to a silver halide emulsion or a layer adjacent thereto.

The amount of the nucleation accelerator added to the material is preferably about 10^{-6} to 10^{-2} mol, more preferably about 10^{-5} to 10^{-2} mol, per mol of a silver halide in the layer or adjacent layer.

If the nucleation accelerator is added to a process ing liquid, i.e., a developing solution or a bath prior to a processing liquid, the amount of the nucleation accelerator is about 10^{-8} to 10^{-3} mol, preferably about 10^{-7} to 10^{-4} mol, per liter of the processing liquid.

Two or more nucleation accelerators can be used in combination.

The color developing solution used for developing the present photosensitive material is substantially free from a silver halide solvent and is preferably an alkaline solution whose major component is an aromatic primary amine color developing agent. As the color developing agent, aminophenol type compounds are useful, and p-phenylenediamine type compounds are preferred. Typical examples thereof are 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline, 3-methyl-4-amino-N-ethyl-N-(β-hydroxyethyl)-aniline and 3-methyl-4-amino-N-ethyl-N-methoxyethylaniline and their sulfates and hydrochlorides. As the color developing agent, compounds described by L.F.A. Mason in Photographic Processing Chemistry, pages 226 to 229 (Focal Press, 1966); U.S. Patents 2,193,015 and 2,592,364; and Japanese Patent Application (OPI) No. 64933/73 can also be used. If desired, two or more color developing agents can be used in combination.

The amount of the color developing agent is preferably about 0.1 to 20 g, more preferably about 0.5 to 15 g, per liter of the developing solution.

The developer can contain preservatives including, for example, aromatic polyhydroxy compounds described in Japanese Patent Application (OPI) Nos. 49828/77, 47038/81, 32140/81 and 160142/84 and U.S. Patent 3,746,544; hydroxyacetones described in U.S. Patent 3,615,503 and British Patent 1,306,176; α-aminocarbonyl compounds described in Japanese Patent Application (OPI) Nos. 143020/77 and 89425/78; metals described, for example, in Japanese Patent Application (OPI) Nos. 44148/82 and 53749/82; sugars described in Japanese Patent Application (OPI) No. 102727/77; hydroxamic acids described in Japanese Patent Application (OPI) No. 27638/77, α,α'-dicarbonyl compounds described in Japanese Patent Application (OPI) No. 160141/84; salicylic acids described in Japanese Patent Application (OPI) No. 180588/84; alkanolamines described in Japanese Patent Application (OPI) No. 3532/79; poly(alkyleneimines) described in Japanese Patent Application (OPI) No. 94349/81; and gluconic acid derivatives described in Japanese Patent Application (OPI) No. 75647/81, which may be used in combination if required. Particularly, the addition of 4,5-dihydroxy-m-benzenedisulfonic acid, poly(ethyleneimine) and triethanolamine is preferred. The addition of substituted phenols such as p-nitrophenol is also preferred. The use of alkylhydroxylamine compounds described in Japanese Patent Appli cation (OPI) No. 3532/79 is also preferred. Particularly, it is preferred that alkylhydroxylamine compounds are used in combination with the above preservatives.

The amount of the preservative to be used is about 0.1 to 20 g, preferably about 0.5 to 10 g, per liter of the developing solution.

The pH of the color developing solution in the present invention is preferably about 9.5 to 11.3, more preferably about 10.0 to 10.8. To maintain the pH mentioned above, various buffers can be used, including carbonates such as potassium carbonate, phosphates such as potassium phosphate and compounds described in Japanese Patent Application (OPI) No. 215272/87, pages 11 to 22.

The color developing solution can contain various chelating agents as agents for preventing calcium and magnesium from precipitating or for improving the stability of the color developing solution.

Chelating agents include, for example, aminopolycarboxylic acids described in Japanese Patent Publication Nos. 30496/73 and 30232/69; organic phosphonic acids described in Japanese Patent Application (OPI) No. 97347/81, Japanese Patent Publication No. 39359/81 and West German Patent No. 2,227,639; phosphonocarboxylic acids described in Japanese Patent Application (OPI) Nos. 102726/77, 42730/78, 121127/79, 126241/80 and 65956/80; and other compounds de scribed in Japanese Patent Application (OPI) Nos. 195845/83 and 203440/83 and Japanese Patent Publication No. 40900/78, which can be used in combination if required. The amount of the chelating agents to be added is that sufficient to form complexes with metal ions present in the color developing solution. For example, the amount is on the order of about 0.1 to 10 g per liter.

If desired, any conventional development accelerator can be added to the color developing solution.

Development accelerators include thioether type compounds described, for example, in Japanese Patent Publication Nos. 16088/62, 5987/62, 7826/63, 12380/69 and 9019/70, and U.S. Patent 3,813,247; p-phenylenediamine type compounds described in Japanese Patent Application (OPI) Nos. 49829/77 and 15554/75; quaternary ammonium salts described, for example, in Japanese Patent Application (OPI) No. 137726/75, Japanese Patent Publication No. 30074/69 and Japanese Patent Application (OPI) Nos. 156826/81 and 43429/77; p-aminophenols described in U.S. Patents 2,610,122 and 4,119,462; amine type compounds described, for example, in U.S. Patents 2,494,903, 3,128,182, 4,230,796 and 3,253,919, Japanese Patent Publication No. 11431/66, U.S. Patents 2,482,546, 2,596,926 and 3,582,346; and 1-phenyl-3-pyrazolidone, hydrazines, meso-ionic compounds, thionic compounds, imidazoles and polyalkylene oxides described, for example, in Japanese Patent Publication Nos. 16088/62 and 25201/67, U.S. Patent 3,128,183, Japanese Patent Publication Nos. 11431/66 and 23883/67 and U.S. Patent 3,532,501. Particularly, thioether type compounds and 1-phenyl-3-pyrazolidones are preferred.

If required, any conventional antifoggant can be added to the color developing solution in the present invention. Such antifoggants include an alkali metal halide such as potassium bromide, sodium chloride and potassium iodide or an organic antifoggant. As an organic antifoggant can be used, for example, a nitrogen-containig heterocyclic ring compound such benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethyl-benzimidazole and hydroxyazaindolizine; a mercapto-substituted heterocyclic compound such as 2-mercaptobenzimidazole and 2-mercaptobenzythiazole; and a mercapto-substituted aromatic compound such as thiosalicyclic acid and adenine. Although these antifoggants may dissolve out of the color photosensitive material during processing and may accumulate in the color developing solution, it is preferred that the amount of the accumulation be limited to reduce their discharge amount of the developer.

It is preferable that the color developing solution in the present invention contain a brightening agent. It is preferred to use, as a brightening agent, a 4,4-diamino2,2'-disulfostilbene type compound. The amount of the brightening agent to be added is 0 to about 5 g/liter, preferably about 0.1 to 2 g/liter.

If required, surface active agents may be added, such as alkylhosphonic acids, arylphosphonic acids, aliphatic carboxylic acids and aromatic carboxylic acids.

Generally, after color development, the photographic emulsion layer is bleached. The bleaching may be carried out simultaneously with fixing as a one-bath bleach-fixing or the bleaching and the fixing can be carried out separately. To reduce the processing time, bleach-fixing can be performed either after the bleaching or after the fixing. Generally, the bleaching solution or the bleach-fix solution in the present invention uses, as a bleaching agent, an aminopolycarboxylic acid iron complex salt. The bleaching solution or the bleach-fix solution in the present invention can contain various additive compounds described in Japanese Patent Application (OPI) No. 21572/87, pages 22 to 30. After the desilvering (bleach-fix or bleaching), washing and/or stabilizing is carried out. It is preferred to use, for washing water or for a stabilizing liquid, water that has been subjected to a water softening treatment, such as a method using an ion exchange resin or a reverse osmosis apparatus described in Japanese Patent Application No. 131632/86. More specifically, the method described in Japanese Patent Application No. 13132/86 is preferably used.

Further, additives that can be used in a washing step and a stabilizing step include various compounds described in Japanese Patent Application (OPI) No. 215272/87, pages 30 to 36.

It is preferable that the amount of the replenishing solution in each step is small. Preferably the amount of the replenishing solution is about 0.1 to 50 times, more preferably about 3 to 30 times the amount of the solution carried over from the preceding bath per unit area of the photosensitive material.

The present invention is not illustrated in greater detail by reference to the following Example, but the present invention is not to be construed as being limited thereto. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLE

EXAMPLE 1

Emulsion-A

An aqueous 10 wt% solution of potassium bromide and an aqueous 10 wt% solution of silver nitrate were simultaneously added at 65°C over a period of about 30 minutes with vigorous stirring to an aqueous 7 wt% gelatin solution containing 0.3 g of 3,4-dimethyl-1,3-thiazoline-2-thion per mol of Ag to obtain an octahedral monodispersed silver bromide emulsion having an average grain diameter of 0.45 µm. 16 mg each of sodium thiosulfate and chloroauric acid (tetrahydrate) were added to the emulsion per mol of silver and the emulsion was heated at 75°C for 80 minutes to be chemically sensitized. The thus prepared silver bromide grains were used as cores and were treated for a further 40 minutes while adding additional potassium bromide and silver nitrate under the same precipitation conditions described above to be further grown thereby producing an octahedral monodispersed (coefficient of variation: 11%) core/shell silver bromide emulsion having an average grain diameter of 0.8 µm. To the emulsion was added hydrogen peroxide in an amount of 1.5 g per mol of Ag, then the emulsion was heated for 8 minutes at 75°C, and washed with water to desalt it; 2.2 mg of each of sodium thiosulfate and chloroauric acid (tetrahydrate) were added per mol of silver thereto; and the emulsion was heated at 60°C for 60 minutes to be chemically sensitized thereby producing an internal latent image type silver halide emulsion A.

Using the core/shell type internal latent image emulsion, each color photographic paper having the layer structure shown in Table 1 was prepared using a paper base with opposite surfaces laminated with polyethylene. The coating liquids were prepared as follows.

Preparation of a first coating liquid: 10 g of a cyan coupler (shown in Table 2) and 2.3 g of a dye image stabilizer (b) were dissolved in 10 ml of ethyl acetate and 4 ml of a solvent (c), and the solution was emulsified and dispersed in 90 ml of a 10% aqueous gelatin solution containing 5 ml of 10% of sodium dodecylbenzenesulfonate to prepare an emulsion dispersion. Separately to the above silver halide emulsion (containing 70 g of Ag/kg) was added a red sensitizing dye shown below in an amount of 2.0×10^{-4} mol per mol of the silver halide to produce 90 g of a red sensitive emulsion. The emulsified dispersion, the red-sensitive emulsion and a development accelerator were mixed and dissolved and the concentrations were adjusted using gelatin to have the composition shown in Table 1, and a nucleating agent (N-I-9) in an amount of 4.5×10^{-6} mol per mol of Ag and a nucleation accelerator (A-15) in an amount of 1×10^{-4} mol per mol of Ag were added thereto to prepare a coating liquid for a first layer.

Coating liquids for the second to seventh layers were prepared in the same way as the coating liquid for the first layer. As a gelatin hardening agent, each layer contained 0.03 g/m^2 of 1-oxy-3,5-dichloro-s-triazine sodium salt.

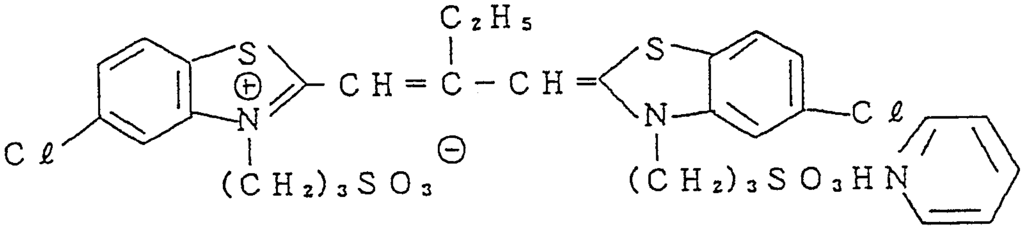
The spectral sensitizers for the emulsions are described below.

Table 1

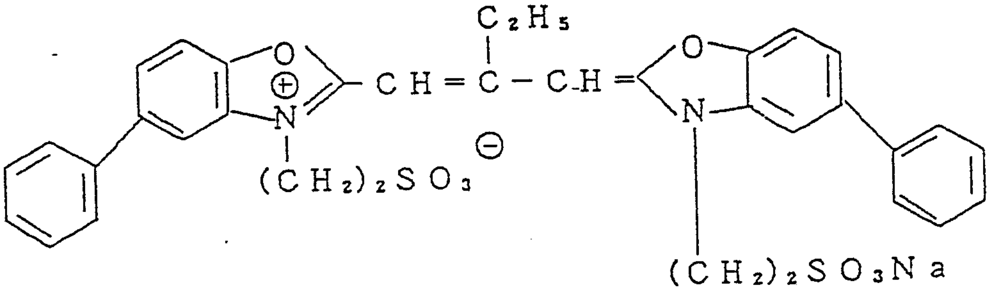
Layer	Major Components	Amount
Seventh Layer (Protective layer)	Gelatin	1.33 g/m^2
	Latex particles of poly methylmethacrylate (average particle diameter: 2.8 μm)	0.55 g/m^2
	Acryl-modified copolymer of polyvinyl alcohol (degree of modification: 17%)	0.17 g/m^2
Sixth Layer (Ultraviolet absorbing layer)	Gelatin	0.54 g/m^2
	Ultraviolet absorbing agent (i)	5.10×10^{-4} mol/m^2
	Solvent (k)	0.08 g/m^2
Fifth Layer (Blue-sensitive layer)	Emulsion (calculated as silver)	0.40 g/m^2
	Gelatin	1.35 g/m^2
	Yellow coupler (ℓ)	6.91×10^{-4} mol/m^2
	Dye stabilizer (m)	0.13 g/m^2
	Solvent (h)	0.02 g/m^2
	Nucleating agent and nucleation accelerator	
Fourth Layer (Ultraviolet absorbing layer)	Gelatin	1.60 g/m^2
	Colloidal silver (diameter 0.01 μm; calculated as silver)	0.10 g/m^2
	Ultraviolet absorber (i)	1.70×10^{-4} mol/m^2
	Color mixing preventing agent (j)	1.60×10^{-4} mol/m^2
	Solvent (k)	0.24 g/m^2

Third Layer (Green-sensitive layer)	Emulsion (calculated as silver)	0.39 g/m^2
	Gelatin	1.56 g/m^2
	Magenta coupler (f)	4.60x10^{-4} mol/m^2
	Dye stabilizer (g)	0.14 g/m^2
	Solvent (h)	0.42 g/m^2
	Nucleator and nucleation accelerator	
Second Layer (Color mixing preventing layer)	Gelatin	0.90 g/m^2
	Colloidal silver (diameter: 0.01 μm; calculated as silver)	0.02 g/m^2
	Color mixing preventing agent (e)	2.33x10^{-4} mol/m^2
First Layer (Red-sensitive layer)	Emulsion (calculated as silver)	0.39 g/m^2
	Gelatin	0.09 g/m^2
	Cyan coupler (see Table 2)	7.05x10^{-4} mol/m^2
	Dye stabilizer (b)	5.20x10^{-4} mol/m^2
	Solvent (c)	0.22 g/m^2
	Nucleating agent and nucleation accelerator	
Base	Polyethylene-laminated paper [the polyethylene on the first layer side contained white pigments (TiO$_2$, etc.) and blue dyes (ultramarine, etc.)]	
Curing preventing layer	Gelatin	2.70 g/m^2

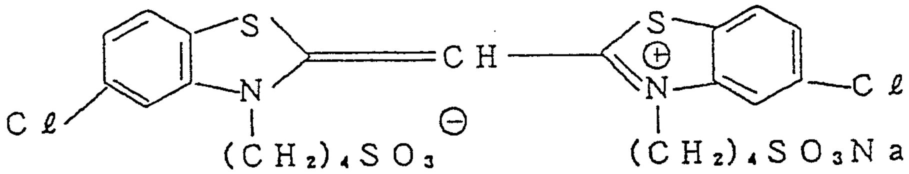
Red-sensitizing Dye:



Green-sensitizing Dye:

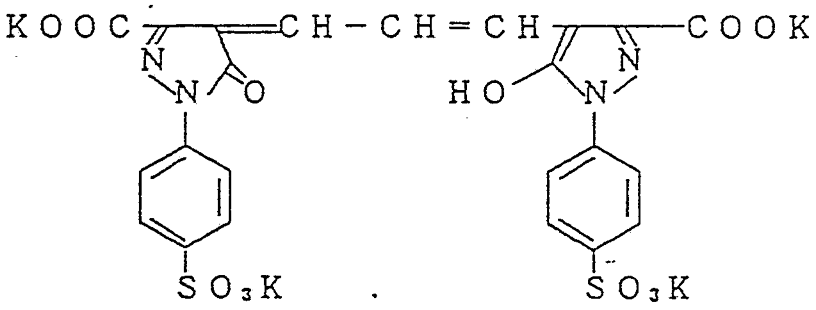


Blue-sensitizing Dye:

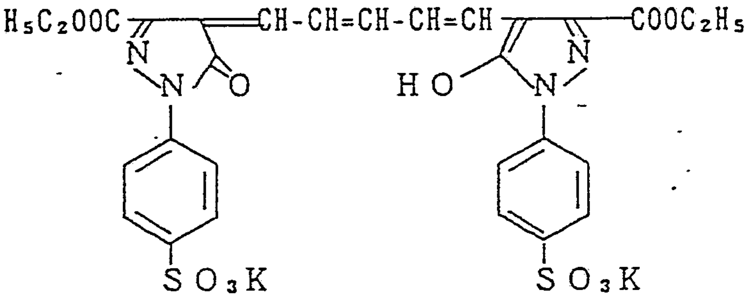


The following dyes were used as irradiation preventive dyes.

Irradiation preventing dye for the green-sensitive emulsion:

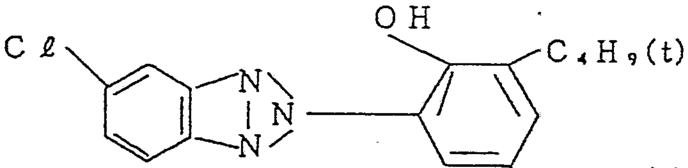


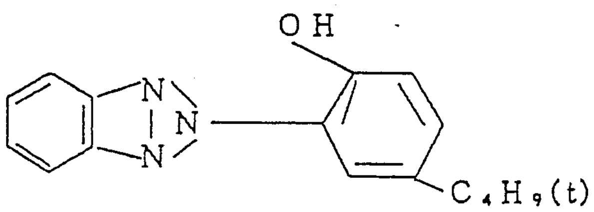
Irradiation preventing dye for the red-sensitive emulsion:



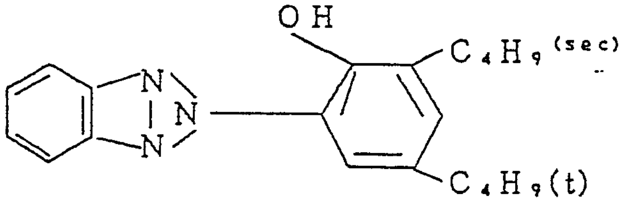
The structures of the compounds used in the Example including couplers are shown below.

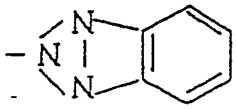
(b) Dye image stabilizer: a 1:3:3 (by mol) mixture of

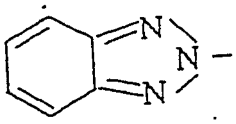




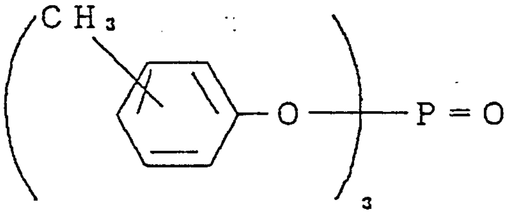
and



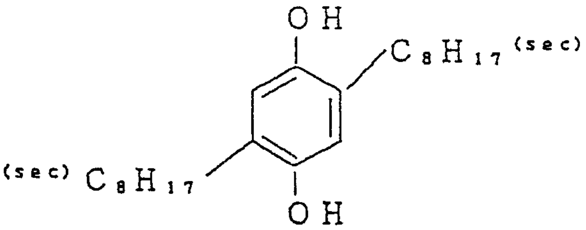
(The  skeleton has the resonance structure of

 in this and other example compounds.)

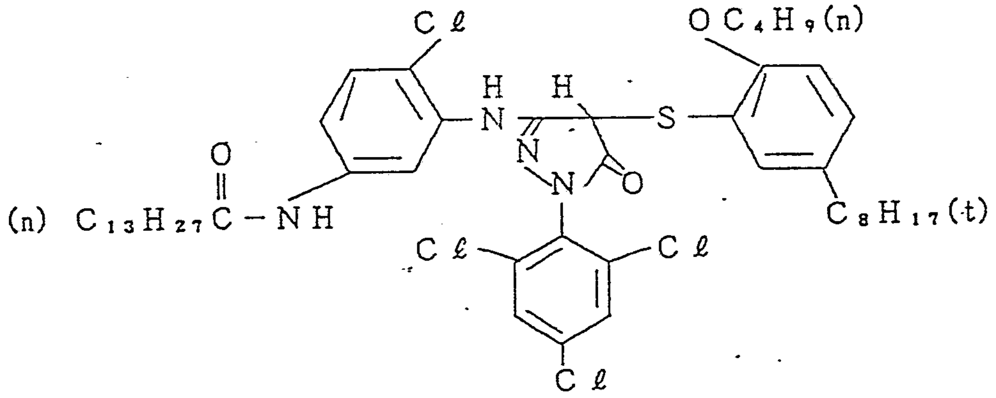
(c) Solvent



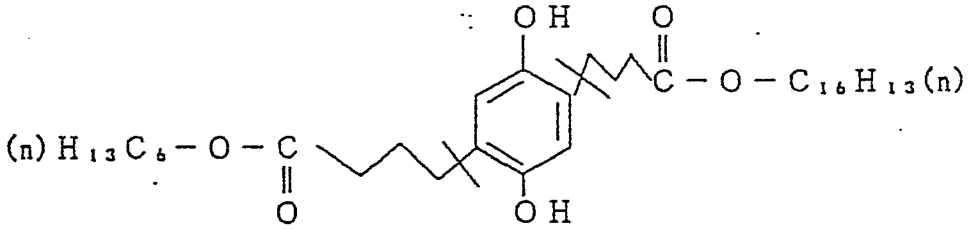
(e) Color mixing preventing agent:



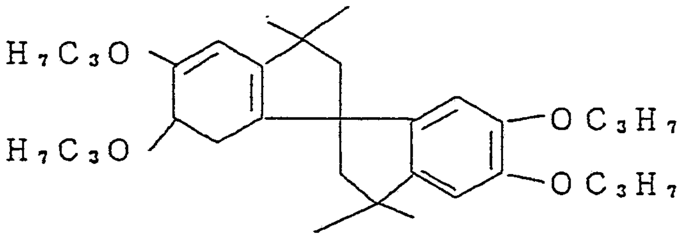
(f) Magenta coupler:



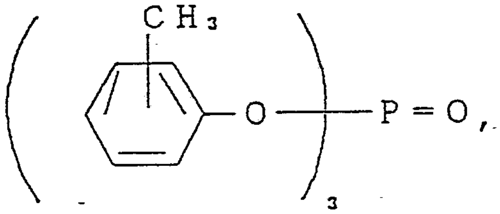
(g) Dye image stabilizer: a 1:1.5 (by weight) mixture of

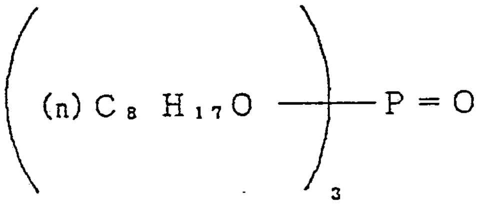


and

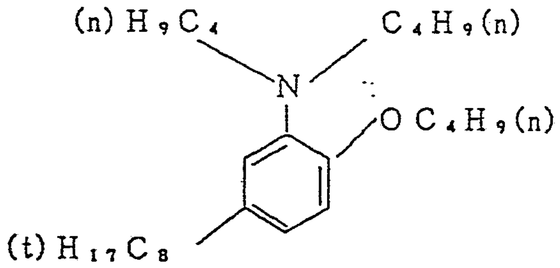


(h) Solvent: a 1:2:2 (by weight) mixture of

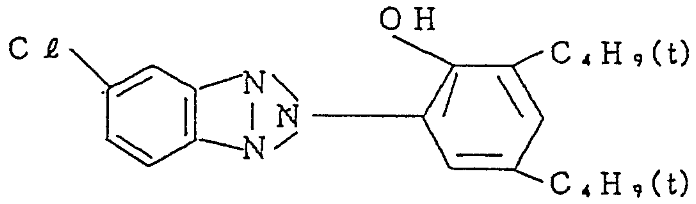


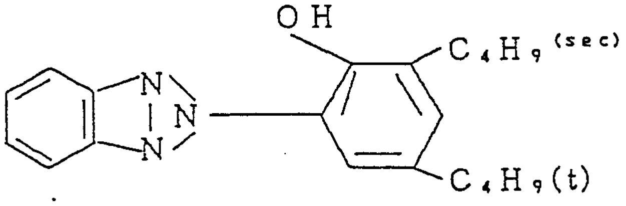


$((n)C_8H_{17}O)_3P=O$ and

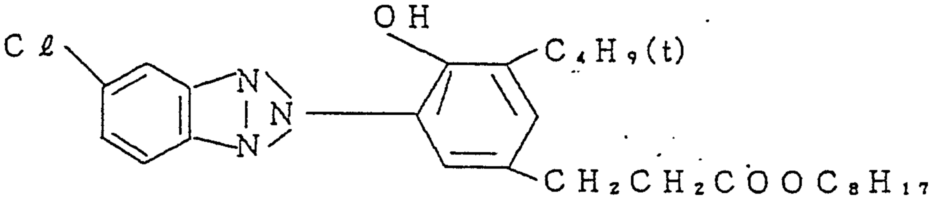


(i) Ultraviolet absorbing agent: a 1:5:3 (by mol) mixture of

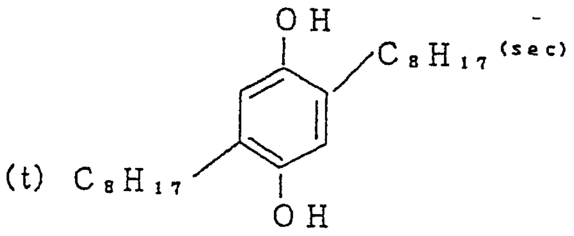




and



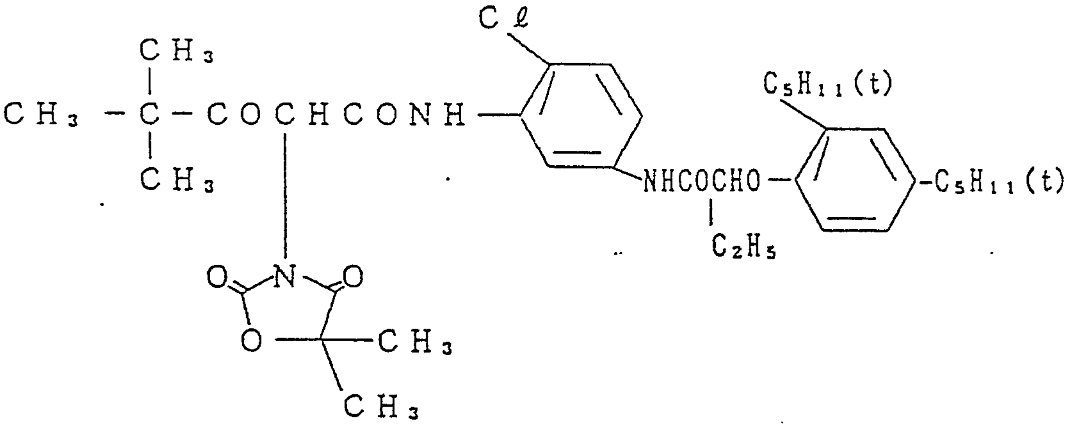
(j) Color mixing preventing agent:



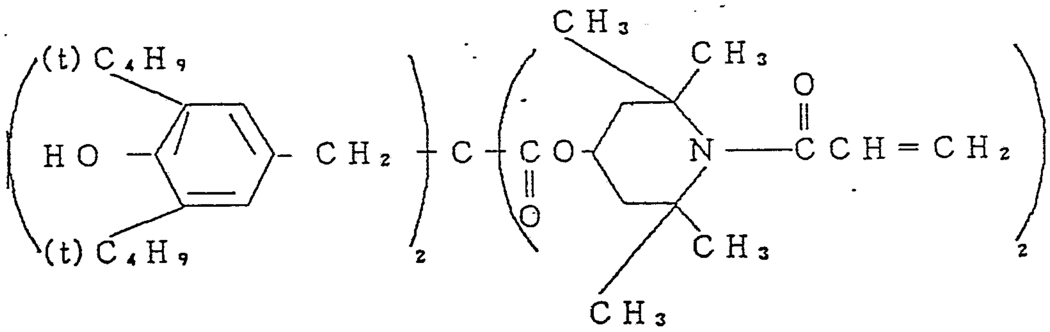
(k) Solvent:

$(\mathrm{iso}\ C_9H_{19}O)_3 - P = O$

(ℓ) Yellow coupler:



(m) Dye stabilizer:



After each of the thus prepared color photographic papers was subjected to wedge exposure (1/10 sec, 10 CMS), the photographic paper was separately subjected to steps (a) and (b) described below, the minimum color image densities of the cyan images were measured, and the difference between the Dmin's obtained in steps (a) and (b) is given in Table 2.

Step (a)

	Time	Temperature
Color development	3 min 30 sec	33°C
Bleach-fix	1 min 30 sec	33°C
Stabilization (1)	1 min	33°C
Stabilization (2)	1 min	33°C
Stabilization (3)	1 min	33°C

The replenishing method of the stabilizing bath was a countercurrent replenishing method, i.e., the replenishing solution was supplied to stabilizing bath (3), the overlfow from stabilizing bath (3) was fed to stabilizing bath (2), and the overflow from stabilizing bath (2) was fed to stabilizing bath (1).

[Color developing solution]

Diethylenetriaminepentaacetic acid	2.0 g
Benzyl alcohol	12.8 g
Diethylene glycol	3.4 g
Sodium sulfite	2.0 g
Sodium bromide	0.26 g
Hydroxylamine sulfate	2.60 g
Sodium chloride	3.20 g
3-methyl-4-amino-N-ethyl-(β-methanesulfonamidoethyl)aniline	4.25 g
Potassium carbonate	30.0 g
Brightening agent (stilbene)	1.0 g

Water to make	1000 ml
pH	10.20

The pH was adjusted using potassium hydroxide or hydrochloric acid.

[Bleach-fix solution]

Ammonium thiosulfate	110 g
Sodium hydrogensulfite	10 g
Ammonium diethylenetriaminepentaacetato ferrate monohydrate	56 g
Disodium ethylenediaminetetraacetate dihydrate	5 g
2-mercapto-1,3,4-triazole	0.5 g
Water to make	1000 ml
pH	6.5

The pH was adjusted using ammonia water or hydrochloric acid.

[Stabilizing solution]

1-hydroxyethylidene-1,1'-diphosphonic acid (60%)	1.6 ml
Bismuth chloride	0.35 g
Polyvinyl pyrrolidone	0.25 g
Ammonia water	2.5 ml
Nitrilotriacetic acid.3Na	1.0 g
5-chloro-2-methyl-4-isothiazoline-3-one	50 mg
2-octyl-4-isothiazoline-3-one	50 mg
Brightening agent (4,4'-diaminostilbene)	1.0 g
Water to make	1000 ml
pH	7.5

The pH was adjusted using potassium hydroxide or hydrochloric acid.

Step (b)

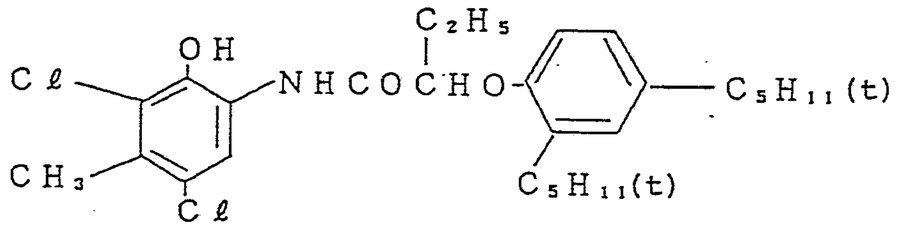
Using the same processing liquids used in step (a) without replenishing, an automatic developing processing machine was run one day and the step (a) was repeated.

Table 2

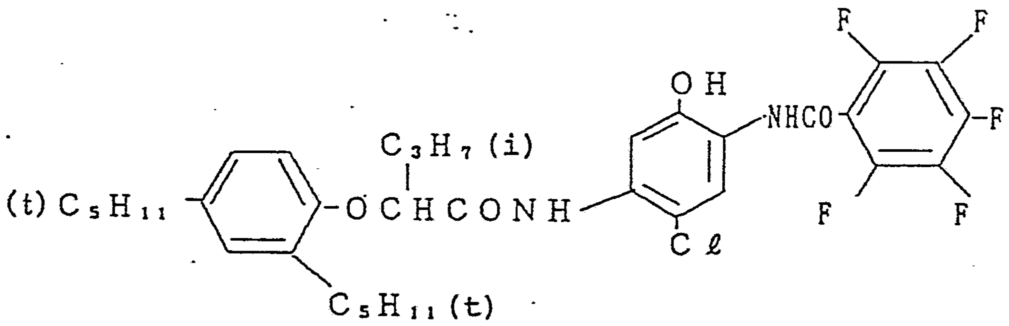
Photosensitive Material	Cyan Coupler	Dmin (b) - Dmin (a)	Remarks
Comparative example: 1-1	C-1*	0.07	Comaprison
" 1-2	C-2*	0.08	Comparison
This invention: 1-1	C-I-2**	0.02	Invention
" 1-2	C-I-3**	0.03	Invention
" 1-3	C-I-5**	0.03	Invention
" 1-4	C-I-9**	0.02	Invention
" 1-5	C-I-12**	0.03	Invention

* Comparative cyan coupler

(C-1):



(C-2):



** These structures are set forth above.

From these results, it can be understood that when the photosensitive materials containing a cyan coupler according to the invention were processed after the automatiic developing processing machine was run one day, the increase in the minimum image density was clearly suppressed.

The color formation of the photosensitive materials containing a cyan coupler according to the invention was good in both steps (a) and (b). The values of the minimum density obtained using cyan couplers according to the invention and comparative cyan couplers in the step (a) were all the same, i.e., 0.21.

EXAMPLE 2

To prepare color photographic papers, Example 1 was repeated, except that an emulsion (B) given below was used; the nucleating agent and the nucleation accelerator were omitted; the cyan couplers shown in Table 3 were used in the first layer.

The thus obtained color photographic papers were subjected to wedge exposure in the same manner as in Example 1, processed by steps (c) and (d), and evaluated in the same way as in Example 1. The results are given in Table 3.

Emulsion (B)

1.2 liter of a silver nitrate solution (0.7 mol/liter) was added to 1.3 liter of a mixture liquid containing 30 g of gelatin, 0.7 mol of KBr, 0.25 mol of NaCl and 0.002 mol of KI at 65°c over a period of 20 minutes and the emulsion was physically ripened for 20 minutes. To 700 ml of that emulsion were added simultaneously 800 ml of each of an aqueous silver nitrate solution (0.6 mol/liter) and an aqueous solution of sodium chloride and potassium bromide (0.8 mol/liter, molar ratio: 1.3 to 1) at 60°C to precipitate silver chloride shells followed by washing with water. A silver halide emulsion (B) having an average grain diameter of 0.75 μm was obtained.

Steps (c) and (d): steps (a) and (c) were repeated, except that light of 0.5 lux (5400 K) was used to expose the photosensitive material surface for 20 seconds, beginning 15 seconds after the start of the development.

Table 3

Photosensitive Material	Cyan Coupler	Dmin (d) - Dmin (c)
Comparative Example: 2-1	C-1*	0.15
Comparative Example: 2-2	C-2*	0.14
This invention: 2-1	C-I-2**	0.04
This invention: 2-2	C-I-5**	0.03
This invention: 2-3	C-I-9**	0.03

*) and **): The structures are set forth below.

The color formation of the photosensitive materials according to the invention processed in the steps (c) and (d) was good, and the Dmin values of the photosensitive materials of the comparative examples and the photosensitive materials according to the invention obtained in the step (c) were all 0.22.

These results were similar to those obtained in Example 1.

EXAMPLE 3

Example 1 was repeated, except that an emulsion (C) given below was used and the cyan couplers shown in Table 4 were used in the first layer.

Emulsion (C)

An aqueous 10 wt% solution of potassium bromide an aqueous 10 wt% solution of silver nitrate were simultaneously added to an aqueous 7 wt% gelatin solution containing 3,4-dimethyl-1,3-thiazoline-2-thione in an amount of 0.56 g per mol of Ag, at 75°C over a period of about 40 minutes to produce an octahedral monodispersed silver bromide emulsion having an average grain diameter of 0.5 µm. To that emulsion were added sodium thiosulfate and chlorauric acid (tetrahydrate), each in an amount of 30 mg per mol of silver, and the emulsion was chemically sensitized by heating at 75°C for 80 minutes. Using the thus obtained silver bromide grains as cores, the silver bromide grains were further treated for 40 minutes under the same precipitation conditions as those for the first time to grow them further thereby obtaining an octahedral monodispersed core/shell silver bromide emulsion having an average grain diameter of 1.1 µm. After the emulsion was washed with water to desalt it, to the emulsion were added sodium thiosulfate and chlorauric acid (tetrahydrate) each in an amount of 2.1 mg per mol of silver, and the emulsion was chemically sensitized by heating at 60°C for 60 minutes to produce an internal latent image type silver halide emulsion (C).

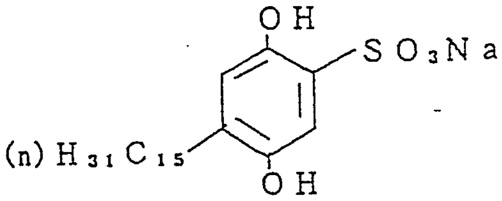
Table 4

Photosensitive Material	Cyan Coupler	Dmin (c)-Dmin (d)
This invention: 3-1	C-I-1	0.01
This invention: 3-2	C-I-3	0.02
This invention: 3-3	C-I-4	0.04
This invention: 3-4	C-I-6	0.01
This invention: 3-5	C-I-7	0.02
This invention: 3-6	C-I-8	0.01
This invention: 3-7	C-I-10	0.01
This invention: 3-8	C-I-11	0.02
This invention: 3-9	C-I-12	0.01
This invention: 3-10	C-I-13	0.02

When they were processed in the same manner as step (b) in Example 1, the increase in the minimum image density was suppressed while good color formation was maintained.

Example 4

Examle 1 was repeated, except that a compound (hg) shown below was added in an amount of 32 mg per m^2 of the photosensitive material to the first, third and fifth layers of the photosensitive material; and the cyan couplers shown in Table 5 were added to the first layer to prepare color photographic papers, which were subjected to steps (e) and (f).



(hg)

Step (e)

	Time	Temperature
Color development	2 min 30 sec	38°C
Bleach-fix	40 sec	38°C
Stabilization (1)	20 sec	38°C
Stabilization (2)	20 sec	38°C
Stabilization (3)	20 sec	38°C

The processing liquids were the same as those used in step (a) in Example 1. The photosensitive materials were processed in steps (e) and (f) using an automatic developing processing machine after the automatic developing processing machine was run at 38°C for one day without replenishment.

Table 5

Photosensitive Material	Cyan Coupler	Dmin (f) - Dmin (e)
Comparative Example: 3-1	C-1	0.06
Comparative Example: 3-2	C-2	0.07
This invention: 3-1	C-I-2	0.00
This invention: 3-2	C-I-3	0.01
This invention: 3-3	C-I-5	0.01
This invention: 3-4	C-I-7	0.00
This invention: 3-5	C-I-13	0.01

It can be understood that when a cyan coupler according to the invention was used in combination with a hydroquinone compound having a sulfonic acid group, the increase in the minimum image density was even further suppressed, in spite of the fact that the running temperature of an automatic development processing machine was raised for one day. Good color formation was maintained. The values of Dmin of the photographic materials according to the present invention and the photographic materials of the comparative examples processed in processing step (e) were all 0.23.

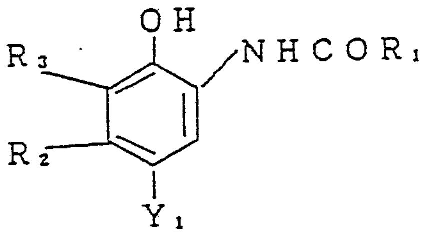
When a cyan coupler according to the present inven tion is used in a photosensitive material, if the temperature or the pH of a color developing solution changes, the maximum image density and the minimum image density scarcely deviate from the optimum values, and an excellent direct positive color image can be formed. Particularly, when an automatic development processing machine was run for one day without replenishment or at high temperatures, an unexpectedly limited increase in minimum density resulted.

The effect was even more remarkable when a hydroquinone compound having a sulfonic acid group was additionally present in the photosensitive material.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A direct positive color photosensitive material comprising a support having thereon at least one photographic emulsion layer containing nonprefogged internal latent image silver halide grains and at least one nondiffusible cyan coupler represented by formula (C-I):



(C-I)

wherein R_1 represents an aliphatic group, an aromatic group, a heterocyclic group, an aromatic amino group or a heterocyclic amino group; R_2 represents an aliphatic group containing 2 to 20 carbon atoms; R_3 represents a hydrogen atom, a halogen atom, an aliphatic group, an aliphatic oxy group or an acylamino group; and Y_1 represents a hydrogen atom or a coupling-off group.

2. The direct positive color photographic material as claimed in claim 1, wherein R_1 represents a substituted or unsubstituted aliphatic group containing 1 to 36 carbon atoms, a substituted or unsubstituted aromatic group containing 6 to 36 carbon atoms, a substituted or unsubstituted heterocyclic group, a substituted or unsubstituted aromatic amino group or a substituted or unsubstituted heterocyclic amino group; R_2 represents a substituted or unsubstituted aliphatic group; R_3 represents a hydrogen atom, a halogen atom, a substituted or unsubstituted aliphatic group containing 1 to 20 carbon atoms, a substituted or unsubstituted aliphatic oxy group containing 1 to 20 carbon atoms, or a substituted or unsubstituted acylamino group containing 1 to 20 carbon atoms; each said substituted group being substituted with a substituent selected from the group consisting of an alkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, an alkenyloxy group, an acyl group, an ester group, an amido group, a sulfamido group, an imido group, a ureido group, an aliphatic sulfonyl group, an aromatic sulfonyl group, an aliphatic thio group, an aromatic thio group, a hydroxyl group, a cyano group, a carboxyl group a nitro group, a sulfo group and a halogen atom.

3. The direct positive color photographic material as claimed in claim 2, wherein R_1 represents an unsubstituted alkyl group; and alkyl group substituted with a halogen atom; an alkyl group substituted with a substituted phenoxy group; an alkyl group substituted with a substituted phenoxy group wherein the phenoxy group substituent is selected from the group consisting of an alkyl group, an alkoxy group, a halogen atom, a sulfonamido group and a sulfamido group; an unsubstituted aryl group; or an aryl group substituted with at least one member of the group consisting of a halogen atom, an alkyl group, a sulfonamido group and an acylamino group.

4. The direct positive color photographic material as claimed in claim 2, wherein R_2 represents an unsubstituted alkyl group or an alkyl group substituted with a substituent selected from the group consisting of an alkoxy group, an aryloxy group, an acylamino group, an alkylthio group, an arylthio group, an imido group, a ureido group, an alkylsulfonyl group and an arylsulfonyl group.

5. The direct positive color photographic material as claimed in claim 2, wherein said coupling-off group is selected from the group consisting of a halogen atom, an aromatic azo group, and a group linked to the coupling active carbon of said cyan coupler by at least one of an oxygen atom, a nitrogen atom, a sulfur atom or a carbon atom, selected from an aliphatic group, an aromatic group, a heterocyclic group, an aliphatic sulfonyl group, an aromatic sulfonyl group, a heterocyclic sulfonyl group, an aliphatic carbonyl group, an aromatic carbonyl group, and a heterocyclic carbonyl group.

6. The direct positive color photographic material as claimed in claim 5, wherein said coupling-off group is selected from the group consisting of a halogen atom, an alkoxy group, an aryloxy group, an acyloxy group, an ali phatic sulfonyloxy group, an aromatic sulfonyloxy group, an acylamino group, an aliphatic sulfonamido group, an aromatic sulfonamido group, an alkoxycarbonyloxy group, an aryloxycarbonyloxy group, an aliphatic thio group, an aromatic thio group, a heterocyclic thio group, a carbamoylamino group, a 5-membered nitrogen-containing heterocyclic group, a 6-membered nitrogen-containing heterocyclic group, an imido group and an aromatic azo group.

7. The direct positive color photographic material as claimed in claim 2, wherein R_3 represents a hydrogen atom, a halogen atom or an acylamino group; and Y_1 represents a halogen atom.

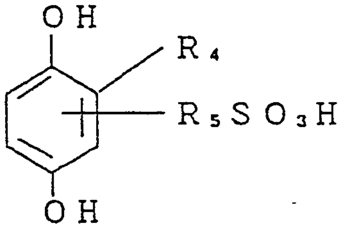
8. The direct positive color photographic material as claimed in claim 7, wherein R_2 represents an alkyl group containing from 2 to 4 carbon atoms; R_3 represents a fluorine atom or a chlorine atom; and Y_1 represents a chlorine atom.

9. The direct positive color photographic material as claimed in claim 1, wherein a plurality of said cyan couplers represented by formula (C-I) is linked by any of R_1, R_2, R_3 and Y_1 to form a dimer or higher polymer thereof.

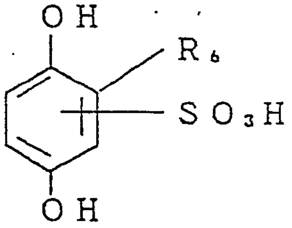
10. The direct positive color photographic material as claimed in claim 1, wherein said polymer comprises a monomer containing said cyan coupler and at least one non-color-forming ethylenically unsaturated monomer.

11. The direct positive color photographic material as claimed in claim 1, further comprising at least one hydroquinone compound substituted with at least one sulfonic acid group, or an ammonium or alkali metal salt thereof.

12. The direct positive color photographic material as claimed in claim 11, wherein said hydroquinone compound is represented by formulae (HQ-I) or (HQ-II):



(HQ-I)



(HQ-II)

wherein R_4 represents an alkyl group, an acylamino group, a hydrogen atom or a sulfonic acid group; R_5 represents an alkylene group or an acylamino group; and R_6 represents an alkyl group or an acylamino group.

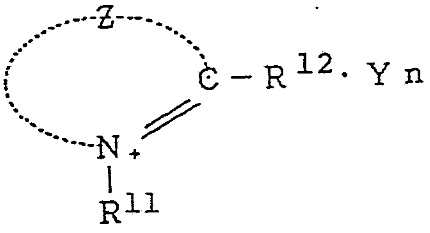
13. The direct positive color photographic material as claimed in claim 12, wherein said acylamino group represented by R_4, R_5 and R_6 is selected from the group consisting of $-NH-\overset{O}{\overset{\|}{C}}-R_7$ or $-NH-\overset{O}{\overset{\|}{C}}-R_8$, wherein R_7 and R_8 each represents an aryl group, an alkyl group, a hydrogen atom or a sulfonic acid group.

14. The direct positive color photographic material as claimed in claim 1, wherein said cyan coupler is present in an amount of from about 0.02 to 0.5 mol per mol of said silver halide.

15. The direct positive color photographic material as claimed in claim 11, wherein said hydroquinone compound is present in an amount of from about 1 to 100 mg per m^2 of said photosensitive material.

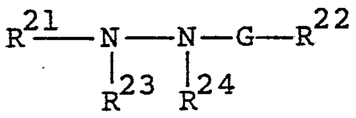
16. The direct positive color photographic material as claimed in claim 1, further comprising at least one layer containing a nucleating agent.

17. The direct positive color photographic material as claimed in claim 16, wherein said nucleating agent is represented by formulae (N-I) or (N-II):



(N-I)

wherein Z represents a non-metallic atomic group necessary for forming a 5-membered or 6-membered heterocyclic ring; R^{11} represents an aliphatic group R^{12} represents a hydrogen atom, an aliphatic group or an aromatic group; provided that at least one of R^{11} and R^{12} comprises an alkynyl group, an acyl group, a hydrazine group or a hydrazone group, or R^{11} and R^{12} are linked to form a 6-membered ring required to form a dihydropyridinium skeleton; Y represents a counter ion necessary for charge balance and n is 0 or 1; and



$$R^{21}-\underset{R^{23}}{\underset{|}{N}}-\underset{R^{24}}{\underset{|}{N}}-G-R^{22} \qquad \text{(N-II)}$$

wherein R^{21} represents an aliphatic group, an aromatic group or a heterocyclic group; R^{22} represents a hydrogen atom, an alkyl group, an aralkyl group, an aryl group, an alkoxy group, an aryloxy group or an amino group; G represents a carbonyl group, a sulfonyl group, a sulfoxy group, a phosphoryl group or an iminomethylene group; one of R^{23} and R^{24} represents a hydrogen atom, and the other represents a hydrogen atom, an alkylsulfonyl group, an arylsulfonyl group or an acyl group.

18. The direct positive color photographic material as claimed in claim 17, wherein at least one of R^{11}, R^{12} and G comprises a group $X^1 -\!\!(L^1)_{m}-$, wherein X^1 represents a group capable of accelerating adsorption onto a silver halide grain, L^1 represents a divalent linking group and m is 0 or 1; and at least one of R^{21} and R^{22} comprises a group $X^2 -\!\!(L^2)_{m}-$ 2, wherein X^2 has the same definition as X^1, L^2 has the same defintion as L^1, and m^2 is 0 or 1.

19. The direct positive color photographic material as claimed in claim 16, wherein said nucleating agent is present in an amount of from about 10^{-8} to 10^{-2} mol per mol of said silver halide.