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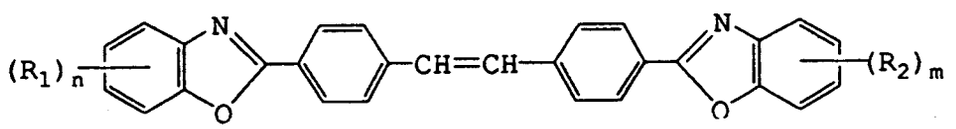
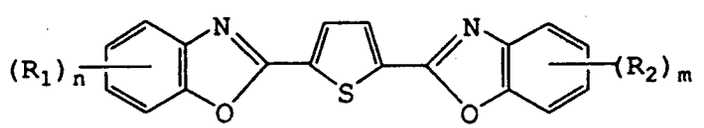
(54) A silver halide color photographic light-sensitive material.

(57) A silver halide color photographic light-sensitive material is disclosed, which is excellent in whiteness, anticoloring property with aging, sharpness of image and color reproducibility. The light-sensitive material comprises a reflective paper support laminated with a polyolefine resin layer which contains a specified amount of white pigment and a specified amount of whitening agent represented by the formula 1, 2 or 3;



(1)



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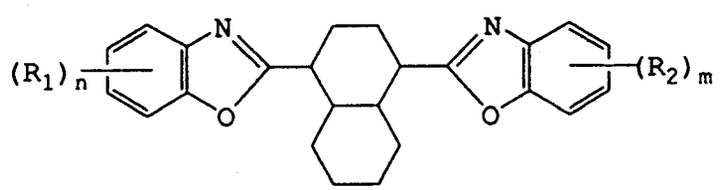

(3)

wherein R_1 and R_2 are each an alkyl group having 1 to 5 carbon atoms, a halogen atom, a hydrogen atom, or an alkoxy group having 1 to 5 carbon atoms; m and n are each an integer of from 1 to 4. And a green sensitive emulsion layer of the light-sensitive material contains a specified magenta coupler.

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FIELD OF THE INVENTION

The present invention relates to a silver halide color photographic light-sensitive material, more particularly to a silver halide color photographic light-sensitive material for printing which is high in whiteness, less coloring in aging and excellent in sharpness and color reproducibility.

BACKGROUND OF THE INVENTION

In general, silver halide color photographic light-sensitive materials for printing comprise a reflective support bearing thereon three types of silver halide emulsion layers subjected to spectral sensitization selectively so as to have sensitivities to blue light, green light and red light.

Meanwhile, there is a continuing demand for color prints of high quality images, and therefore intensive studies are conducted to improve the sharpness, whiteness and hue reproducibility.

Addition of a large amount of an inhibitor in photographic emulsions aimed at an improved whiteness reduces fogging, but it liable to lower sensitivity and gradation. As another measure to improve the whiteness, Japanese Pat. Exam. Pub. Nos. 21189/1971, 27692/1973, 28225/1976 and 32254/1977 propose to use a fluorescent brightener in photographic emulsions. But this method is not effective and has a defect of increasing fog that deteriorates the whiteness.

Japanese Pat. O.P.I. Pub. Nos. 71256/1990, 66234/1975 and U.S. Pat. Nos. 3,501,298, 4,794,071 disclose a technique to enhance the whiteness by adding a specific fluorescent brightener in the polyolefine resin layer on the side coated with silver halide emulsions of a double-side polyolefine-resin-coated paper support. While this method can improve the whiteness of the support, a light-sensitive material having silver halide emulsion layers formed on such a support has a defect of poor sharpness. It is easily conceived that use of a white pigment in a polyolefine-resin layer on the photographic emulsion side of a support improves the sharpness, as described in Japanese Pat. O.P.I. Pub. Nos. 46035/1979, 18144/1989 and 71256/1990. But light-sensitive materials whose silver halide emulsion layers are formed on such a support are not immune from a fatal defect that white portions are degraded with aging.

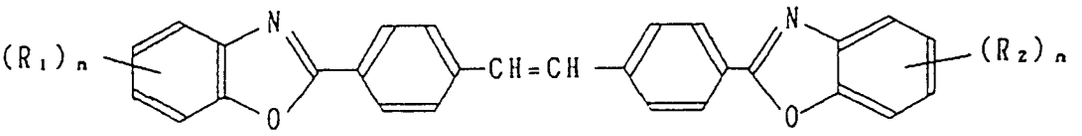
SUMMARY OF THE INVENTION

The present invention is attained as a means to solve the above problems and to provide a silver halide color photographic light-sensitive material for printing excellent in whiteness, anticoloring property with aging, sharpness and color reproducibility.

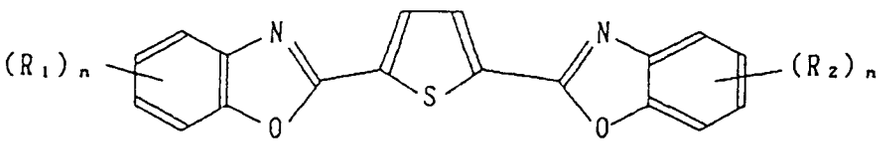
Accordingly, the first object of the invention is to provide a silver halide color photographic light-sensitive material having an excellent whiteness and causing no degradation in whiteness over a long time. The second object of the invention is to provide a silver halide color photographic light-sensitive material excellent in the sharpness and color reproducibility and suitable for printing.

The silver halide color photographic light-sensitive material of the invention comprises a photographic layer including a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red-sensitive emulsion layer provided on a side of a reflective support which comprises a raw paper coated with a polyolefine resin on both sides, wherein the polyolefine resin layer provided on the side of the reflective support coated with photographic emulsions contains a compound represented by the following Formula 1, 2 or 3 in an amount of 0.01 to 0.2% by weight of the polyolefine resin of the polyolefine resin layer and a white pigment in an amount of 13 to 20% by weight of the polyolefine resin of the polyolefine resin layer, and the green-sensitive emulsion layer contains a compound represented by the following Formula M-1.

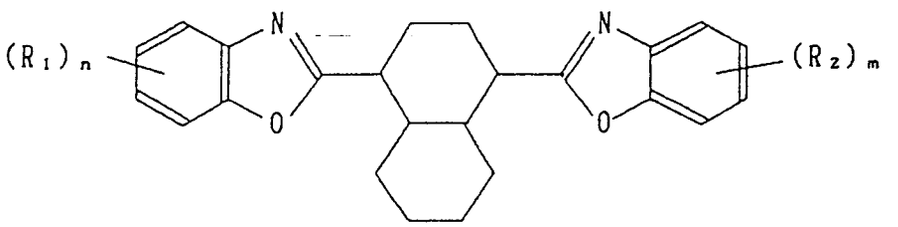
Formula 1



Formula 2

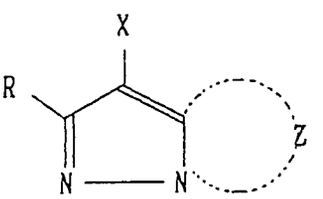


Formula 3



In Formulas 1, 2 and 3, R_1 and R_2 each represent an alkyl group having 1 to 5 carbon atoms, a halogen or hydrogen atom, or an alkoxy group having 1 to 5 carbon atoms. m and n each represent an integer of 1 to 4.

Formula M-1



In Formula M-1, Z represents a group of non-metallic atoms necessary to form a nitrogen-containing heterocycle, which may have a substituent. X represents a hydrogen atom or a substituent capable of splitting off upon reaction with an oxidation product of a color developing agent. R represents a hydrogen atom or a substituent.

DETAILED DESCRIPTION OF THE INVENTION

The raw paper used as the support in the invention may be made of materials used commonly; that is, there may be used singly or in combination natural pulps such as needle-leaf bleached sulfite pulp, broad-leaf bleached sulfite pulp, needle-leaf bleached kraft pulp and broad-leaf bleached kraft pulp. When two or more kinds of pulps are used in combination, a preferable blending ratio of broad-leaf pulp/needle-leaf pulp

ranges from 95/5 to 60/40. Further, straw pulp, esparto pulp or bamboo pulp, or synthetic fiber if necessary, may be blended in the above natural pulps. Though the thickness of the base paper is determined according to uses, the basis weight is generally within the range from 50 to 250 g/m^2.

It is preferable that the base paper be enriched its physical properties including water restance by the addition of various additives shown below. As sizing agents, for example, a fatty acid salt of an alkylketene dimer, rosin, maleated rosin, alkenyl succinate, alkyl succinate and polysaccharide are employed in amounts of 0.2 to 2% of pulp.

As dry strength improver, there are used a cationic starch, cationic polyacrylamide, anionic polyacrylamide and carboxyl-modified polyvinyl alcohol.

As wet strength improver, there are used a melamine resin, urea resin and epoxylated polyamide resin.

Further, polyvalent metallic salts such as aluminium sulfate, aluminium chloride and cationic polymers such as cationic starch are used as fixing agents.

Clay, talc, calcium carbonate, titanium dioxide and barium sulfate may also be contained as white pigments when necessary.

In general, the pulp is subjected to tab sizing or size press sizing on its surface with a solution containing a water-soluble polymer additive. As such a water-soluble polymer, cationic starch, polyvinyl alcohol, carboxyl-modified polyvinyl alcohol, hydroxymethyl cellulose, hydroxyethyl cellulose, polyacrylamide or gelatin can be used.

In addition, there employed sodium chloride or sodium sulfate as inorganic electrolytes, glycerol or polyethylene glycol as a moisture absorbent, and hydrochloric acid, sodium hydroxide or sodium carbonate as a pH conditioner; moreover, additives such as dyes, fluorescent brighteners, antistatic agents and defoamers are used in combination.

After being beaten to a desired degree, the pulp is made up to a pulp slurry containing the above additives according to a specific requirement, then it is formed into paper on a paper machine such as Fourdrinier paper machine, dried and subjected to super calendering. And surface sizing is performed before or after the drying.

The support according to the invention is prepared by coating both sides of the raw paper obtained as above with a polyolefine resin.

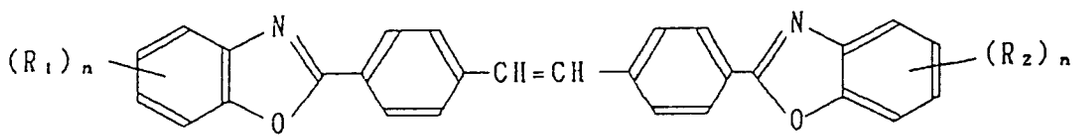
This polyolefine resin is, for example, an α-olefine homopolymer such as polyethylene or polypropylene, or a mixture of such polymers. And high density polyethylene, low density polyethylene and a mixture thereof are particularly preferred. The molecular weight of these polyolefines is not particularly limited, but polyolefines having molecular weights ranging from 20,000 to 200,000 are generally used. The thickness of the polyolefine resin coating layer is not particularly limited, but usually within the range from 15 to 50 μm.

The white pigment used in the polyolefine resin layer of the invention may be any of anatase-type and rutile-type titanium dioxide, barium sulfate, zinc oxide, calcium carbonate, aluminium oxide, magnesium oxide and talc, but titanium dioxide is particularly preferred.

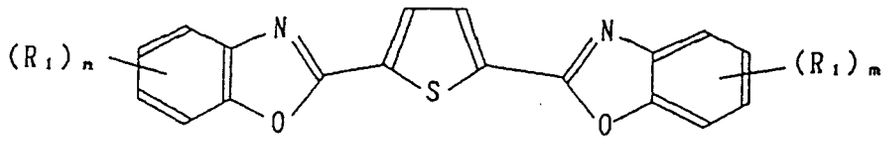
The titanium oxide may be surface-treated with aluminium hydroxide, alcohols or surfactants, or may not be surface-treated. These white pigments are used in amounts of 13 to 20%, preferably 15 to 18% by weight of the polyolefine resin of the polyolefine resin layer of a reflective support on the side coated with photographic emulsions.

The polyolefine resin layer of the invention contains a compound represented by Formula 1, 2 or 3, hereinafter occasionally referred to as the fluorescent brightener of the invention.

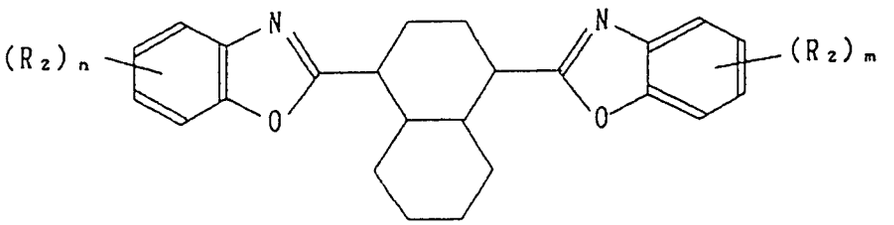
Formula 1



Formula 2



Formula 3

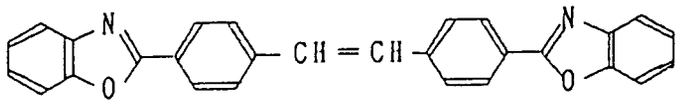


In Formulas 1 through 3, R_1 and R_2 each represent an alkyl group having 1 to 5 carbon atoms, a halogen or hydrogen atom, or an alkoxy group having 1 to 5 carbon atoms. m and n each represent an integer of 1 to 4.

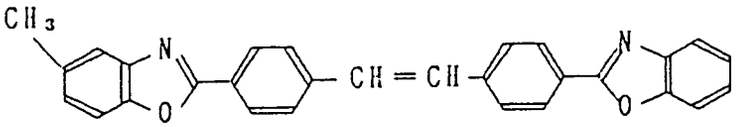
In Formula 1, the alkyl group represented by R_1 or R_2 and having 1 to 5 carbon atoms is, for example, a methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, amyl or t-amyl group. And a methyl group is particularly preferred. The halogen atom is preferably a chlorine atom. The alkoxy group having 1 to 5 carbon atoms is preferably a methoxy, or ethoxy group. Among them, an alkyl group and a hydrogen atom are preferred. A methyl group and a hydrogen atom are particularly preferred.

Typical examples of the compounds represented by Formula 1 are as follows:

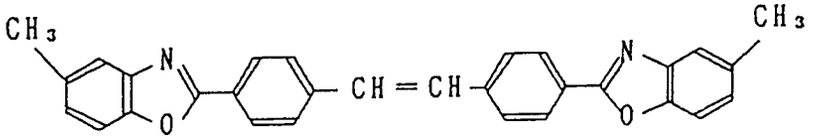
1 − 1



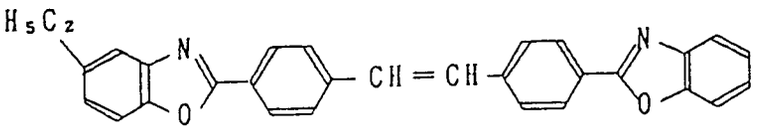
1 − 2



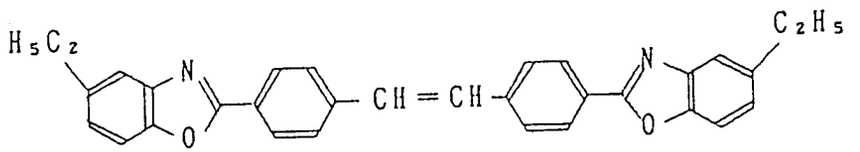
1 − 3



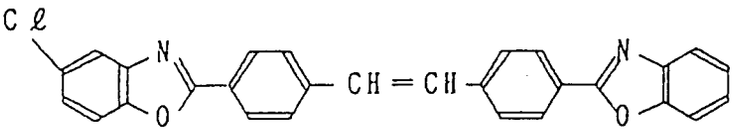
1 − 4



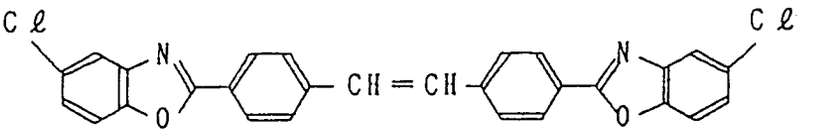
1 − 5



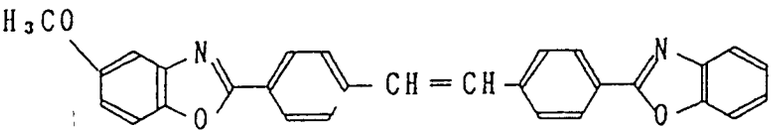
1 − 6



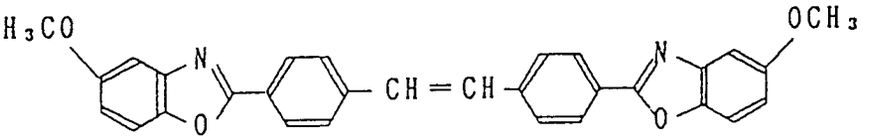
1 − 7



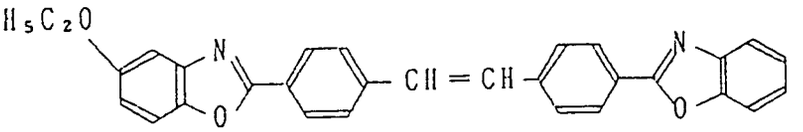
1 − 8



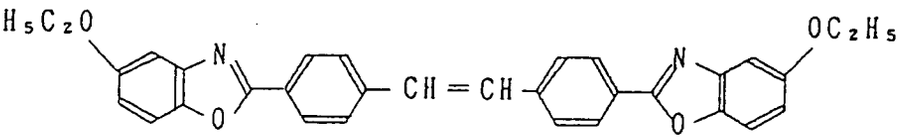
1 − 9



1 − 1 0



1 − 1 1



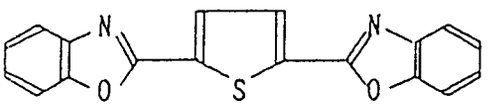
The compound represented by Formula 1 can be synthesized by known methods as shown in U.S. Pat. No. 4,794,071 and Japanese Pat. O.P.I. Pub. No. 71256/1990 and is contained, together with a white pigment and a colored pigment, in the polyolefine resin coating layer on the side to be coated with photographic emulsions in an amount of 0.01 to 0.2% by weight of the polyolefine resin.

In Formula 2, the alkyl group represented by R_1 or R_2 having 1 to 5 carbon atoms is, for example, a methyl, ethyl, propyl, butyl, isobutyl, t-butyl, amyl, isoamyl or t-amyl group. Among them,a t-butyl group and a t-amyl groups are particularly preferred.

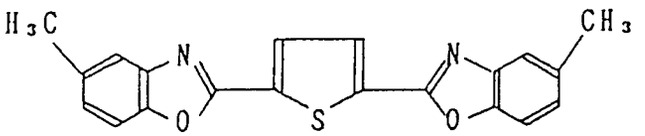
Examples of the halogen atom include a chlorine atom. Examples of the alkoxy group having 1 to 5 carbon atoms include a t-buthoxy group and t-pentyloxy group. Among them, an alkyl group and a hydrogen atom are preferred; a t-butyl group, a t-amyl group and a hydrogen atom are particularly preferred.

Typical examples of the compounds represented by Formula 2 are as follows:

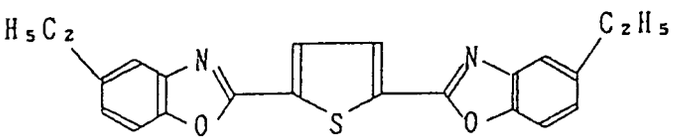
2 − 1



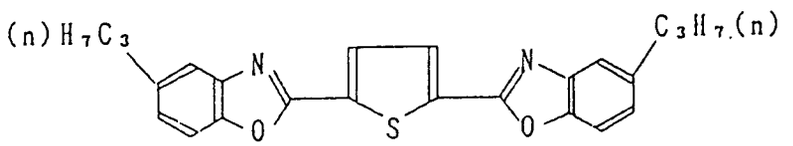
2 − 2



2 − 3



2 − 4



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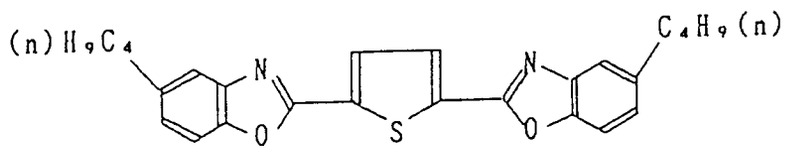
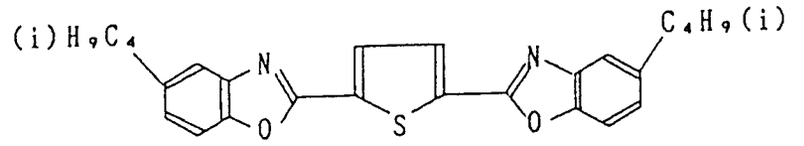
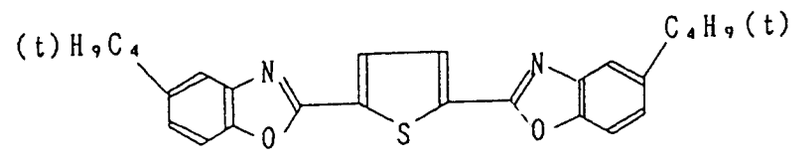

(n)H9C4
C4H9(n)
N
O
S
N
O

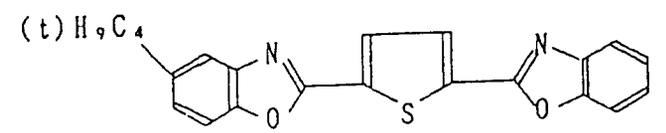
2 − 6


(i)H9C4
C4H9(i)
N
O
S
N
O

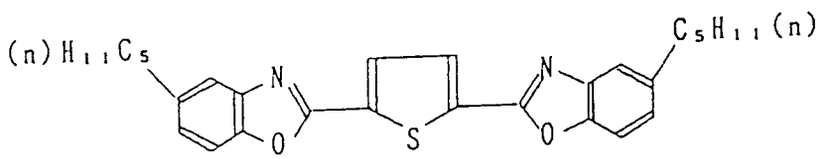
2 − 7


(t)H9C4
C4H9(t)
N
O
S
N
O

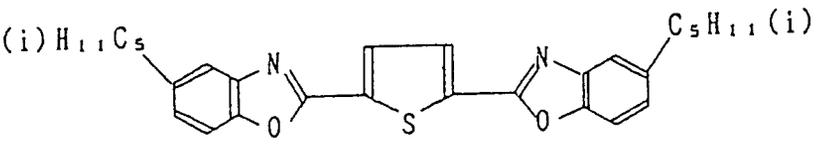
2 − 8


(t)H9C4
N
O
S
N
O

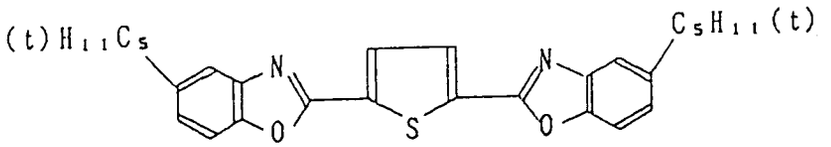
2 − 9


(n)H11C5
C5H11(n)
N
O
S
N
O

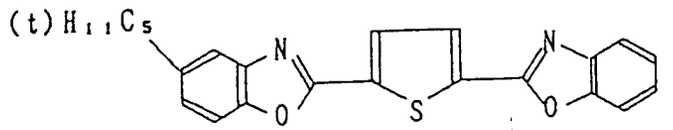
2 − 1 0



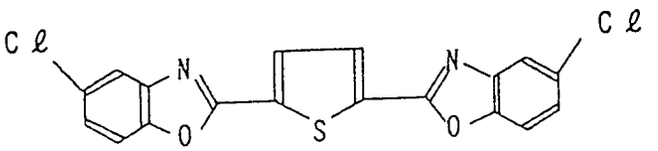
2 − 1 1



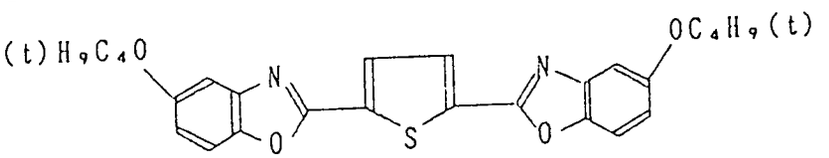
2 − 1 2



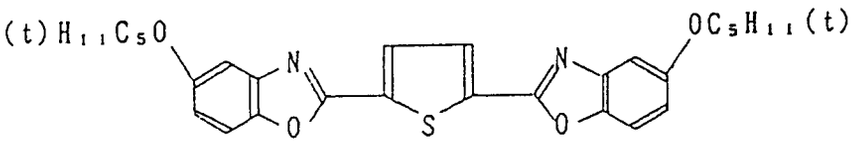
2 − 1 3



2 − 1 4



2 − 1 5

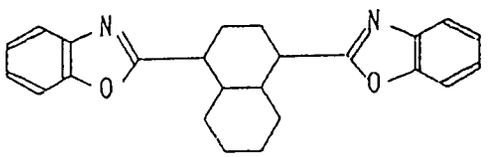


The compound represented by Formula 2 can be synthesized by known methods as shown in U.S. Pat. No. 3,501,298 and is contained, together with a white pigment and a colored pigment, in the polyolefine resin coating layer on the side to be coated with photographic emulsions in an amount of 0.01 to 0.2% by weight of the polyolefine resin.

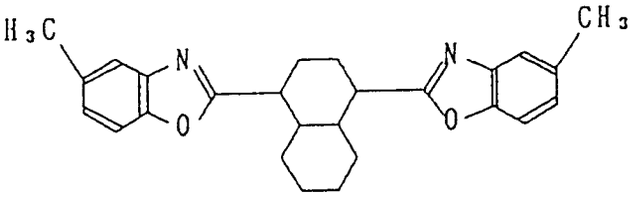
In Formula 3, the alkyl group represented by R_1 or R_2 and having 1 to 5 carbon atoms is, for example, a methyl, ethyl, propyl, butyl or amyl group. And a methyl group is preferred. An suitable example of the halogen atom is a chlorine atom. Examples of the alkoxy group having 1 to 5 carbon atoms include a methoxy group and ethoxy group. Among them, an alkyl group and a hydrogen atom are preferred. A methyl group and a hydrogen atom are particularly preferred.

Typical examples of the compounds represented by Formula 3 are as follows:

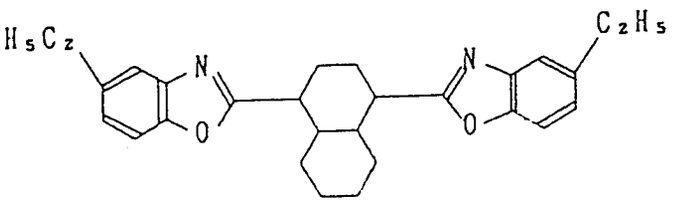
3 − 1



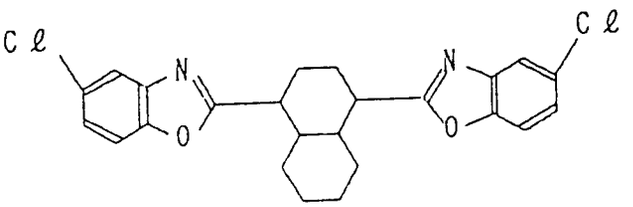
3 − 2



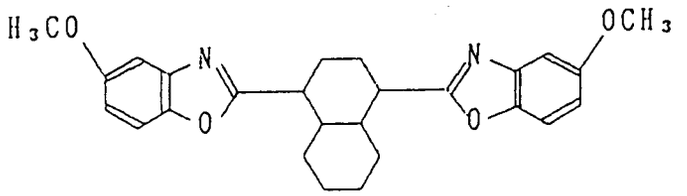
3 − 3



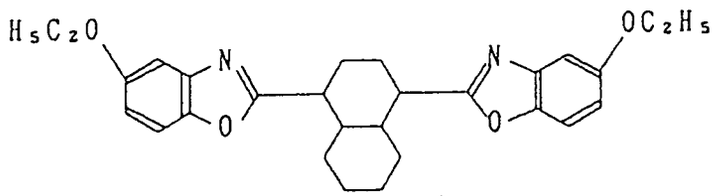
3 − 4



3 − 5



3 − 6



The compound represented by Formula 3 can be synthesized by known methods as shown in German Pat. Nos. 1,282,592, 1,302,052 and Japanese Pat. O.P.I. Pub. No. 66234/1975 and is contained, together with a white pigment and a colored pigment, in a polyolefine resin coating layer on the side to be coated with photographic emulsions, in an amount of 0.01 to 0.2% by weight of the polyolefine resin.

The polyolefine resin layer of the invention may contain a fatty acid metallic salt such as zinc stearate or magnesium stearate. Further, there may also be contained an anti-oxidant such as hindered phenol-type anti-oxidant, a coloring pigment such as ultramarine, cobalt blue or red iron oxide, and a fluorescent brightener such as bisbenzoxazole or stilbene.

The support of the invention is prepared by extruding, from a slit die, a resin composition containing the above additives including pigments and molten at 200 to 350 ° C in the form of film, on a running raw paper which is subjected beforehand to surface treatment such as corona discharge.

In a silver halide color photographic light-sensitive material according to the invention, the amount of a binder used in an silver halide emulsion layer and a nonlight-sensitive layer is generally 6.0 to 7.8 g/m^2, preferably 6.5 to 7.5 g/m^2.

Though gelatin is advantageously used as a binder or as a protective colloid, there may also be employed other hydrophilic colloids such as gelatin derivatives, graft copolymers of gelatin and other polymers, proteins other than gelatin, sugar derivatives, cellulose derivatives, and hydrophilic synthetic homopolymers and copolymers.

Besides lime-treated gelatins, usable gelatins include acid-treated gelatins and enzyme-treated gelatins described in Bulletin of Society of Science of Photography of Japan, No. 16, p. 30 (1966). Further, hydrolysis products or enzyme-catalyzed decomposition products of gelatin can also be used.

As gelatin derivatives, there are used reaction products of gelatin and compounds such as acid halides, acid anhydrides, isocyanates, bromoacetic acid, alkane sultones, vinyl sulfonamides, maleinimides, polyalkylene oxides and epoxides. Typical examples of gelatin derivatives can be seen in U.S. Pat. Nos. 2,614,928, 3,132,945, 3,186,846, 3,312,553, British Pat. Nos. 861,414, 1,033,189, 1,005,784 and Japanese Pat. Exam. Pub. No. 26845/1967.

Usable proteins are albumin and casein; usable cellulose derivatives are hydroxyethyl cellulose, carboxymethyl celluloser and cellulose sulfates; and usable sugar derivatives are sodium alginate and starch derivatives.

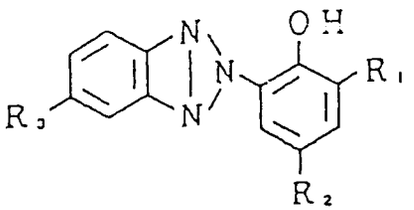
As the foregoing graft polymers between gelatin and other polymers, there can be employed ones obtained by grafting on gelatin homopolymers or copolymer of vinyl monomers such as acrylic acid, methacrylic acid, deridatives of these acids including esters and amides, acrylonitrile and styrene. Among them, the preferred are ones obtained by grafting polymers having a little compatibility with gelatin such as polymers of acrylic acid, acrylamide, methacrylamide or hydroxyalkyl methacrylate. Typical examples thereof are described in U.S. Pat. Nos. 2,763,625, 2,831,767 and 2,956,884.

Typical synthetic hydrophilic polymers usable in the invention are homo- or co-polymers such as polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole and polyvinylpyrazole. Examples thereof can be seen in German Pat. Appl. (OLS) No. 2,12,708, U.S. Pat. Nos. 3,620,751, 3,879,205 and Japanese Pat. Exam. Pub. No. 7561/1968.

In order to improve the light-fastness of printed dye images, it is preferable that a non-light-sensitive layer containing an UV absorbent be provided on the emulsion coated side of the silver halide color photographic light-sensitive material of the invention.

Though usable UV absorbents are not particularly limited, the preferred are those represented by the following Formula UV-I

Formula UV-I



wherein R_1, R_2 and R_3 independently represent a hydrogen or halogen atom, or an alkyl, aryl, alkoxy, aryloxy, alkenyl, nitro or hydroxyl group.

In Formula UV-I, the halogen atom represented by R_1, R_2 or R_3 is a fluorine, chlorine or bromine atom, and a chlorine atom is particularly preferred.

The alkyl group or alkoxy group represented by R_1, R_2 or R_3 is one having 1 to 20 carbon atoms, the alkenyl group so-represented is one having 2 to 20 carbon atoms, and each of them may be of straight chain or branched chain.

These alkyl, alkenyl and alkoxy groups may have a substituent such as halogen atom, or aryl, cyano, heterocyclic, cycloalkyl or cycloalkenyl group, or spiro compound residue or bridged hydrocarbon residue; other examples of the substituent include ones which substitute via a carbonyl group such as acyl, carboxyl, carbamoyl, alkoxycarbamoyl and aryloxycarbamoyl groups, and ones which substitute via a hetero atom examples include ones which substitute via an oxygen atom such as hydroxyl, alkoxy, aryloxy, heterocyclic oxy, siloxy, acyloxy and carbamoyloxy groups, ones which substitute via a nitrogen atom such as nitro, amino including dialkylamino, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, acylamino, sulfonamide, imido and ureido groups, ones which substitute via a sulfur atom such as alkylthio, heterocyclic thio, sulfonyl, sulfinyl and sulfamoyl groups, and ones which substitute via a phosphorus atom such as phosphonyl group .

Typical examples of such substituents are methyl, ethyl, isopropyl, t-butyl, sec-butyl, n-butyl, n-amyl, sec-amyl, t-amyl, α,α-dimethylbenzyl, octyloxycarbonylethyl, methoxy, ethoxy, octyloxy and allyl groups.

As the aryl group or aryloxy group represented by R_1, R_2 or R_3, phenyl and phenyloxy groups are preferred, and these may have a substituent, e.g., alkyl or alkoxy. Typical examples thereof are phenyl, 4-t-butylphenyl and 2,4-di-t-amylphenyl groups.

Among the groups represented by R_1 or R_2, preferred ones are hydrogen atoms and alkyl, alkoxy, and aryl groups; hydrogen atoms, and alkyl and alkoxy groups are particularly preferred.

Among the groups represented by R_3, hydrogen and halogen atoms as well as alkyl and alkoxy groups are preferred.

Next, the UV absorbent represented by Formula UV-1 is described in detail.

As the UV absorbent represented by Foprmula UV-1, a mixture of one being liquid at ordinary temperatures and one being solid at ordinary temperatures is preferably used. The melting point of the UV absorbent being liquid at ordinary temperatures is preferably less than 30 °C, especially less than 15 °C. Such a liquid UV absorbent may be a single compound or a mixture of structural isomers.

In a mixed UV absorbent, the ratio of a UV absorbent being liquid at ordinary temperatures is usually more than 30%, preferably more than 30% and less than 99%, and especially more than 30% and less than 95% by weight of the total UV absorbents. For the UV absorbent being solid at ordinary temperatures,

the ratio of a solid UV absorbent, in which the total number of carbon atoms contained in groups R_1 and R_2 of Formula UV-1 is 8 or more, is required to be more than 35% by weight of the total solid UV absorbents. This ratio is preferably within a range from 35% to 100%, especially from 50% to 100%.

For the UV absorbent which is solid at ordinary temperatures and may be a mixture of several UV absorbents, it is necessary that at least one of the constituent solid UV absorbents have 8 or more carbon atoms in total of groups R_1 and R_2 of Formula UV-1; while the upper limit thereof varies depending upon groups R_1 and R_2 as well as group R_3, it is preferably 12 at most. The total addition amount of the UV absorbent is within a range from 0.1 to 300%, preferably from 1 to 200%, and especially from 5 to 100% by weight of a binder of a non-light-sensitive layer in which the UV absorbent is contained.

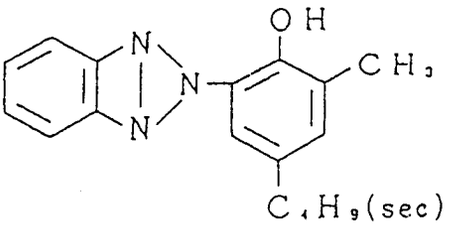
As binders used in a non-light-sensitive layer containing the UV absorbent, hydrophilic binders are preferred. While gelatin, gelatin derivatives, e.g., acetylated gelatin, phthalated gelatin, albumin and collodion can be used, gelatin is preferred. In incorporating the UV absorbent in the non-light-sensitive layer, there can be used various methods such as an aqueous alkaline solution dispersion method, solid dispersion method, latex dispersion method and oil-in-water type emulsification method. Though a suitable method can be selected according to the chemical structure of the UV absorbent, the latex dispersion method and oil-in-water type emulsification method are particularly useful. These dispersing methods are well known in the art. The latex dispersion method and its effect can be seen, for example, in Japanese Pat. Appl. Nos. 74538/1974, 59943/1976, 32552/1979 and Research Disclosure, No. 14,850 (Aug., 1976), pp. 77-79.

Suitable examples of the latex include homopolymers, copolymers and terpolymers of various monomers such as styrene, ethyl acrylate, n-butyl acrylate, n-butyl methacrylate, 2-acetacetoxyethyl methacrylate, ammonium 2-(methacryloyloxy)ethyltrimethyl metasulfate, sodium 3-(methacryoyloxy)-propane-1-sulfonate, N-isopropyl acrylamide, N-[2-(2-methyl-4-oxopentyl)]acrylamide and 2-acrylamide-2-methylpropane sulfonic acid.

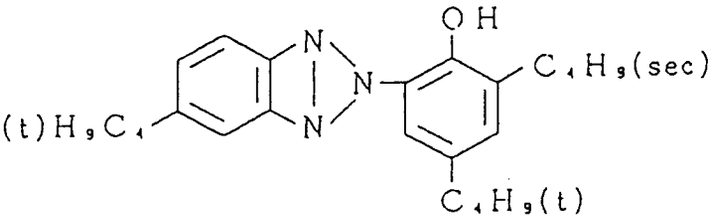
The oil-in-water type emulsification method can be carried out in a conventional manner which comprises a step to disperse hydrophobic additives such as couplers. The UV absorbent can be incorporated in an objective layer, for example, by steps of dispersing it in a high boiling solvent having a boiling point of 175 °C or more, using a low boiling solvent jointly when necessary, emulsifying the solution in a hydrophilic binder such an aqueous solution of gelatin with the aid of surfactants, and then adding the dispersion in a prescribed layer.

The following are typical examples of the 2-(2'-hydroxyphenyl)benzotriazole UV absorbent which are liquid at ordinary temperatures:

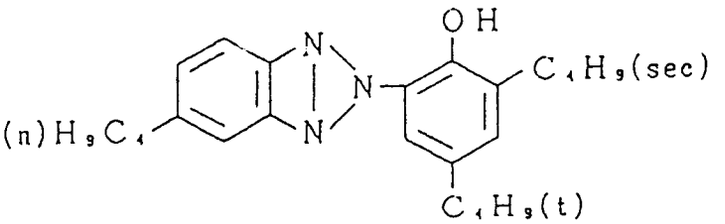
UV-1L



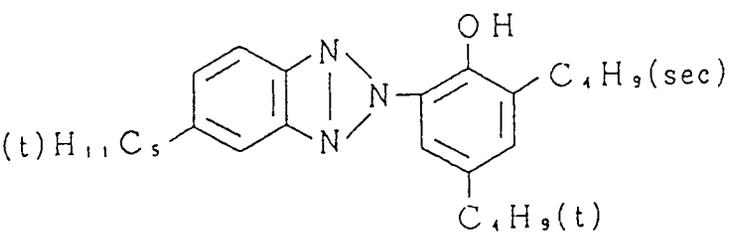
UV-2L



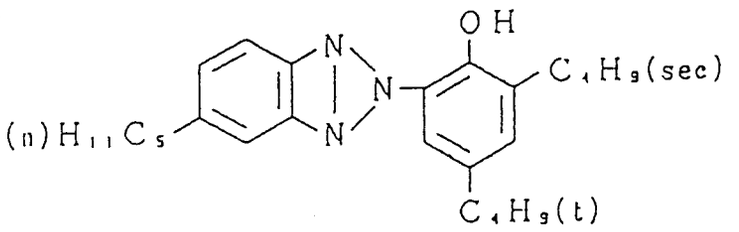
UV-3L



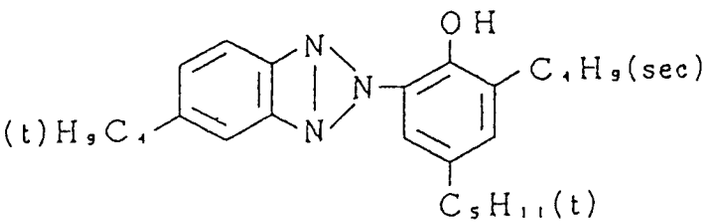
UV-4L



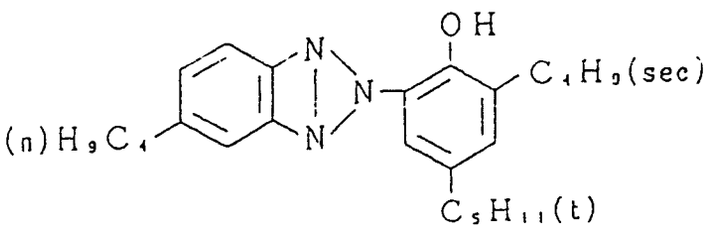
UV-5L



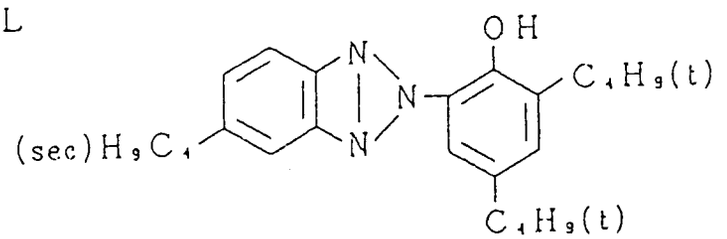
UV-6L



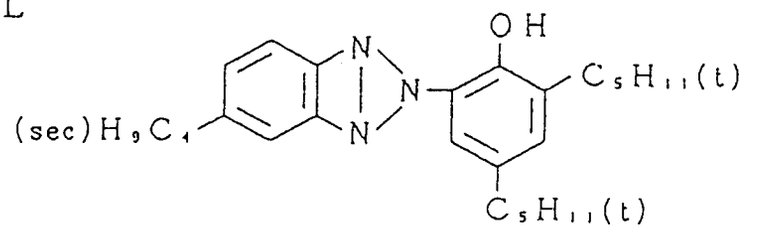
UV-7L



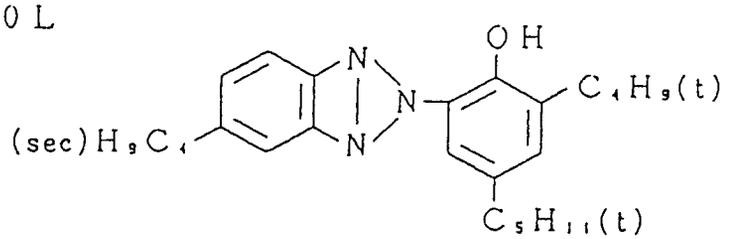
UV-8L



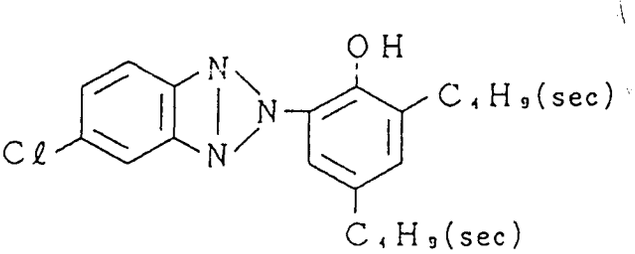
UV-9L



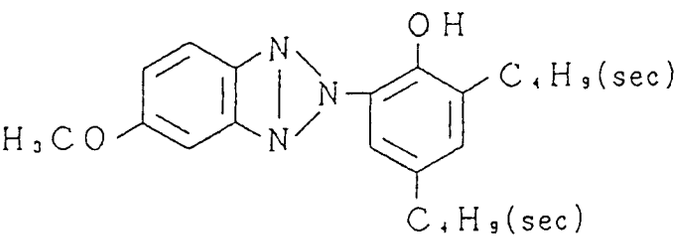
UV-10L



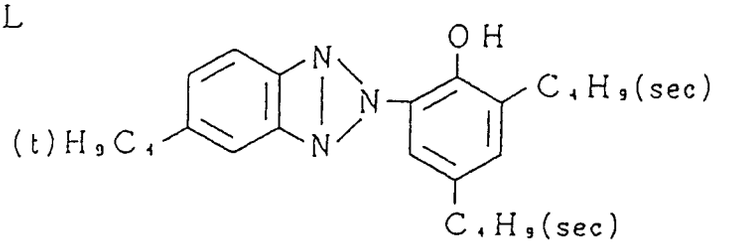
UV-11L



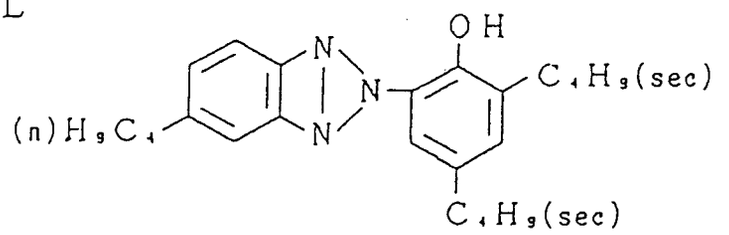
UV-12L



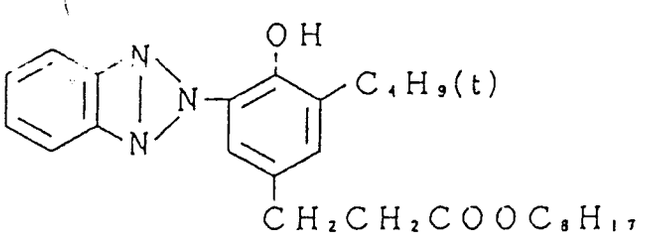
UV-13L



UV-14L

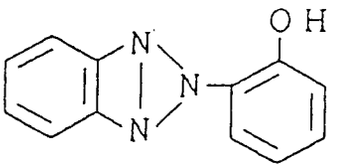


UV-15L

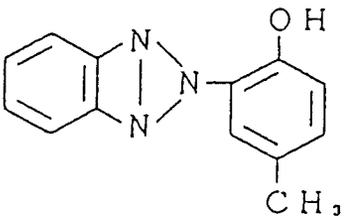


The following are typical examples of the 2-(2'-hydroxyphenyl)benzotriazole UV absorbent which are solid at ordinary temperatures:

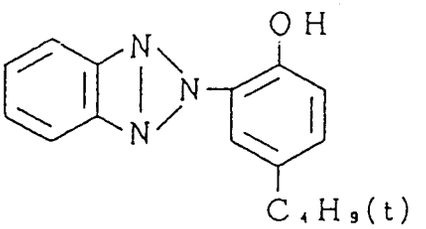
UV-1S



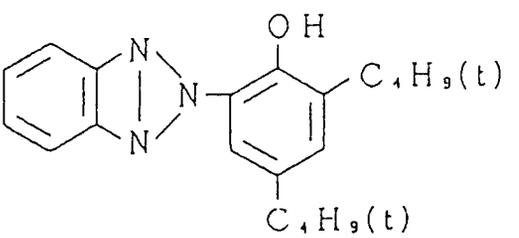
UV-2S



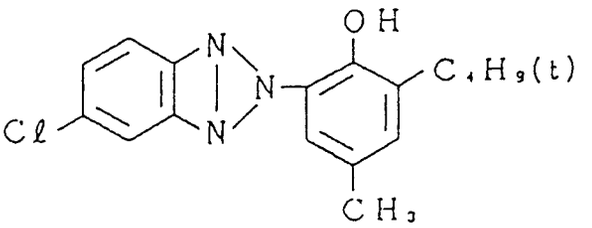
UV-3S



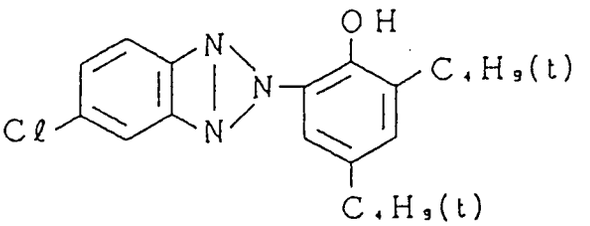
UV-4S



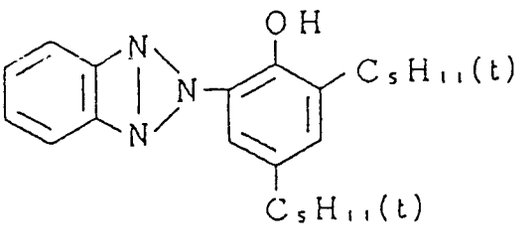
UV-5S



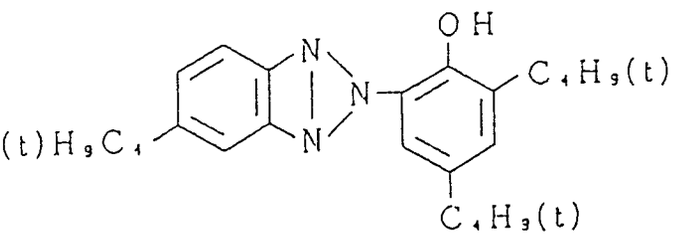
UV-6S



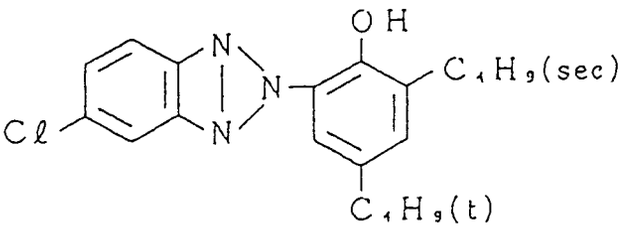
UV-7S



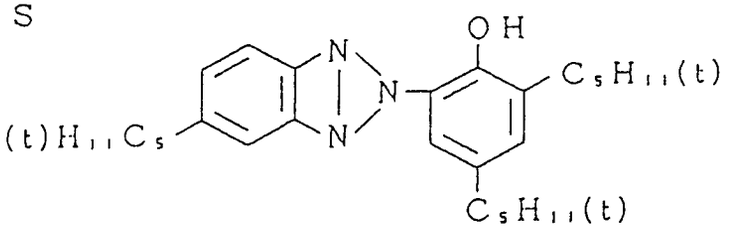
UV-8S



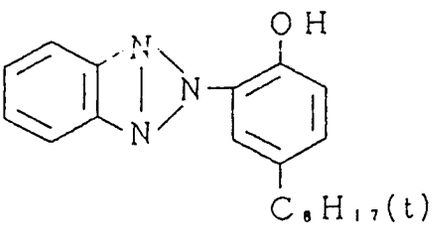
UV-9S



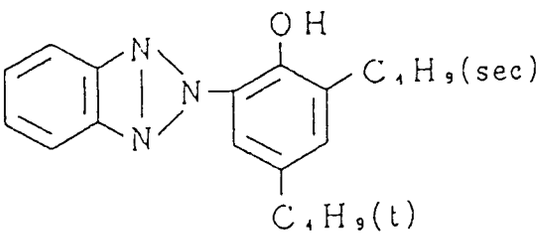
UV-10S



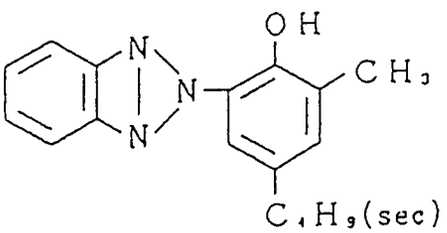
UV-11S



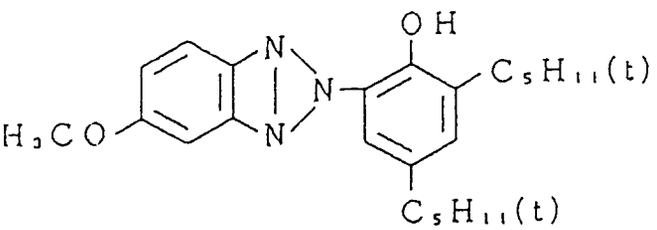
UV-12S



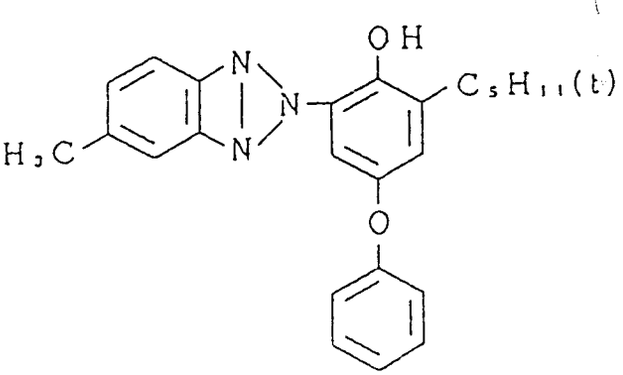
UV-13S



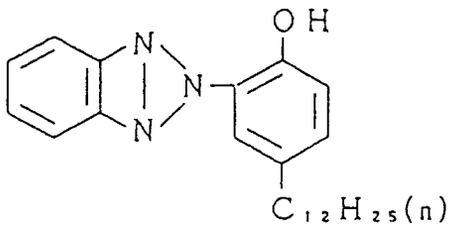
UV-14S



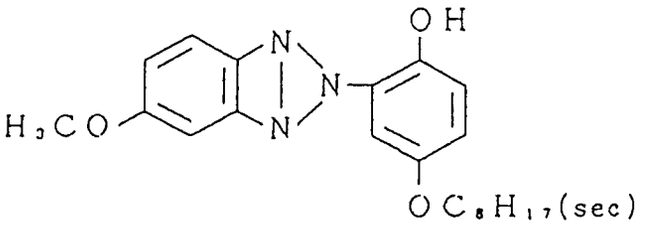
UV-15S



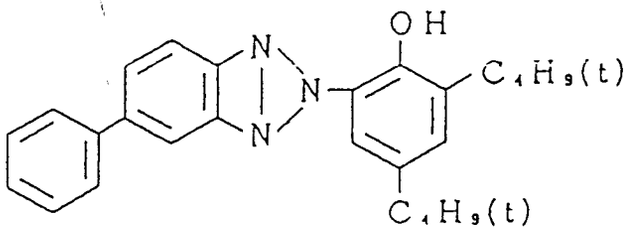
UV-16S



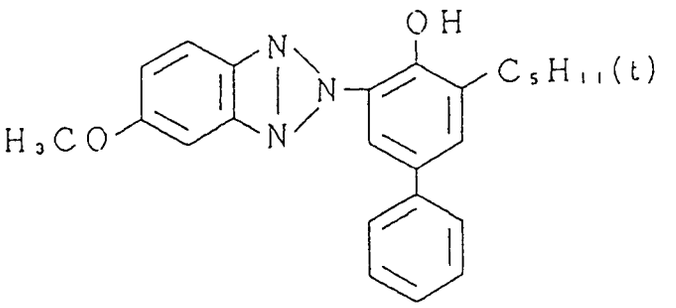
UV-17S



UV-18S



UV-19S



These benzotriazole-type UV absorbents, which are liquid or solid at ordinary temperatures, are described in Japanese Pat. Exam. Pub. Nos. 10466/1961, 26187/1967, 5496/1973, 41572/1973, U.S. Pat. Nos. 3,754,919, 4,220,711, International Pub. No. 01473/1981 and European Pat. Pub. No. 57160.

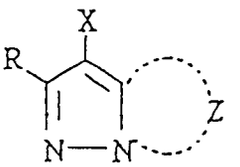
The silver halide color photographic light-sensitive material of the invention contains dye-forming couplers which form dyes in a color developing process by reacting with an oxidation product of an aromatic primary amine developing agent such as p-phenylenediamine derivatives and aminophenol derivatives. In general, said dye forming couplers are selected so as to form dyes which absorb spectral lights to which respective emulsion layers are sensitive; that is, yellow dye forming couplers are used in a blue-sensitive emulsion layer, magenta dye forming couplers in a green-sensitive emulsion layer, and cyan

dye forming couplers in a red-sensitive emulsion layer. In making a silver halide color photographic light-sensitive material, however, combinations other than the above may also be used according to specific requirements.

It is preferred for these dye forming couplers to have, in the molecule, a group having 8 or more carbon atoms, which is called ballast group and makes the coupler non-diffusible. These dye forming couplers may be four-equivalent ones which requires reduction of 4 silver ions to form 1 dye molecule, or two-equivalent ones which requires reduction of only 2 silver ions to form 1 dye molecule.

As magenta dye forming couplers, compounds represented by following Formula M-I are used.

Formula M-I



In the magenta coupler represented by Formula M-I, Z is a group of non-metallic atoms necessary to form a nitrogen-containing heterocycle, which may have a substituent.

X is a hydrogen atom, or a group capable of splitting off upon reaction with an oxidation product of a color developing agent.

R is a hydrogen atom or a substituent.

The substituent represented by R is not particularly limited. Typical examples thereof include alkyl, aryl, anilino, acylamino, sulfonamido, alkylthio, arylthio, alkenyl and cycloalkyl groups; other examples are halogen atoms, and cycloalkenyl, alkynyl, heterocyclic, sulfonyl, sulfinyl, phosphonyl, acyl, carbamoyl, sulfamoyl, cyano, alkoxy, aryloxy, heterocycloxy, siloxy, acyloxy, carbamoyloxy, amino, alkylamino, imido, ureido, sulfamoylamino, alkoxycarbonylamino, aryloxycarbonylamino, alkocycarbonyl, aryloxycarbonyl and heterocyclothio groups, and spiro compound residues and bridged hydrocarbon residues.

The alkyl group represented by R is preferably one having 1 to 32 carbon atoms and may be of straight chain or branched chain.

Preferable example of the aryl group represented by R is a phenyl group.

Examples of the acylamino group represented by R include alkylcarbonylamino and arylcarbonylamino groups.

Examples of the sulfonamido group represented by R include alkylsulfonylamino and arylsulfonylamino groups.

The alkyl component and aryl component in the alkylthio group and arylthio group represented by R are the same as the alkyl group and aryl group-defined for the above R.

The alkenyl group represented by R is preferably one having 2 to 32 carbon atoms; the cycloalkyl group is preferably one having 3 to 12, especially 5 to 7 carbon atoms; the alkenyl group may be of straight chain or branched chain.

The cycloalkenyl group represented by R is preferably one having 3 to 12, especially 5 to 7 carbon atoms.

Examples of the sulfonyl group represented by R include alkylsulfonyl and arylsulfonyl groups.

Examples of the sulfinyl group include alkylsulfinyl and arylsulfinyl groups.

Examples of the phosphonyl group include alkylphosphonyl, alkoxyphosphonyl, aryloxyphosphonyl and arylphosphonyl groups.

Examples of the acyl group include alkylcarbonyl and arylcarbonyl groups.

Examples of the carbamoyl group include alkylcarbamoyl and arylcarbamoyl groups.

Examples of the sulfamoyl group include alkylsufamoyl and arylsulfamoyl groups.

Examples of the acyloxy group include alkylcarbonyloxy and arylcarbonyloxy groups.

Examples of the carbamoyloxy group include alkylcarbamoyloxy and arylcarbamoyloxy groups.

Examples of the ureido group include alkylureido and arylureido groups.

Examples of the sulfamoylamino group include alkylsulfamoylamino and arylsulfamoylamino groups.

The heterocyclic group is preferably a 5- to 7-membered one; examples thereof include 2-furyl, 2-thienyl, 2-pyrimidinyl and 2-benzothiazolyl groups.

The heterocycloxy group is preferably one having a 5-to 7-membered heterocycle; examples thereof include 3,4,5,6-tetrahydropyranyl-2-oxy and 1-phenyltetrazole-5-oxy groups.

The heterocyclothio group is preferably a 5- to 7-membered heterocyclothio group; examples thereof include 2-pyridylthio, 2-benzothiazolylthio and 2,4-diphenoxy-1,3,5-triazole-6-thio groups.

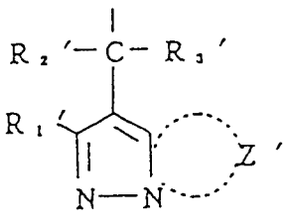
Examples of the siloxy group include trimethylsiloxy, triethylsiloxy and dimethylbutylsiloxy groups.

Examples of the imido group include succinimido, 3-heptadecyl succinimido, phthalimide and glutarimido groups.

Examples of the Spiro compound residue include spiro[3,3]heptane-1-yl.

Examples of the bridged hydrocarbon residue include bicyclo[2,2,1]heptane-1-yl, tricyclo[3,3,1,^{3},^{7}]-decane-1-yl and 7,7-dimethyl-bicyclo[2,2,1]heptane-1-yl.

Examples of the group represented by X and capable of splitting off by reacting with an oxidation product of a color developing agent include halogen atoms such as chlorine, bromine and fluorine atoms; alkoxy, aryloxy, heterocycloxy, acyloxy, sulfonyloxy, alkoxycarbonyloxy, aryloxycarbonyl, alkyloxalyloxy, alkylthio, arylthio, heterocyclothio, alkyloxythio carbonylthio, acylamino, sulfonamido, nitogen-containing heterocycle bonded by the N atom, alkyloxycarbonylamino, aryloxycarbonylamino and carboxyl groups, and

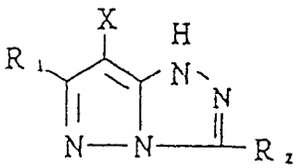


wherein R_1' is the same as the above R; Z' is the same as the above Z; R_2' and R_3' each represent a hydrogen atom, or an aryl, alkyl or heterocyclic group. Among them, the preferred is a halogen atom, especially chlorine atom.

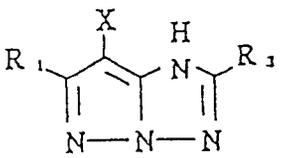
Examples of the nitrogen-containing heterocycle formed by Z or Z' include pyrazole, imidazole, triazole and tetrazole rings. As examples of the substituent each of the above rings may have, those defined for the above R are included.

The compounds represented by Formula M-I are more specifically represented by the following Formulas M-II through M-VII:

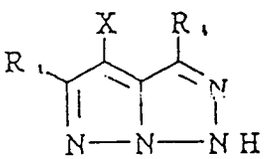
Formula M-II



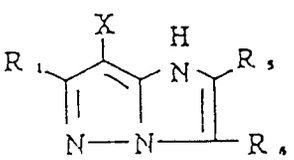
Formula M-III



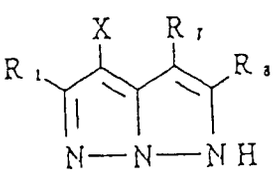
Formula M-IV



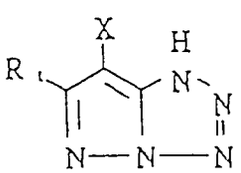
Formula M-V



Formula M-VI



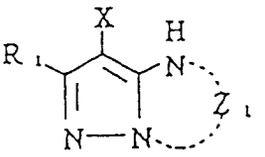
Formula M-VII



In Formulas M-II through M-VII, R_1 through R_8 and X are the same as the foregoing R and X respectively.

Among the compounds represented by Formula M-I, the preferred are those represented by the following Formula M-VIII.

Formula M-VIII

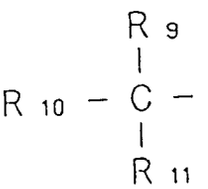


In the formula, R_1, X and Z_1 are the same as R, X and Z in Formula M-I.

Of the magenta couplers represented by Formulas M-II through M-VII, the particularly preferred are magenta couplers represented by Formula M-II.

As the substituent R or R_1 on the foregoing heterocycles, ones represented by the following Formula M-IX are particularly preferred.

Formula M-IX



In the formula, R_9, R_{10} and R_{11} are the same as the foregoing R.

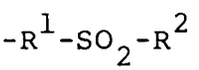
Two of the above R_9, R_{10} and R_{11} -- for example, R_9 and R_{10} -- may be linked to each other to form a saturated or unsaturated ring e.g., cycloalkane, cycloalkene or heterocycle, and further, R_{11} may be linked to said ring to form a bridged hydrocarbon residue.

With respect to Formula M-IX, it is preferable that (i) at least two of R_9 through R_{11} be alkyl groups, or that (ii) one of R_9 through R_{11} -- for example, R_{11} -- be a hydrogen atom, while the other two -- namely, R_9 and R_{10} -- be linked to form a cycloalkyl together with the root carbon atom.

In case (i), it is particularly preferable that two of R_9 through R_{11} be alkyl groups and the other one be a hydrogen atom or an alkyl group.

As the substituents the ring formed by Z of Formula M-I and the ring formed by Z_1 of Formula M-VIII may have, and as the substituents represented by R_2 through R_8 of Formulas M-II through M-VI, ones represented by the following Formula M-X are preferred.

Formula M-X



In the formula, R^1 is an alkylene group, R^2 is an alkyl, cycloalkyl or aryl group.

The alkylene group represented by R^1 is preferably one having 2 or more, especially 3 to 6 carbon atoms on the straight chain portion and may be of straight chain or branched chain.

The cycloalkyl group represented by R_2 is preferably a 5- or 6-membered one.

Next, typical examples of the compounds according to the invention are illustrated.

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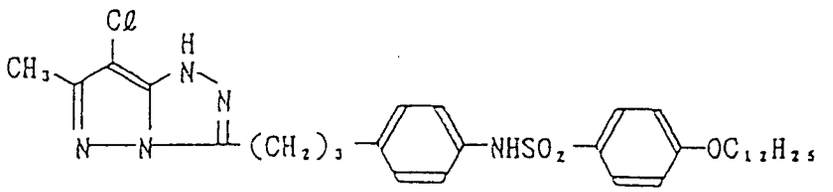

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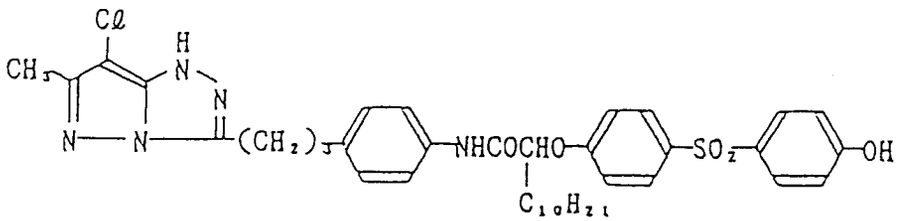

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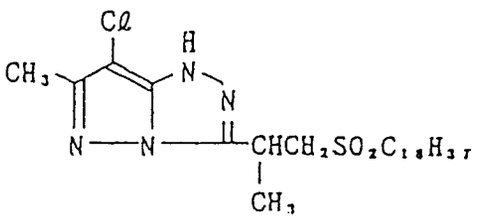

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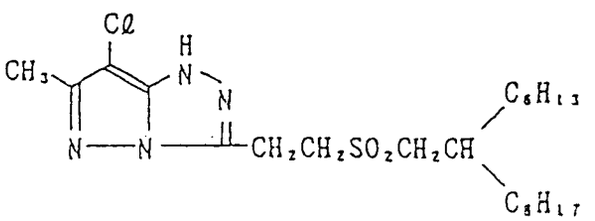

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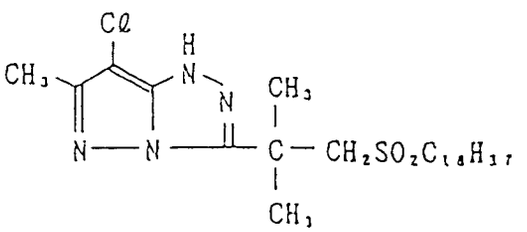

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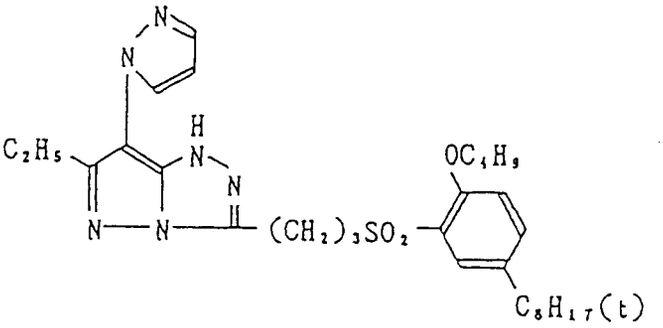

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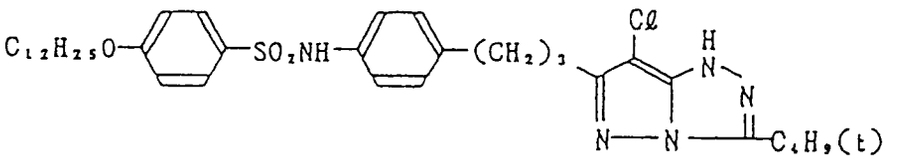

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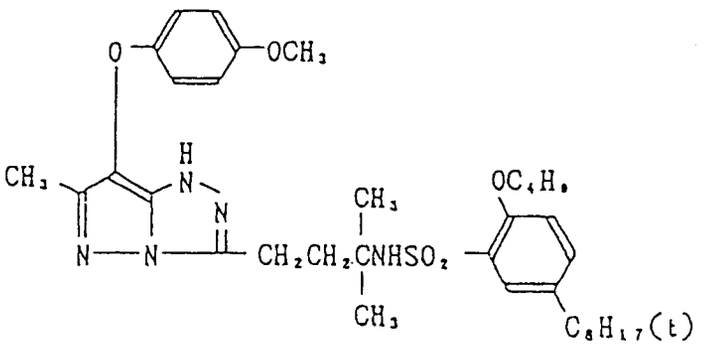

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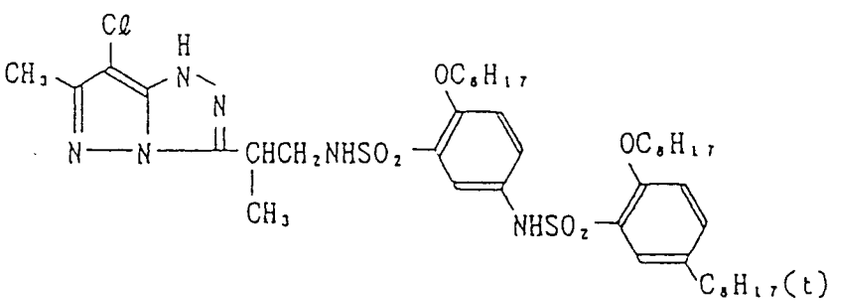

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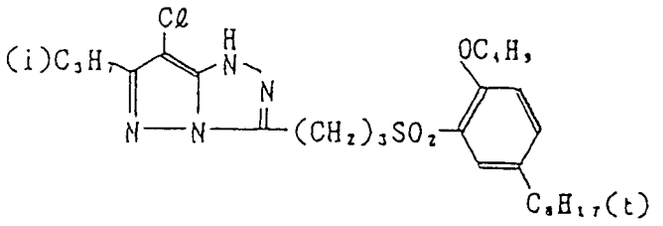

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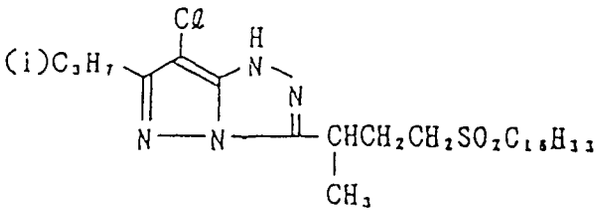

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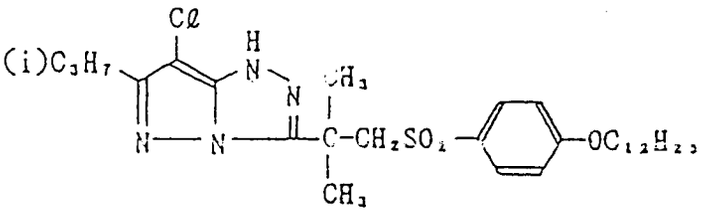

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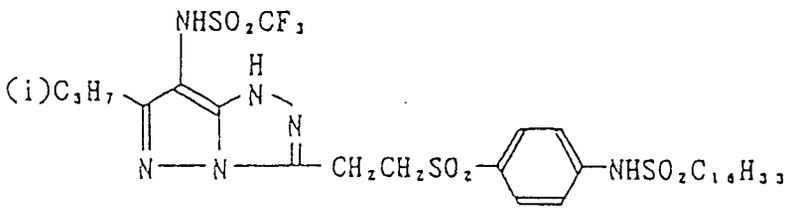

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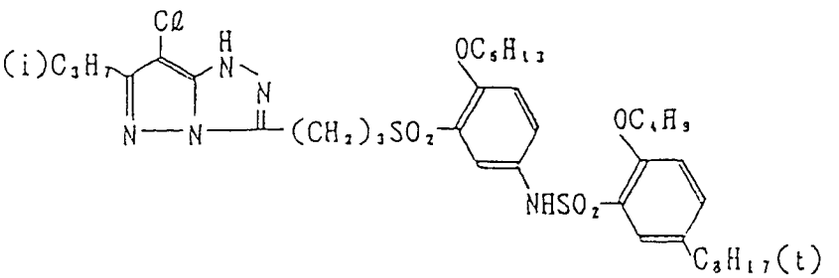

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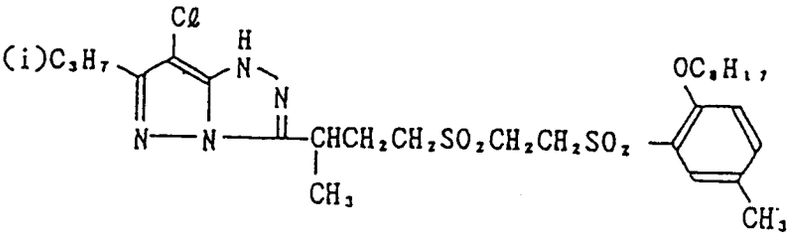

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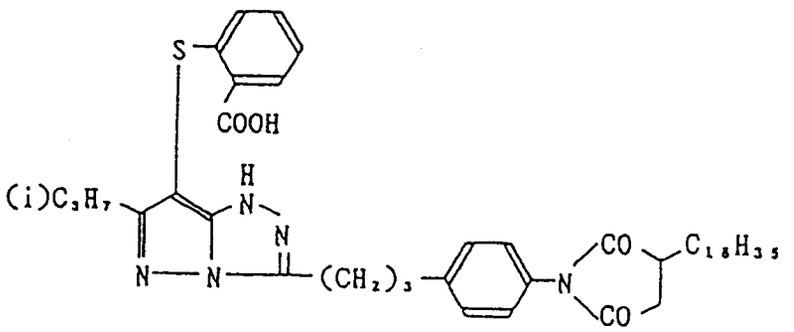

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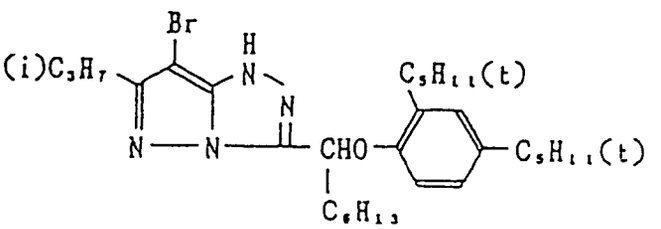

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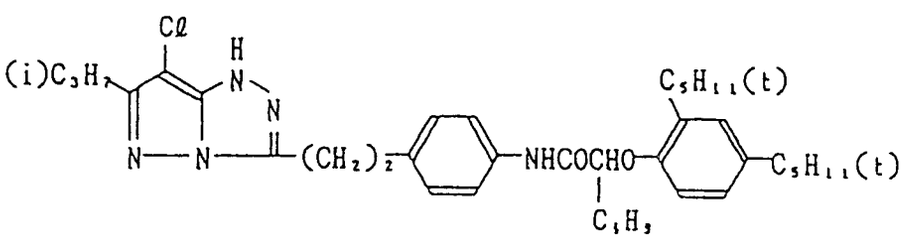

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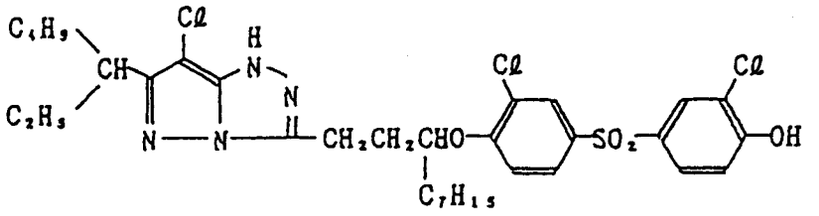

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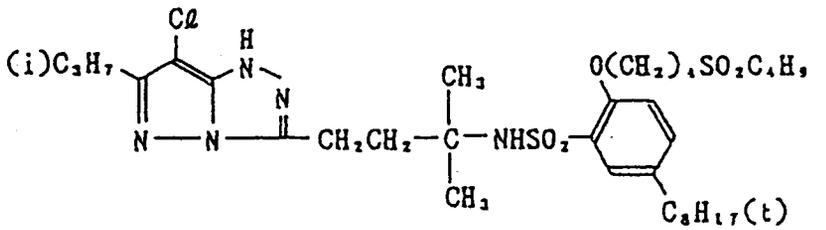

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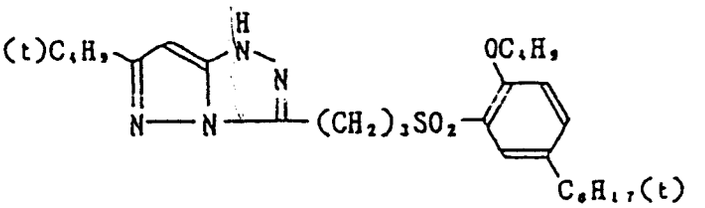

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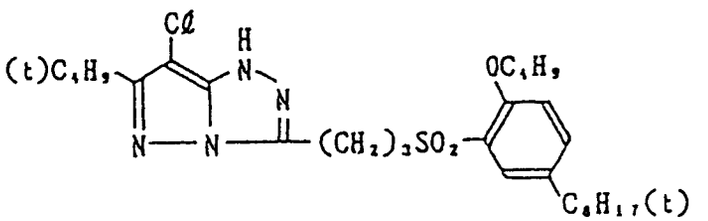

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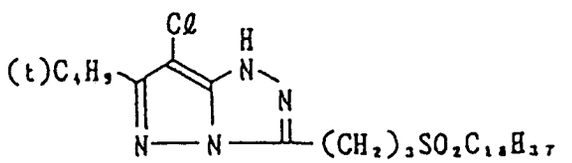

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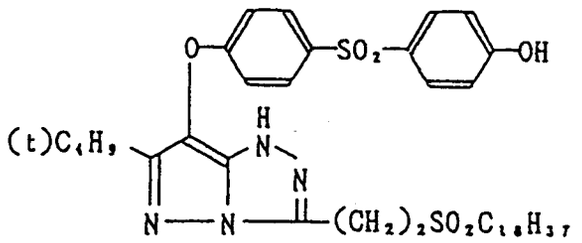

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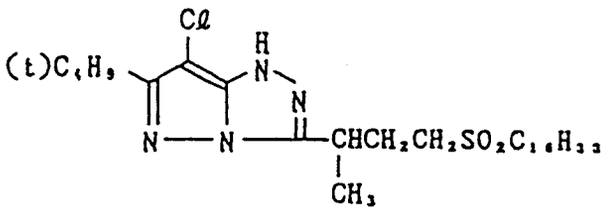

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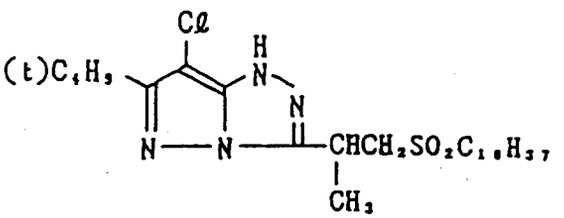

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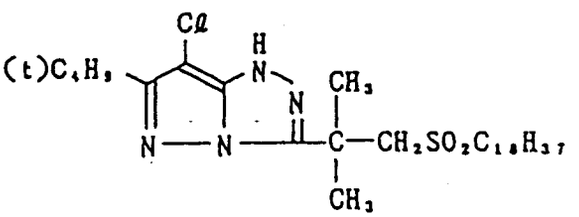

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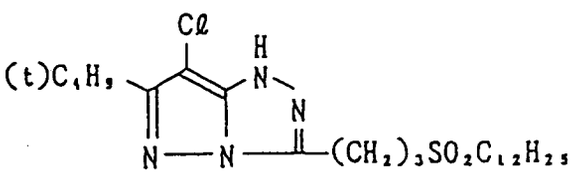

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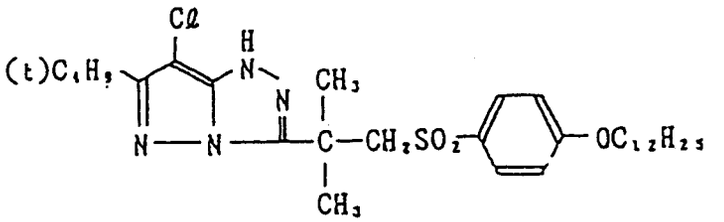

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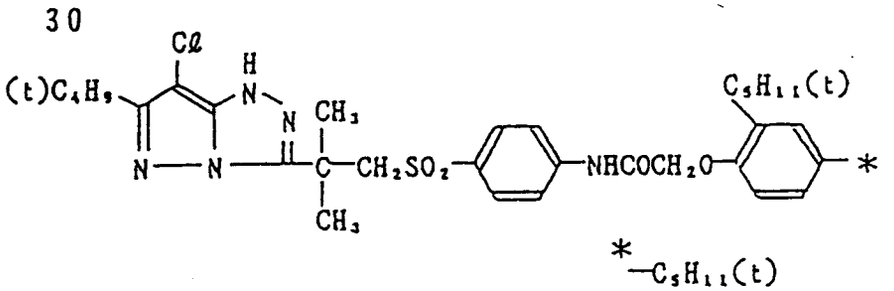

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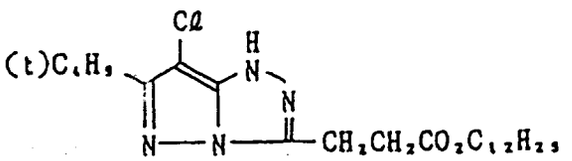

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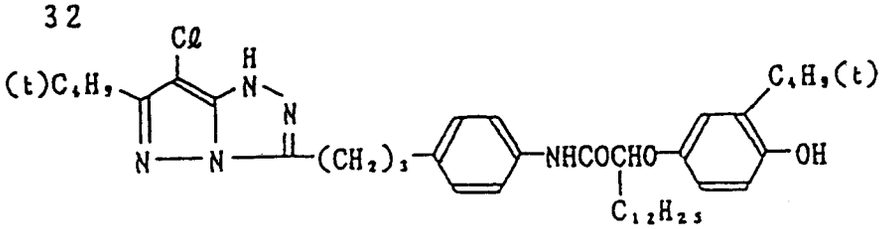

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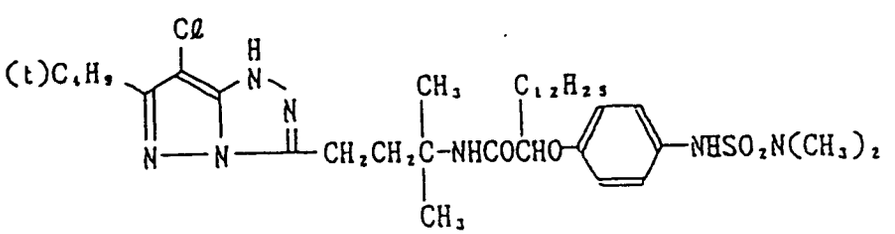

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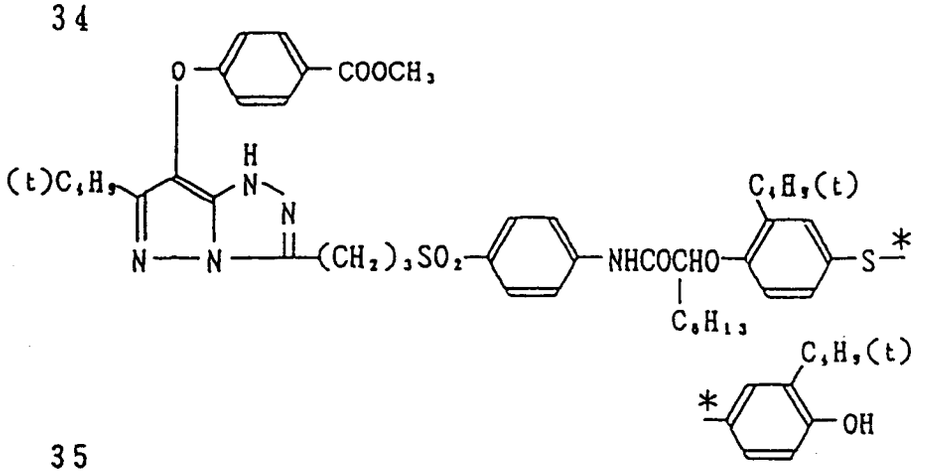

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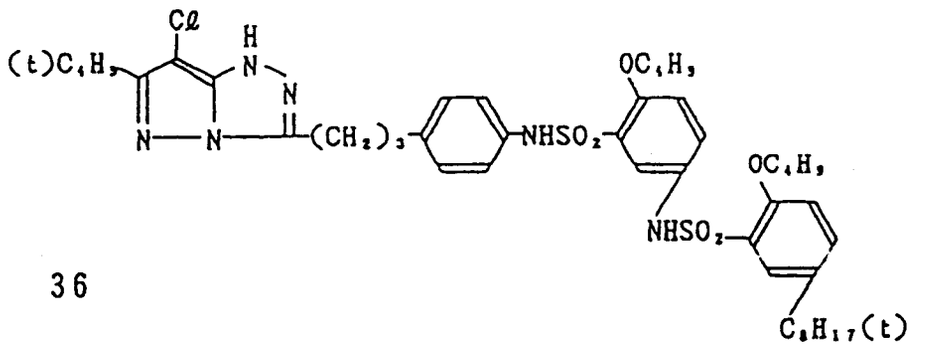

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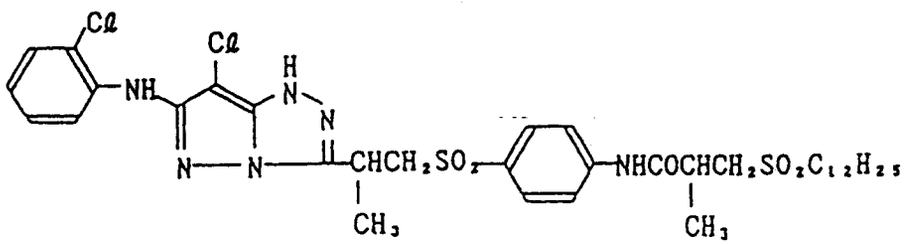

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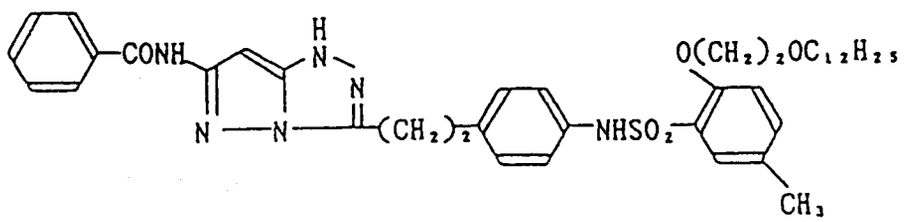

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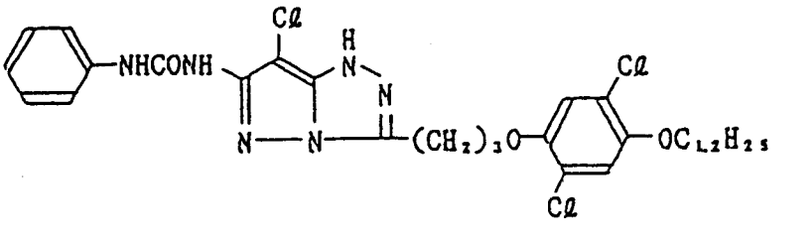

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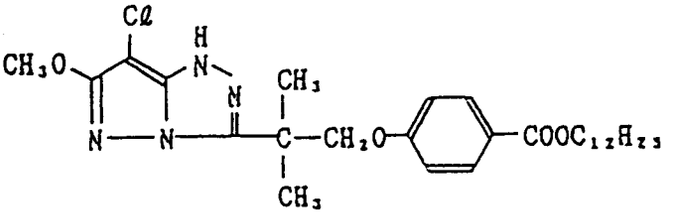

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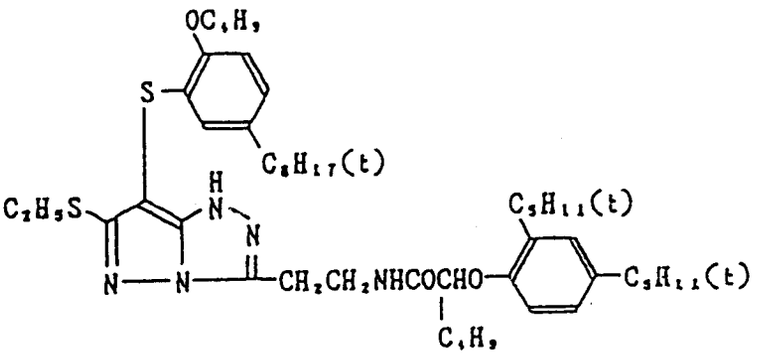

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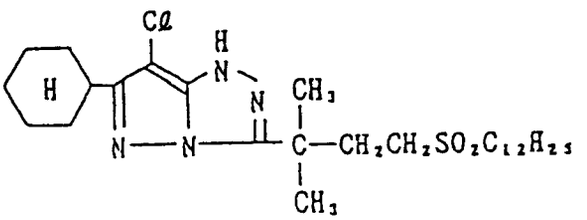

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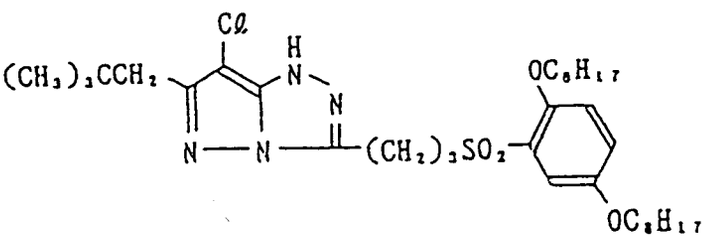

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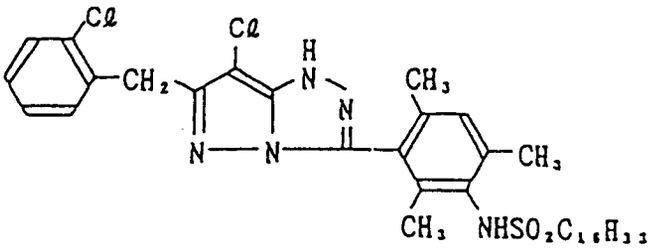

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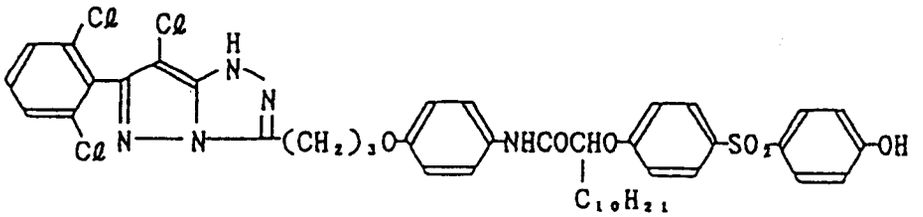

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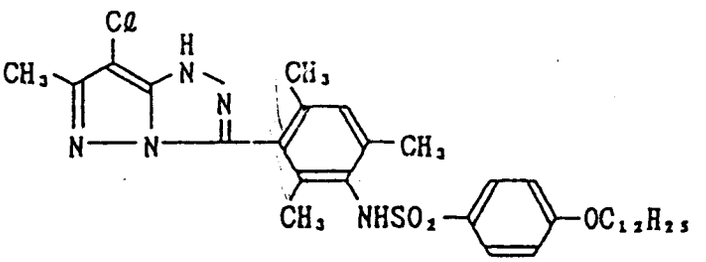

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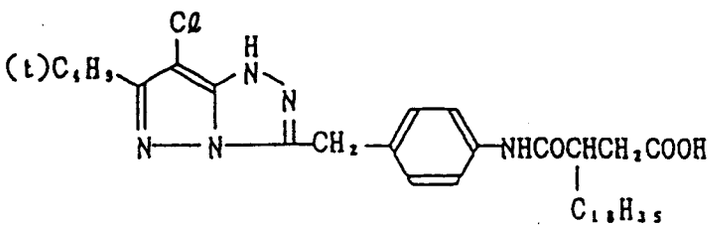

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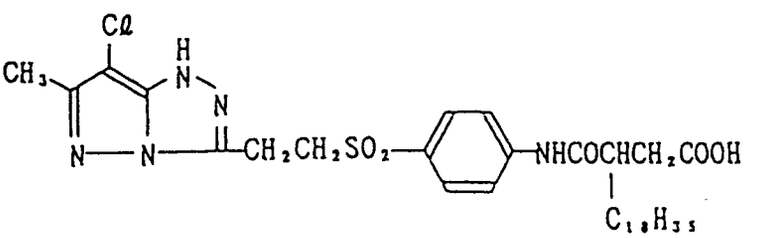

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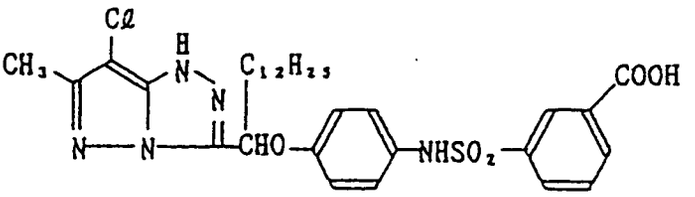

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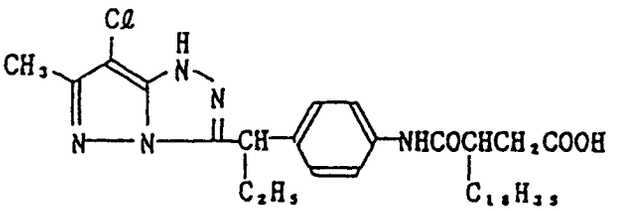

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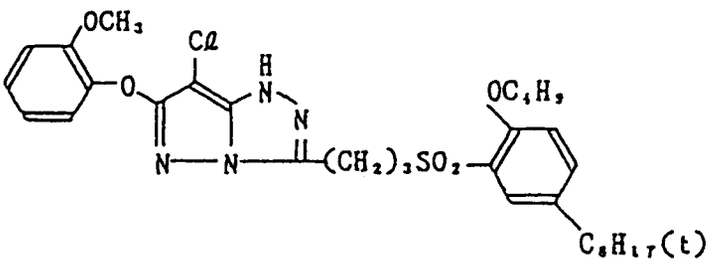

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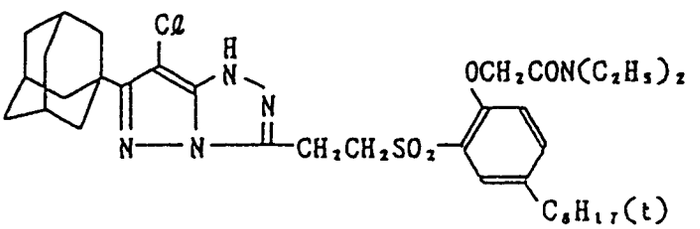

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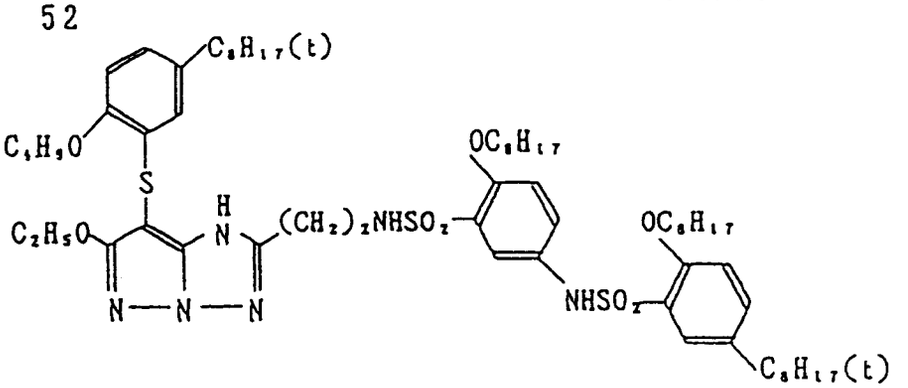

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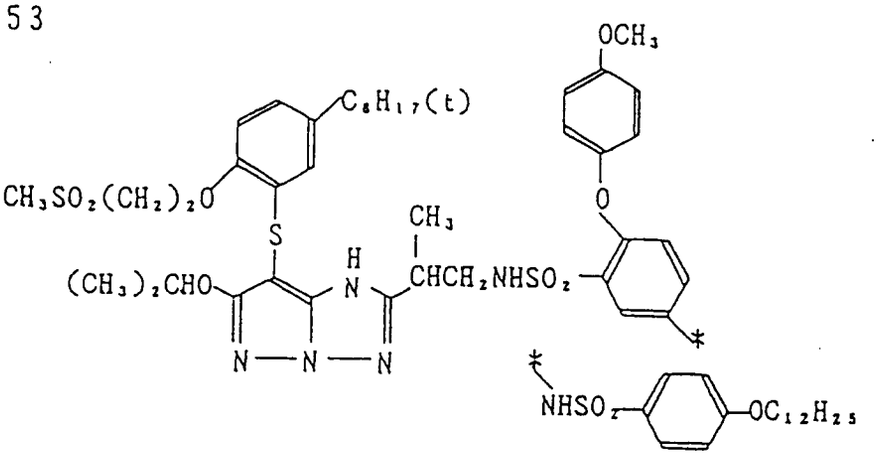

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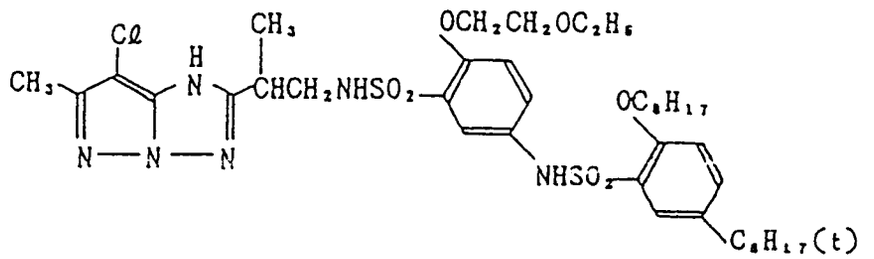

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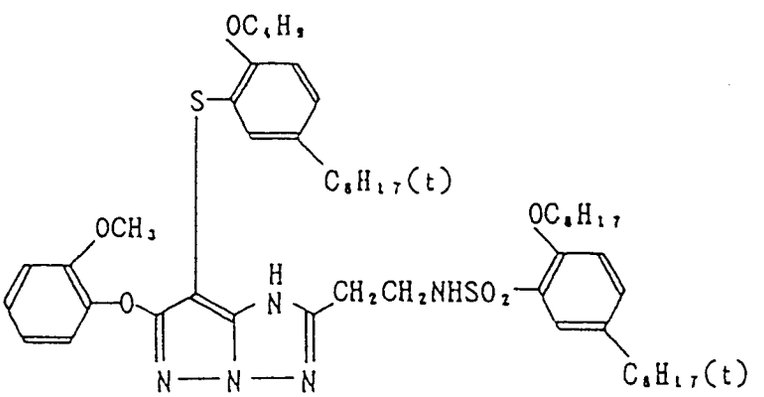

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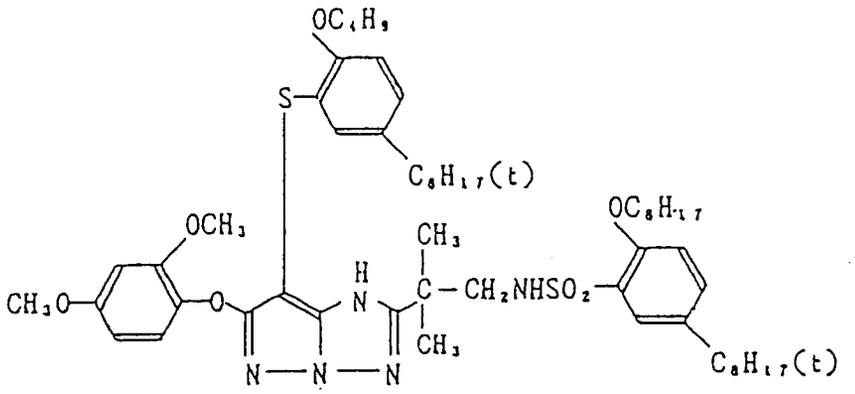

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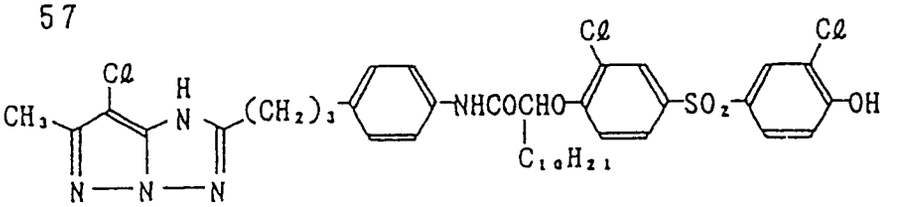

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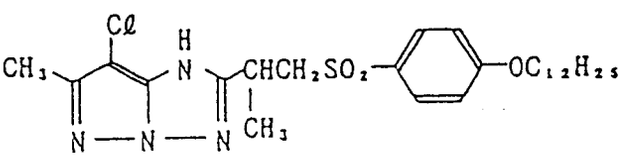

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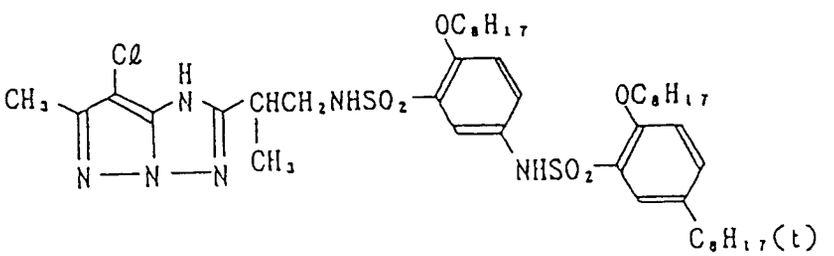

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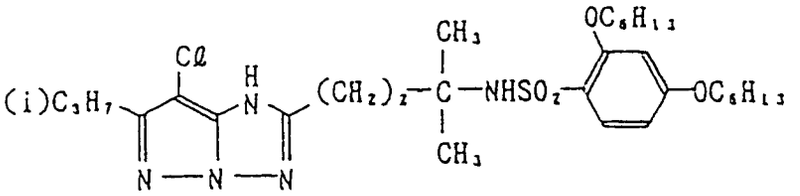

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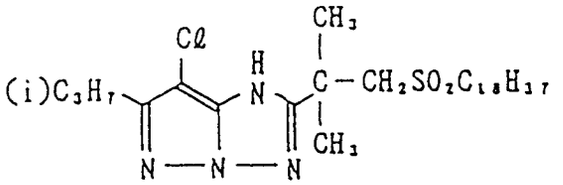

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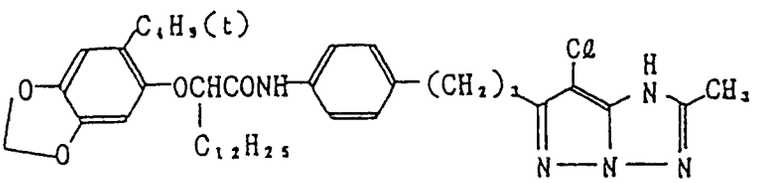

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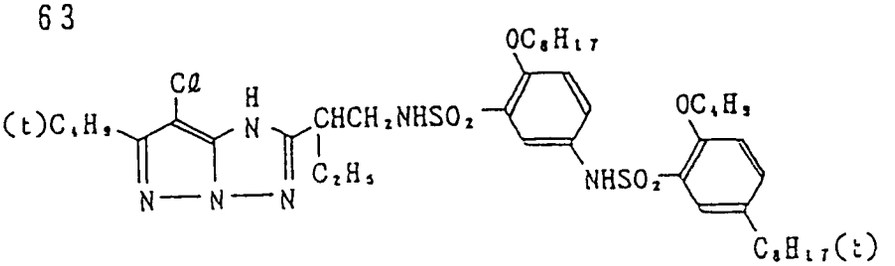

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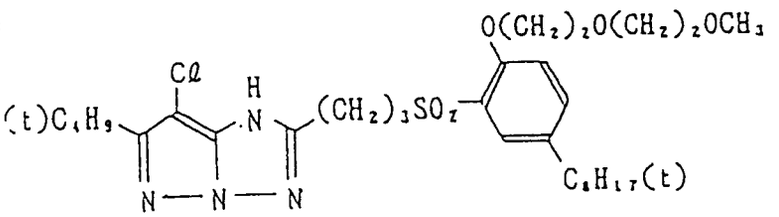

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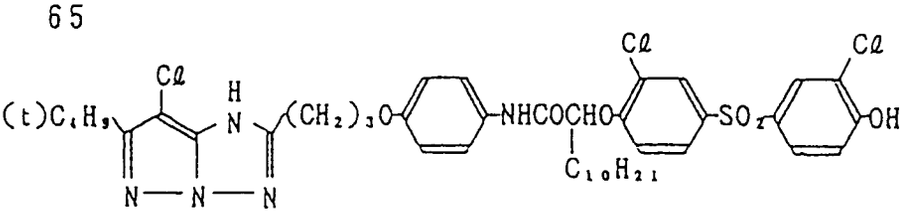

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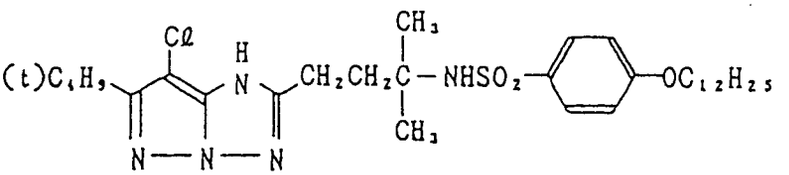

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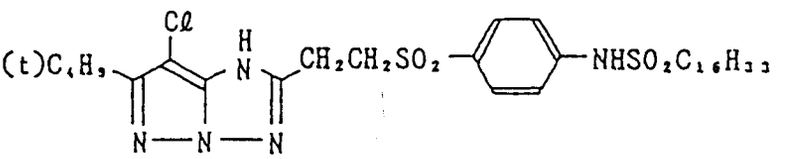

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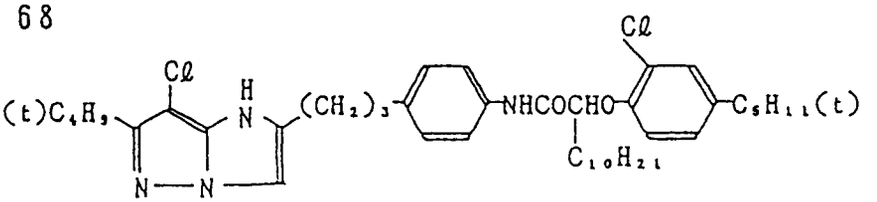

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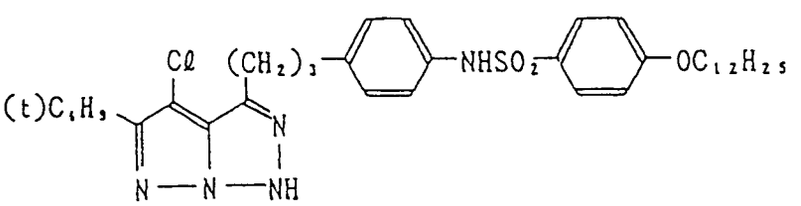

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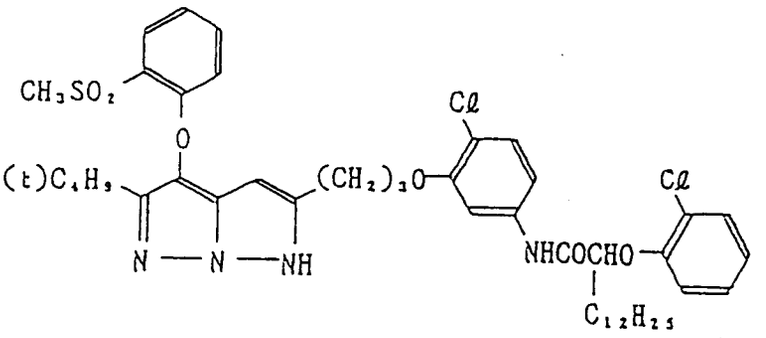

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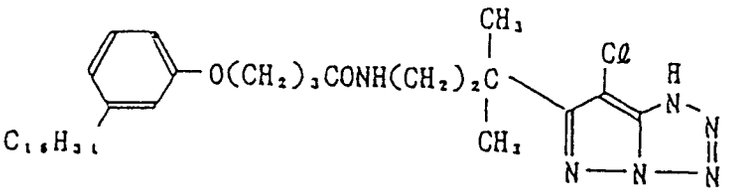

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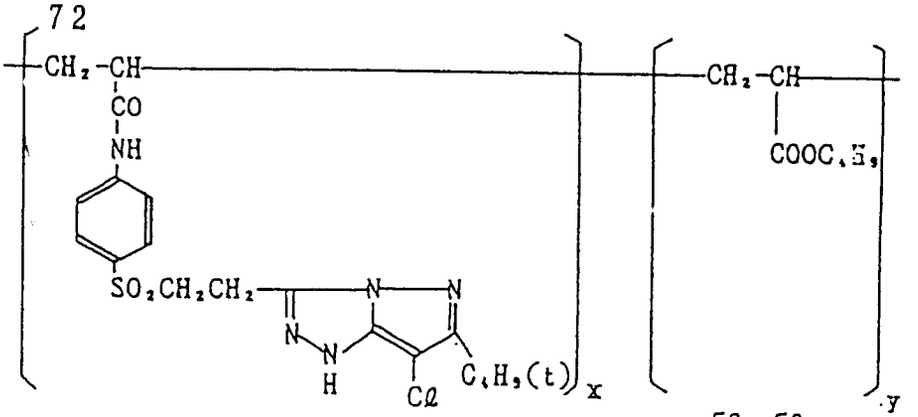

x : y = 50 : 50

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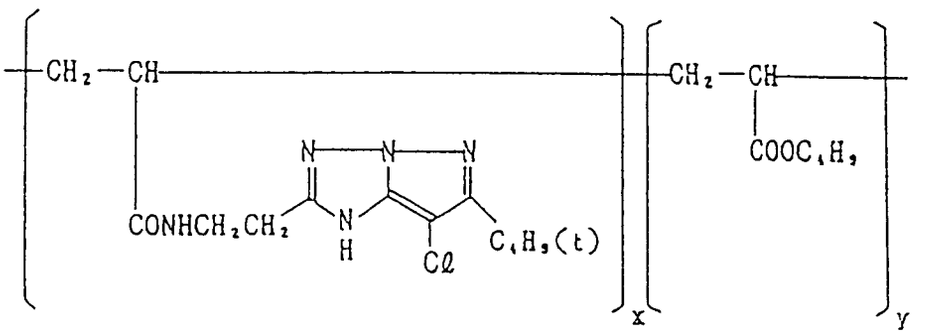


x : y = 50 : 50

Besides the typical examples illustrated above, other examples of the compounds according to the invention are those illustrated on pages 18-32 of the specification of Japanese Pat. O.P.I. Pub. No. 166339/1987 by Nos. 1-4, 6, 8-17, 19-24, 26-43, 45-59, 61-104, 106-121, 123-162 and 164-223.

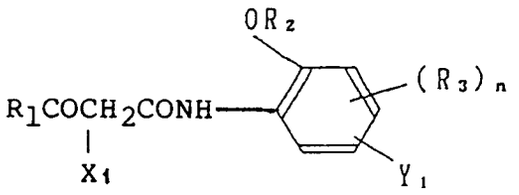
The above couplers can be synthesized by referring to Journal of the Chemical Society, Perkin I (1977), pp. 2047-2052; U.S. Pat. No. 3,725,067 and Japanese Pat. O.P.I. Pub. Nos. 99437/1984, 42045/1983, 162548/1984, 171956/1984, 335552/1985, 43659/1985, 172982/1985, 190779/1985, 209457/1987, 307453/1988.

The couplers of the invention are usually used in an amount of 1×10^{-3} to 1 mol, preferably 1×10^{-2} to 8×10^{-1} mol per of silver halide.

The couplers of the invention can be used together with other types of magenta couplers.

The yellow dye forming couplers used in a blue-sensitive emulsion layer of the silver halide color photographic light-sensitive material of the invention are not particularly limited, but the compounds represented by the following Formula Y-I are advantageously used.

Formula Y-I



In the formula, R_1 is an alkyl, cycloalkyl or aryl group; R_2 is an alkyl, cycloalkyl, acyl or aryl group; R_3 is a group capable of substituting on benzene ring; n is an integer of 0 or 1; X_1 is a hydrogen atom or a substituent capable of splitting off by reaction with an oxidation product of a developing agent; and Y_1 is an organic group.

The yellow coupler represented by Formula Y-I is hereunder described in detail.

In Formula Y-I, examples of the alkyl group represented by R_1 include a methyl, ethyl, isopropyl, t-butyl or dodecyl group, each of which may have a substituent; examples of such a substituent are halogen atoms, and aryl, alkoxy, aryloxy, alkylsulfonyl, acylamino and hydroxyl groups.

Examples of the cycloalkyl group represented by R_1 include cyclopropyl and cyclohexyl groups as well as organic hydrocarbon residues formed by condensation of two or more of cycloalkyls such as adamantyl group. The cycloalkyl group represented by R_1 may have a substituent, of which examples are those exemplified for the substituent of the alkyl group represented by R_1. Examples of the aryl group represented by R_1 include a phenyll group; said aryl group may have a substituent. Examples of said substituent include those which are exemplified as substituents for the alkyl group represented by R_1 and an alkyl group. Among these groups available as R_1, the preferred is a branched alkyl group.

With respect to Formula Y-I, examples of the alkyl, cycloalkyl and aryl groups represented by R_2 are those exemplified for R_1, and any of them may have a substituent among those exemplified as substituents for R_1. Examples of the acyl group include acetyl, propionyl, butylyl, hexanoyl and benzoyl groups, said acyl group may have a substituent. Of these groups available as R_2, desirable ones are alkyl and aryl groups, more desirable ones are alkyl groups, and the most desirable ones are lower alkyl groups having carbon atoms of 5 or less.

In Formula Y-I, the group represented by R_3 and capable of substituting on benzene ring is a halogen atom, or an alkyl group, e.g., ethyl, isopropyl, t-butyl, alkoxy group, e.g., methoxy, aryloxy group, e.g., phenoxy, acyloxy group, e.g., acetyloxy, benzoyloxy, acylamino group, e.g., acetamido, benzylamino, carbamoyl group, e.g., N-methylcarbamoyl, N-phenylcarbamoyl, alkylsulfonamido group, e.g., ethylsulfonamido, arylsulfonamido, e.g., phenylsulfonamido, sulfamoyl group, e.g., N-propylsulfamoyl, N-phenylsulfamoyl or imido group, e.g., succinimido, glutarimido.

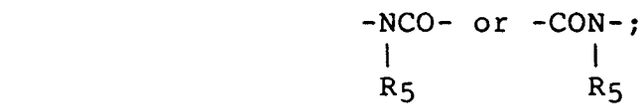
In Formula Y-I, Y_1 is an organic group and preferably one represented by the following Formula Y-II.

Formula Y-II $-(J)_p-R_4$

In Formula Y-II, R_4 is an organic group containing one interlinking group consisting of a carbonyl unit or sulfonyl unit; and p is 0 or 1.

Examples of the group having a carbonyl unit include ester, amido, carbamoyl, ureido and urethane groups; examples of the group having a sulfonyl unit include sulfonyl, sulfonylamino, sulfamoyl and aminosulfonylamino groups.

J represents



where R_5 is a hydrogen atom, or an alkyl, aryl or heterocyclic group.

Examples of the alkyl group represented by R_5 include methyl, ethyl, isopropyl, t-butyl and dodecyl groups. Examples of the aryl group represented by R_5 include phenyl and naphthyl groups. Examples of the heterocyclic group represented by R_5 include pyridyl group.

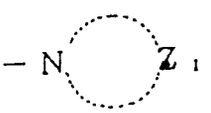
The groups represented by R_5 may have a substituent. While the substituent is not particularly limited, typical examples are halogen atoms, e.g., chlorine atom alkyl groups, e.g., ethyl, t-butyl, aryl groups, e.g., phenyl, p-methoxyphenyl, naphthyl, alkoxy groups, e.g., ethoxy, benzyloxy, aryloxy groups, e.g., phenoxy, alkylthio group, e.g., ethylthio, arylthio, e.g., phenylthio, alkylsulfonyl group, e.g., β-hydroxyethylsulfonyl, arylsulfonyl groups, e.g., phenylsulfonyl, acylamino groups, e.g., alkylcarbonylamino groups such as acetamide, arylcarbonylamino groups such as benzoylamino, carbamoyl groups, e.g., alkylcarbamoyl groups such as N-methylcarbamoyl, arylcarbamoyl groups such as N-phenylcarbamoyl, acyl groups, e.g., alkylcarbonyl groups such as acetyl, arylcarbonyl groups such as benzoyl, sulfonylamino groups, e.g., alkylsulfonylamino groups such as methylsulfonylamino, arylsulfonylamino groups such as phenylsulfonylamino, sulfamoyl groups, e.g., alkylsulfamoyl groups such as N-methylsulfamoyl, arylsulfamoyl groups such as N-phenylsulfamoyl, hydroxy group and nitrile group.

Examples of the group represented by X_1 in Formula Y-I and capable of splitting off upon coupling with an oxidation product of a developing agent are those represented by the following Formula Y-III or Y-IV.

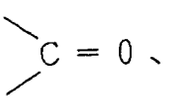
Formula Y-III $-OR_6$

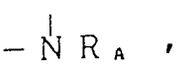
In Formula Y-III, R_6 represents an aryl or heterocyclic group which may have a substituent.

Formula Y-IV



In Formula Y-IV, Z_1 is a group of non-metallic atoms necessary to form a 5- or 6-membered ring in conjunction with a nitrogen atom. An atomic group which constitutes said non-metal atomic group is, for example, a substituted or unsubstituted methylene or methine, or



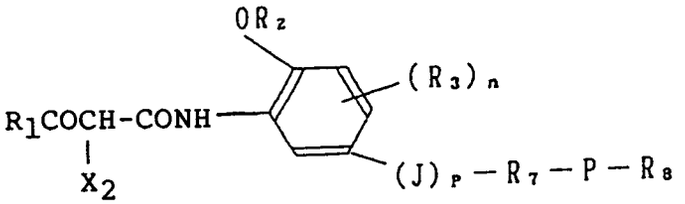


R_A is the same as the above R_5, -N=, -O-, -S-or $-SO_2-$.

The yellow dye forming coupler represented by Formula Y-I may form a bis-compound by interlinking at the part of R_1, R_3 or Y_1.

Particularly preferred yellow couplers of the invention are those represented by the following Formula Y-V.

Formula Y-V



In Formula Y-V, R_1, R_2, R_3, n and J are the same as R_1, R_2, R_3 and n in Formula Y-I and J in Formula Y-II. R_7 is an alkylene, arylene, alkylene-arylene or arylene-alkylene group, or -A-V_1-B- in which A and B each represent an alkylene, arylene, alkylene-arylene or arylene-alkylene group; and V_1 represents a divalent interlinking group. R_8 is an alkyl, cycloalkyl, aryl or heterocyclic group. p is a bonding group having a carbonyl unit or sulfonyl unit. X_2 is a group capable of splitting off upon coupling with an oxidation product of a developing agent.

Examples of the alkylene group represented by R_7, A or B of Formula Y-V include methylene, ethylene, trimethylene, butylene, hexylene, methylmethylene, methylethylene, ethylethylene, 1-methylethylene, 1-methyl-2-ethylethylene, 2-decylethylene and 3-hexylpropylene groups, which may be of straight chain or branched chain. The alkylene group may have a substituent, e.g., aryl; examples thereof are 1-benzylethylene, 2-phenylethylene and 3-naphthylpropylene groups.

Examples of the arylene group include phenylene and naphthylene groups, each of which may have a substituent.

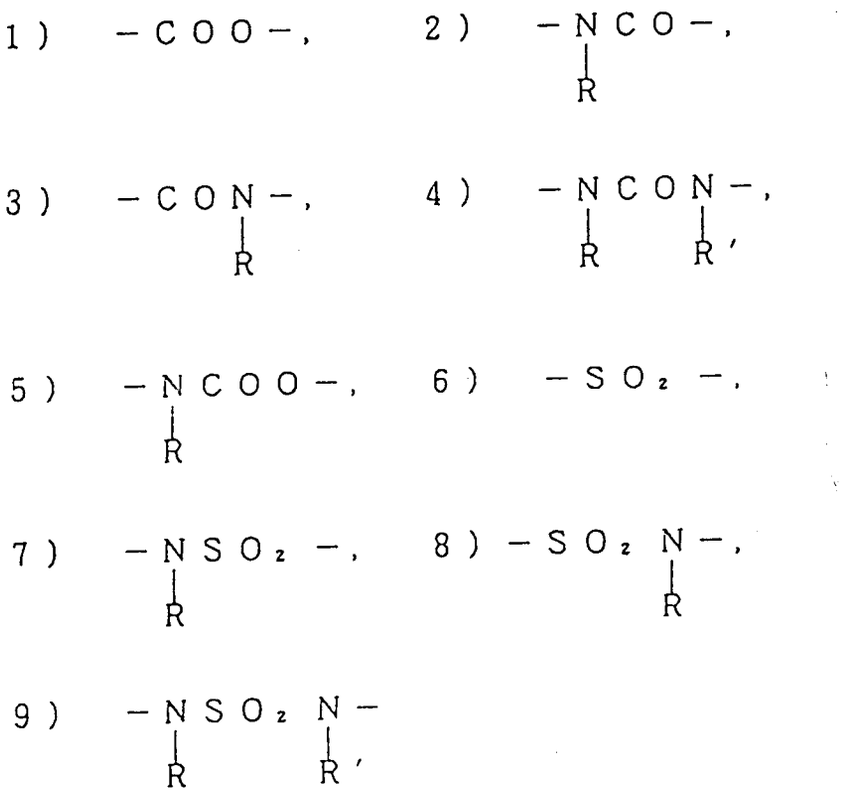
Examples of the alkylene-arylene group include methylene-phenylene groups; examples of the arylene-alkylene group include phenylene-methylene groups; and each of these groups may have a substituent. The divalent interlinking group represented by V_1 is, for example, -O- or -S- group.

Among alkylene, arylene, alkylene-arylene and arylene-alkylene groups and -A-V_1-B- represented by R_7 respectively, the particularly preferred are alkylene groups.

In Formula Y-V, the alkyl group represented by R_8 includes, for example, ethyl, butyl, hexyl, octyl, 2-ethylhexyl, dodecyl, hexadecyl, 2-hexyldecyl and octadecyl groups, which may be of straight chain or branced chain. Examples of the cycloalkyl group include cyclohexyl groups; examples of the aryl group include phenyl and naphthyl groups;and examples of the heterocyclic group include pyridyl groups. These alkyl, cycloalkyl, aryl and heterocyclic groups represented by R_8 may have a substituent. The substituent is not particularly limited in types, except that organic groups containing a dissociative hydrogen atom having a pKa value of 9.5 or less, e.g., dissociative phenolic hydrogen atom, are unsuitable. Preferred substituents are those exemplified as substituents for R_5.

In Formula Y-V, p is a bonding group having a carbonyl or sulfonyl unit, preferably one of the groups represented by the following Groups Y-VI-1) through Y-VI-9).

Groups Y-VI-1) through 9)

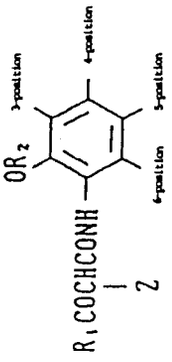


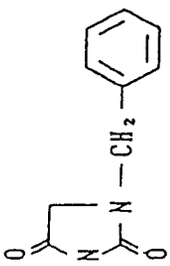
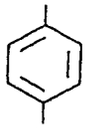
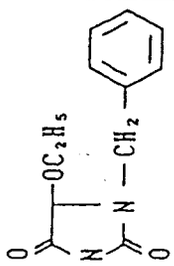
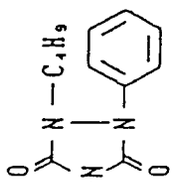
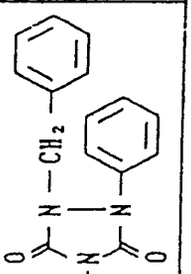
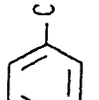
In these groups, R and R' each represent a hydrogen atom, or an alkyl, aryl or heterocyclic group.

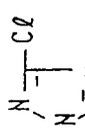
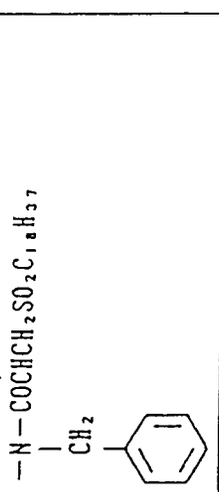
Examples of the group represented by R or R' are those exemplified for the foregoing R_5, and these groups may have a substituent. Examples of the substituent are those exemplified as substituents for R_5. Among ones exemplified as R or R^1, a hydrogen atom is preferred.

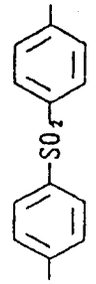
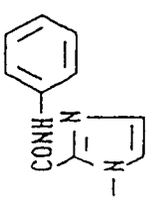
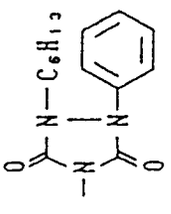
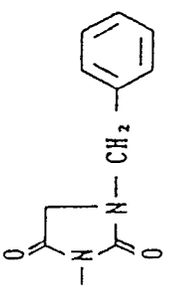
The yellow coupler of the invention represented by Formula Y-I is used in an amount of 1×10^{-3} to 1 mol, preferably 1×10^{-2} to 8×10^{-1} mol per mol of silver halide.

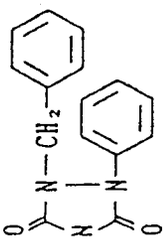
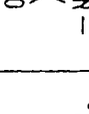
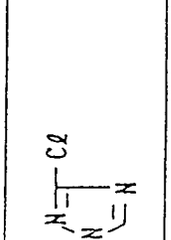
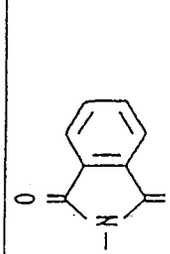
Typical examples of the yellow coupler represented by Formula Y-I are illustrated below.

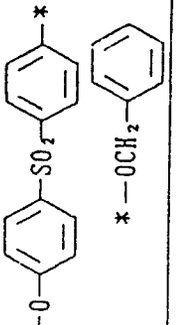
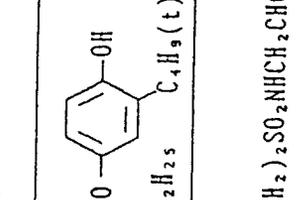
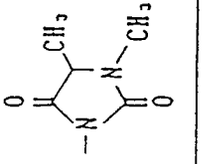
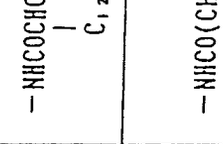
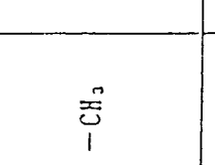
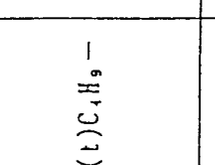
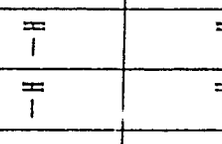


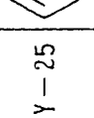
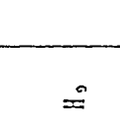
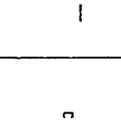
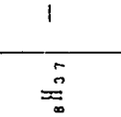
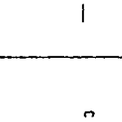
NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-1	(t)C_4H_9-	$-CH_3$		-H	-H		-H
Y-2	(t)C_4H_9-	$-CH_3$		-H	-H		-H
Y-3	(t)C_4H_9-	$-CH_3$		-H	-H	CH_3 $-NHCOCHCH_2SO_2C_{12}H_{25}$	-H
Y-4	(t)C_4H_9-	$-CH_3$		-H	-H		-H

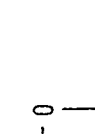
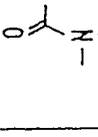
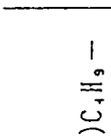
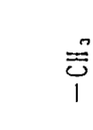
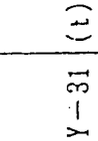
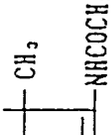
NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-5	(t)C_4H_9-	$-CH_3$			—H	—H	—H
Y-6	(t)C_4H_9-	$-CH_3$		$-NHCOCHCH_2SO_2C_{12}H_{25}$ | CH_3	—H	—H	—H
Y-7	(t)C_4H_9-	$-CH_3$		$-NHCO(CH_2)_2CONHC_{12}H_{25}$ | C_2H_5	—H	—H	—H
Y-8	(t)C_4H_9-	$-C_3H_7$(iso)		$-CONH(CH_2)_3CONH-C_{12}H_{25}$	—H	—H	—H
Y-9	(t)C_4H_9-	$-CH_3$		$-CONH-NHCOC_{12}H_{25}$	—H	—H	—H

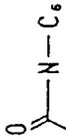
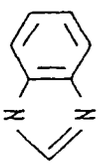
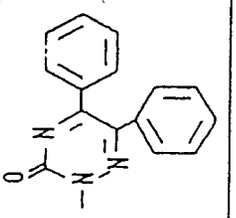
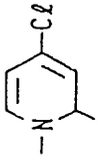
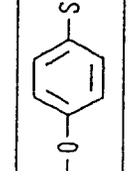
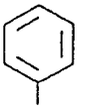
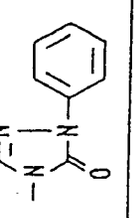
NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-10	(t)C_4H_9-	$-C_{12}H_{25}$		$-CONHCHCH_2SO_2C_2H_5$ | CH_3	-H	-H	-H
Y-11	(t)C_4H_9-	$-C_{18}H_{37}$		CH_3 | $-NHCOCCH_2SO_2C_4H_9$ | CH_3	-H	-H	-H
Y-12	(t)C_4H_9-	$-CH_3$		$-NHCOCHNHCO-C_6H_3(OC_{12}H_{25})$ | CH_3	-H	-H	-H
Y-13	(t)C_4H_9-	$-C_4H_9$		$-NHCOCHO-C_6H_3(SO_2NHC_4H_9)$ | $C_{12}H_{25}$	-H	-H	-H
Y-14	(t)C_4H_9-	$-CH_3$		$-NHCOCHCH_2SO_2C_{12}H_{25}$ | CH_3	-H	-H	-H

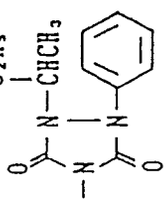
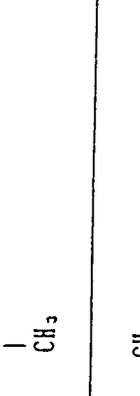
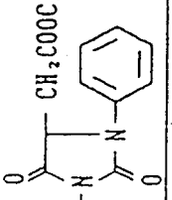
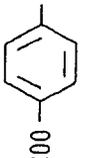
NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-15	(t)C_4H_9-	$-CH_3$		—H	—H	$-CONH(CH_2)_2NHSO_2C_{12}H_{25}$	—H
Y-16	(t)C_4H_9-	$-CH_3$		—H	—H	$-CONHCHCH_2SO_2CH_2CHC_8H_{17}$ (CH$_3$; C_6H_{13})	—H
Y-17	(t)C_4H_9-	$-CH_3$		—H	—H	$-SO_2NH(CH_2)_3O-$ (C_5H_{11}(t); C_5H_{11}(t))	—H
Y-18	(t)C_4H_9-	$-CH_3$		—H	—H	$-NHCOCH(CH_2)_2NHCO-$ ($OC_{12}H_{25}$; CH$_3$)	—H
Y-19	$C_2H_5OCH_2C(CH_3)_2$-	$-CH_3$		—H	—H	$-NHCO(CH_2)_{10}COOC_2H_5$	—H

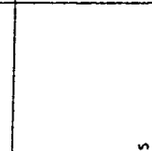
NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-20	(t)C_4H_9-	$-CH_3$		-H	-H		-H
Y-21	(t)C_4H_9-	$-CH_3$		-H	-H	-NHCOCHCH$_2$SO$_2$C$_{12}$H$_{25}$ (CH$_3$)	-H
Y-22	(t)C_4H_9-	$-CH_3$		-H	-H		-H
Y-23	(t)C_4H_9-	$-C_{12}H_{25}$		-H	-H	-NHCO(CH$_2$)$_3$SO$_2$NHCH$_2$CHC$_4$H$_9$ (C_2H_5)	-H
Y-24	(t)C_4H_9-	$-C_2H_5$		-H	-H		-H

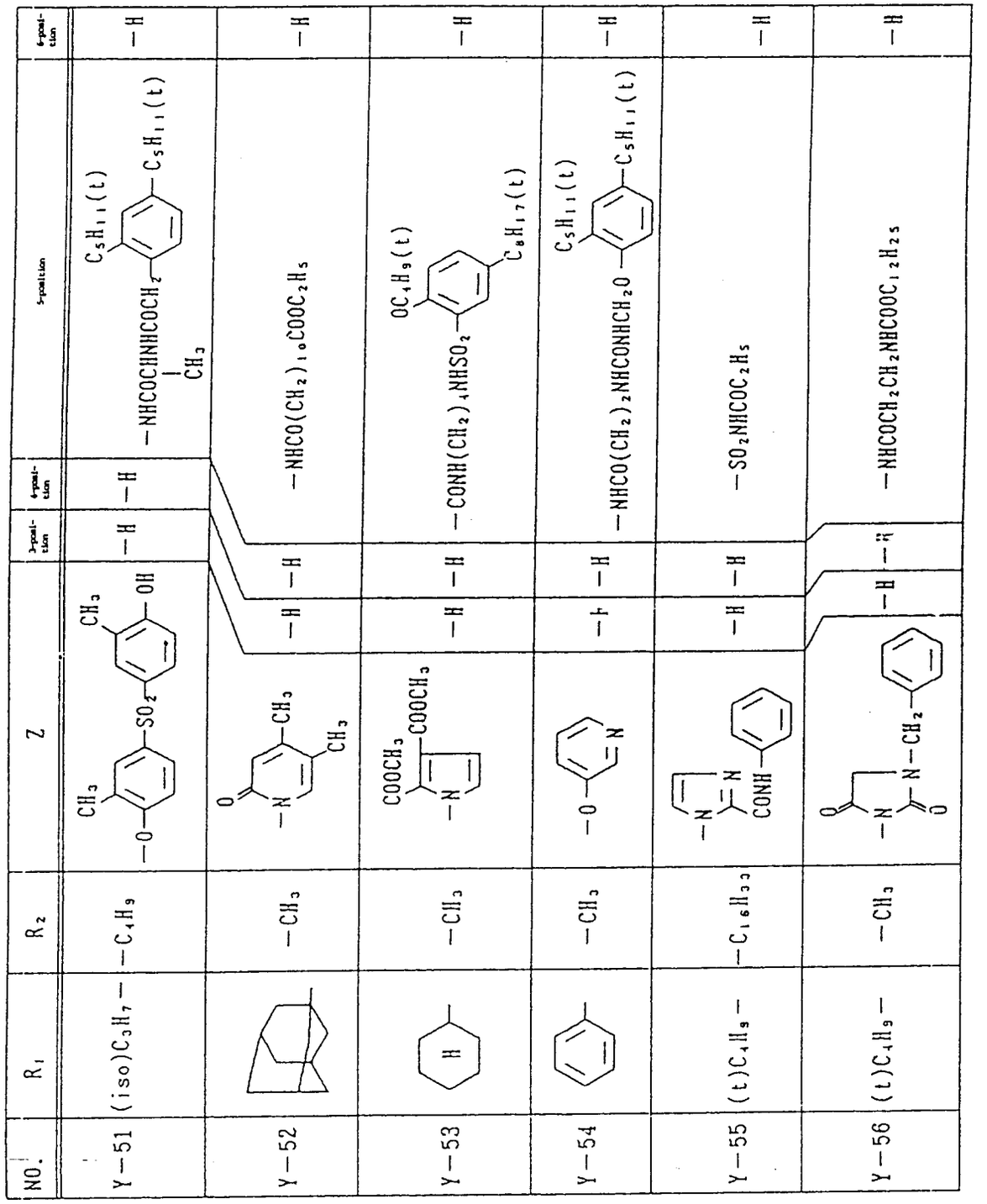
NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-25		$-C_4H_9$		—H	—H	$-NHSO_2C_{16}H_{33}$	—H
Y-26	$(t)C_5H_{11}$—	$-C_2H_5$	—H	—H	—H		—H
Y-27	$(t)C_4H_9$—	$-CH_3$		—H	—H		—H
Y-28	$(t)C_4H_9$—	$-C_{18}H_{37}$		—H	—H		—H
Y-29	$(t)C_4H_9$—	$-CH_3$		—H	—H		—H

NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-30	(t)C_4H_9-	$-CH_3$		-H	-H	$-CONHCHCH_2SO_2NHC_{12}H_{25}$ | C_6H_{13}	-H
Y-31	(t)C_4H_9-	$-CH_3$		-H	-H	$-COOC_{14}H_{29}(n)$	-H
Y-32		$-C_{12}H_{25}$		-H	-H	C_2H_5 | $-NHCO(CH_2)_3NHCONHCH_2CHC_4H_9$	-H
Y-33	(t)C_5H_{11}-	$-CH_3$		-H	-H		-H
Y-34	(t)C_4H_9-	$-CH_3$		-H	-H	$-COOC_{18}H_{35}$	-H

NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-35	(t)C_4H_9—	—CH_3		—H	—H	—NHCO$(CH_2)_3$NHCOCH$_2$CHC$_6H_{13}$ (C$_8H_{17}$)	—H
Y-36	(t)C_4H_9—	—CH_3		—H	—Cℓ	CH_3 — C($C_{12}H_{25}$) — $NHCOCCH_2NHCON$ — C(C_2H_5) — CH_3	—H
Y-37	(t)C_4H_9—	—$COOC_2H_5$		—H	—H	—$CONHCH_2CHSO$— C($C_{18}H_{37}$) — C_2H_5	—H
Y-38	(t)C_4H_9—	—C_4H_9		—H	—$NHCOCHSO_2NHC_{12}H_{25}$ — C($C_{16}H_{33}$)	—Cℓ	—H
Y-39	(t)C_4H_9—	—CH_3		—H	—Cℓ	—$NHCO(CH_2)_2NHCO$— C($C_{12}H_{25}$)	—H
Y-40	(t)C_4H_9—			—H	—H	CH_2 — C — $CONHCCH_2CONH$ — C(CH_2) — $OC_{12}H_{25}$	—H

NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-41	(t)C_5H_{11}	$-\overset{O}{\overset{\|}{C}}-CH_3$		—H	$-OCH_3$		—H
Y-42	(t)C_4H_9—	$-\overset{O}{\overset{\|}{C}}-C_2H_5$		—H	—H	$-COOCHCOOC_{12}H_{25}$ | CH_3	—H
Y-43	(t)C_4H_9—	$-CH_3$		—H	—H	CH_3 | $-CONHC(CH_2)_2COO$—  | CH_3	—H
Y-44	(t)C_4H_9—	$-CH_3$		—H	$-CONH(CH_2)_4NHSO_2CHC_4H_9$ | CH_3	$-OCH_3$	—H
Y-45	(t)C_4H_9—	$-CH_3$		—H	—H	$-CONH$— $-SO_2NHC_{12}H_{25}$	—H

NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-46	(t)C_4H_9-	$-CH_3$		-H	-H		-H
Y-47	(t)C_4H_9-	$-CH_3$		-H	-H		-H
Y-48		$-C_2H_5$		-H	-H		-H
Y-49	(t)C_4H_9-			-H	-H		-H
Y-50		$-CH_3$		-H	-H		-H



NO.	R_1	R_2	Z	3-position	4-position	5-position	6-position
Y-51	(iso)C_3H_7-	$-C_4H_9$		-H	-H		-H
Y-52		$-CH_3$		-H	-H	$-NHCO(CH_2)_{10}COOC_2H_5$	-H
Y-53		$-CH_3$		-H	-H		-H
Y-54		$-CH_3$		-H	-H		-H
Y-55	(t)C_4H_9-	$-C_{16}H_{33}$		-H	-H	$-SO_2NHCOC_2H_5$	-H
Y-56	(t)C_4H_9-	$-CH_3$		-H	-H	$-NHCOCH_2CH_2NHCOOC_{12}H_{25}$	-H

As cyan dye forming couplers used in a red-sensitive emulsion layer of the silver halide color photographic light-sensitive material of the invention, naphthol-type couplers and phenol-type couplers are preferably used.

Compounds such as dye forming couplers for the silver halide color photographic light-sensitive material of the invention are usually dissolved in a high boiling organic solvent having a boiling point higher than about 160 °C or in a water-insoluble polymer, using a low boiling and/or water-soluble organic solvent in combination if necessary, the solution is dispersed in a hydrophilic binder such as aqueous gelatin solution with the aid of surfactants, and then the dispersion obtained is added in an objective hydrophilic colloid layer. A process to remove the low boiling solvent may be provided after or in the course of dispersing.

It is desirable that the high boiling organic solvent be a compound having a dielectric constant not more than 6.5. Suitable ones are esters such as phthalaters and phosphates, amides of organic acids, ketones and hydrocarbons each having a dielectric constant not more than 6.5. It is more desirable that the high boiling organic solvent be a compound having a dielectric constant not more than 6.5 and not less than 1.9 and a vapor pressure not more than 0.5 mmHg at 100 °C. Among the solvent exemplified above, phthalates and phosphates are preferred, and dialkyl phthalates containing alkyl groups having 9 or more carbon atoms are particularly preferred. Such a high boiling organic solvent may be a mixture of two or more kinds.

The dielectric constant referred to in the invention is a dielectric constant at 30 °C.

These high boiling organic solvents are used generally in an amount of 0 to 400%, preferably 10 to 100% by weight of couplers.

As the silver halide contained in a photographic light-sensitive material of the invention, there may be used any of silver bromide, silver iodobromide, silver iodochloride, silver chlorobromide and silver chloride which are commonly used in silver halide emulsions.

However, it is preferable that silver halide grains used in the invention be a silver chlorobromide having a silver chloride content of not less than 90 mol%, a silver, bromide content of not more than 10 mol% and a silver iodide content of not more than 0.5 mol%. And a silver chlorobromide having a silver bromide content of 0.1 to 2 mol% is particularly preferred.

Said silver halide grains may be used aingly or in combination with other silver halide grains different in composition. Further, silver halide grains containing not less than 90 mol% of silver chloride can be jointly used.

In a silver halide emulsion layer containing silver halide grains having a silver chloride content of not less than 90 mol%, silver halide grains having a silver chloride content of not less than 90 mol% amount to not less than 60% by weight, preferably not less than 80% by weight of the total silver halide grains contained in said emulsion layer.

Silver halide emulsions used in the invention may be chemically sensitized by the sulfur sensitization method, selenium sensitization method, reduction sensitizing method or precious metal sensitizing method.

Silver halide emulsions used in the invention may be spectrally sensitized to desired wavelength regions with dyes known as sensitizing dyes in the art.

The silver halide photographic light-sensitive material of the invention may contain, in its hydrophilic colloid layers such as protective layer and intermediate layers, UV absorbents, to prevent fogging caused by discharge due to frictional electrification of the light-sensitive material and to prevent deterioration in dye images caused by ultraviolet rays.

In the silver halide photographic light-sensitive material of the invention, there may be provided auxiliary layers such as a filter layer, antihalation layer and/or anti-irradiation layer. These auxiliary layers and/or emulsion layers may contain a dye which is washed away from the color light-sensitive material, or bleached out, in the developing process.

To silver halide emulsion layers and/or other hydrophilic colloid layers of the silver halide light-sensitive material of the invention may be added a matting agent, for purposes of reducing the gloss of light-sensitive material, enhancing retouchability, and preventing sticking between light-sensitive materials.

The silver halide photographic light-sensitive material of the invention may contain a lubricant for a reduced sliding friction.

In the silver halide photographic light-sensitive material of the invention may be used an antistatic agent as a preventing measure against electrification. Such an antistatic agent may be contained in an antistatic layer provided on a support in reverse to the emulsion layer side, or in emulsion layers and/or a protective colloid layer other than emulsion layers provided on the side on which emulsion layers are formed.

In photographic emulsion layers and/or other hydrophilic colloid layers of the light-sensitive material according to the invention, various kinds of surfactants may be employed in order to enhance compatibility with a coating solution, antistatic property, sliding capability, emulsification and dispersion, anti-sticking property and photographic characteristics such as developing property, contrast and sensitizing property.

The silver halide light-sensitive materials of the invention may be coated on a support, after subjecting the support to a surface treatment such as corona discharge, ultraviolet irradiation or flame treatment, directly or via a subbing layer. As the subbing layer one or two layers may be formed in order to improve adhesive property at the support's surface, antistatic property, dimensional stability, abrasion resistance, hardness, antihalation property, rubbing characteristics and/or other characteristics.

In coating a photographic light-sensitive material with a silver halide emulsion of the invention, a thickener may be used in the emulsion to improve the coatability. As the coating method, extrusion coating and curtain coating are particularly useful for their capability of simultaneous multilayer coating.

In the invention, color developing agents used in color developers are conventional ones widely used in various coupler photographic processes.

In the invention, the color developing process may be directly followed by the process with a processing solution having a bleaching capability, or said bleaching-capable processing solution may have a fixing capability concurrently, the so-called bleach-fixer. In said bleaching process, metal complex salts of organic acids are used as bleaching agents.

EXAMPLES

Example 1

A paper stock was prepared by mixing, in a refiner, 20% of a needle-leaf bleached sulfite pulp beated to freeness 250 mℓ of Canadian Standard (JIS P-8121-76) and 80% of a broad-leaf bleached kraft pulp beated to freeness 280 mℓ of the above standard.

Additives for paper were added thereto in amounts shown below per absolute dry weight of the pulp.

Cationic starch	2.0%
Alkyl ketenedimer resin	0.4%
Anionic polyacryl amide	0.1%
Polyamide-polyamine epichlorohydrin resin	0.7%
Sodium hydroxide	to adjust the pH to 7.5

The above paper stock containing the additives was formed into a sheet on a Fourdrinier machine, and the sheet obtained was subjected to size pressing and machine calendering to obtain a raw paper having a basis weight of 170 g/m^2, a bulk density of 1.0 and a moisture content of 8%.

In size pressing, a sizing solution, which was prepared by dissolving a 2:1 mixture of carboxyl-modified PVA and sodium chloride in water at a concentration of 5%, was coated on both sides of the paper sheet in a coating weight of 2.2 g/m^2.

The raw paper prepared as above was subjected to corona discharge, and then a 35 μm-thick polyolefine resin coating layer was formed thereon by extrusion coating of high density polyethylene (specific gravity: 0.94, melt index: 6.8) containing anatase-type titanium dioxide and a fluorescent brightener in amounts shown in Table 2, on the reverse side thereof was formed a polyethylene resin coating layer by co-extrusion coating of polyethylene containing no titanium dioxide at 280 °C. The laminated product thus obtained was pressed against a cleaning roll having a smooth face of 20 °C by applying a line pressure of 20 kg/cm, so that a support for photographic printing paper was prepared.

Then, a multilayered silver halide color photographic light-sensitive material was prepared by forming the following layers on the support's polyolefine resin coating layer containing titanium dioxide and a fluorescent brightener. The coating solutions used were prepared in the following procedures.

Coating solution for 1st layer

There were dissolved 26.7 g of yellow coupler Y-3, 10.0 g of image stabilizer ST-1, 6.67 g of image stabilizer ST-2 and 0.67 g of antistain agent HQ-1 in 6.67 g of high boiling solvent DNP and 60 mℓ of ethyl acetate, the solution was added to 220 mℓ of a 10% aqueous gelatin containing 7 mℓ of a 20% surfactant SU-1 solution and emulsified with a supersonic homogenizer to prepare a coupler dispersion. The dispersion was then mixed with a blue-sensitive silver halide emulsion (containing 10 g of silver) prepared in the following manner to obtain a coating solution for the 1st layer.

Coating solutions for the 2nd through 7th layers were prepared in similar manners as in the coating solution for the 1st layer.

As hardeners, H-1 was added in the 2nd and 4th layers, and H-2 was used in the 7th layer. Surfactant SU-2 and SU-3 were employed as coating aids to adjust surface tension.

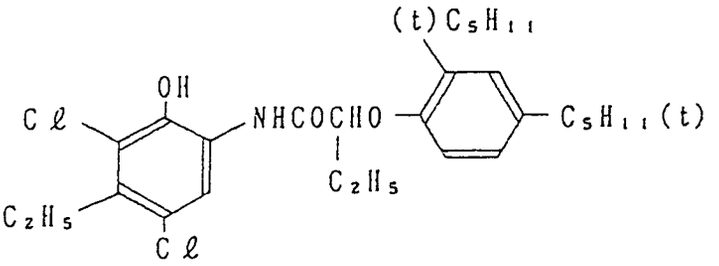
Table 1

Layer	Constituents	Addition amount (g/m^2)
7th layer (protective layer)	gelatin	0.002
	antistain agent HQ-2	0.002
	antistain agent HQ-3	0.004
	antistain agent HQ-4	0.02
	antistain agent HQ-5	0.005
	antistain agent HQ-6	0.002
	antimold F-1	
6th layer (UV absorbing layer)	gelatin	0.40
	UV absorbent (shown in Table 2)	
	antistain agent HQ-5	0.04
	DNP	0.20
	PVP	0.03
	anti-irradiation dye AI-2	0.02
	anti-irradiation dye AI-4	0.01
5th layer (red-sensitive layer)	gelatin	1.30
	red-sensitive silver chlorobromide emulsion Em-R	0.21
	cyan coupler C-1	0.17
	cyan coupler C-2	0.25
	dye image stabilizer ST-1	0.20
	antistain agent HQ-1	0.01
	HBS-1	0.20
	DOP	0.20
4th layer (UV absorbing layer)	gelatin	0.94
	UV absorbent (shown in Table 2)	
	antistain agent HQ-5	0.10
	DNP	0.40

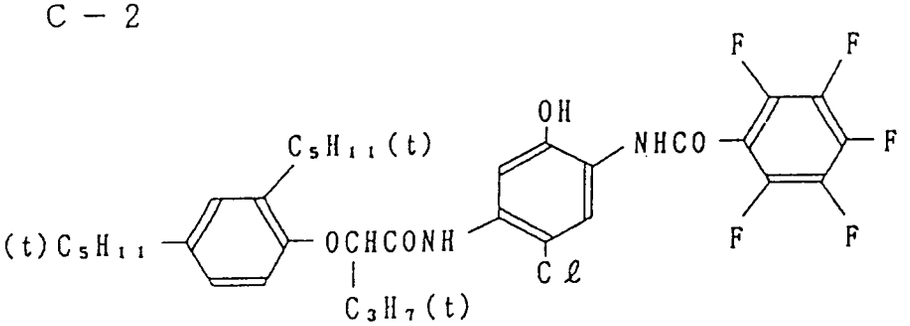
Layer	Constituents	Addition amount (g/m^2)
3rd layer (green-sensitive layer)	gelatin	1.40
	green-sensitive silver chlorobromide emulsion Em-G	0.17
	magenta coupler (shown in Table 2)	
	dye image stabilizer ST-3	0.20
	dye image stabilizer ST-4	0.17
	DIDP	0.13
	DBP	0.13
	anti-irradiation dye AI-1	0.01
2nd layer (intermediate layer)	gelatin	1.20
	antistain agent HQ-2	0.03
	antistain agent HQ-3	0.03
	antistain agent HQ-4	0.05
	antistain agent HQ-5	0.23
	DIDP	0.06
	antimold	0.002
1st layer (blue-sensitive layer)	gelatin	1.20
	blue-sensitive silver chlorobromide emulsion Em-B	0.26
	yellow coupler Y -3	0.80
	dye image stabilizer ST-1	0.30
	dye image stabilizer ST-2	0.20
	antistain agent HQ-1	0.02
	anti-irradiation dye AI-3	0.01
	DNP	0.20
Support	polyethylene laminated paper	

Notes: addition amounts of silver halide emulsions are shown in amounts of silver present.

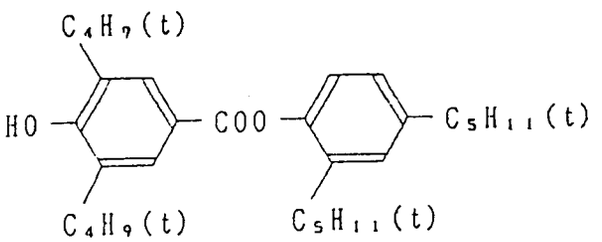
C − 1



C − 2



S T − 1



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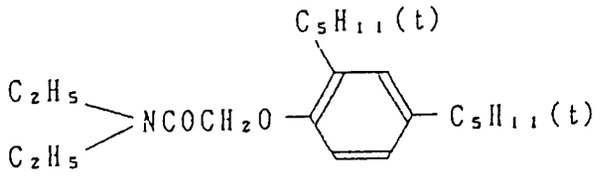

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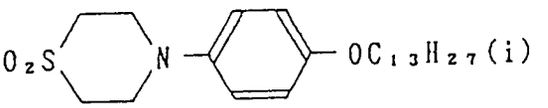
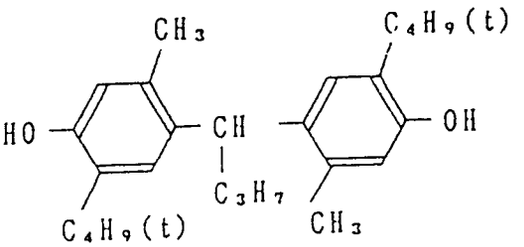
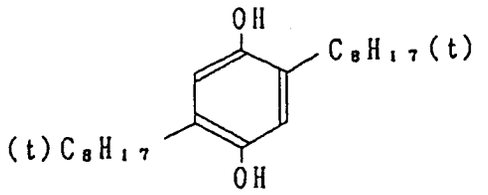


S T − 4

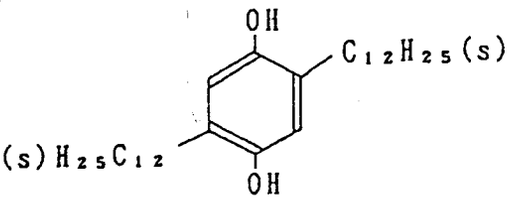


DBP : dibutyl phthalate
DOP : dioctyl phthalate
DNP : dinonyl phthalate
DIDP: diisodecyl phthalate
PVP : polyvinyl pyrrolidone

HQ－1


OH
C8H17(t)
(t)C8H17
OH

HQ－2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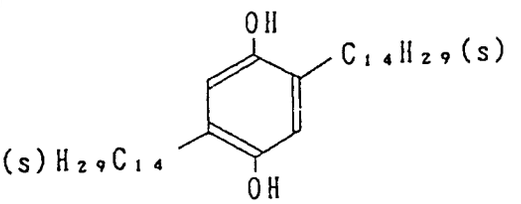
C12H25(s)
(s)H25C12
OH

HQ－3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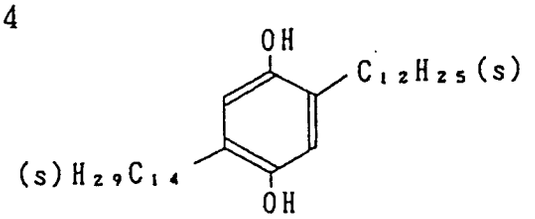
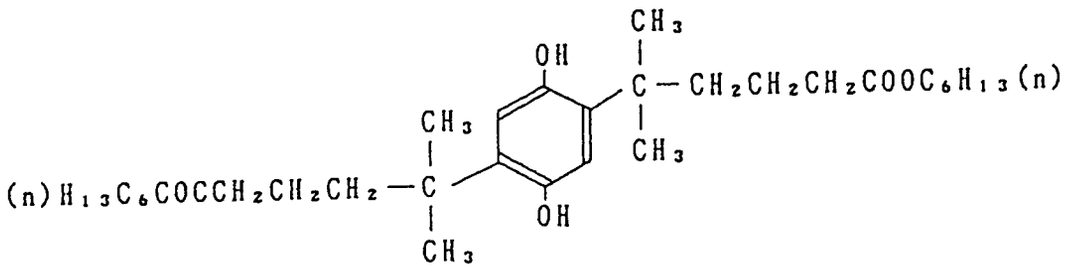
(s)H29C14
OH

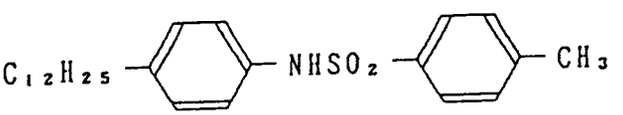
HQ－4



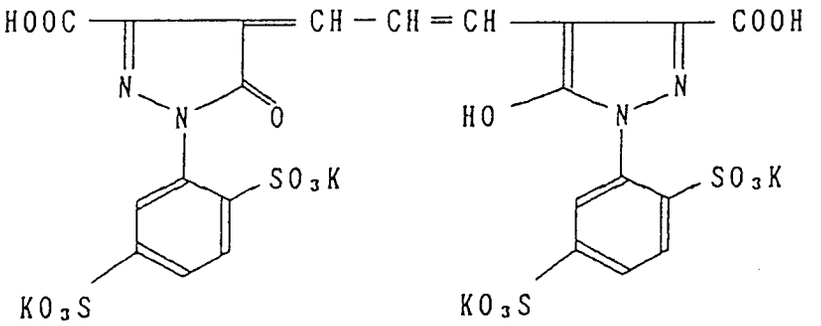
HQ－5



HBS－i



A I − 1



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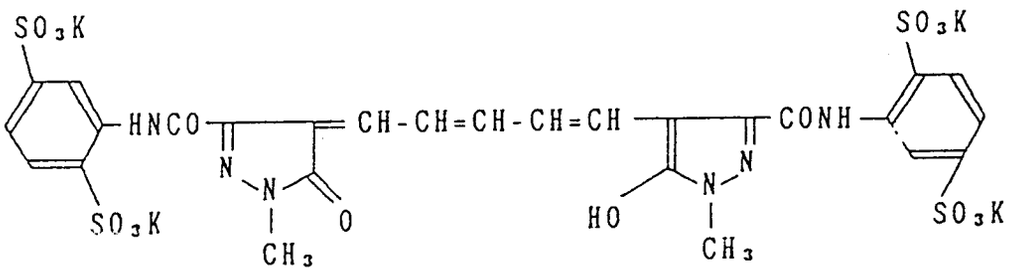

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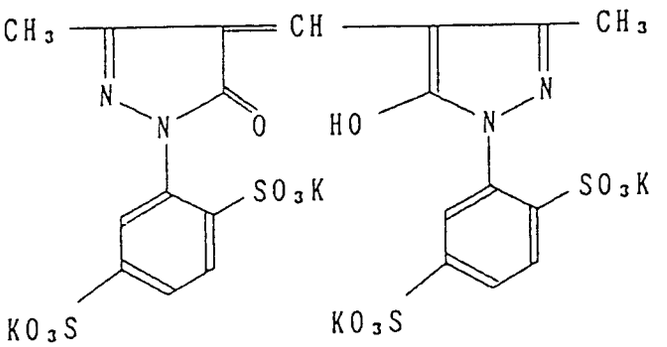
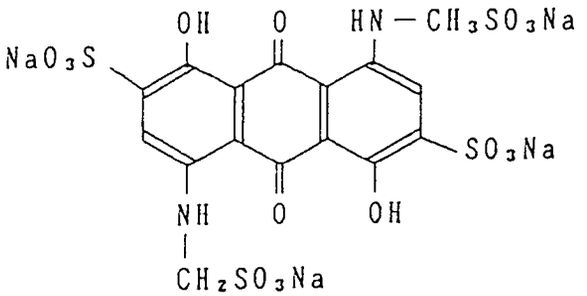
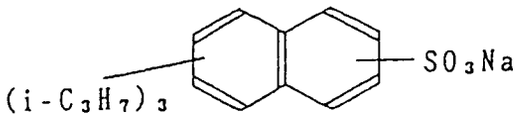


AI－4



SU－1



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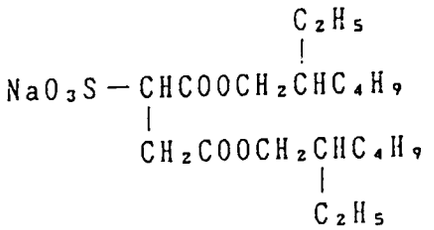
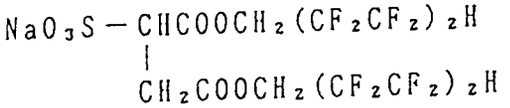
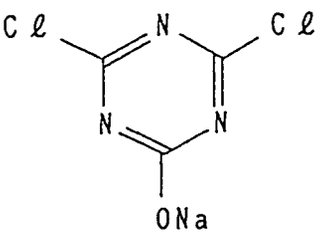


SU－3

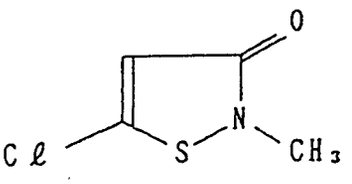


H − 1

H − 2



F − 1



Preparation of blue-sensitive silver halide emulsion

The following solutions A and B were simultaneously added over a period of 30 minutes to 1,000 mℓ of a 2%-aqueous gelatin maintained at 40 °C, while keeping the pAg and pH at 6.5 and 3.0, respectively. Further, the following solutions C and D were simultaneously added thereto over a period of 180 minutes, while controlling the reaction liquor at pAg 7,3 and pH 5.5. In the addition, the pAg was controlled in the manner described in Japanese Pat. O.P.I. Pub. No. 45437/1984, and the pH was controlled with an aqueous solution of sulfuric acid or sodium hydroxide.

Solution A	
Sodium chloride	3.42 g
Potassium bromide	0.03 g
Water to make	200 mℓ

Solution B	
ilver nitrate	10 g
Water to make	200 mℓ

Solution C	
Sodium chloride	102.7 g
Potassium bromide	1.0 g
Water to make	600 mℓ

Solution D	
Silver nitrate	300 g
Water to make	600 mℓ

After addition, the product was subjected to desalination using a 5%-aqueous solution of Demol N (product of Kao Atlas) and a 20% aqueous solution of magnesium sulfate, and then mixed with an aqueous gelatin. The obtained was a monodispersed cubic emulsion EMP-1 having an average grain size of 0.85 μm, a distribution variation coefficient ($\sigma/\bar{r}$) of 0.07 and a silver chloride content of 99.5 mol%. The above σ and $\bar{r}$ are standard deviation of grain size distribution and average grain size of silver halide grains of the emulsion, respectively.

Then, emulsion EMP-1 was subjected to chemical sensitization for 90 minutes at 50 °C with the following compounds to obtain a blue-sensitive silver halide emulsion Em-B.

Sodium thiosulfate	0.8 mg/mol AgX
Chloroauric acid	0.5 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye BS-1	4×10^{-4} mol/mol AgX
Sensitizing dye BS-2	1×10^{-4} mol/mol AgX

Preparation of green-sensitive silver halide emulsion

There was prepared a monodispersed cubic emulsion EMP-2 having an average grain size of 0.43 μm, a distribution variation coefficient ($\sigma/\bar{r}$) of 0.08 and a silver chloride content of 99.5 mol%, in the same procedure as in EMP-1 except that the addition time of solutions A and B as well as that of solutions C and D were changed.

EMP-2 was chemically sensitized for 120 minutes at 55 °C using the following compounds to obtain a green-sensitive silver halide emulsion Em-G.

Sodium thiosulfate	1.5 mg/mol AgX
Chloroauric acid	1.0 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye GS-1	4×10^{-4} mol/mol AgX

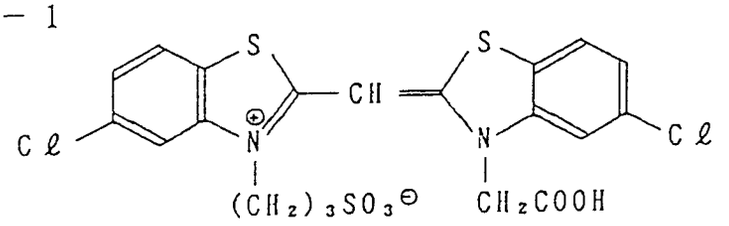
Preparation of red-sensitive silver halide emulsion

There was prepared a monodispersed cubic emulsion EMP-3 having an average grain size of 0.50 μm, a distribution variation coefficient ($\sigma/\bar{r}$) of 0.08 and a silver chloride content of 99.5 mol%, in the same procedure as in EMP-1 except that the addition time of solutions A and B as well as that of solutions C and D were changed.

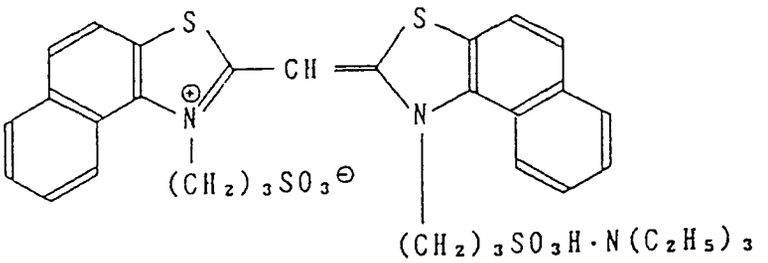
Subsequently, EMP-3 was chemically sensitized for 90 minutes at 50 °C using the following compounds to obtain a red-sensitive silver halide emulsion Em-R.

Sodium thiosulfate	1.8 mg/mol AgX
Chloroauric acid	2.0 mg/mol AgX
Stabilizer STAB-1	6×10^{-4} mol/mol AgX
Sensitizing dye RS-1	1×10^{-4} mol/mol AgX

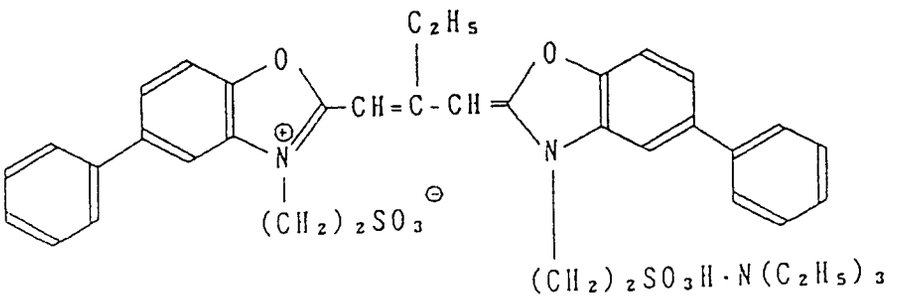
BS－1



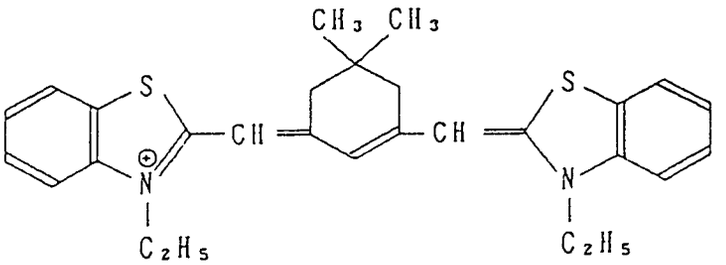
BS－2



GS－1



R S − 1



S T A B − 1

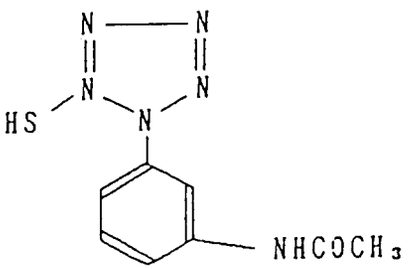
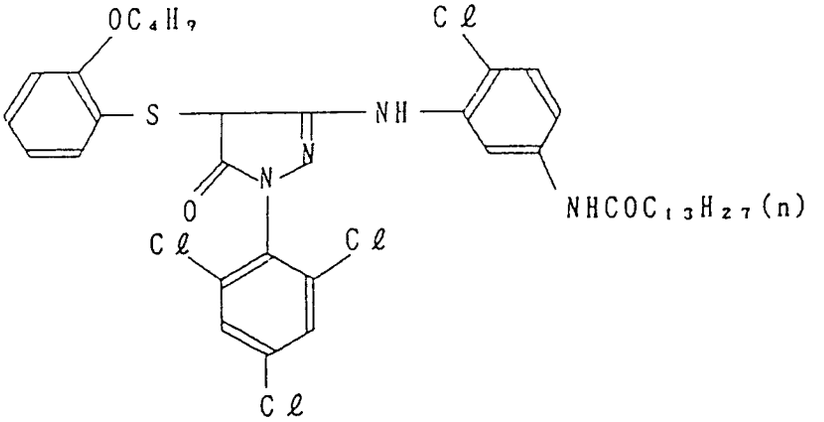


Table 2

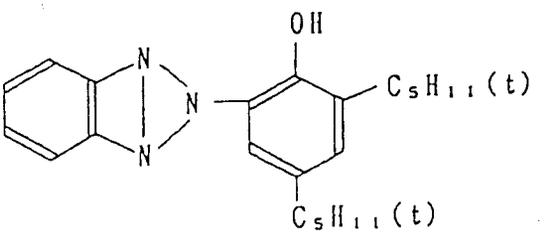
Sample No.	Polyolefine resin coating layer: Titanium dioxide conc. (%)	Polyolefine resin coating layer: Fluorescent brightener Kind	Polyolefine resin coating layer: Fluorescent brightener Conc. (%)	3rd layer: Magenta coupler Kind	3rd layer: Magenta coupler Coating weight (g/m2)	4th layer: UV absorbent Kind	4th layer: UV absorbent Coating weight (g/m2)	6th layer: UV absorbent Kind	6th layer: UV absorbent Coating weight (g/m2)
1	10	-	0	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
2	15	-	0	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
3	15	(1)-3	0.005	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
4 Invention	15	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
5 Invention	15	(1)-3	0.15	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
6	15	(1)-3	0.3	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
7	10	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
8 Invention	13	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
9 Invention	17	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
10 Invention	20	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
11	25	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
12 Invention	15	(1)-2	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
13 Invention	15	(2)-7	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
14 Invention	15	(1)-3	0.05	(4)-28	0.23	UV-2L	0.75	UV-7L	0.38
15 Invention	15	(1)-2	0.05	(4)-10	0.23	UV-2L	0.75	UV-7L	0.38
16 Invention	15	(1)-2	0.05	(4)-20	0.23	UV-2L	0.75	UV-7L	0.38
17	15	(1)-2	0.05	M-1	0.23	UV-2L	0.75	UV-7L	0.38
18 Invention	15	(1)-2	0.05	(4)-28	0.23	UV-a	0.75	UV-a	0.38

Notes: In sample No. 14, the following Y-a was used as the yellow coupler.

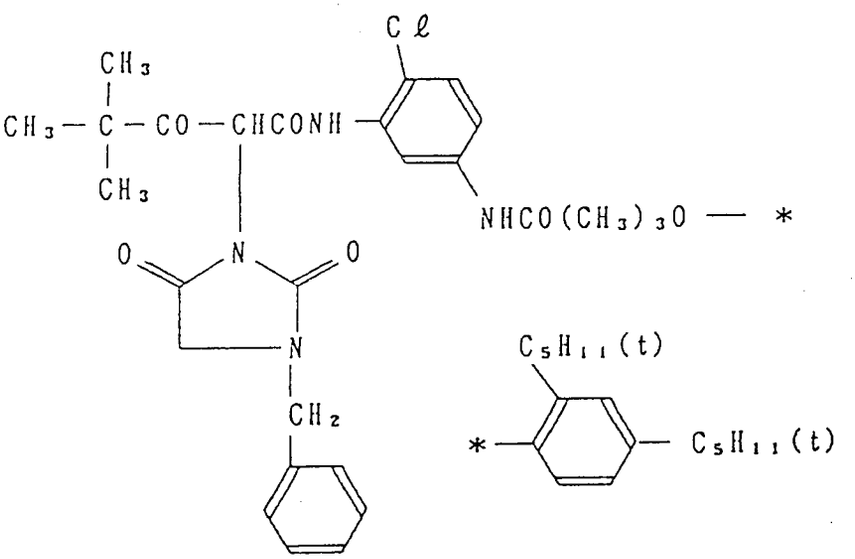
M − 1



U V − a



Y − a



Each of 18 samples (Nos. 1 through 18) prepared as above was subjected to the processing shown below and then evaluated for whiteness, coloring with aging and sharpness of images according to the method described later. The results are summarized in Table 3.

Processing	Temperature	Time
Color developing	35.0 ±0.3 °C	45 sec
Bleach-fixing	35.0 ±0.5 °C	45 sec
Stabilizing	30 - 34 °C	90 sec
Drying	60 - 80 °C	60 sec

Color developer	
Demineralized water	800 mℓ
Triethanolamine	10 g
N,N-diethylhydroxylamine	5 g
Potassium bromide	0.02 g
Potassium chloride	2 g
Potassium sulfite	0.3 g
1-hydroxylethylidene-1,1-diphosphonic acid	1.0 g
Ethylenediaminetetracetic acid	1.0 g
Disodium catechol-3,5-diphosphonate	1.0 g
N-ethyl-N-β-methanesulfonamido-ethyl-3-methyl-4-aminoaniline sulfate	4.5 g
Fluorescent brightener (4,4'-diaminostilbene-sulfonic acid derivative)	1.0 g
Potassium carbonate	27 g

Water is added to make up to 1 liter, then the pH is adjusted to 10.10.

Bleach-fixer	
Ammonium ferric ethylenediaminetetracetate dihydrate	60 g
Ethylenediaminetetracetic acid	3 g
Ammonium thiosulfate (70% aqueous solution)	100 mℓ
Ammonium sulfite (40% aqueous solution)	27.5 mℓ

Water is added to make up to 1 liter, then the pH is adjusted to 5.7 with potassium carbonate or glacial acetic acid.

Stabilizer	
5-Chloro-2-methyl-4-isothiazoline-3-one	1.0 g
Ethylene glycol	1.0 g
1-Hydroxyethylidene-1,1-diphosphonic acid	2.0 g
Ethylenediaminetetracetic acid	1.0 g
Aqueous ammonia (20% solution)	3.0 g
Fluorescent brightener (4,4'-diaminostilbenesulfonic acid derivative)	1.5 g

Water is added to make up to 1 liter, then the pH is adjusted to 7.0 with sulfuric acid or potassium hydroxide.

(1) Whiteness

The whiteness of a processed sample's white portion was visually evaluated.

(2) Coloring with aging

The samples were allowed to stand for 3 months at 30 °C and 50% RH and then evaluated for the whiteness as in (1).

(3) A resolution testing chart was printed on each sample using blue, green and red lights. After developing each sample, yellow, magenta and cyan images obtained were subjected to densitometry with a microphotometer. The sharpness was given as the average of values shown by the following expression:

$$\text{Sharpness of a large pattern (\%)} = \frac{\text{(maximum density - minimum density) of a contact printed image of 3 lines/mm}}{\text{(maximum density - minimum density) of a large area portion}}$$

The expression means that the sharpness becomes larger as the value increases.

Table 3

Sample No.	Whiteness (visual check)	Coloring with aging (visual check)	Sharpness (average of exposures using blue, green and red lights)
1	C	C	38
2	C	C	83
3	C	C	80
4 Invention	A	A	75
5	A	A	71
6	C	C	60
7	A	A	37
8 Invention	A	A	55
9 Invention	A	A	82
10 Invention	B	B	85
11	C	C	86
12 Invention	A	A	78
13 Invention	A	A	68
14 Invention	B	B	75
15 Invention	A	B	77
16 Invention	A	B	75
17	B	C	77
18 Invention	B	B	70

Criteria for judgement

Whiteness, coloring with aging

A: good

B: lowest allowable level in practical use

C: not allowable

Sharpness

More than 60%: good

50 to 60%: lowest allowable level in practical use

Less than 50%: not allowable

It is understood from the results shown in Table 3 that only the samples of the invention, Nos. 4, 8-10, 12-16, and 18, satisfy all the properties.

Example 2

Supports for photographic printing paper shown in Table 5 were prepared in similar manners as in Example 1. Then, the following layers were formed, on each of the supports, on the side provided with the polyethylene coating layer containing titanium dioxide and a fluorescent brightener to obtain multilayered silver halide color photographic light-sensitive materials. Coating solutions used were prepared as follows:

Coating solution for 1st layer

There were dissolved 19.1 g of yellow coupler Y-3 and 4.4 g of image stabilizer ST-5 in 27.2 mi of ethyl acetate and 7.7 mℓ of high boiling organic solvent Solv-1. And the solution was emulsified in 185 mℓ of a 10% aqueous gelatin containing 8 mℓ of a 10% aqueous solution of sodium dodecylbenzene sulfonate. The dispersion was then mixed with a blue-sensitive silver halide emulsion prepared in the following manner to obtain a coating solution for the 1st layer.

Coating solutions for the 2nd through 7th layers were prepared in similar manners as in the coating solution for the 1st layer.

As a gelatin hardener, H-2 of Example 1 was used in each layer.

Layer	Constituent	Addition amount (g/m^2)
7th layer (protective layer)	gelatin	1.26
	acryl-modified polyvinyl alcohol copolymer (modification degree: 17%)	0.17
	liquid paraffin	0.03
6th layer (UV absorbing layer)	gelatin	0.62
	UV absorbent (shown in Table 5)	
	high boiling organic solvent Solv-3	0.08
5th layer (red-sensitive layer)	gelatin	1.26
	red-sensitive silver chlorobromide emulsion (silver chloride content:99.5%)	0.20
	cyan coupler C-1	0.07
	cyan coupler C-3	0.07
	cyan coupler C-4	0.07
	cyan coupler C-5	0.14
	dye image stabilizer ST-6	0.07
	polymer Ply-1	0.17
	high boiling organic solvent Solv-4	0.40
	anti-irradiation dye AI-6	0.23
	anti-irradiation dye AI-7	0.02
		0.02
4th layer (UV absorbing layer)	gelatin	1.45
	UV absorbent (shown in Table 5)	
	antistain agent HQ-1	0.05
	high boiling organic solvent Solv-3	0.24

Layer	Constituent	Addition amount (g/m^2)
3rd layer (green-sensitive layer)	gelatin	1.62
	green-sensitive silver chlorobromide emulsion (silver chloride content:98.5%)	0.13
	magenta coupler (shown in Table 5)	
	dye image stabilizer ST-7	0.20
	dye image stabilizer ST-8	0.02
	dye image stabilizer ST-9	0.03
	dye image stabilizer ST-10	0.01
	high boiling organic solvent Solv-2	0.65
	anti-irradiation dye AI-5	0.01
2nd layer (intermediate layer)	gelatin	0.79
	antistain agent HQ-5	0.08
	high boiling organic solvent Solv-5	0.08
1st layer (blue-sensitive layer)	gelatin	1.65
	blue-sensitive silver chlorobromide emulsion (silver chloride content:98.6%)	0.26
	yellow coupler Y -3	0.83
	dye image stabilizer ST-5	0.19
	high boiling organic solvent Solv-2	0.35
	anti-irradiation dye AI-4	0.01
Support	polyethylene laminated paper	

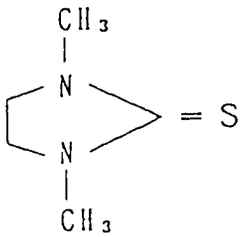
Preparation of blue-sensitive silver halide emulsion

After adding the following solutions A and B to 1,000 mℓ of a 2.5% aqueous gelatin maintained at 58 °C, solutions C and D were simultaneously added thereto over a period of 45 minutes. Ten minutes later, solutions E and F were simultaneously added over a period of 15 minutes. Further, solution G was added thereto and 10 minutes after that, solutions H and I were simultaneously added over a period of 20 minutes. Five minutes after the addition, the reaction liquor was cooled and desalted. After adding water and dispersed gelatin, the pH was adjusted to 6.2. The obtained was a monodispersed silver chlorobromide emulsion EMP-4 having an average grain size of 0.92 μm, a distribution variation coefficient ($\sigma/\bar{r}$) of 0.10 and a silver chloride content of 99.6%.

Solution A	
Sulfuric acid (1N)	20 mℓ

Solution B

The following silver halide solvent (1%) 2 mℓ



Solution C	
NaCl	1.7 g
H_2O to make	140 mℓ

Solution D	
$AgNO_3$	5.0 g
H_2O to make	140 mℓ

Solution E	
NaCl	41.1 g
H_2O to make	320 mℓ

Solution F	
$AgNO_3$	119.5 g
H_2O to make	320 mℓ

Solution G	
BS-3	4×10^{-4} mol
Ethyl alcohol	20 mℓ

Solution H	
KBr	0.35 g
K_2IrCl_6	0.012 g
H_2O to make	50 mℓ

Solution I	
$AgNO_3$	0.5 g
H_2O to make	50 mℓ

The above EMP-4 was subjected to an optimum chemical ripening at 58°C using the following compounds to obtain a blue-sensitive silver halide emulsion.

Triethyl thiourea	1 mg/mol AgX
Stabilizer STAB-2	3.8×10^{-4} mol/mol AgX

Preparation of green-sensitive silver halide emulsion

There was prepared a monodispersed silver chlorobromide emulsion EMP-5 having an average grain size of 0.51 μm, a distribution variation coefficient ($\sigma/\bar{r}$) of 0.78 and a silver chloride content of 98.5%, in the same manner as in EMP-4 except that the addition time of solutions C and D was changed and that solutions E, F, G, H and I were replaced by solutions J, K, L, M and M respectively.

Solution J	
NaCl	40.6 g
H_2O to make	320 mℓ

Solution K	
$AgNO_3$	118.1 g
H_2O to make	320 mℓ

Solution L	
GS-2	3×10^{-4} mol
GS-3	5×10^{-4} mol
Ethyl alcohol	20 mℓ

Solution M	
KBr	1.3 g
K_2IrCl_6	0.024 g
H_2O to make	50 mℓ

Solution N	
$AgNO_3$	1.9 g
H_2O to make	50 mℓ

The above EMP-5 was subjected to an optimum chemical ripening at 58°C using the following compounds to obtain a green-sensitive silver halide emulsion.

Triethyl thiourea	1 mg/mol AgX
Stabilizer STAB-2	5.3×10^{-4} mol/mol AgX

Preparation of red-sensitive silver halide emulsion

There was prepared a monodispersed silver chlorobromide emulsion EMP-6 having an average grain size of 0.60 μm, a distribution variation coefficient ($\sigma/\bar{r}$) of 0.72 and a silver chloride content of 99.5%, in the same manner as in EMP-4 except that the addition time of solutions C and D was changed and that solutions E, F, G, H and I were replaced by solutions O, P, Q, R and S respectively.

Solution O	
NaCl	41.06 g
H_2O to make	320 mℓ

Solution P	
$AgNO_3$	119.4 g
H_2O to make	320 mℓ

Solution Q	
RS-2	7×10^{-5} mol
Ethyl alcohol	20 mℓ

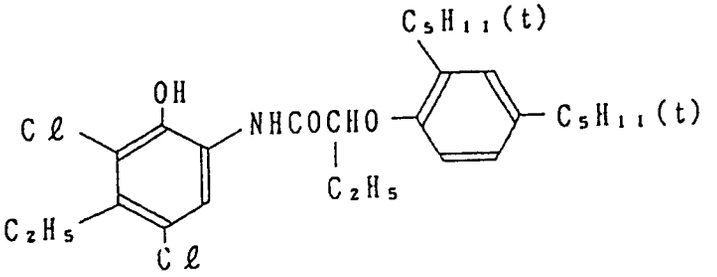
Solution R	
KBr	0.44 g
K_2IrCl_6	0.10 g
H_2O to make	50 mℓ

Solution S	
$AgNO_3$	0.63 g
H_2O to make	50 mℓ

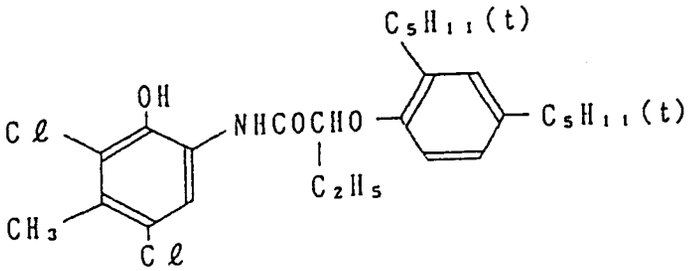
The above EMP-6 was subjected to an optimum chemical ripening at 60°C using the following compounds to obtain a red-sensitive silver halide emulsion.

Triethyl thiourea	1 mg/mol AgX
Stabilizer STAB-2	5.3×10^{-4} mol/mol AgX
Supersensitizer SS-1	2.6×10^{-4} mol/mol AgX

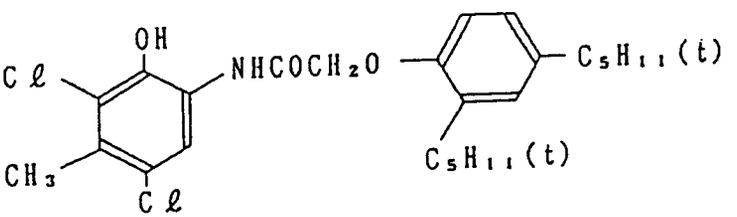
(C − 1)



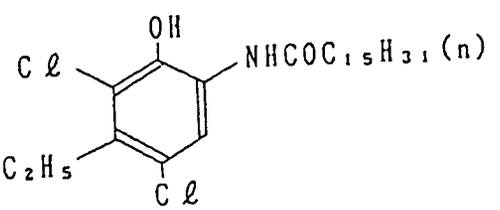
(C − 3)



(C − 4)

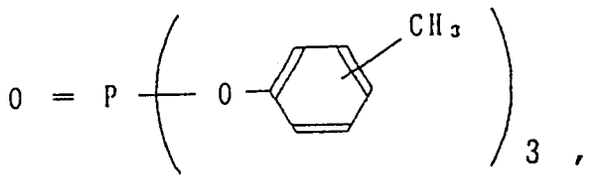


(C − 5)



Solvent Solv-1

a 1:1:2 mixture (weight ratio) of



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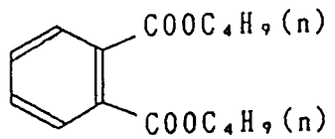

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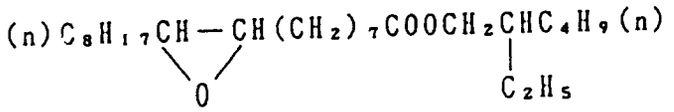
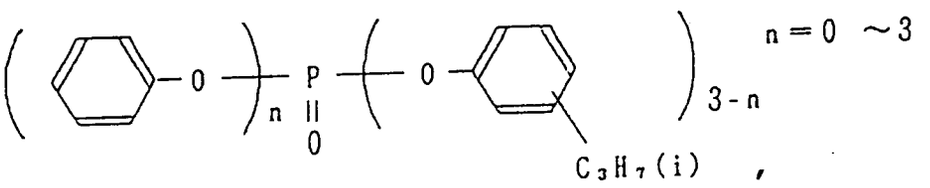
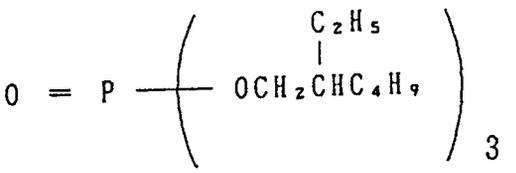


Solvent solv-2

a 2:1:1 mixture (weight ratio) of





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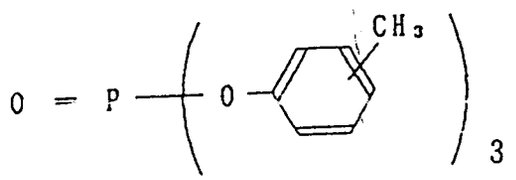
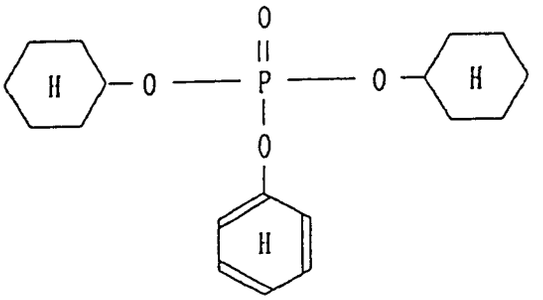


Solvent solv-3

a 5:3:1:1 mixture (weight ratio) of



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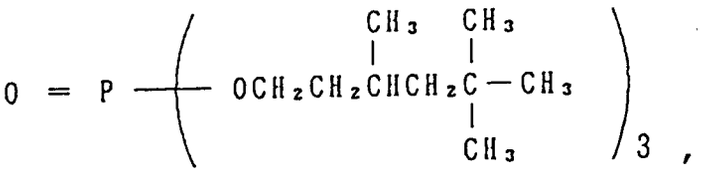

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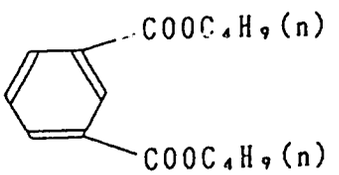
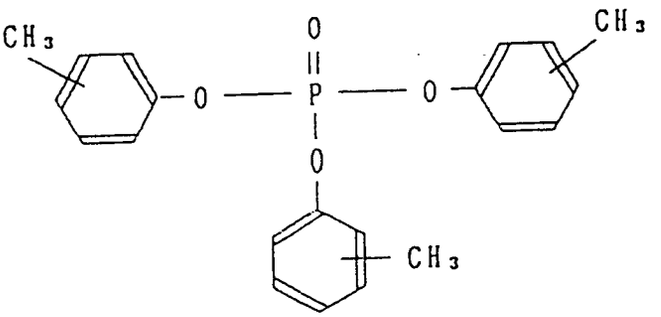
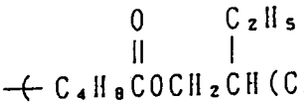


and

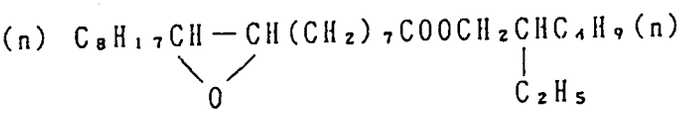


Solvent solv-4

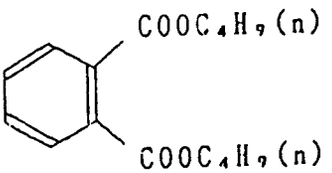
a 3:2 mixture (weight ratio) of



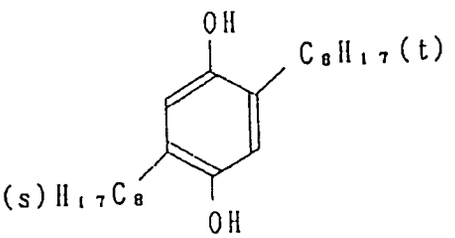
and



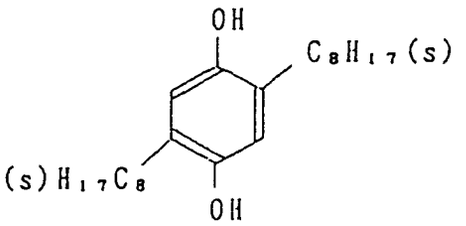
Solvent solv-5



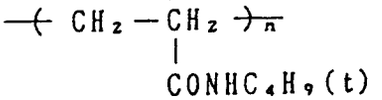
HQ-1



HQ－5

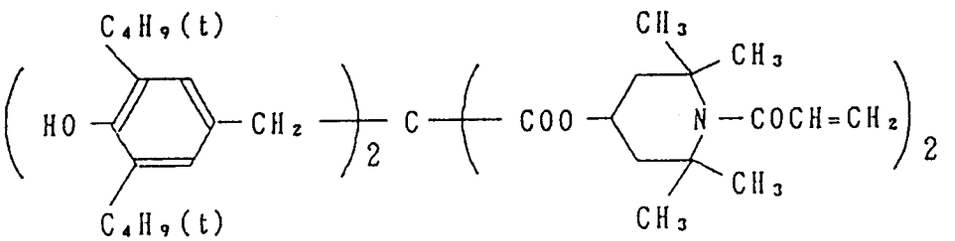


Polymer Ply-1



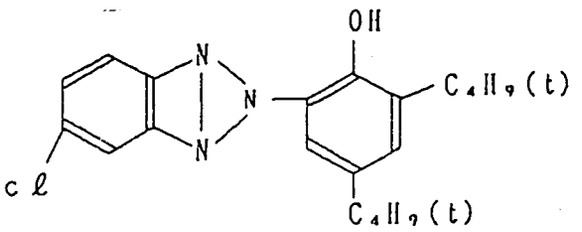
average molecular weight: 80,000

ST－5

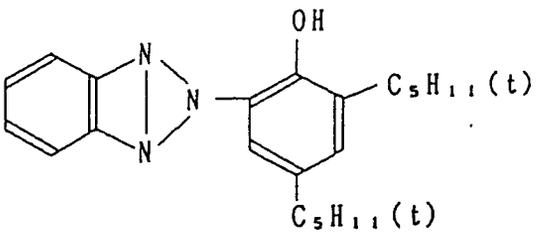


S T − 6

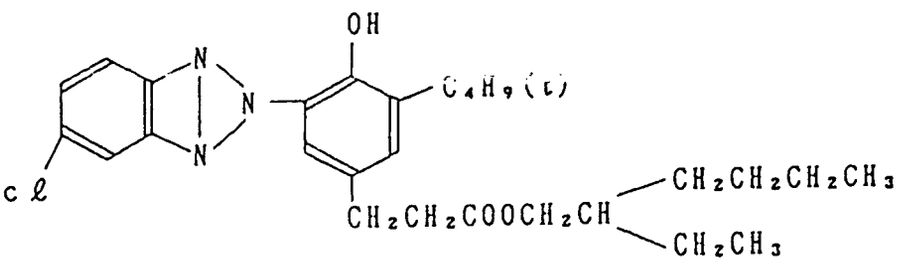
a 8:9:5 mixture (weight ratio) of



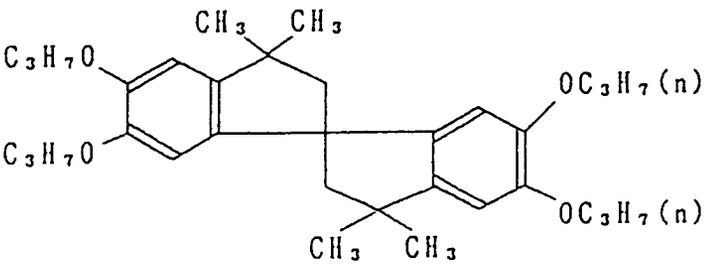
,



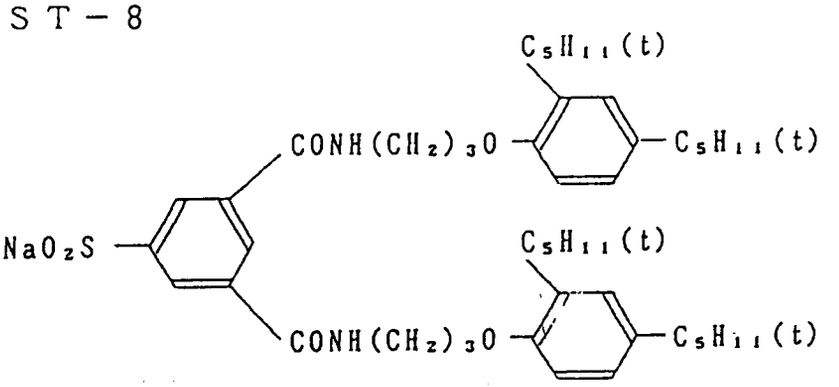
and



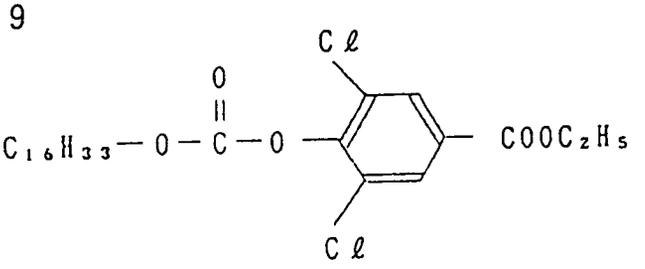
S T − 7



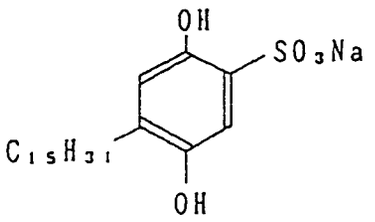
S T − 8



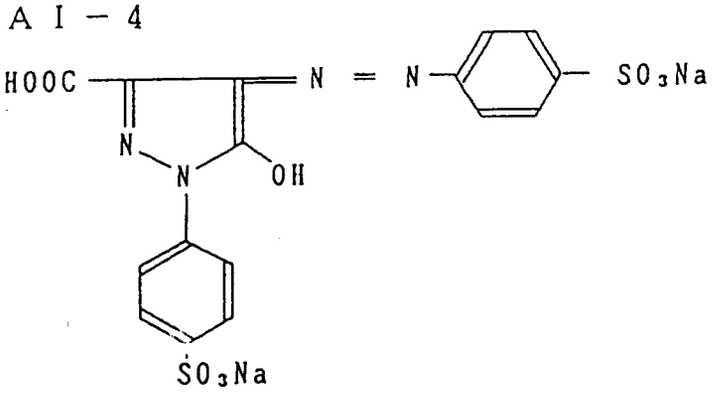
S T − 9



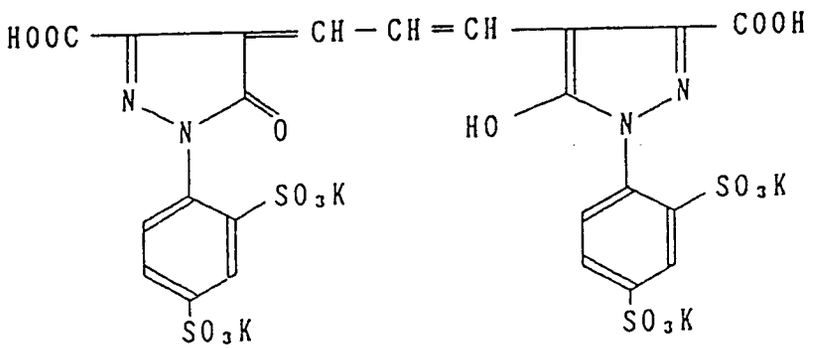
S T − 1 0



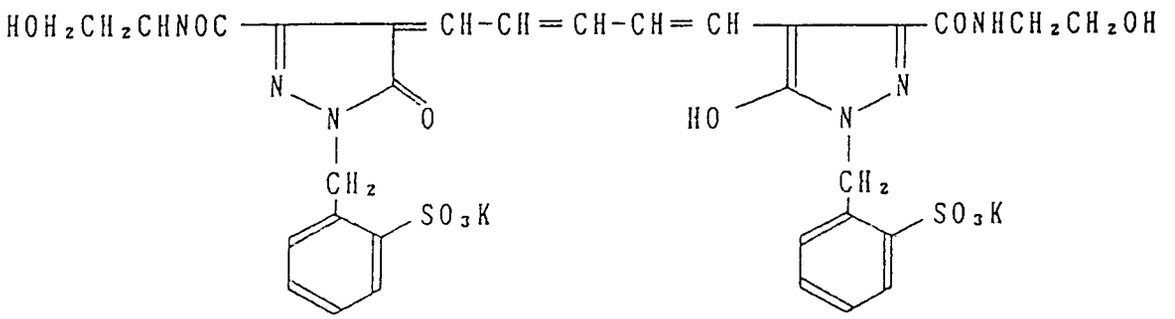
A I − 4



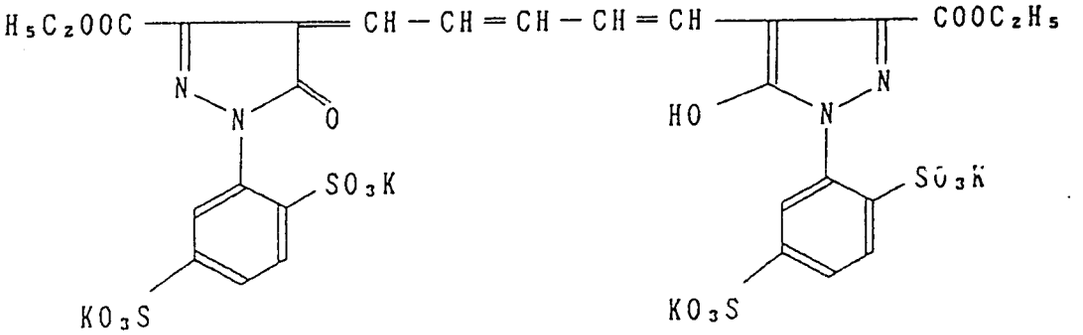
A I − 5



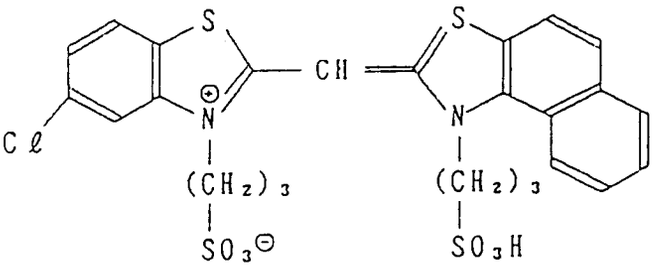
A I − 6



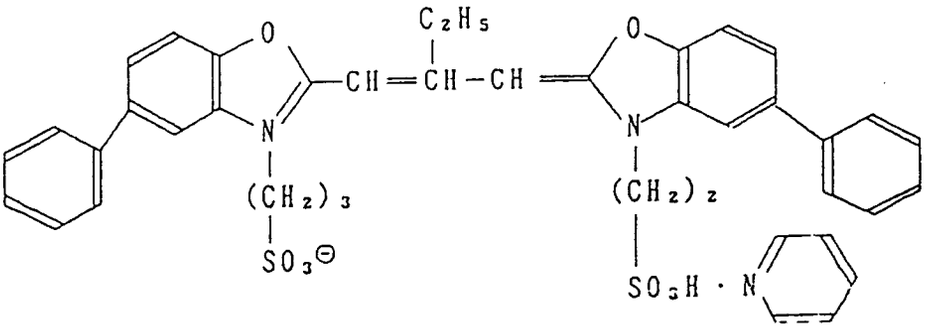
A I − 7



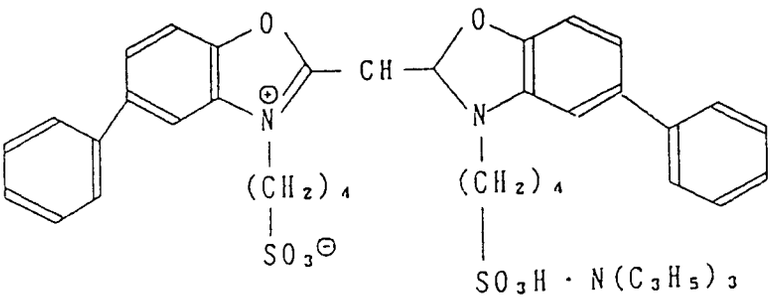
B S − 3



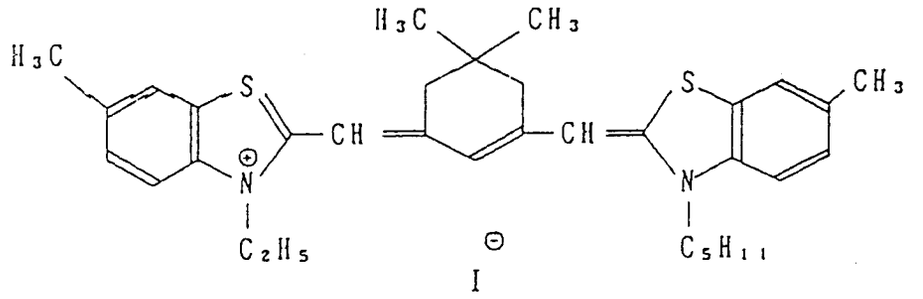
G S − 2



G S − 3

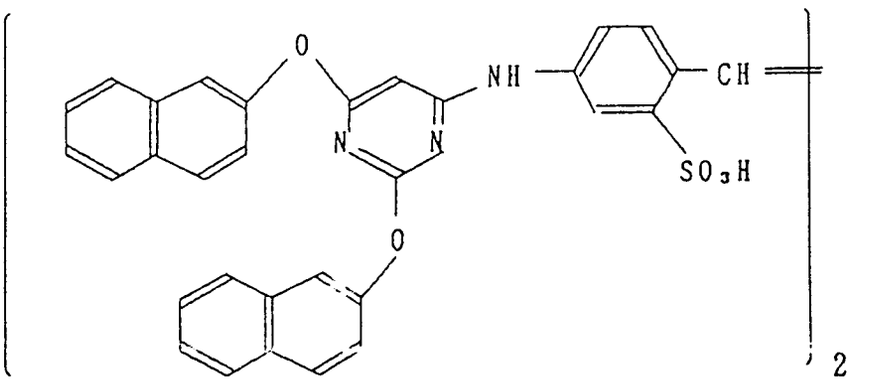


R S − 2



I

S S − 1



S T A B − 2

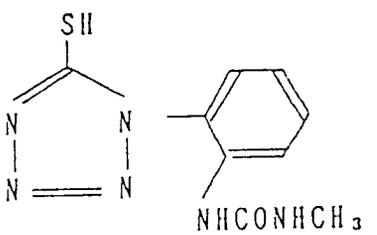


Table 5

Sample No.	Surface polyethylene layer		3rd layer	4th layer	6th layer
	Titanium dioxide conc. (%)	Fluorescent brightener Kind Conc. (%)	Magenta coupler Kind Coating weight (g/m^2)	UV absorbent Kind Coating weight (g/m^2)	UV absorbent Kind Coating weight (g/m^2)
19	15	-	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
20	10	(1)-2 0.05	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
21 Invention	15	(1)-2 0.05	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
22 Invention	15	(1)-2 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
23	15	(1)-2 0.25	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
24 Invention	15	(1)-1 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
25 Invention	15	(1)-3 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
26 Invention	15	(1)-4 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
27 Invention	15	(1)-2 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
28 invention	15	{(1)-1 0.05 (1)-2 0.05 (1)-3 0.05	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
29 Invention	15	(1)-8 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
30 Invention	15	(2)-11 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21
31 Invention	15	(3)-2 0.15	(4)-54 0.32	UV-15L 0.62	UV-15L 0.21

Thirteen kinds of samples prepared as above, Nos. 19-31 were evaluated in the same procedure as in Example 1, the results are summarized in Table 6.

Y − b

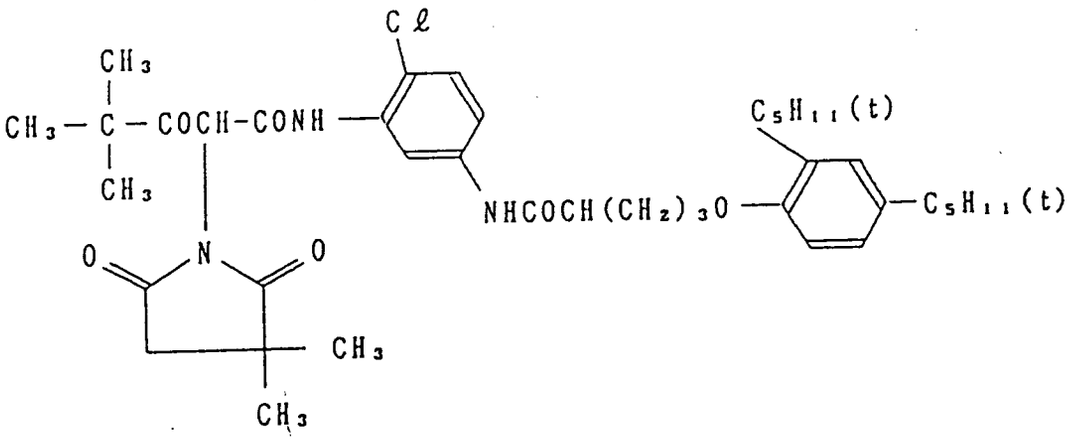


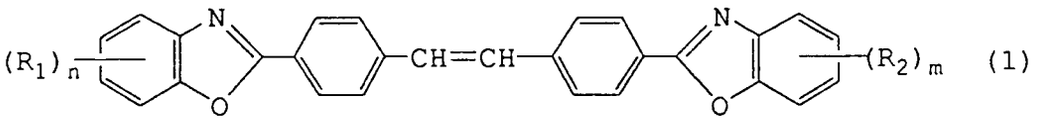
Table 6

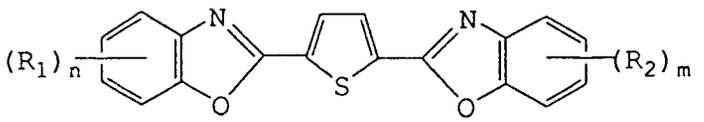
Sample No.	Whiteness (visual check)	Coloring with aging (visual check)	Sharpness (average of exposures using blue, green and red lights)
19	C	C	75
20	A	A	30
21 Invention	A	A	71
22 Invention	A	A	66
23	C	C	55
24 Invention	A	A	69
25 Invention	A	A	67
26 Invention	A	B	65
27 Invention	B	B	64
28 Invention	A	A	85
29 Invention	A	B	68
30 Invention	A	B	65
31 Invention	B	B	69

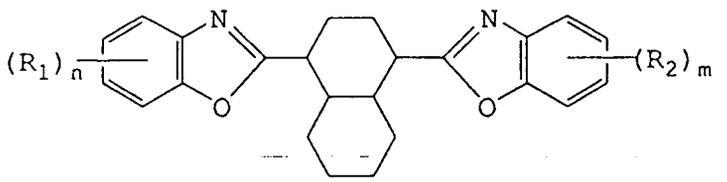
It is understood from the results shown in Table 5 that only the samples of the invention, Nos. 21, 22 and 24-31, satisfy all the properties.

Claims

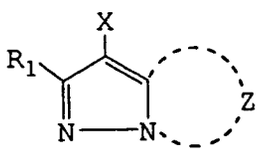
1. A silver halide color photographic light-sensitive material comprising a photographic layer including a blue-sensitive emulsion layer, a green-sensitive emulsion layer and a red-sensitive emulsion layer, coated on one side of a reflecting support which comprises a raw paper coated with a polyolefine resin on both sides thereof, wherein the polyolefine layer provided on the side of said reflective support coated with said emulsion layers contains a compound represented by the following formula 1, 2 or 3 in an amount of 0.01 % to 0.2 % by weight of polyolefine resin and a white pigment in an amount of 13 % to 20 % by weight of polyolefine resin, and said green-sensitive silver halide emulsion layer contains a magenta coupler represented by the following formula M-1:


(1)


(2)


(3)

wherein R_1 and R_2 are each an alkyl group having 1 to 5 carbon atoms, a halogen atom, a hydrogen atom, or an alkoxy group having 1 to 5 carbon atoms; m and n are each an integer of from 1 to 4;

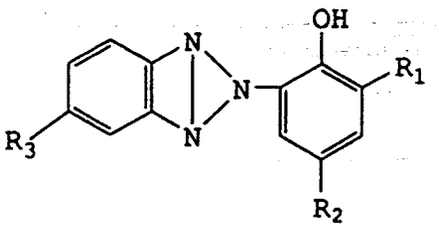

(M-I)

wherein Z is a group of non-metal atoms necessary for forming a nitrogen-containing heterocyclic ring which may have a substituent; X is a hydrogen atom or a substituent capable of splitting of upon reaction with the oxydation product of a color developing agent; and R is a hydrogen atom or a substituent.

2. A light-sensitive material of claim 1, wherein said white pigment is contained in said polyolefine resin layer in an amount of from 15 % to 18 % of said polyolefine resin.

3. A light-sensitive material of claim 1 or 2, wherein said polyolefine resin layer contains a compound represented by formula 1.

4. A light-sensitive material of claim 1, 2 or 3, wherein said photographic layer further includes a non-light-sensitive layer containing a UV absorbent represented by the following formula UV-I which is liquid at an ordinary temperature;

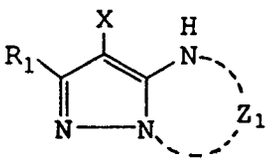


(UV-I)

wherein R_1, R_2 and R_3 are each a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkenyl group, a nitro group or hydroxyl group.

5. A light-sensitive material of claims 1 or 2 to 4, wherein said photographic layer contains a binder in an amount of 6.0 g/m^2 to 7.8 g/m^2 in total.

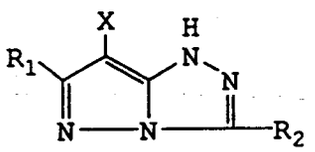
6. A light-sensitive material of claims 1 or 2 to 5, wherein said magenta coupler is represented by the following formula M-VIII;



(M-VIII)

wherein R_1, X and Z_1 are each the same as R, X and Z defined in formula M-I, respectively.

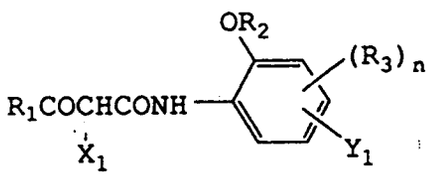
7. A light-sensitive material of claim 6, wherein said magenta coupler is represented by the following formula M-II;



(M-II)

wherein R_1 and R_2, and X are each the same as R and Z defined in formula M-I, respectively.

8. A light-sensitive material of claims 1 or 2 to 7, wherein said blue-sensitive emulsion layer contains a yellow coupler represented by the following formula Y-I;

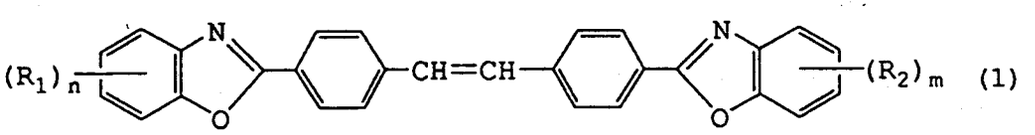


(Y-I)

wherein R_1 is an alkyl group, a cycloalkyl group or an aryl group; R_2 is an alkyl group, a cycloalkyl group, an acyl group or an aryl group; R_3 is a substituent; n is an integer of 0 or 1; Y_1 is an organic group and X_1 is a hydrogen group or a substituent capable of splitting off upon reaction with an oxidation product of a color developing agent.

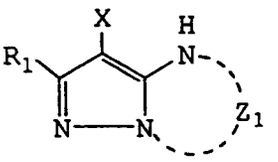
9. A silver halide color photographic light-sensitive material comprising a photographic layer including a blue-sensitive emulsion layer, a green-sensitive emulsion layer, a red-sensitive emulsion layer and a non-light-sensitive layer coated on one side of a reflecting support which comprises a raw paper coated

with a polyolefine resin on both sides thereof, wherein the polyolefine layer provided on the side of said reflective support coated with said photographic layer contains a compound represented by the following formula 1 in an amount of 0.01 % to 0.2 % by weight of polyolefine resin and a white pigment in an amount of 15 % to 18 % by weight of polyolefine resin, said green-sensitive silver halide emulsion layer contains a magenta coupler represented by the following formula M-VIII, said blue-sensitive layer contains a yellow coupler represented by the following formula Y-I, said non-light-sensitive layer contains a UV absorbent represented by the following formula UV-I which is a liquid at an ordinary temperature, and said photographic layer contains a binder in an amount of from 6.0 g/m^2 to 7.8 g/m^2 in total.



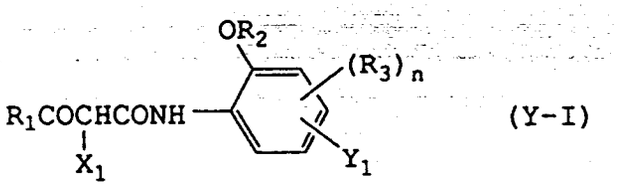
(1)

wherein R_1 and R_2 are each an alkyl group having 1 to 5 carbon atoms, a halogen atom, a hydrogen atom, or an alkoxy group having 1 to 5 carbon atoms; m and n are each an integer of from 1 to 4;



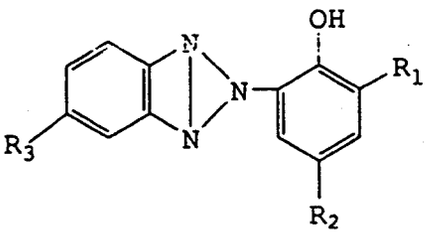
(M-VIII)

wherein Z is a group of non-metal atoms necessary for forming a nitrogen-containing heterocyclic ring which may have a substitutent; X is a hydrogen atom or a substituent capable of splitting of upon reaction with the oxydation product of a color developing agent, and R is a hydrogen atom or a substituent,



(Y-I)

wherein R_1 is an alkyl group, a cycloalkyl group or an aryl group; R_2 is an alkyl group, a cycloalkyl group, an acyl group or an aryl group; R_3 is a substituent; n is an integer of 0 or 1; Y_1 is an organic group and X_1 is a hydrogen group or a substituent capable of splitting off upon reaction with an oxidation product of a color developing agent,



(UV-I)

wherein R_1, R_2 and R_3 are each a hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, an alkenyl group, a nitro group or hydroxyl group.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 11 8823

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 307 868 (KONICA) * page 23, line 16 - line 28 * * page 24, line 13 - line 20 * * page 29, line 16 - line 18 * * page 31, line 18 - line 33 *	1-9	G03C1/79 G03C1/815 G03C7/32
Y	EP-A-0 283 324 (KONICA) * page 3, line 23 - page 31, line 62 *	1-9	
Y	EP-A-0 266 733 (KONICA) * page 4, line 51 - page 5, line 24; claim 1 *	1-9	
Y	JP-B-6 148 147 (FUJI) * column 6, line 39 - line 41 * * column 11, line 28 - line 33 * * column 18, line 1 - line 5 * * column 18; table 3 *	1,4,5,9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 JANUARY 1992	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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