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(54) **Encased photographic material.**

(57) An encased photographic material includes a silver halide light-sensitive material (24) having at least one silver halide emulsion layer on a support. The emulsion layer contains gold- and chalcogen-sensitized silver halide grains. A lightproof container (22) contains the light-sensitive material (24) such that an end portion (25) of the light-sensitive material (24) is positioned outside the lightproof container (22), and that a gas can pass between an inside and an outside of the lightproof container (22). A light-transmitting case (26) encases and seals the lightproof container (22) containing the light-sensitive material (24). A hydrogen cyanide gas scavenger is present inside the case (26).

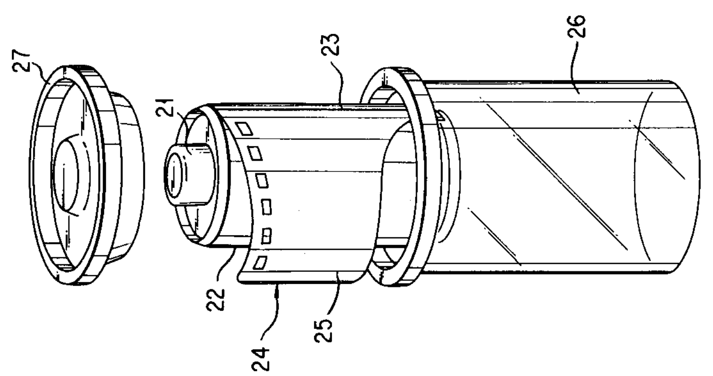

FIG. 2

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The present invention relates to an encased photographic material and, more particularly, to an encased photographic material in which the storage stability of a silver halide photographic light-sensitive material encased in a light-transmitting case is improved.

Silver halide photographic light-sensitive materials are sensitive to light. Therefore, such materials are generally shielded from light during storage before used in photographing. For example, the light-sensitive material is set in a lightproof container such as a magazine or cartridge, such as a film cartridge of 135-format color negative film. The cartridge containing the light-sensitive material is often encased in a light-transmitting or transparent case. The transparent case allows easy observation of the cartridge encased therein without requiring indications of the type of film on the case, leading to a lower cost. Further, the transparent case can be conveniently reused as a case for keeping small articles.

Recently, a surprising phenomenon has been found: photographic film products placed on shelves in stores for long periods of time vary in film performance depending on brightness with which they are placed. An analysis of this phenomenon revealed that a certain kind of gas was generated by light incident on the leader portion of a film in a cartridge, through a paper box containing a transparent case encasing the cartridge and this gas diffused to a film portion shielded from light in the cartridge, changing the performance of the film. No such phenomenon has been conventionally known to those skilled in the art. To analyze this gas, a photographic film was forced to be irradiated with intense light and gas produced was collected. The gas was found to contain hydrogen cyanide gas.

Meanwhile, silver halide photographic emulsions for use in silver halide photographic light-sensitive materials are normally subjected to chemical sensitization using various chemical substances in order to obtain, e.g., desired sensitivities and gradations. Representative methods of the chemical sensitization are chalcogen sensitization such as sulfur sensitization or selenium sensitization, noble metal sensitization such as gold sensitization, reduction sensitization, and combinations of these sensitization methods.

Recently, strong demands have arisen for a high sensitivity, a good graininess, and a high sharpness of a silver halide photographic light-sensitive material, and for rapid processing obtained by increasing, e.g., the rate of development of the material, and so various improvements have been made for the above sensitization methods.

Among the above sensitization methods, the selenium sensitization is disclosed in, e.g., U.S. Patents 1,574,944, 1,602,592, 1,623,499, 3,297,446, 3,297,447, 3,320,069, 3,408,196, 3,408,197, 3,442,653, 3,420,670 and 3,591,385, French Patents 2,093,038 and 2,093,209, JP-B-52-34491 ("JP-B" means Published Examined Japanese Patent Application), JP-B-52-34492, JP-B-53-295, JP-B-57-22090, JP-A-59-180536 ("JP-A" means Published Unexamined Japanese Patent Application), JP-A-59-185330, JP-A-59-181337, JP-A-59-187338, JP-A-59-192241, JP-A-60-150046, JP-A-60-151637, JP-A-61-246738, JP-A-3-111838, JP-A-3-148648, British Patents 255,846 and 861,984, and H.E. Spencer et al., "Journal of Photographic Science," Vol. 31, pages 158 to 169 (1983). Generally, the selenium sensitization has a larger sensitizing effect than that obtained by the sulfur sensitization commonly performed in this field of art, but often tends to increase fog and to readily cause soft tone. Although many of the above known patents are for improving these drawbacks, they can provide only unsatisfactory results so far.

In addition, a significant increase in sensitivity can be obtained by especially when the chalcogen sensitization, e.g., the sulfur sensitization or the selenium sensitization is combined with the gold sensitization. However, the deterioration caused by hydrogen cyanide gas is significant when the grains are sensitized with gold and chalogen.

It is considered that the deterioration is caused by hydrogen cyanide gas because gold is moved from the gold- and sulfur-sensitized, or gold-, (sulfur-) and selenium-sensitized silver halide emulsion by the action of hydrogen cyanide gas, leaving silver sulfide or silver selenide fog centers having high fog activity, as described in JP-A-3-505263.

It is known that the silver selenide fog centers have a higher fog activity than the silver sulfide fog centers. Because of this, the gold-, (sulfur-) and selenium-sensitized emulsion is more significantly deteriorated than the gold- and sulfur-sensitized emulsion.

The present inventors believe that a reaction presented below takes place in a portion irradiated with light to produce hydrogen cyanide gas:

$$AgBr + h\nu \text{ (irradiation with light)}$$
$$\rightarrow 2Ag + Br_2 \text{ (print out)}$$
$$2AgSCN + Br_2 \rightarrow 2AgBr + (SCN)_2$$
$$(SCN)_2 \xrightarrow{\text{hydrolysis}} HCN$$

It will be understood from this reaction formula that a scavenger for a halogen gas is also effective.

Further, it is predicted that the amount of bromine gas generated at print out, leading to an increase in the amount of hydrogen cyanide gas, when a silver halide emulsion having a higher sensitivity. It is also predicted that an amount of hydrogen cyanide gas produced increases when the humidity is high.

It is therefore an object of the present invention to provide an encased photographic material in which the storage stability of a silver halide photographic light-sensitive material containing a gold- and chalcogen-sensitized emulsion together with a thicyanate salt, which is encased in a light-transmitting case, is improved, by eliminating the adverse effect of hydrogen cyanide generated by light irradiation on the silver halide light-sensitive material.

According to the present invention, there is provided an encased photographic material comprising:

a silver halide light-sensitive material including at least one silver halide emulsion layer on a support, the emulsion layer containing gold- and chalcogen-sensitized silver halide grains and a thiocyanate salt therein;

a lightproof container containing the light-sensitive material such that an end portion of the light-sensitive material is positioned outside the lightproof container, and that a gas can pass between an inside and an outside of the lightproof container;

a light-transmitting case encasing and sealing the lightproof container; and

a hydrogen cyanide gas scavenger present inside the case.

In a preferred embodiment, the encased photographic material of the invention further comprises a halogen gas scavenger.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 shows a hydrogen cyanide trapping device for measuring an amount of hydrogen cyanide gas generated; and

Fig. 2 is a perspective view showing a light-transmittng case encasing a silver halide light sensitive material contained in a lightproof container with its cap open.

The present invention will be described in detail below.

An encased photographic material of the present invention comprises a silver halide light-sensitive material including at least one silver halide emulsion layer on a support. The emulsion layer contains silver halide grains sensitized with gold and chalcogen, and a thiocyanate salt therein.

The light-sensitive material is contained in a lightproof container such that an end portion of the light-sensitive material is positioned outside the lightproof container. Therefore, the end portion of the light-sensitive material is not shielded from light by the lightproof container. A gas can pass between an inside and an outside of the lightproof container.

The lightproof container containing the light-sensitive material is encased and sealed in a light-transmitting case.

The present invention provides means for eliminating adverse effect of hydrogen cyanide gas generated by light incident upon the unshielded end portion of the light-sensitive material. The generated hydrogen cyanide gas diffuses to the shielded portion of the light-sensitive material and deteriorates the performance of the light-sensitive material. More specifically, according to the present invention, a hydrogen cyanide gas scavenger is present inside the light-transmitting case to capture the generated hydrogen cyanide gas.

If a silver halide is deteriorated to change its photographic performance under the influence of hydrogen cyanide gas, a scavenger for hydrogen cyanide gas is expected to be effective. JP-A-3-505263 discloses that compounds of palladium, gold, and platinum are effective as scavengers for hydrogen cyanide gas. It describes that fog resulting frog hydrogen cyanide gas produced from carbon black can be prevented by adding a hydrogen cyanide gas scavenger to a position at which a light-sensitive emulsion can be protected from the gas. JP-A-3-505263 also describes that the addition position of a scavenger is preferably closer to carbon black, the source of the gas.

JP-A-3-505263 has, however, no description indicating that hydrogen cyanide gas is produced when light is radiated onto a light-sensitive material.

JP-A-3-505263, therefore, has, of course, no description indicating that hydrogen cyanide gas produced from a portion irradiated with light has an influence on photographic properties of a portion shielded from light.

Moreover, there is no description in JP-A-3-505263 that a thiocyanate salt contained in a light-sensitive material involves the generation of hydrogen cyanide gas.

As disclosed in, e.g., U.S. Patents 2,566,245 and 2,566,263, addition of Pd compounds to silver halide photographic light-sensitive materials is a well-known conventional technique. In effect, addition of Pd to emulsion layers or interlayers of silver halide color photographic light-sensitive materials is widely put into practical use. For example, Kodacolor VR-G100 Brownie Film (EMUL. NO. 24 031 13) good through November, 1988, manufactured in the factory of Eastman Kodak Co., Rochester, New York, U.S.A., contains approximately 3×10^{-5} g of Pd per a roll of film. This film is shielded from light by light-shielding black paper containing carbon black in an amount of about 8% (about 0.7 g per a roll of film) with respect to the weight of paper. So it is believed that the film is free from an influence of hydrogen cyanide gas produced upon irradiation with light.

It is impossible to predict that this Pd is effective against fog which is likely to occur when the same light-sensitive material as described above is made into a product with a film format having a portion exposed to light before photographing, such as those in the present invention.

The above description explains that a thiocyanate salt causes the generation of hydrogen cyanide gas by the light irradiation on a silver halide. However, the present invention can also be effectively applied to a photographic material containing a compound which can directly or indirectly generate hydrogen cyanide gas upon light irradiation.

The direct or indirect generation of hydrogen cyanide gas means that the mechanism of the generation of hydrogen cyanide gas is complicated, and can not be identified simply. However, the generation of hydrogen cyanide gas can be easily determined. For example, the amount of hydrogen cyanide gas generated can be measured by the following method.

Fig. 1 shows a hydrogen cyanide gas trapping device. The trapping device has scrubbing bottles 11, 12, 13 and 14, which are connected with glass tubes 15, 16 and 17 having an inner diameter of 5 mm. Each of the bottles 11, 13 and 14 has an inner volume of 250 cc, and the bottle 12 has an inner volume of one litter. The bottles are available from Shibata Scientific Instrument Industry K.K., Japan.

Each of the bottles 11, 13 and 14 contains 100 cc of 1N NaOH, and the bottle contains a sample to be measured. The glass tube 16 is provided with a glass ball 18 having small through pores (G 3) at the end immersed in the liquid in the bottle 13 to improve the trapping efficiency of hydrogen cyanide gas. Likewise, the glass tube 17 is provided with a glass ball 18 having small through pores (G 3) at the end immersed in the liquid in the bottle 14.

An air pump 20 (Iwaki Air Pump (AP-220 ZN)) is connected to the bottle 14 through a glass tube 19. The flow rate of air is adjusted to 700 ± 400 cc/min. The variation of the air flow rate does not largely affect quantitative accuracy of hydrogen cyanide gas.

The bottle 11 and 12 are set in a thermostatic chamber at 25°C. When the ambient temperature is within a range of 10 to 30°C, the temperature control of the bottles 13 and 14 is not necessary.

A sample of 1 m^2 is finely cut and placed in the bottle 12. While light is irradiated on the sample at 10,000 lux for 24 hours, the air pump 20 is operated to trap hydrogen cyanide gas in the bottles 13 and 14.

According to the Test Method For Industrial Waste Water specified in JIS K 0102, Item 38: Cyanide Compounds, 38.2 Pyridine-Pyrazolone Absorptiometric Method, an absorbance at 620 nm is measured. From the measured value, an absorbance value obtained on a blank is subtracted. Thus, cyanide ions in the trapping liquids are quantitatively determined.

In the method described above, the sample is placed at a relative humidity of about 75%. Preferably, the air flow rate is controlled to attain a relative humidity of 75 ± 15%, more preferably 75 ± 10%.

When light-sensitive layers and back layers of a color photographic light-sensitive material exist, these layers also are preferably adjusted to a pH of 5.5 ± 0.5. If a pH of the light-sensitive layers is 6.0 or less, 90% or more of cyanides generated in the light-sensitive layers by light irradiation volatile as hydrogen cyanide.

In the present invention, a more remarkable effect can be obtained if the amount of hydrogen cyanide gas is 0.1 μg or more, particularly 0.3 μg or more, more particularly 0.6 μg or more.

Fog is more readily generated in a color photographic light-sensitive material than in a black-and-white photographic light-sensitive material, and the color photographic light-sensitive material is more damaged than the black-and-white photographic light-sensitive material.

An encased photographic light-sensitive material is contained in an outer box having a product name printed thereon. The above-mentioned phenomenon of hydrogen cyanide generation occurs by light transmitted through the box. Therefore, it is possible to suppress the phenomenon by lowering the light transmissivity of the box. For this purpose, it is, however, necessary for the box to be printed with an ink having a large light absorptivity, i.e., a dark ink. This is not practical since the box must be so designed as to attract attention. If the box is constructed of a composite material of paper and light-shielding material, the problem can be solved. However, the use of such a composite material increases the cost of the photographic product.

The present invention provides an effective method for without increasing the cost of the product.

A hydrogen cyanide gas scavenger according to the present invention is a compound that converts hydrogen cyanide gas, produced when a light-sensitive material is irradiated with light, into a photographically inert substance. The hydrogen cyanide gas scavenger of the present invention has no chemical sensitization effect. The scavenger should not release any substance having an adverse effect on silver halide light-sensitive materials, as a result of trapping of hydrogen cyanide gas. An appropriate hydrogen cyanide gas scavenger can be selected from inorganic or organic compounds of noble metals. Most preferred are compounds of palladium (II or IV) and platinum (II or IV). A compound of gold (I or III) is also preferable. Although compounds of rhodium (III), iridium (III or IV), and osmium (II, III, or IV) are also effective, a larger amount is required to obtain an equivalent effect when these compounds are used.

Practical examples of effective inorganic or organic noble metal compounds are described in detail in, e.g., Gmelin Handbook. These commercially available products, synthetic products, and in situ synthetic products must be used with purity with which they do not have any adverse effect on photographic light-sensitive materials.

Representative examples of useful palladium compounds are palladium (II) chloride, palladium (II) bromide, palladium (II) hydroxide, palladium (II) sulfate, palladium (II) thiocyanate, tetrachloropalladate (II) (sodium salt, potassium salt, and ammonium salt), hexachloropalladate(IV), tetrabromopalladate(II), hexabromopalladate(IV), bis(salicylato)palladate(II), bis(dithiooxalato-S,S')palladate(II), trans-dichlorobis-(thioether)palladium(II), tetraamminepalladium(II) salt, dichlorodiamminepalladium(II), dibromodiamminepalladium(II), oxalatodiamminepalladium(II), dinitrodiaminepalladium(II), bis-(ethylenediamine)palladium(II) salt, dichloroethylenediaminepalladium(II), bis(2,2'-bipyridine)palladium(II) salt, bis(1,10-phenanthroline)palladium(II) salt, tetranitropalladate(II), bis(glycinato)palladium(II), tetrakis-(thiocyanato)palladate(II), dichlorobis(phosphine)palladium(II), di-μ-chloro-bis[chloro(phosphine)palladium(II)], di-μ-chloro-bis[chloro(arsine)palladium(II)], and dinitrobis(arsine)palladium(II).

Representative examples of useful platinum compounds are platinum(II) chloride, platinum(IV) chloride, hexafluoroplatinate(IV), tetrachloroplatinate(II), hexachloroplatinate(IV), trichlorotrifluoroplatinate(IV), tetrabromoplatinate(II), hexabromoplatinate(IV), dibromodichloroplatinate(II), hexahydroxoplatinate(IV), bis-(oxalato)platinate(II), dichlorobis(oxalato)platinate(IV), bis(thiooxalato)platinate(II), bis(acetylacetonato)-platinum(II), bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)platinum(II), bis(1,1,1-trifluoro-2,4-pentanedionato)-platinum(II), tetrakis(thiocyanato)platinate(II), hexakis(thiocyanato)platinate(IV), bis{(Z)-1,2-dicyanoethylene-1,2-dithiolato}platinate(II), dichlorobis(diethylsulfido)platinum(II), tetrachlorobis(diethylsulfide)platinum(IV), bis(glycinato)platinum(II), dichloroglycinatoplatinate(II), dichlorobis(triethylphosphine)platinum(II), chlorohydridobis(triethylphosphine)platinum(II), tetraammineplatinum(II) salt, tetrachloroplatinate(II), dichlorodiammineplatinum(II), trichloroammineplatinum(II) salt, hexaammineplatinum(IV) salt, chloropentammineplatinum(IV) salt, tetrachlorodiammineplatinum(IV), dinitrodiammineplatinum(II), dichlorotetrakis(methylamine)platinum(IV) salt, dichloro(ethylenediamine)platinum(II), bis(ethylenediamine)-platinum(II) salt, tris(ethylenediamine)platinum(IV) salt, dichlorobis(ethylenediamine)platinum(IV) salt, dichlorodihydroxo(ethylenediamine)platinum(IV), tetrakis(pyridine)platinum(II) salt, dichlorobis(pyridine)-platinum(II), bis(2,2'-bipyridine)platinum(II) salt, tetranitroplatinate(II), chlorotrinitroplatinate(II), dichlorodinitroplatinate(II), dibromodinitroplatinate(II), hexanitroplatinate(IV), chloropentanitroplatinate(IV), dichlorotetranitroplatinate(IV), trichlorotrinitroplatinate(IV), trichlorodinitroplatinate(IV), dibromodichlorodinitroplatinate(IV), tetrachloro(ethylene)platinate(II), di-μ-chloro-bis{chloro(ethylene)-platinum(II)}, trans-dichloro(ethylene)(pyridine)platinum(II), bis[bis(β-mercaptoethylamine)nickel(II)-S,S'-]platinum (II) salt, and dichlorodicarbonylplatinum(II).

Examples of compounds of gold(I or III), rhodium(III), iridium(III or IV), and osmium(II, III, or IV) are potassium tetrachloroaurate(III), rhodium(III) chloride, potassium hexachloroiridate(IV), potassium tetrachloroiridate(III), and potassium hexachloroosmate(IV).

Inorganic or organic compounds of noble metals are not limited to the above examples as long as the effect of the present invention can be obtained.

In the present invention, the hydrogen cyanide gas scavenger can be present at any position inside the sealed case; the hydrogen cyanide gas scavenger can be coated on or incorporated in the inner surface of the sealed case or coated on or incorporated in a part forming a cartridge. Most preferably, the hydrogen cyanide gas scavenger is present in a photographic light-sensitive material. A photographic light-sensitive material is normally constituted by a support, a back layer, emulsion layers, surface protective layers, interlayers, and an antihalation layer. The hydrogen cyanide gas scavenger of the present invention is added directly to these layers and coated in the form of layers, or coated separately together with an appropriate solvent or binder.

As a method of adding the hydrogen cyanide gas scavenger to the light-sensitive material, methods normally used to add additives to photographic light-sensitive materials are applicable. For example, a water-soluble scavenger can be added in the form of an aqueous solution with a proper concentration. A scavenger which is insoluble or sparingly soluble in water can be dissolved in an appropriate organic solvent, such as alcohols, glycols, ketone, esters, or amides, that is miscible with water and has no adverse effect on photographic properties, and added in the form of a solution.

A back layer, emulsion layers, a surface protective layer, interlayers, and an antihalation layer are generally dispersions using binders. Examples of useful binders are a naturally produced polymeric vehicle, such as gelatin and a cellulose derivative, and a synthetic vehicle, such as polyvinyl alcohol and its derivative, acrylate and methacrylate polymers, and a butadiene-styrene polymer and a similar substance. When the hydrogen cyanide gas scavenger is to be added directly to these layers, the conditions, such as the concentration and the pH of a binder must be selected carefully in accordance with the type and the amount of the hydrogen cyanide gas scavenger to be used. Generally, a noble metal compound and gelatin interact, and this sometimes significantly raises the viscosity of the system depending on the conditions. For example, the interaction between palladium(II) ions and gelatin is described in detail in Journal of Japan Photographic Society, Vol. 34, page 159 (1971), Keiichi Tanaka; Journal of Japan Photographic Society, Vol. 37, page 133 (1974), Keiichi Tanaka; Journal of Japan Photographic Society, Vol. 39, page 73 (1976), Keiichi Tanaka; Journal of Photographic Science, Vol. 21, page 134 (1973), Keiichi Tanaka; and Journal of Photographic Science, Vol. 26, page 222 (1978), Keiichi Tanaka.

Palladium(II) ions strongly bond with amide linkage and amino acid residues of gelatin, and hence sometimes form a bulk foreign matter of gelatin depending on the conditions. Therefore, it is preferable to select a proper palladium compound described above in accordance with the conditions.

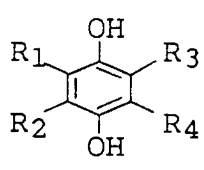
In the present invention, the addition amount of the hydrogen cyanide gas scavenger must be so determined as to fall within a range over which the effect of the present invention can be obtained significantly. The addition amount is preferably 1/10 mol or more, more preferably 1/2 to 100 mol, and most preferably 1 to 10 mol per mol of thiocyanate contained in that portion of a silver halide light-sensitive material which may be irradiated with light during storage or before photographing.

As has been pointed above, a halogen gas scavenger is also effective in eliminating the adverse effect of hydrogen cyanide produced light irradiation upon the light-sensitive material before photographing of the material.

The halogen gas scavenger of the invention is a compound that converts halogen gas, produced when a light-sensitive material is irradiated with light, into a photographically inert substance. The scavenger, therefore, should not release any substance having an adverse effect on silver halide light-sensitive materials, as a result of trapping of halogen gas.

It is generally known that gelatin acts as a halogen gas scavenger and its actions are the functions of the pH and the pAg of the system. In the present invention, however, it is preferable to use a compound given below be present as a halogen gas scavenger at a position inside the sealed case encasing the light-sensitive material. Preferred halogen scavengers are sulfide compounds, nitrite salts, semicarbazides, sulfite salts, hydroquinones, ethylenediamine, acetonesemicarbazone, and p-hydroxyphenylglycine. Particulary preferred halogen gas scavengers are those represented by Formula (H) below:

Formula (H)



where each of R_1, R_2, R_3, and R_4 represents a hydrogen atom or a group substitutable on the benzene nucleus.

Preferable examples of the substituent in Formula (H) are a halogen atom (e.g., a fluorine atom, a chlorine atom, and a bromine atom), an alkyl group (most preferably one having 1 to 32 carbon atoms, e.g., methyl, ethyl, n-propyl, t-butyl, n-amyl, i-amyl, n-octyl, n-dodecyl, and n-octadecyl), an alkenyl group, an aryl group, an acyl group, a cycloalkyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an alkylacylamino group, an arylacylamino group, an alkylcarbamoyl group, an arylcarbamoyl group, an alkylcarbonamido group, an arylcarbonamido group, an alkylsulfonamido group, an arylsulfonamido group, an alkylsulfamoyl group, an arylsulfamoyl group, an alkylsulfonyl group, an arylsulfonyl group, an alkyloxycarbonyl group, an aryloxycarbonyl group, an alkylacyloxy group, and an arylacyloxy group.

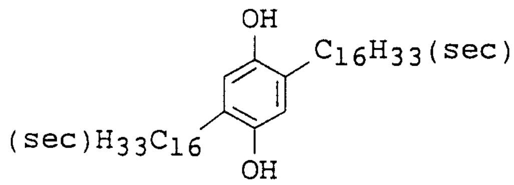
These substituent groups may be further substituted with substituents similar to those enumerated above.

The halogen gas scavenger of the present invention may be present either in a non-light-sensitive layer, such as a protective layer, an interlayer, or a back layer formed on a surface of film opposite to the emulsion surface, or a silver halide emulsion layer. The halogen gas scavenger is more preferably added to a layer formed on the emulsion layer side of a support and farther from the support.

The addition amount of the halogen gas scavenger is preferably 0.05 to 1 g/m^2, and more preferably 0.1 to 0.5 g/m^2.

Practical examples of a compound represented by Formula (H) are shown below.

(H-1)



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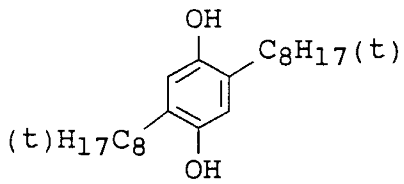

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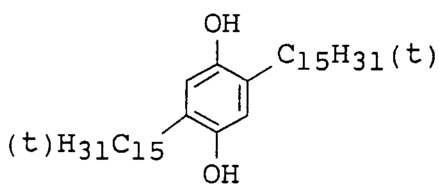
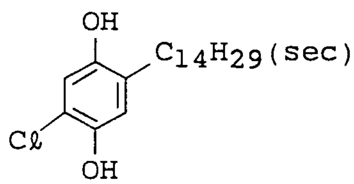
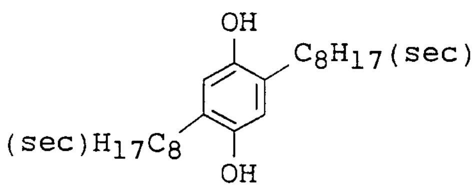


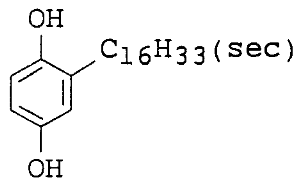
(H-4)



(H-5)



(H-6)



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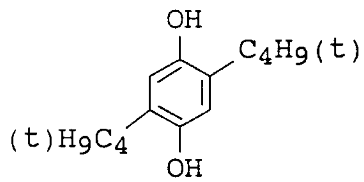
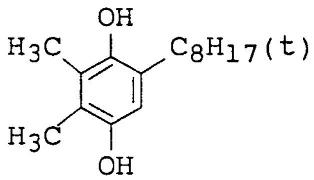


(H-8)



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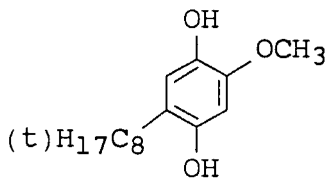

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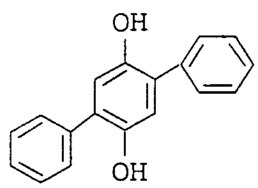

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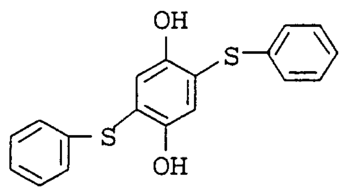

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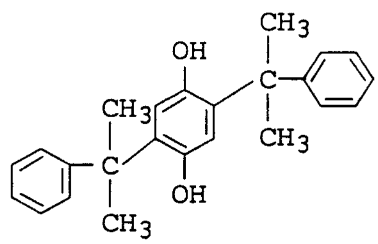

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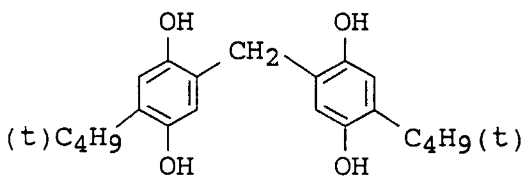

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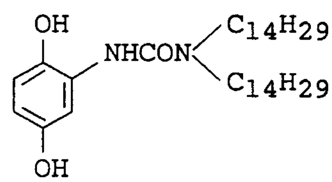

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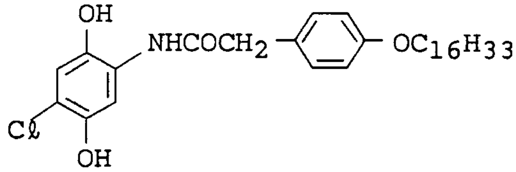

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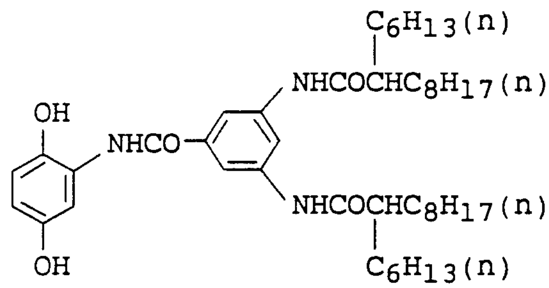

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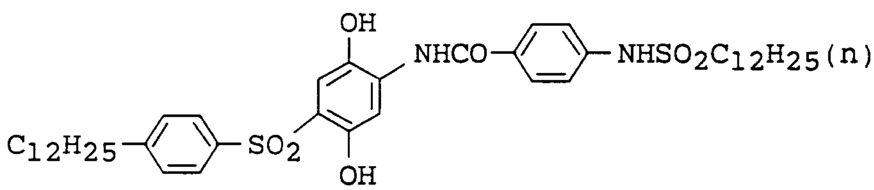

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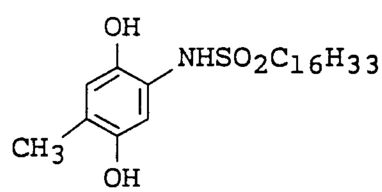
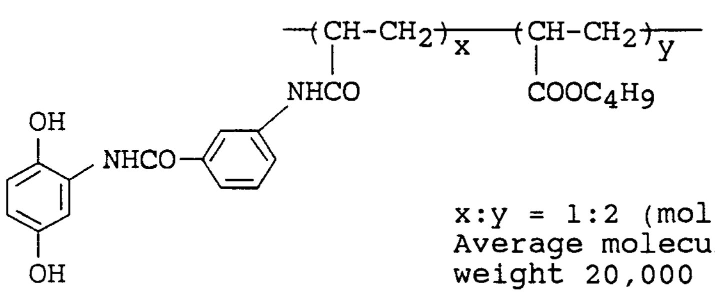


(H-20)

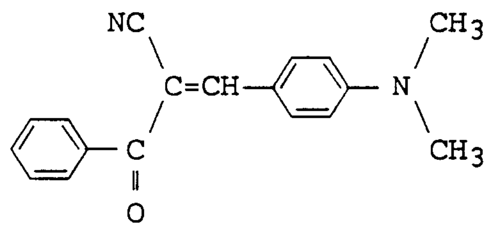


x:y = 1:2 (molar ratio)
Average molecular weight 20,000

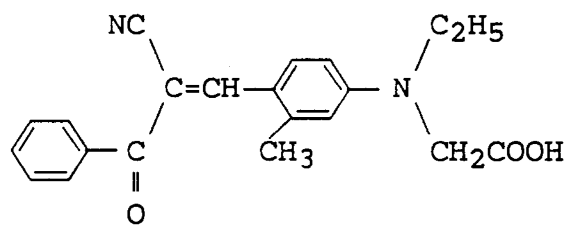
A compound which can directly or indirectly generate hydrogen cyanide gas upon light irradiation on the light-sensitive material includes an inorganic compound such as a selenocyanate salt, a cyano complex salt or a selenocyano complex salt, and an organic compound having a cyano group.

Examples of the organic compound having a cyano group are listed below:

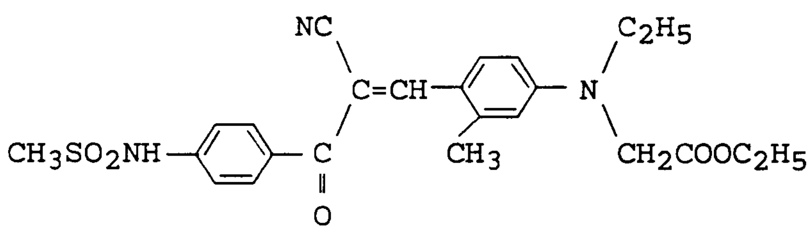
Y-1



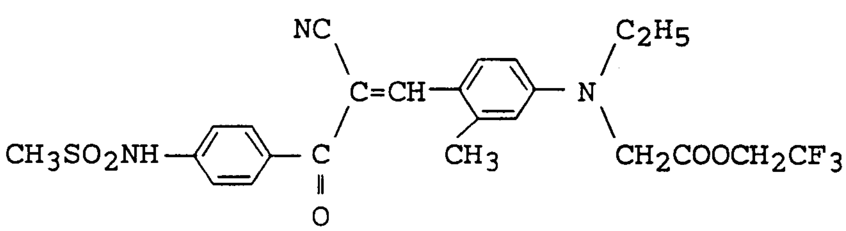
Y-2



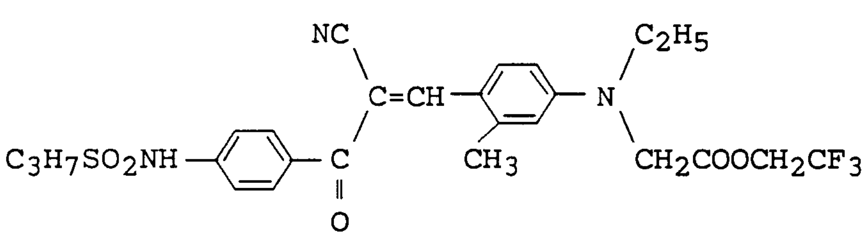
Y-3



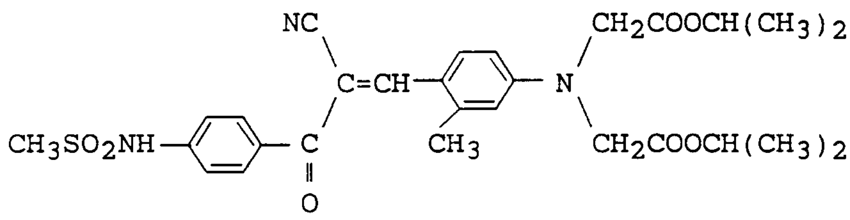
Y-4



Y-5



Y-6



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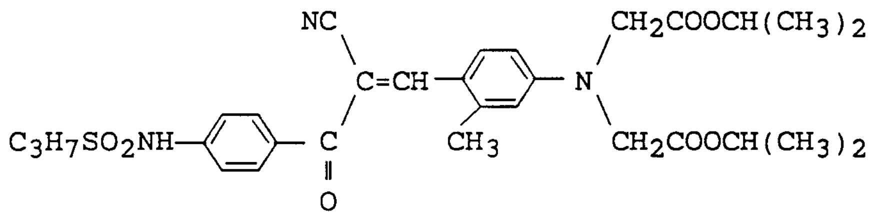

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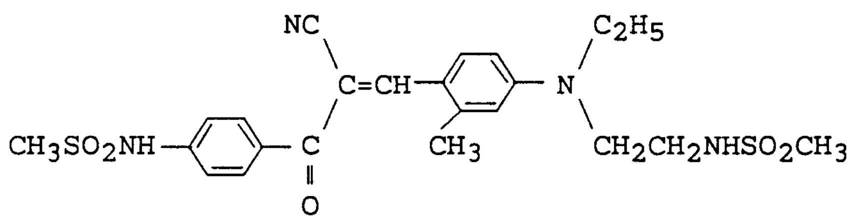
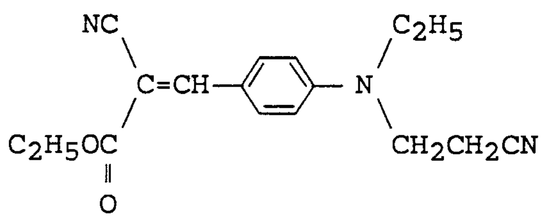


Y-9



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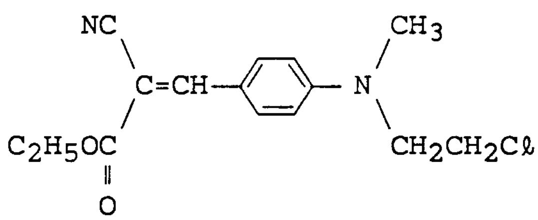

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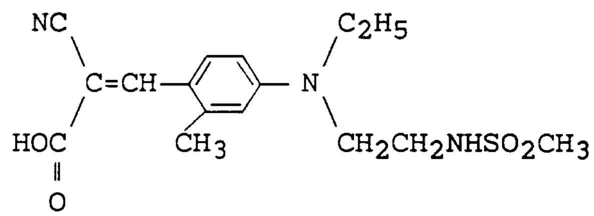

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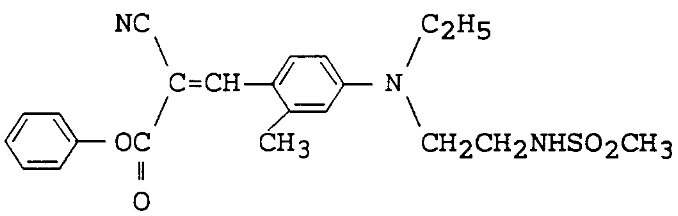

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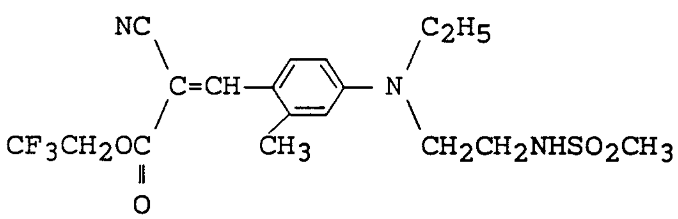

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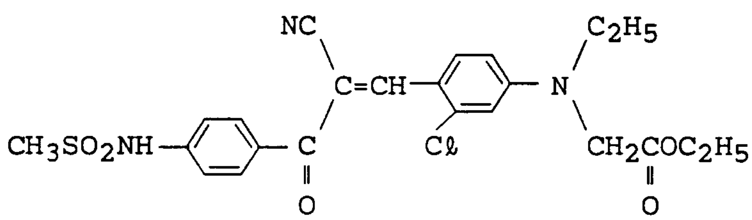

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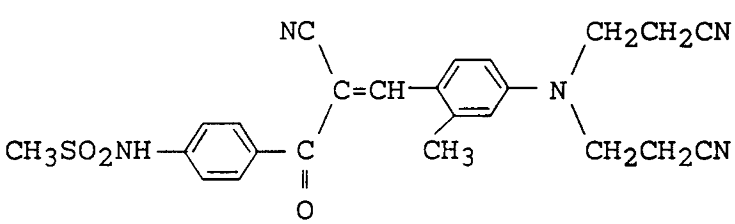

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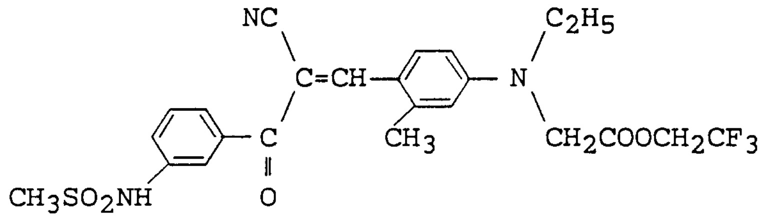

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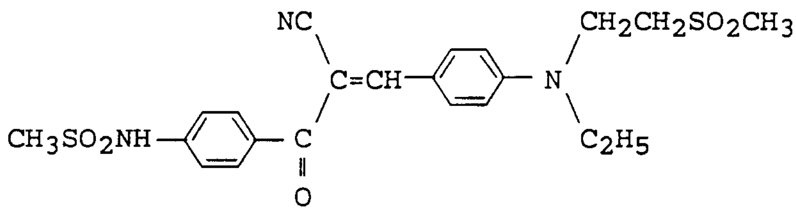

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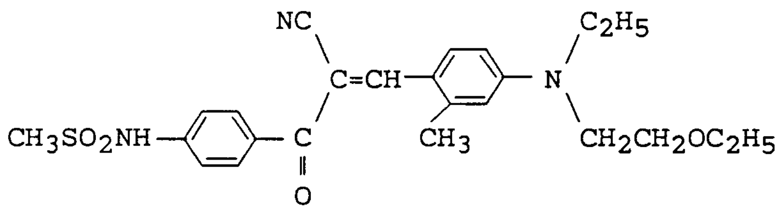

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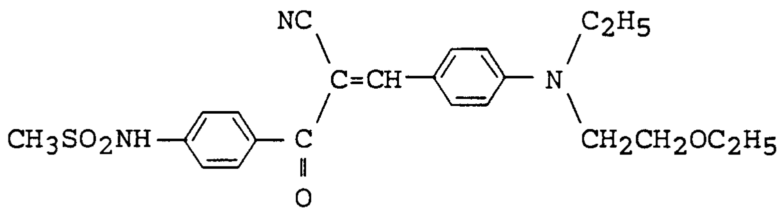

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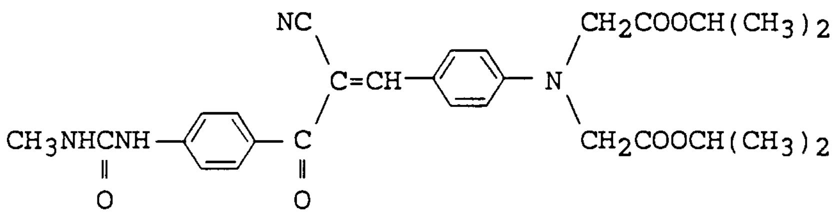

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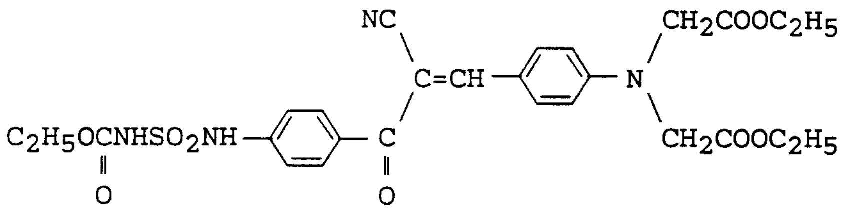

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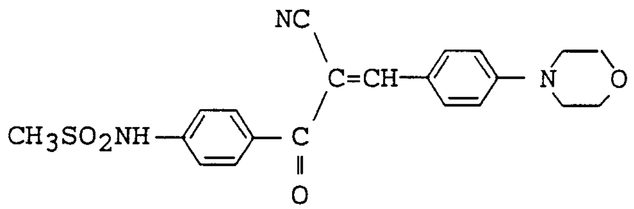

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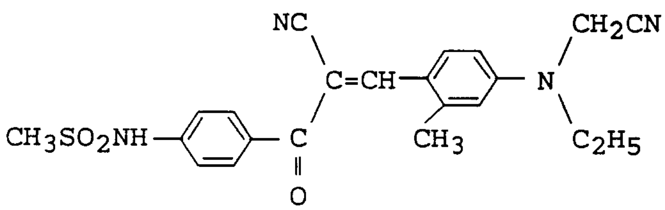

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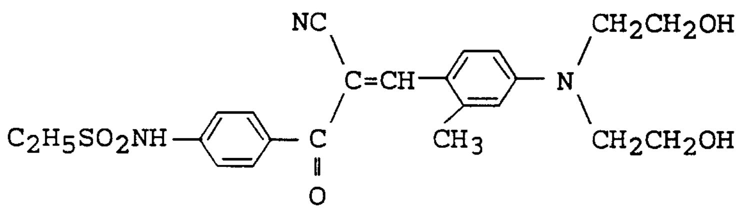

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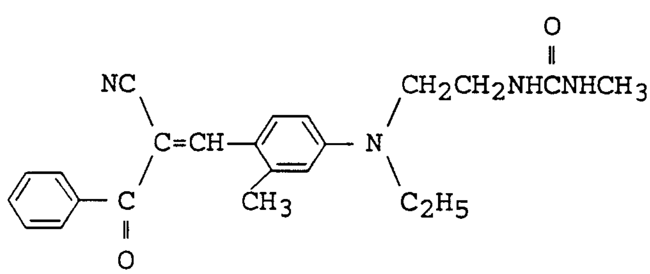

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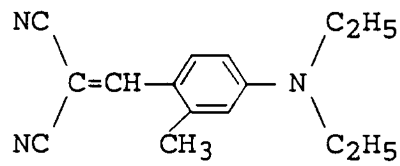

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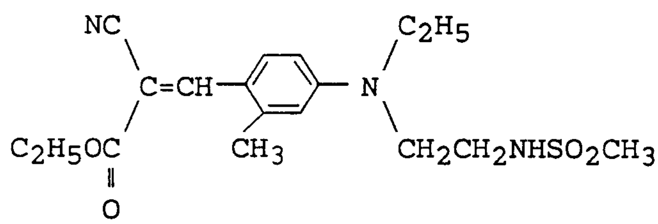

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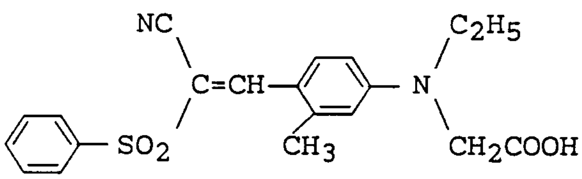

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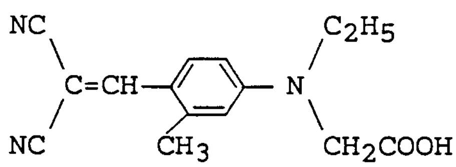

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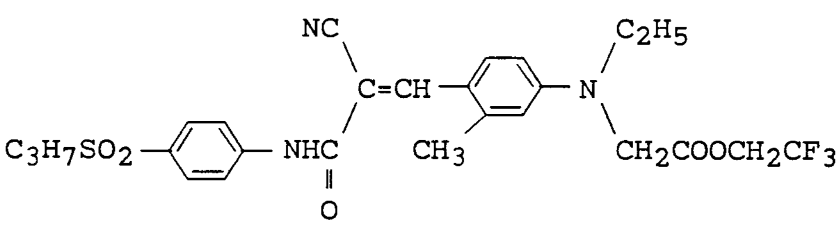

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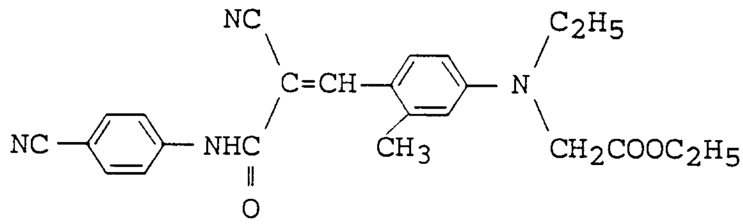

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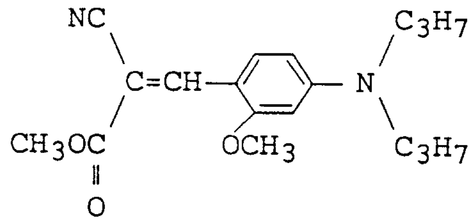

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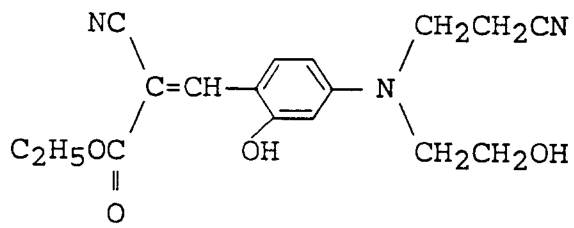

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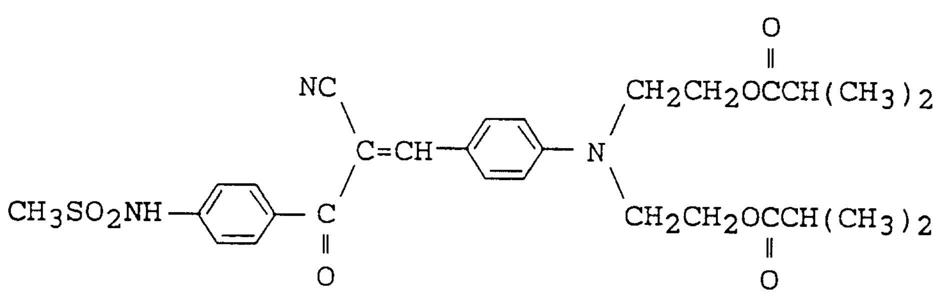

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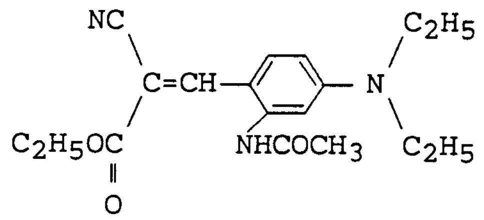

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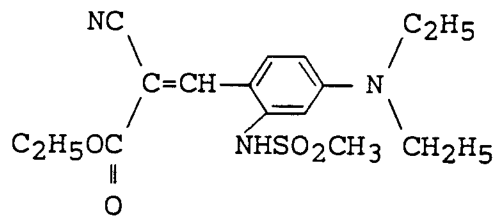

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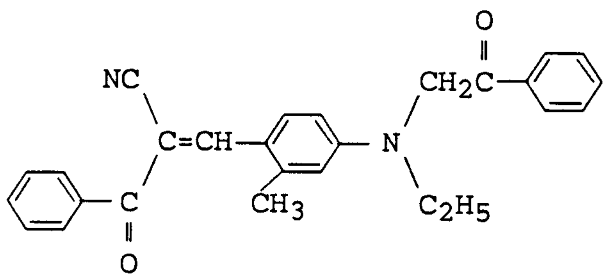

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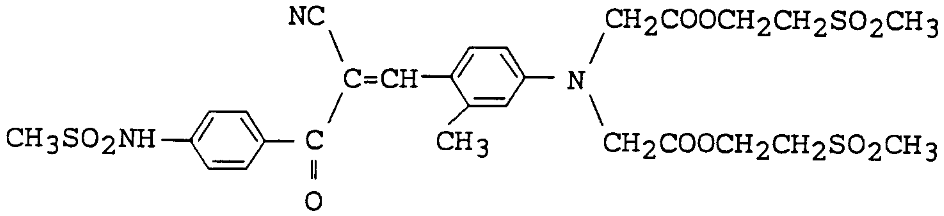

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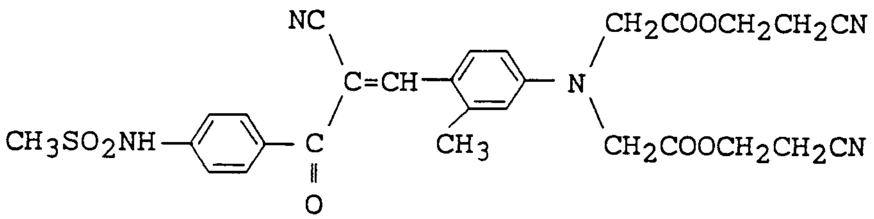

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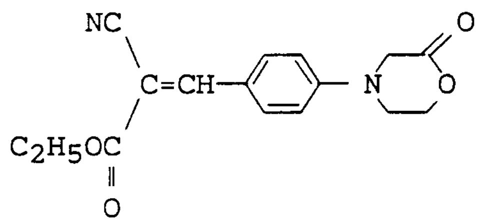

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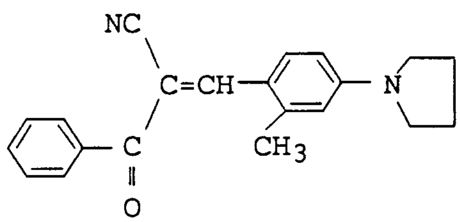

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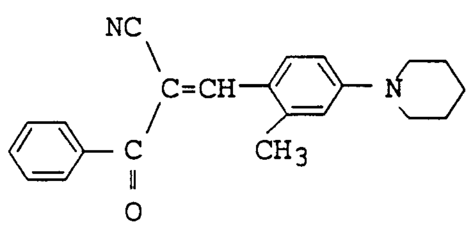

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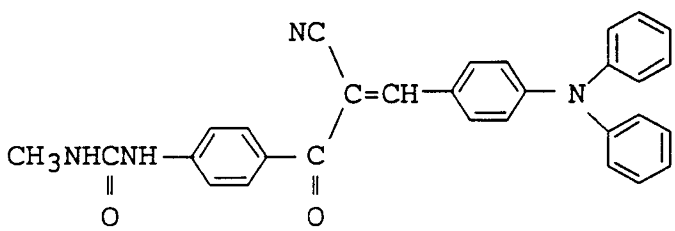

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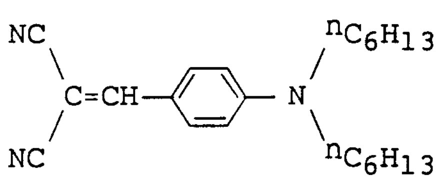

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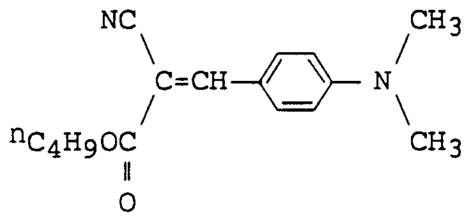

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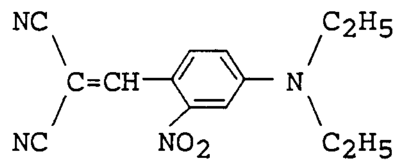

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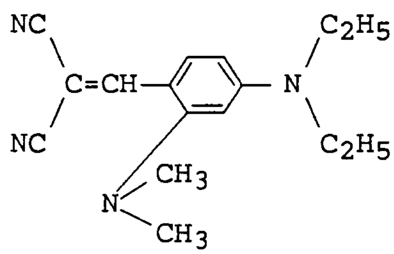

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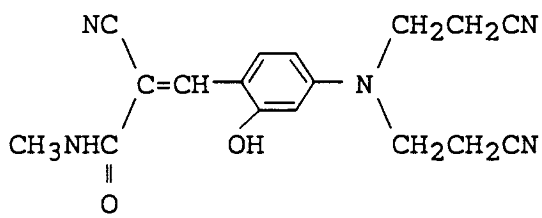

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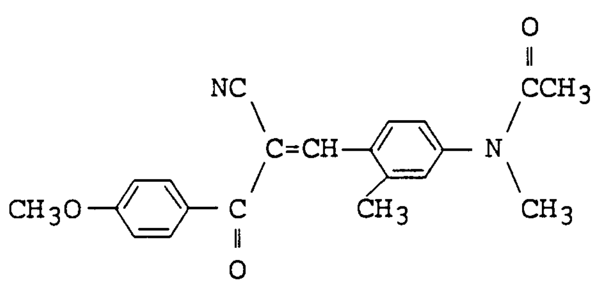

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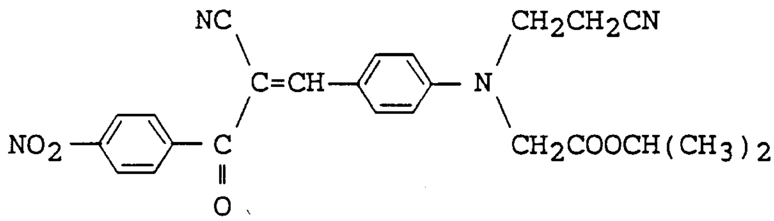

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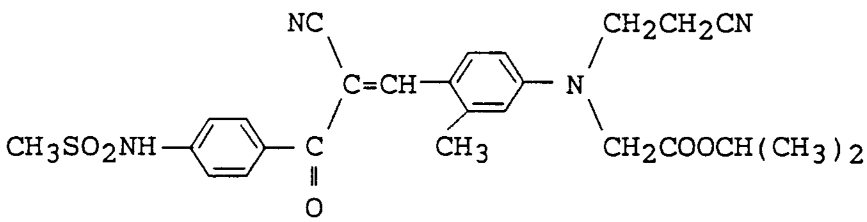

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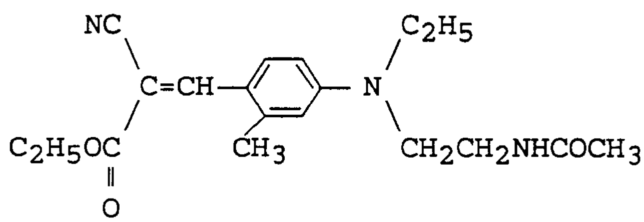
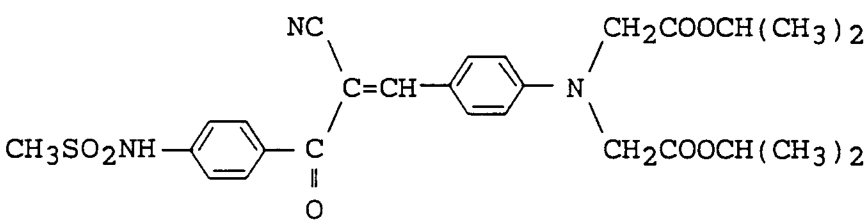


Y-56



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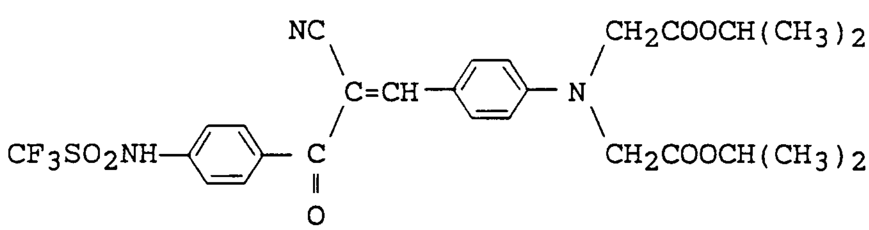
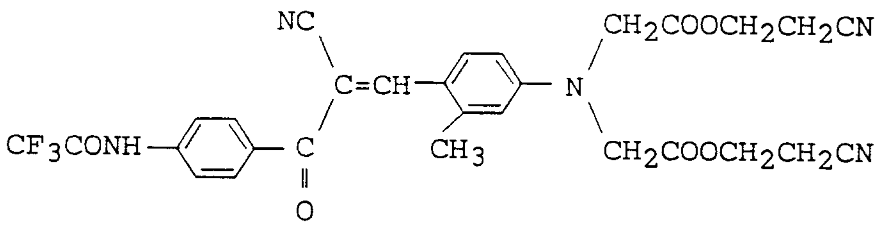
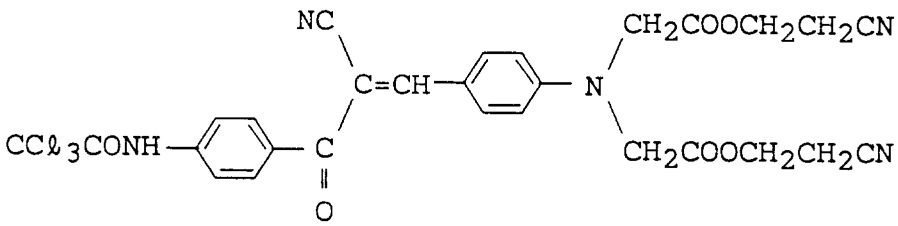


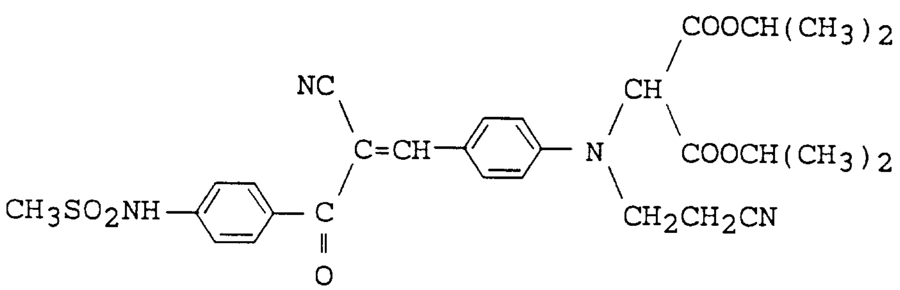
Y-58



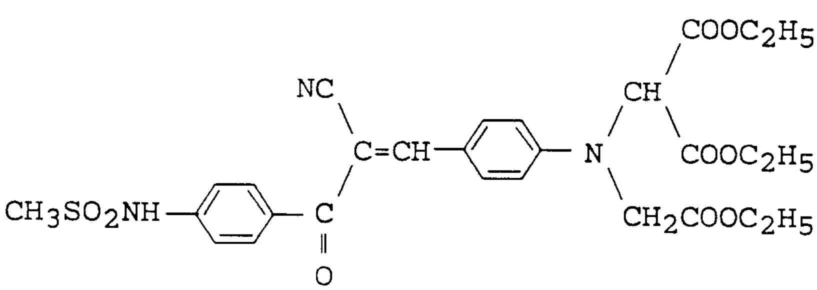
Y-59



Y-60



Y-61



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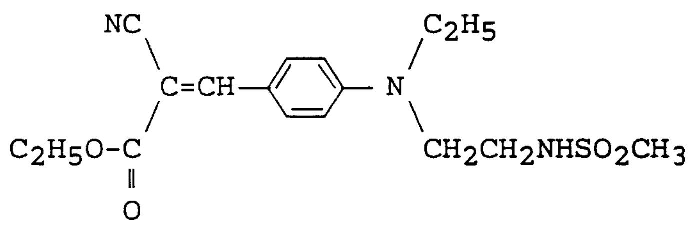
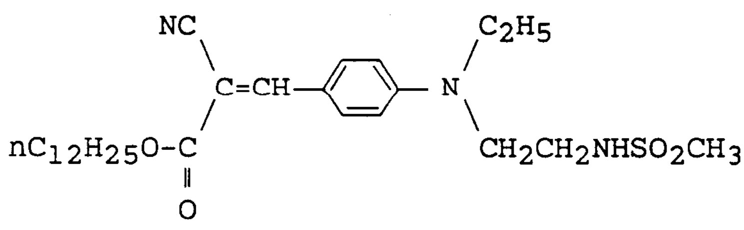
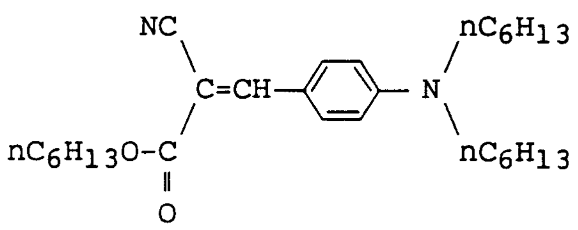


Y-63



Y-64



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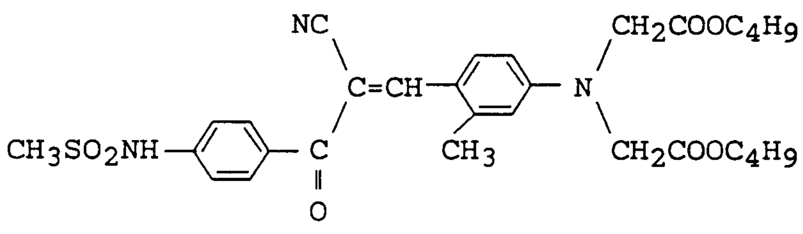

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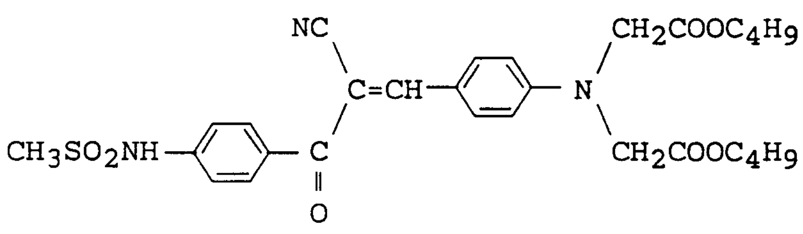

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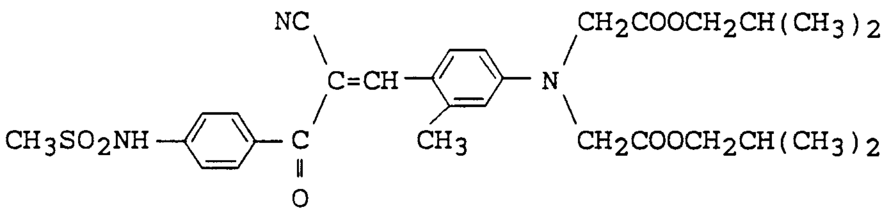

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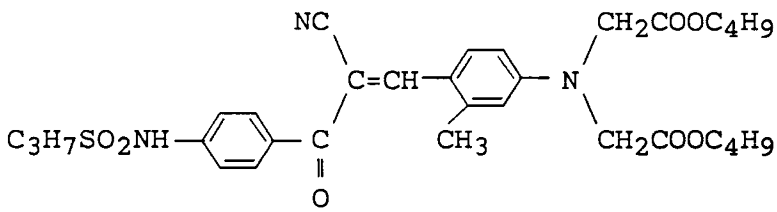

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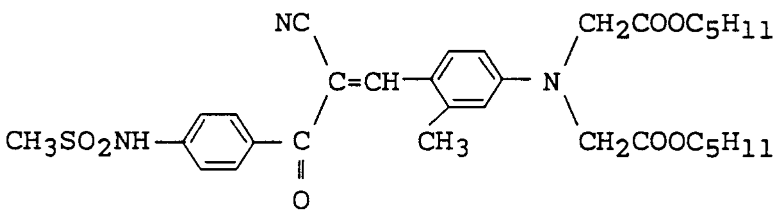

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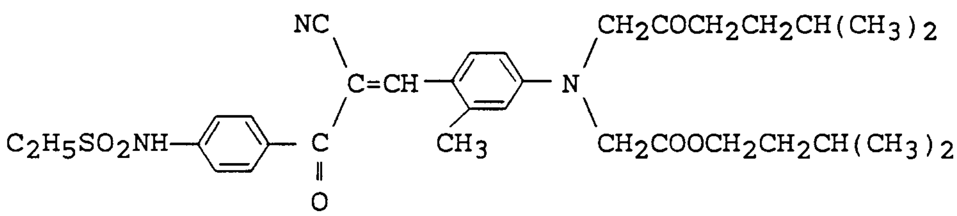

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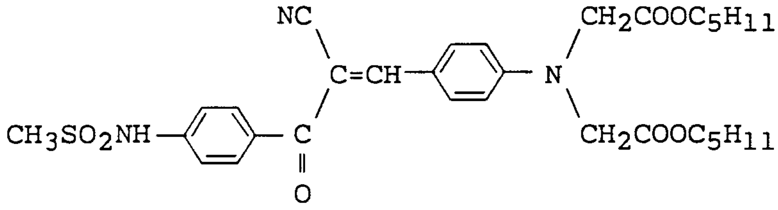

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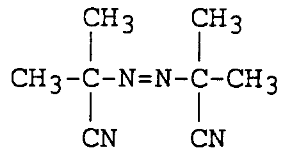

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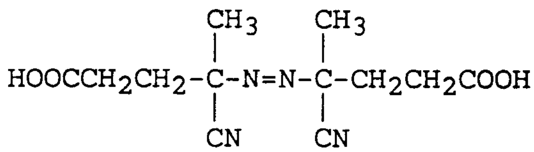

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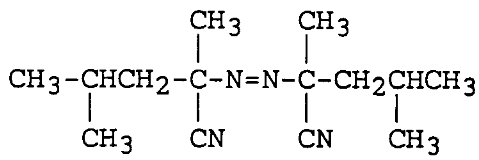

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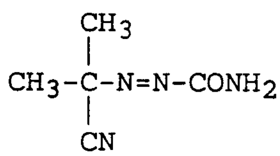

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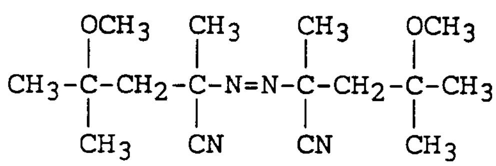
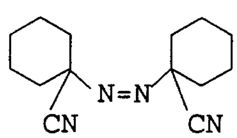


(X-6)



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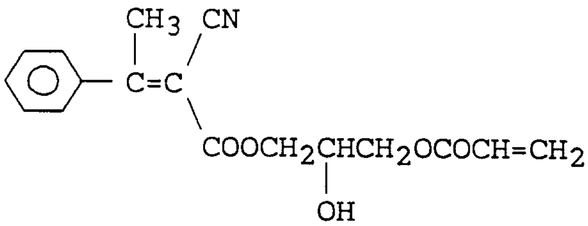

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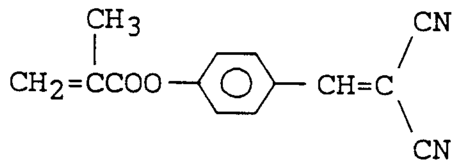

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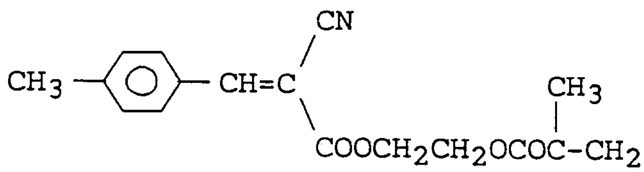

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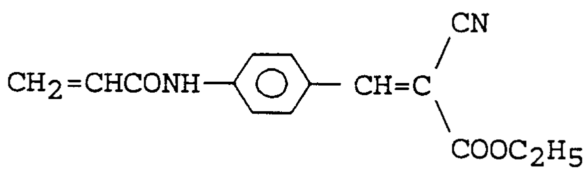

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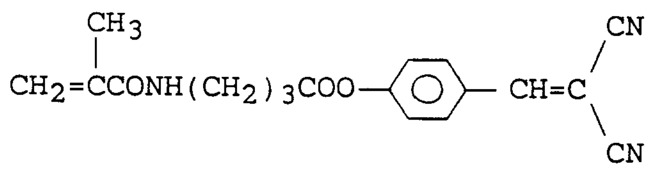

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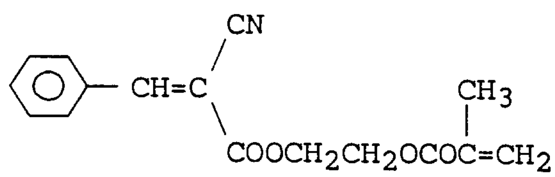

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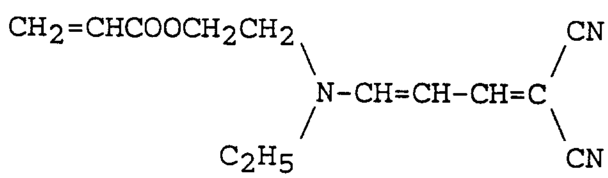


As has been described, the silver halide photographic light sensitive material in the present invention has a silver halide emulsion layer on a support. The support is described in Research Disclosure (RD) No. 17643, page 28, RD No. 18716, page 647, right column to page 648, left column and RD No. 307105, page 879. The silver halide emulsion used in the present invention is subjected to gold sensitization and chalcogen sensitization. The chalcogen sensitization is performed by using at least one of selenium, sulfur, and tellurium sensitizers. Thus, the gold-chalcogen sensitization is selected from gold-sulfur, gold-selenium, gold-tellurium, gold-surfur-selenium, gold-sulfur-tellurium, gold-selenium-tellurium, and gold-sulfur-selenium-tellurium sensitizations.

The selenium sensitization is performed by conventionally known methods. That is, the selenium sensitization is normally performed by adding a labile selenium compound and/or a non-labile selenium compound to an emulsion and stirring the emulsion at a high temperature, preferably 40°C or more for a predetermined period of time. Selenium sensitization using the labile selenium compounds described in JP-B-44-15748 ("JP-B" means Published Examined Japanese Patent Application) is preferably performed. Practical examples of the labile selenium sensitizer are aliphatic isoselenocyanates, such as allylisoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylic acids and selenocarboxylate esters, and selenophosphates. Most preferable labile selenium compounds are as follows.

I. Colloidal metal selenium

II. Organic selenium compound (in which a selenium atom is double-bonded to a carbon atom of an organic compound by a covalent bond)

a. Isoselenocyanates
Examples are aliphatic isoselenocyanates, such as allylisoselenocyanate.

b. Selenoureas (including an enol type)

Examples are aliphatic selenourea, such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, octyl, dioctyl, tetraoctyl, N-(β-carboxyethyl)-N',N'-dimethyl, N,N-diethyl, diethyl, and dimethyl selenoureas; aromatic selenourea having one or more aromatic groups such as phenyl and tolyl; and heterocyclic selenourea having a heterocyclic group such as pyridyl and benzothiazolyl.

c. Selenoketones

Examples are selenoacetone, selenoacetophenone, selenoketone in which an alkyl group is bonded to >C=Se, and selenobenzophenone.

d. Selenoamides

An example is selenoamide.

e. Selenocarboxylic acids and selenocarboxylate esters

Examples are 2-selenopropionic acid, 3-selenobutylic acid, and methyl 3-selenobutyrate.

III. Others

a. Selenides

Examples are diethylselenide, diethyldiselenide, and triphenylphosphineselenide.

b. Selenophosphates

Examples are tri-p-tolylselenophosphate and tri-n-butylselenophosphate.

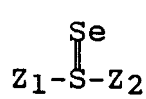
Although preferable examples of the labile selenium compound are described above, the present invention is not limited to these examples. It is generally understood by those skilled in the art that the structure of a labile selenium compound used as a sensitizer for a photographic emulsion is not so important as long as selenium is labile, and that the organic part of the molecule of the selenium sensitizer has no important role except the role of carrying selenium and keeping it in a labile state in an emulsion. In the present invention, therefore, labile selenium compounds in this broad concept are advantageously used.

Selenium sensitization using non-labile selenium sensitizers described in JP-B-46-4553, JP-B-52-34491, and JP-B-52-34492 can also be used. The non-labile selenium compounds include selenious acid, potassium selenocyanide, selenazoles, quaternary ammonium salts of selenazoles, diarylselenide, diaryldiselenide, 2-selenazolidinedione, 2-selenoxazolidinethione, and derivatives of these compounds.

Non-labile selenium sensitizers and thioselenazolidinedione compounds described in JP-B-52-38408 are also useful.

Among these selenium compounds, those preferably used in the present invention are compounds represented by Formulas (I) and (II) below.

Formula (I)



wherein Z_1 and Z_2 may be the same or different and each represents an alkyl group (e.g., methyl, ethyl, t-butyl, adamantyl, and t-octyl), an alkenyl group (e.g., vinyl and propenyl), an aralkyl group (e.g., benzyl and phenethyl), an aryl group (e.g., phenyl, pentafluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 4-octylsulfamoylphenyl, and α-naphthyl), a heterocyclic group (e.g., pyridyl, thienyl, furyl, and imidazolyl), $-NR_1(R_2)$, $-OR_3$, or $-SR_4$.

R_1, R_2, R_3, and R_4 may be the same or different and each represents an alkyl group, an aralkyl group, an aryl group, or a heterocyclic group. Examples of the alkyl group, the aralkyl group, the aryl group, and the heterocyclic group can be the same as those enumerated above for Z_1. Note that each of R_1 and R_2 can be a hydrogen atom or an acyl group (e.g., acetyl, propanoyl, benzoyl, heptafluorobutanoyl, difluoroacetyl, 4-nitrobenzoyl, α-naphthoyl, and 4-trifluoromethylbenzoyl).

In Formula (I), Z_1 preferably represents an alkyl group, an aryl group, or $-NR_1(R_2)$ and Z_2 preferably represents $-NR_5(R_6)$ wherein R_1, R_2, R_5, and R_6 may be the same or different and each represents a hydrogen atom, an alkyl group, an aryl group, or an acyl group.

More preferable examples of a selenium compound represented by Formula (I) are N,N-dialkylselenourea, N,N,N'-trialkyl-N'-acylselenourea, tetraalkylselenourea, N,N-dialkyl-arylselenoamide, and N-alkyl-N-aryl-arylselenoamide.

Formula (II)

$$\left.\begin{matrix}Z_3\\Z_4\\Z_5\end{matrix}\right\rangle P{=}Se$$

wherein Z_3, Z_4, and Z_5 may be the same or different and each represents an aliphatic group, an aromatic group, a heterocyclic group, $-OR_7$, $-NR_8(R_9)$, $-SR_{10}$, $-SeR_{11}$, X, or a hydrogen atom.

Each of R_7, R_{10}, and R_{11} represents an aliphatic group, an aromatic group, a heterocyclic group, a hydrogen atom, or a cation, and each of R_8 and R_9 represents an aliphatic group, an aromatic group, a heterocyclic group, or a hydrogen atom. X represents a halogen atom.

In Formula (II), an aliphatic group represented by Z_3, Z_4, Z_5, R_7, R_8, R_9, R_{10}, or R_{11} represents a straight-chain, branched, or cyclic alkyl, alkenyl, alkynyl, or aralkyl group (e.g., methyl, ethyl, n-propyl, isopropyl, t-butyl, n-butyl, n-octyl, n-decyl, n-hexadecyl, cyclopentyl, cyclohexyl, allyl, 2-butenyl, 3-pentenyl, propargyl, 3-pentynyl, benzyl, and phenethyl).

In Formula (II), an aromatic group represented by Z_3, Z_4, Z_5, R_7, R_8, R_9, R_{10}, or R_{11} represents a monocyclic or condensed-ring aryl group (e.g., phenyl, pentafluorophenyl, 4-chlorophenyl, 3-sulfophenyl, α-naphthyl, and 4-methylphenyl).

In Formula (II), a heterocyclic group represented by Z_3, Z_4, Z_5, R_7, R_8, R_9, R_{10}, or R_{11} represents a 3- to 10-membered saturated or unsaturated heterocyclic group (e.g., pyridyl, thienyl, furyl, thiazolyl, imidazolyl, and benzimidazolyl) containing at least one heteroatom selected from a nitrogen atom, an oxygen atom, and a sulfur atom.

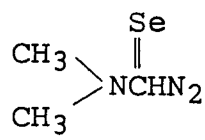
In Formula (II), a cation represented by R_7, R_{10}, or R_{11} represents an alkali metal atom or ammonium, and a halogen atom represented by X represents a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom.

In Formula (II), Z_3, Z_4, or Z_5 preferably represents an aliphatic group, an aromatic group, or $-OR_7$, and R_7 preferably represents an aliphatic group or an aromatic group.

More preferable examples of a compound represented by Formula (II) are trialkylphosphineselenide, triarylphosphineselenide, trialkylselenophosphate, and triarylselenophosphate.

Practical examples of compounds represented by Formulas (I) and (II) are presented below, but the present invention is not limited to these examples.

1.



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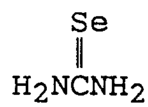

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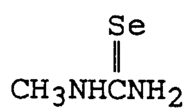

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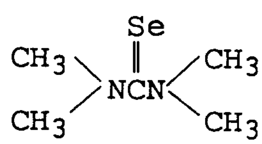

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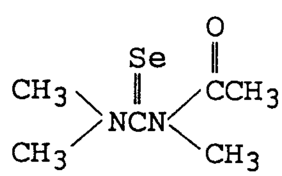

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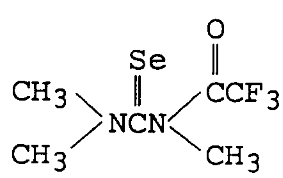

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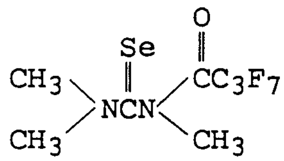

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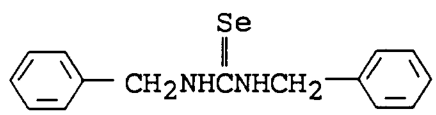

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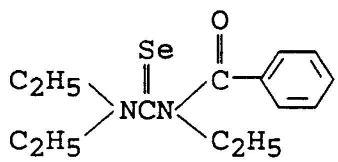

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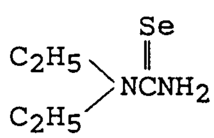

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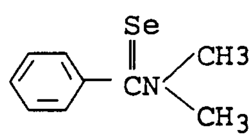

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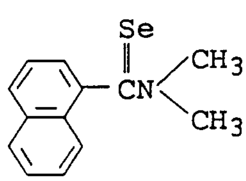

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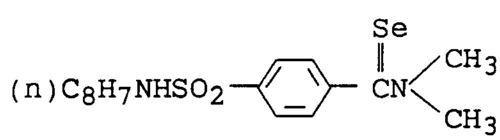

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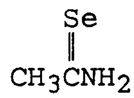

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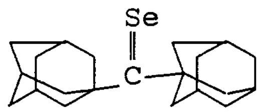

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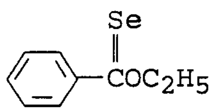

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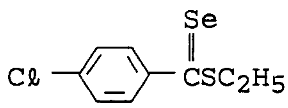

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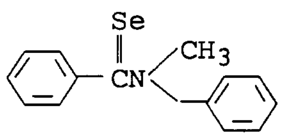

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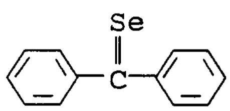

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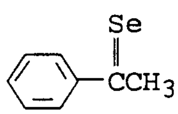

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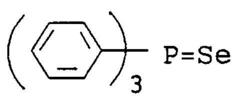

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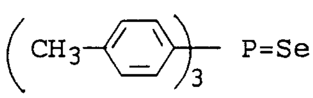
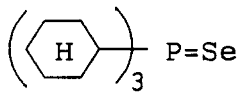


23.

$(nC_4H_9)_3 P{=}Se$

24.



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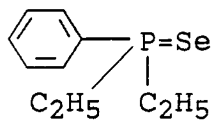

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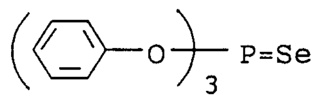

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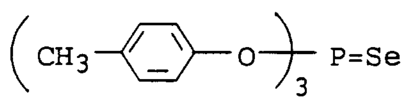
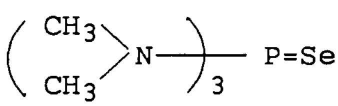


28.

$(nC_4H_9O)_3 P{=}Se$

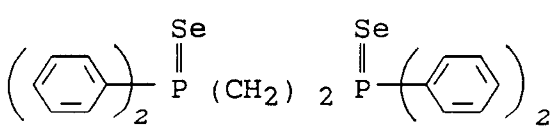
29.



30.

$(C_2H_5O) P{=}Se$

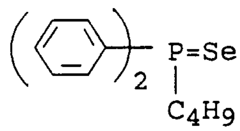
31.



32.

$(nC_8H_{17}O)_3$ P=Se

33.



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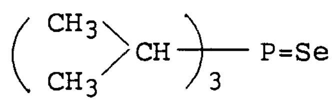

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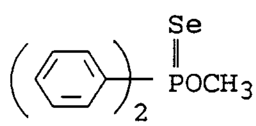

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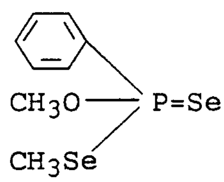

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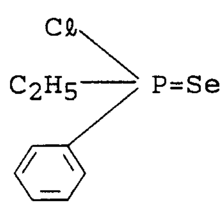

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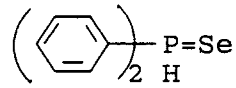

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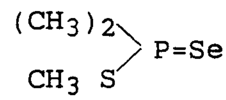

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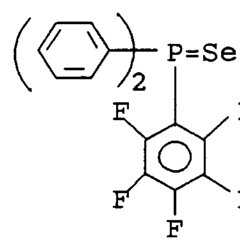

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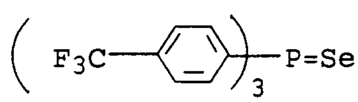
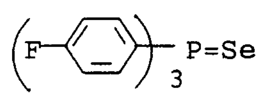


42.



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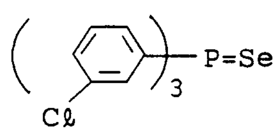


The selenium sensitization is disclosed in, e.g., U.S. Patents 1,574,944, 1,602,592, 1,623,499, 3,297,446, 3,297,447, 3,320,069, 3,408,196, 3,408,197, 3,442,653, 3,420,670 and 3,591,385, French Patents 2,093,038 and 2,093,209, JP-B-52-34491, JP-B-52-34492, JP-B-53-295, JP-B-57-22090, JP-A-59-180536, JP-A-59-185330, JP-A-59-181337, JP-A-59-187338, JP-A-59-192241, JP-A-60-150046, JP-A-60-151637, JP-A-61-246738, JP-A-3-111838, JP-A-3-148648, British Patents 255,846 and 861,984, and H.E. Spencer et al., "Journal of Photographic Science," Vol. 31, pages 158 to 169 (1983).

These selenium sensitizers are added in the form of a solution by dissolving in water, an organic solvent, such as methanol or ethanol, or a solvent mixture of these solvents, or in the form described in JP-A-4-140738 or JP-A-4-140739, so that they may be present during chemical sensitization. The selenium sensitizers are preferably added before start of chemical sensitization. A selenium sensitizer to be used is not limited to one type, but two or more of the selenium sensitizers described above can be used together. A combination of the labile selenium compound and the non-labile selenium compound may be used.

The addition amount of the selenium sensitizer used in the present invention varies depending on the activity of each selenium sensitizer used, the type or grain size of a silver halide, and the temperature and time of ripening. The addition amount, however, is preferably 1×10^{-8} mole or more, and more preferably 1×10^{-7} to 1×10^{-4} mole per mole of silver halide. When the selenium sensitizer is used, the temperature of chemical ripening is preferably 45°C or more, and more preferably 50°C to 80°C. The pAg and the pH can be set as desired. For example, the effect of the present invention can be obtained by a pH over a wide range of 4 to 9.

In the present invention, the selenium sensitization can be performed more effectively in the presence of a silver halide solvent.

Examples of the silver halide solvent usable in the present invention are (a) organic thioethers described in U.S. Patents 3,271,157, 3,531,289, and 3,574,628, JP-A-54-1019 ("JP-A" means Published Unexamined Japanese Patent Application), and JP-A-54-158917, (b) thiourea derivatives described in JP-A-53-82408, JP-A-55-77737, and JP-A-55-2982, (c) silver halide solvents having a thiocarbonyl group sandwiched between an oxygen or sulfur atom and a nitrogen atom, described in JP-A-53-144319, (d) imidazoles described in JP-A-54-100717, (e) sulfite salts, and (f) thiocyanates. Most preferable silver halide solvents are thiocyanate and tetramethylthiourea.

Although the amount of the silver halide solvent varies depending on the type of solvent, a preferable amount of, e.g., thiocyanate is 1×10^{-4} to 1×10^{-2} mol per mol of silver halide.

The sulfur sensitization is normally performed by adding a sulfur sensitizer to an emulsion and stirring the emulsion at a high temperature, preferably 40°C or more for a predetermined time.

The gold sensitization is normally performed by adding a gold sensitizer to an emulsion and stirring the emulsion at a high temperature, preferably 40°C or more for a predetermined time.

Sulfur sensitizers known to those skilled in the art can be used in the sulfur sensitization. Examples of the sulfur sensitizer are thiosulfate salts, allylthiocarbamidothioureas, allylisothiacyanate, cystine, p-toluenethiosulfonate salts, and rhodanine. It is also possible to use sulfur sensitizers described in, e.g., U.S. Patents 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313, and 3,656,955, German Patent 1,422,869, JP-B-56-24937, and JP-A-55-45016. The sulfur sensitizer is used in an amount sufficient to effectively increase the sensitivity of an emulsion. Although this amount varies over a wide range depending on various conditions such as the pH, the temperature, and the size of silver halide grains, it is preferably 1×10^{-7} to 1×10^{-4} mol per mol of silver halide.

The gold sensitizer for use in the gold sensitization of the present invention can be any gold compound having an oxidation number of gold of +1 or +3, and it is possible to use gold compounds normally used as gold sensitizers. Representative examples of the gold sensitizer are chloroaurate, potassium chloroaurate, auric trichloride, potassium auricthiocyanate, potassium iodoaurate, tetracyanoauric acid, ammonium aurothiacyanate, and pyridyltrichlorogold.

Although the addition amount of the gold sensitizers varies depending on various conditions, it is preferably 1×10^{-7} and 1×10^{-4} mol per mol of silver halide.

The thiocyanate salt is used in any of these gold-chalcogen sensitizations. Preferable examples of the thiocyanate salt are an ammonium salt, a potassium salt, and a sodium salt.

The thiocyanate salt can be added either singly or in the form of a mixture with gold sensitizers in the gold-chalcogen sensitization. In addition, the thiocyanate salt can be added either in portions or continuously.

In the present invention, the thiocyanate salt is more preferably used not only in the gold-chalcogen sensitization, but in grain formation or desalting. The use of a thiocyanate salt during grain formation is described in U.S. Patents 3,320,069 and 4,434,226.

A silver halide light-sensitive material of the present invention has an ISO sensitivity of preferably 100 to 3,200, and more preferably 400 to 3,200.

In the encased photographic material according to the present invention, a photographic light-sensitive material is contained in a lightproof container such that an end portion of the light-sensitive material is located at a position at which it may be irradiated with light (outside the container) and the remaining portion is located at a position at which it is shielded from light (within the container). Air circulates through the portion to be irradiated with light and the portion to be shielded therefrom. The light-sensitive material contained in the lightproof container is encased in a light-transmitting case.

Although the lightproof container of the present invention includes a cassette for sheet film, it is typically a cartridge for roll film. The cartridge for roll film has a spool around which a silver halide light-sensitive material is wound into the form of a roll, a film slit through which the light-sensitive material is inserted and extracted, and a cartridge main body for housing the spool such that the spool is rotatable around the axis. The spool has a flange for shielding light: the flange prevents external light from entering the cartridge through a gap formed between a cap, which is arranged on one end portion of the cartridge main body, typically a cylindrical body portion, and the spool. It is also preferable to provide a light-shielding member at the film slit to allow smooth extraction and rewind of film. This light-shielding member is described in Published Examined Japanese Utility Model Application No. 61-34526.

A currently widely distributed 135-format roll film corresponds to a photographic material of this type. That is, as shown in Fig. 2, a silver halide photographic light-sensitive material 24 is contained in a metal cartridge 22 having a plastic spool 21 as its shaft and is in part extracted from a film extraction portion 23 via a light-shielding ribbon. For convenience of film loading, several centimeters of film are normally extracted, and this portion 25 corresponds to the position which may be irradiated with light before photographing. Air circulates from the portion 25 to a portion to be shielded from light through the film extraction portion 23 or a gap formed in the cartridge 22.

The cartridge 22 containing the silver halide photographic light-sensitive material 24 is encased and sealed in a cartridge case 26 and a cap 27. The sealed case 26 is so designed as to shield gas that is harmful to light-sensitive materials and suppress permeation of excess water vapor. However, the permeabilities to gas and water vapor largely depend on the structures and the materials of the cartridge case 26 and the cap 27.

The humidity inside the sealed case 26 is preferably maintained constant. To obtain more advantageous effect of the present invention, a relative humidity inside the sealed case at 25°C is preferably 55% or more, more preferably 55% to 70%, and most preferably 55% to 65%.

"The humidity inside the sealed case is maintained constant" means that when the difference in humidity between the atmosphere and the interior of the case is 20%, a change in humidity inside the case is 10% or less when the case is left to stand at 25°C for 12 months.

The equilibrium humidity in the present invention is a value measured at 25°C and can be measured by conventional methods (the equilibrium humidity can be measured by a capacitance humidity measurement device, such as a HUMICAP humidity sensor available from VAISALA K.K.)

In the present invention, the cartridge case 26 and/or the cap 27 is light-transmitting, i.e., transparent or semitransparent. "Transparent or semitransparent" means that the portion 25 extracted from the film extraction portion 23 may be exposed essentially to external light before photographing. More specifically, when the film is left to stand under radiation of light of 10,000 lux for 24 hours, an increase in fog in the portion 25 extracted from the film extraction portion 23 is 0.1 or more, preferably 0.3 or more, and more preferably 0.5 or more, or overall fog is caused.

Plastic materials for forming the transmitting case 26 or cap 27 can be manufactured by addition polymerization of an olefin having a carbon-carbon double bond, ring-opening polymerization of a small number-membered cyclic compound, polycondensation (condensation polymerization) of two or more types of polyfunctional compounds, polyaddition, or addition condensation of a phenol derivative, a urea derivative or a melamine derivative with a compound having an aldehyde.

Representative examples of the olefin having a carbon-carbon double bond, as the raw material for forming the plastic material of the present invention, are styrene, α-methylstyrene, butadiene, methyl methacrylate, butyl acrylate, acrylonitrile, vinyl chloride, vinylidene chloride, vinylpyridine, N-vinylcarbazole, N-vinylpyrrolidone, vinylidene cyanide, ethylene, and propylene. Representative examples of the small number-membered cyclic compound are ethylene oxide, propylene oxide, glycidol, 3,3-bischloromethyloxetane, 1,4-dioxane, tetrahydrofuran, trioxane, ϵ-caprolactam, β-propiolactone, ethyleneimine, and tetramethylsiloxane.

Representative examples of the polyfunctional compound are carboxylic acids, such as terephthalic acid, adipic acid, and glutaric acid; isocyanates, such as toluenediisocyanate, tetramethylenediisocyanate, and hexamethylenediisocyanate; alcohols, such as ethyleneglycol, propyleneglycol, and glycerin; amines, such as hexamethylenediamine, tetramethylenediamine, and paraphenylenediamine; and epoxy. Representative examples of the phenol derivative, the urea derivative, and the melamine derivative are phenol, cresol, methoxyphenol, chlorophenol, urea, and melamine. Representative examples of the compound having an aldehyde are formaldehyde, acetaldehyde, octanal, dodecanal, and benzaldehyde. Two or more types of these raw materials can be used together in accordance with the target performance.

A catalyst or a solvent is sometimes used in the manufacture of the plastic material using these raw materials.

Examples of the catalyst are a free-radical polymerization catalyst, such as (1-phenylethyl)-azodiphenylmethane, dimethyl-2,2'-azobisisobutylate, 2,2'-azobis(2-methylpropane), benzoylperoxide, cyclohexanone peroxide, and potassium persulfate; a cation polymerization catalyst, such as sulfuric acid, toluenesulfonic acid, trifluorosulfuric acid, perchloric acid, trifluoroboric acid, and tin tetrachloride; an anion polymerisation catalyst, such as n-butyllithium, sodium/naphthalene, 9-fluorenyllithium, and phenylmagnesium bromide; a triethylaluminum/tetrachlorotitanium-based Ziegler-Natta catalyst; sodium hydroxide; potassium hydroxide; and a potassium metal.

The solvent is not particularly limited as long as it does not inhibit polymerization. Examples are hexane, decalin, benzene, toluene, cyclohexane, chloroform, acetone, methylethylketone, ethyl acetate, butyl acetate, and tetrahydrofuran.

In molding of plastic material, a plasticizer is mixed in plastic material as needed. Representative examples of the plasticizer are trioctylphosphate, tributylphosphate, dibutylphthalate, diethylsebacate, methylamylketone, nitrobenzene, γ-valerolactone, di-n-octylsuccinate, bromonaphthalene, and butylpalmitate.

Practical examples of the plastic material used in the present invention are shown below, but the material is not limited to these examples.

P-1 Polystyrene
P-2 Polyethylene
P-3 Polypropylene
P-4 Polymonochlorotrifluoroethylene
P-5 Vinylidene chloride resin
P-6 Vinyl chloride resin
P-7 Vinyl chloride-vinyl acetate copolymer resin
P-8 Acrylonitrile-butadiene-styrene copolymer resin
P-9 Methyl methacrylic resin
P-10 Vinylformal resin
P-11 Vinylbutyral resin
P-12 Polyethylenephthalate
P-13 Teflon
P-14 Nylon
P-15 Phenolic resin
P-16 Melamine resin

Examples of a plastic material most preferable for the present invention are polystyrene, polyethylene, and polypropylene.

The light-sensitive material in the present invention needs only to have at least one of silver halide emulsion layers, i.e., a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, formed on a support. The number or order of the silver halide emulsion layers and the non-light-sensitive layers are particularly not limited. A typical example is a silver halide photographic light-sensitive material having, on a support, at least one unit light-sensitive layer constituted by a plurality of silver halide emulsion layers which are sensitive to essentially the same color but have different sensitivities or speeds. The unit light-sensitive layer is sensitive to blue, green or red light. In a multi-layered silver halide color photographic light-sensitive material, the unit light-sensitive layers are generally arranged such that red-, green-, and blue-sensitive layers are formed from a support side in the order named. However, this order may be reversed or a layer having a different color sensitivity may be sandwiched between layers having the same color sensitivity in accordance with the application.

Non-light-sensitive layers such as various types of interlayers may be formed between the silver halide light-sensitive layers and as the uppermost layer and the lowermost layer.

The interlayer may contain, e.g., couplers and DIR compounds as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038 or a color mixing inhibitor which is normally used.

As a plurality of silver halide emulsion layers constituting each unit light-sensitive layer, a two-layered structure of high- and low-speed emulsion layers can be preferably used as described in West German Patent 1,121,470 or British Patent 923,045. In this case, layers are preferably arranged such that the sensitivity or speed is sequentially decreased toward a support, and a non-light-sensitive layer may be formed between the silver halide emulsion layers. In addition, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, layers may be arranged such that a low-speed emulsion layer is formed remotely from a support and a high-speed layer is formed close to the support.

More specifically, layers may be arranged from the farthest side from a support in an order of low-speed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)-/low-speed green-sensitive layer (GL)/high-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RL), an order of BH/BL/GL/GH/ RH/RL, or an order of BH/BL/GH/GL/RL/RH.

In addition, as described in JP-B-55-34932, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GH/RH/GL/RL. Furthermore, as described in JP-A-56-25738 and JP-A-62-63936, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GL/RL/GH/RH.

As described in JP-B-49-15495, three layers may be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an intermediate layer, and a silver halide emulsion layer having sensitivity lower than that of the intermediate layer is arranged as a lower layer. In other words, three layers having different sensitivities may be arranged such that the sensitivity is sequentially decreased toward the support. When a layer structure is constituted by three layers having different sensitivities or speeds, these layers may be arranged in an order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer from the farthest side from a support in a layer having the same color sensitivity as described in JP-A-59-202464.

Also, an order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer, or low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer may be adopted. Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

To improve the color reproduction, a donor layer (CL) of an interlayer effect can be arranged directly adjacent to, or close to, a main light-sensitive layer such as BL, GL or RL. The donor layer has a spectral sensitivity distribution which is different from that of the main light-sensitive layer. Donor layers of this type are disclosed in U.S. Patent 4,663,271, U.S. Patent 4,705,744, U.S. Patent 4,707,436, JP-A-62-160448, and JP-A-63-89850.

As described above, various layer configurations and arrangements can be selected in accordance with the application of the light-sensitive material.

A preferable silver halide contained in photographic emulsion layers of the photographic light-sensitive material of the present invention is silver bromoiodide, silver chloroiodide, or silver chlorobromoiodide containing about 30 mol% or less of silver iodide. The most preferable silver halide is silver bromoiodide or silver chlorobromoiodide containing about 2 mol% to about 10 mol% of silver iodide.

Silver halide grains contained in the photographic emulsion may have regular crystals such as cubic, octahedral, or tetradecahedral crystals, irregular crystals such as spherical, or tabular crystals, crystals having defects such as twin planes, or composite shapes thereof.

The silver halide may consist of fine grains having a grain size of about 0.2 μm or less or large grains having a projected-area diameter of up to 10 μm, and the emulsion may be either a polydisperse emulsion or a monodisperse emulsion.

The silver halide photographic emulsion which can be used in the present invention can be prepared by methods described in, for example, Research Disclosure (RD) No. 17643 (December 1978), pp. 22 to 23, "I. Emulsion preparation and types", RD No. 18716 (November 1979), page 648, and RD No. 307105 (November 1989), pp. 863 to 865; P. Glafkides, "Chemie et Phisique Photographique", Paul Montel, 1967; G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1964.

Monodisperse emulsions described in, for example, U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748 are also preferred.

Also, tabular grains having an aspect ratio of about 3 or more can be used in the present invention. The tabular grains can be easily prepared by methods described in, e.g., Gutoff, "Photographic Science and Engineering", Vol. 14, PP. 248 to 257 (1970); U.S. Patents 4,434,226; 4,414,310; 4,433,048 and 4,499,520, and British Patent 2,112,157.

The crystal structure may be uniform, may have different halogen compositions in the interior and the surface thereof, or may be a layered structure. Alternatively, silver halides having different compositions may be joined by an epitaxial junction, or a compound other than a silver halide such as silver rhodanide or zinc oxide may be joined. A mixture of grains having various types of crystal shapes may be used.

The above emulsion may be of any of a surface latent image type in which a latent image is mainly formed on the surface of each grain, an internal latent image type in which a latent image is formed in the interior of each grain, and a type in which a latent image is formed on the surface and in the interior of each grain. However, the emulsion must be of a negative type. When the emulsion is of an internal latent image type, it may be a core/shell internal latent image type emulsion described in JP-A-63-264740. A method of preparing this core/shell internal latent image type emulsion is described in JP-A-59-133542. Although the thickness of a shell of this emulsion changes in accordance with development or the like, it is preferably 3 to 40 nm, and most preferably, 5 to 20 nm.

A silver halide emulsion layer is normally subjected to physical ripening, chemical ripening, and spectral sensitization steps before it is used. Additives for use in these steps are described in RD Nos. 17,643; 18,716 and 307,105 and they are summarized in the table represented later.

In the light-sensitive material of the present invention, two or more types of emulsions different in at least one of features such as a grain size, a grain size distribution, a halogen composition, a grain shape, and sensitivity can be mixed and used in the same layer.

Surface-fogged silver halide grains described in U.S. Patent 4,082,553, internally fogged silver halide grains described in U.S. Patent 4,626,498 or JP-A-59-214852, and colloidal silver can be preferably used in a light-sensitive silver halide emulsion layer and/or a substantially non-light-sensitive hydrophilic colloid layer. The internally fogged or surface-fogged silver halide grains are silver halide grains which can be uniformly (non-imagewise) developed despite the presence of a non-exposed portion and exposed portion of the light-sensitive material. A method of preparing the internally fogged or surface-fogged silver halide grain is described in U.S. Patent 4,626,498 or JP-A-59-214852.

The silver halides which form the core of the internally fogged or surface-fogged core/shell silver halide grains may be of the same halogen composition or different halogen compositions. Examples of the internally fogged or surface-fogged silver halide are silver chloride, silver bromochloride, silver bromoiodide, and silver bromochloroiodide. Although the grain size of these fogged silver halide grains is not particularly limited, an average grain size is preferably 0.01 to 0.75 μm, and most preferably, 0.05 to 0.6 μm. The grain shape is also not particularly limited, and may be a regular grain shape. Although the emulsion may be a polydisperse emulsion, it is preferably a monodisperse emulsion (in which at least 95% in weight or number of silver halide grains have a grain size falling within a range of ±40% of the average grain size).

Photographic emulsions used in the present invention may be subjected to spectral sensitization by methine dyes and the like. Usable dyes include a cyanine dye, a merocyanine dye, a composite cyanine dye, a composite merocyanine dye, a holopolar cyanine dye. a hemicyanine dye, a styryl dye, and a hemioxonole dye. Most useful dyes are those belonging to a cyanine dye, a merocyanine dye, and a composite merocyanine dye. Any nucleus commonly contained as a basic heterocyclic nucleus in cyanine dyes can be contained in these dyes. Examples of an applicable nucleus are a pyrroline uncleus, an oxazoline uncleus, a thiozoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, and pyridine nucleus; a nucleus in which an aliphatic hydrocarbon ring is fused to any of the above nuclei; and a nucleus in which an aromatic hydrocarbon ring is fused to any of the above nuclei, e.g., an indolenine nucleus, a benzindolenine uncleus, an indole nucleus, a benzoxazble nucleus, a naphthoxazole nucleus, a benzthiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus, and a quionoline nucleus. These nuclei may have a substitute on a carbon atom.

It is possible for a merocyanine dye or a composite merocyanine dye to have a 5- to 6-membered heterocyclic nucleus as a nucleus having a ketomethylene structure. Examples are a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thiooxazolidin-2,4-dione nucleus, a thiazolidin-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus.

Although these sensitising dyes may be used singly, they can also be used together. The combination of sensitising dyes is often used for a supersensitization purpose. Representative examples of the combination are described in U.S. Patents 2,688,545, 2,977,299, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964. 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, British Patents 1,344,281 and 1,507,803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618, and JP-A-100925.

The emulsions used in the present invention may contain, in addition to the sensitising dyes, dyes having no spectral sensitizing effect or substances not essentially absorbing visible light and presenting supersensitization.

The sensitizing dyes can be added to an emulsion at any point in preparation of an emulsion, which is conventionally known to be useful. Most ordinarily, the addition is performed after completion of chemical sensitization and before coating. However, it is possible to perform the addition at the same time as addition of chemical sensitizing dyes to perform spectral sensitization and chemical sensitization simultaneously, as described in U.S. Patents 3,628,969 and 4,225,666. It is also possible to perform the addition prior to chemical sensitization, as described in JP-A-58-113928, or before completion of formation of a silver halide grain precipitation to start spectral sensitization. Alternatively, as disclosed in U.S. Patent 4,225,666, these dyes described above can be added separately: a portion of the dyes may be added prior to chemical sensitization, while the remaining portion is added after that. That is, the dyes can be added at any time during formation of silver halide grains, including the method disclosed in U.S. Patent 4,183,756.

The addition amount of the sensitizing dye may be 4×10^{-6} to 8×10^{-3} mole per mole of silver halide. However, for a more preferable silver halide grain size of 0.2 to 1.2 μm, an addition amount of about 5×10^{-5} to 2×10^{-3} mole per mole of silver halide is more effective.

In the present invention, a non-light-sensitive fine grain silver halide is preferably used. The non-light-sensitive fine grain silver halide means silver halide fine grains not sensitive upon imagewise exposure for obtaining a dye image and essentially not developed in development. The non-light-sensitive fine grain silver halide is preferably not fogged beforehand.

The fine grain silver halide contains 0 to 100 mol% of silver bromide and may contain silver chloride and/or silver iodide as needed. Preferably, the fine grain silver halide contains 0.5 to 10 mol% of silver iodide.

An average grain size (an average value of equivalent-circle diameters of projected areas) of the fine grain silver halide is preferably 0.01 to 0.5 μm, and more preferably, 0.02 to 0.2 μm.

The fine grain silver halide can be prepared by a method similar to a method of preparing normal light-sensitive silver halide. In this preparation, the surface of a silver halide grain need not be subjected to either chemical sensitization or spectral sensitization. However, before the silver halide grains are added to a coating solution, a known stabilizer such as a triazole compound, an azaindene compound, a benzothiazolium compound, a mercapto compound, or a zinc compound is preferably added. This fine grain silver halide grain-containing layer preferably contains colloidal silver.

A coating silver amount of the light-sensitive material of the present invention is preferably 6.0 g/m^2 or less, and most preferably, 4.5 g/m^2 or less.

Known photographic additives usable in the present invention are also described in the above three RDs, and they are summarized in the following Table:

	Additives	RD17643 [December,1978]	RD18716 [November,1979]
1.	Chemical sensitizers	page 23	page 648, right column
2.	Sensitivity increasing agent		ditto
3.	Spectral sensitizers, super sensitizers	pages 23 - 24	page 648, right column to page 649, right column
4.	Brighteners	page 24	page 647, right column
5.	Antifoggants and stabilizers	pages 24 - 25	page 649, right column
6.	Light absorbent, filter dye, ultraviolet absorbents	pages 25 - 26	page 649, right column to page 650, left column
7.	Stain preventing agents	page 25, right column	page 650, left to right columns
8.	dye image stabilizer	page 25	page 650, left column
9.	Hardening agents	page 26	page 651, left column
10.	Binder	page 26	ditto
11.	Plasticizers, lubricants	page 27	page 650, right column
12.	Coating aids, surface active agents	pages 26 - 27	ditto
13.	Antistatic agents	page 27	ditto
14.	Matting agents		

(Continued)

	Additives	RD307105
1.	Chemical sensitizers	page 866
2.	Sensitivity increasing agents	
3.	Spectral sensitizers, super sensitizers	page 866 - 868
4.	Brighteners	page 868
5.	Antifoggants and stabilizers	pages 868 - 750
6.	Light absorbent, filter dye, ultraviolet absorbents	page 873
7.	Stain preventing agents	page 872
8.	Dye image stabilizer	ditto
9.	Hardening agents	pages 874 - 875
10.	Binder	pages 873 - 874
11.	Plasticizers, lubricants	page 876
12.	Coating aids, surface active agents	pages 875 - 876
13.	Antistatic agents	pages 876 - 877
14.	Matting agents	pages 878 - 879

In order to prevent degradation in photographic properties caused by formaldehyde gas, a compound described in U.S. Patent 4,411,987 or 4,435,503, which can react with formaldehyde and fix the same, is preferably added to the light-sensitive material.

The light-sensitive material of the present invention preferably contains a mercapto compound described in U.S. Patents 4,740,454 and 4,788,132, JP-A-62-18539, and JP-A-1-283551.

The light-sensitive material of the present invention preferably contains compounds which release, regardless of a developed silver amount produced by the development, a fogging agent, a development accelerator, a silver halide solvent, or precursors thereof, described in JP-A-1-106052 .

The light-sensitive material of the present invention preferably contains dyes dispersed by methods described in International Disclosure WO 88/04794 and JP-A-1-502912 or dyes described in European Patent 317,308A, U.S. Patent 4,420,555, and JP-A-1-259358.

Various color couplers can be used in the present invention, and specific examples of these couplers are described in patents described in the above-mentioned RD No. 17643, VII-C to VII-G and RD No. 307105, VII-C to VII-G.

Preferable examples of yellow couplers are described in, e.g., U.S. Patents 3,933,501; 4,022,620; 4,326,024; 4,401,752 and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents 3,973,968; 4,314,023 and 4,511,649, and European Patent 249,473A.

Examples of a magenta coupler are preferably 5-pyrazolone type and pyrazoloazole type compounds, and more preferably, compounds described in, for example, U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, RD No. 24220 (June 1984), JP-A-60-33552, RD No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-18951, U.S. Patents 4,500,630; 4,540,654 and 4,556,630, and WO No. 88/04795.

Examples of a cyan coupler are phenol type and naphthol type ones. Of these, preferable are those described in, for example, U.S. Patents 4,052,212; 4,146,396; 4,228,233; 4,296,200; 2,369,929; 2,801,171; 2,772,162; 2,895,826; 3,772,002; 3,758,308; 4,343,011 and 4,327,173, West German Patent Laid-open Application 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622; 4,333,999; 4,775,616; 4,451,559; 4,427,767; 4,690,889; 4,254,212 and 4,296,199, and JP-A-61-42658. Also, the pyrazoloazole type couplers disclosed in JP-A-64-553, JP-A-64-554, JP-A-64-555 and JP-A-64-556, and imidazole type couplers disclosed in U.S. Patent 4,818,672 can be used as cyan coupler in the present invention.

Typical examples of a polymerized dye-forming coupler are described in, e.g., U.S. Patents 3,451,820; 4,080,211; 4,367,282; 4,409,320 and 4,576,910, British Patent 2,102,173, and European Patent 341,188A.

Preferable examples of a coupler capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Laid-open Patent Application No. 3,234,533.

Preferable examples of a colored coupler for correcting unnecessary absorption of a colored dye are those described in RD No. 17643, VII-G, RD No. 30715, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, and British Patent 1,146,368. A coupler for correcting unnecessary absorption of a colored dye by a fluorescent dye released upon coupling described in U.S. Patent 4,774,181 or a coupler having a dye precursor group which can react with a developing agent to form a dye as a split-off group described in U.S. Patent 4,777,120 may be preferably used.

Those compounds which release a photographically useful residue upon coupling may also be preferably used in the present invention. DIR couplers, i.e., couplers releasing a development inhibitor, are preferably those described in the patents cited in the above-described RD No. 17643, VII-F and RD No. 307105, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 4,248,962 and 4,782,012.

RD Nos. 11449 and 24241, and JP-A-61-201247, for example, disclose couplers which release bleaching accelerator. These couplers effectively serve to shorten the time of any process that involves bleaching. They are effective, particularly when added to light-sensitive material containing tabular silver halide grains. Preferable examples of a coupler which imagewise releases a nucleating agent or a development accelerator are preferably those described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840. In addition, compounds releasing, e.g., a fogging agent, a development accelerator, or a silver halide solvent upon redox reaction with an oxidized form of a developing agent, described in JP-A-60-107029, JP-A-60-252340, JP-A-1-44940, and JP-A-1-45687, can also be preferably used.

Examples of other compounds which can be used in the light-sensitive material of the present invention are competing couplers described in, for example, U.S. Patent 4,130,427; poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler releasing redox compound, or a DIR redox releasing redox compound described in, for example, JP-A-60-185950 and JP-A-62-24252; couplers releasing a dye which restores color after being released described in European Patent 173,302A and 313,308A; a ligand releasing coupler described in, e.g., U.S. Patent 4,553,477; a coupler releasing a leuco dye described in JP-A-63-75747; and a coupler releasing a fluorescent dye described in U.S. Patent 4,774,181.

The couplers for use in this invention can be introduced into the light-sensitive material by various known dispersion methods.

Examples of a high-boiling point organic solvent to be used in the oil-in-water dispersion method are described in, e.g., U.S. Patent 2,322,027. Examples of a high-boiling point organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175°C or more at atmospheric pressure are phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis-(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate, bis(1,1-di-ethylpropyl) phthalate), phosphate or phosphonate esters (e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trichloropropylphosphate, and di-2-ethylhexylphenylphosphonate), benzoate esters (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylate esters (e.g., bis(2-ethylhexyl) sebacate, dioctylazelate, glyceroltributyrate, isostearyllactate, and trioctylcitrate), an aniline derivative (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene). An organic solvent having a boiling point of about 30°C or more, and preferably, 50°C to about 160°C can be used as an auxiliary solvent. Typical examples of the auxiliary solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.

Steps and effects of a latex dispersion method and examples of a immersing latex are described in, e.g., U.S. Patent 4,199,363 and German Laid-open Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

Various types of antiseptics and fungicides agent are preferably added to the color light-sensitive material of the present invention. Typical examples of the antiseptics and the fungicides are phenethyl alcohol, and 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol, and 2-(4-thiazolyl)benzimidazole, which are described in JP-A-63-257747, JP-A-62-272248, and JP-A-1-80941.

The present invention can be applied to various color light-sensitive materials. Examples of the material are a color negative film for a general purpose or a movie, a color reversal film for a slide or a television, a color paper, a color positive film, and a color reversal paper.

A support which can be suitably used in the present invention is described in, e.g., RD. No. 17643, page 28, RD. No. 18716, from the right column, page 647 to the left column, page 648, and RD. No. 307105, page 879.

In the light-sensitive material of the present invention, the sum total of film thicknesses of all hydrophilic colloidal layers at the side having emulsion layers is preferably 28 µm or less, more preferably, 23 µm or less, much more preferably, 18 µm or less, and most preferably, 16 µm or less. A film swell speed $T_{1/2}$ is preferably 30 seconds or less, and more preferably, 20 seconds or less. The film thickness means a film thickness measured under moisture conditioning at a temperature of 25°C and a relative humidity of 55% (two days). The film swell speed $T_{1/2}$ can be measured in accordance with a known method in the art. For example, the film swell speed $T_{1/2}$ can be measured by using a swello-meter described by A. Green et al. in Photographic Science & Engineering, Vol. 19, No. 2, pp. 124 to 129. When 90% of a maximum swell film thickness reached by performing a treatment by using a color developer at 30°C for 3 minutes and 15 seconds is defined as a saturated film thickness, $T_{1/2}$ is defined as a time required for reaching 1/2 of the saturated film thickness.

The film swell speed $T_{1/2}$ can be adjusted by adding a film hardening agent to gelatin as a binder or changing aging conditions after coating. A swell ratio is preferably 150% to 400%. The swell ratio is calculated from the maximum swell film thickness measured under the above conditions in accordance with a relation:

(maximum swell film thickness - film thickness)/film thickness.

In the light-sensitive material of the present invention, a hydrophilic colloid layer (called back layer) having a total dried film thickness of 2 to 20 µm is preferably formed on the side opposite to the side having emulsion layers. The back layer preferably contains, e.g., the light absorbent, the filter dye, the ultraviolet absorbent, the antistatic agent, the film hardener, the binder, the plasticizer, the lubricant, the coating aid, and the surfactant, described above. The swell ratio of the back layer is preferably 150% to 500%.

The color photographic light-sensitive material according to the present invention can be developed by conventional methods described in RD. No. 17643, pp. 28 and 29, RD. No. 18716, the left to right columns, page 651, and RD. No. 307105, pp. 880 and 881.

A color developer used in development of the light-sensitive material of the present invention is an aqueous alkaline solution containing as a main component, preferably, an aromatic primary amine color developing agent. As the color developing agent, although an aminophenol compound is effective, a p-phenylenediamine compound is preferably used. Typical examples of the p-phenylenediamine compound are: 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline, 4-amino-3-methyl-N-methyl-N-(3-hydroxypropyl)aniline, 4-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline, 4-amino-3-methyl-N-ethyl-N-(2-hydroxypropyl)anline, 4-amino-3-ethyl-N-ethyl-N-(3-hydroxypropyl)aniline, 4-amino-3-methyl-N-propyl-N-(3-hydroxypropyl)aniline, 4-amino-3-propyl-N-methyl-N-(3-hydroxypropyl)aniline, 4-amino-3-methyl-N-methyl-N-(4-hydroxybutyl)aniline, 4-amino-3-methyl-N-ethyl-N-(4-hydroxybutyl)aniline, 4-amino-3-methyl-N-propyl-N-(4-hydroxybutyl)aniline, 4-amino-3-methyl-N-ethyl-N-(3-hydroxy-2-methyl-propyl)aniline, 4-amino-3-methyl-N,N-bis(4-hydroxybutyl)aniline, 4-amino-3-methyl-N,N-bis(5-hydroxypentyl)-aniline, 4-amino-3-methyl-N-(5-hydroxypentyl)-N-(4-hydroxybutyl)aniline, 4-amino-3-methoxy-N-ethyl-N-(4-hydroxybutyl)aniline, 4-amino-3-ethoxy-N,N-bis(5-hydroxypentyl)aniline, 4-amino-3-propyl-N-(4-hydroxybutyl)aniline, and the sulfates, hydrochlorides and p-toluenesulfonates thereof. Of these compounds, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 4-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline, 4-amino-3-methyl-N-ethyl-N-(4-hydroxybutyl)aniline, and the sulfates, hydrochlorides and p-toluenesulfonates thereof are preferred in particular. The above compounds can be used in a combination of two or more thereof in accordance with the application.

In general, the color developer contains a pH buffering agent such as a carbonate, a borate or a phosphate of an alkali metal, and a development restrainer or an antifoggant such as a chloride, a bromide, an iodide, a benzimidazole, a benzothiazole, or a mercapto compound. If necessary, the color developer may also contain a preservative such as hydroxylamine, diethylhydroxylamine, a sulfite, a hydrazine such as N,N-biscarboxymethylhydrazine, a phenylsemicarbazide, triethanolamine, or a catechol sulfonic acid; an organic solvent such as ethyleneglycol or diethyleneglycol; a development accelerator such as benzylalcohol, polyethyleneglycol, a quaternary ammonium salt or an amine; a dye-forming coupler; a competing coupler; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity-imparting agent; and a chelating agent such as an aminopolycarboxylic acid, an aminopolyphosphonic acid, an alkylphosphonic acid, or a phosphonocarboxylic acid. Examples of the chelating agent are ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof.

In order to perform reversal development, black-and-white development is performed and then color development is performed. As a black-and-white developer, a well-known black-and-white developing agent, e.g., a dihydroxybenzene such as hydroquinone, a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone, and an aminophenol such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof. The pH of the color and black-and-white developers is generally 9 to 12. Although the quantity of replenisher of the developers depends on a color photographic light-sensitive material to be processed, it is generally 3 liters or less per m^2 of the light-sensitive material. The quantity of replenisher can be decreased to be 500 ml or less by decreasing a bromide ion concentration in a replenisher. When the quantity of the replenisher is decreased, a contact area of a processing tank with air is preferably decreased to prevent evaporation and oxidation of the solution upon contact with air.

The contact area of the processing solution with air in a processing tank can be represented by an aperture defined below:

Aperture = [contact area (cm^2) of processing solution with air]/[volume (cm^3) of the solution]

The above aperture is preferably 0.1 or less, and more preferably, 0.001 to 0.05. In order to reduce the aperture, a shielding member such as a floating cover may be provided on the surface of the photographic processing solution in the processing tank. In addition, a method of using a movable cover described in JP-A-1-82033 or a slit developing method descried in JP-A-63-216050 may be used. The aperture is preferably reduced not only in color and black-and-white development steps but also in all subsequent steps, e.g., bleaching, bleach-fixing, fixing, washing, and stabilizing steps. In addition, the quantity of replenisher can be reduced by using a means of suppressing storage of bromide ions in the developing solution.

A color development time is normally 2 to 5 minutes. The processing time, however, can be shortened by setting a high temperature and a high pH and using the color developing agent at a high concentration.

The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching may be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing may be performed after bleaching. Also, processing may be performed in a bleach-fixing bath having two continuous tanks, fixing may be performed before bleach-fixing, or bleaching may be performed after bleach-fixing, in accordance with the application. Examples of the bleaching agent are compounds of a polyvalent metal, e.g., iron (III); peracids; quinones; and nitro compounds. Typical examples of the bleaching agent are an organic complex salt of iron (III), e.g., a complex salt with an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, and 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid; or a complex salt with citric acid, tartaric acid, or malic acid. Of these compounds, an iron (III) complex salt of an aminopolycarboxylic acid such as an iron (III) complex salt of ethylenediaminetetraacetic acid or 1,3-diaminopropanetetraacetic acid is preferred because it can increase a processing speed and prevent an environmental contamination. The iron (III) complex salt of an aminopolycarboxylic acid is useful in both the bleaching and bleach-fixing solutions. The pH of the bleaching or bleach-fixing solution using the iron (III) complex salt of an aminopolycarboxylic acid is normally 4.0 to 8. In order to increase the processing speed, however, processing can be performed at a lower pH.

A bleaching accelerator can be used in the bleaching solution, the bleach-fixing solution, and their pre-bath, if necessary. Examples of a useful bleaching accelerator are: compounds having a mercapto group or a disulfide group described in, for example, U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and RD No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in JP-B-45-8506, JP-A-52-20832, JP-A-53-32735, and U.S. Patent 3,706,561; iodide salts described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds descried in West German Patents 966,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; compounds descried in JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940; and a bromide ion. Of these compounds, a compound having a mercapto group or a disulfide group is preferable since the compound has a large accelerating effect. In particular, compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are preferred. A compound described in U.S. Patent 4,552,834 is also preferable. These bleaching accelerators may be added in the light-sensitive material. These bleaching accelerators are useful especially in bleach-fixing of a photographic color light-sensitive material.

The bleaching solution or the bleach-fixing solution preferably contains, in addition to the above compounds, an organic acid in order to prevent a bleaching stain. The most preferable organic acid is a compound having an acid dissociation constant (pKa) of 2 to 5, e.g., acetic acid, propionic acid, or hydroxy acetic acid.

Examples of the fixing agent used in the fixing solution or the bleach-fixing solution are a thiosulfate salt, a thiocyanate salt, a thioether-based compound, a thiourea and a large amount of an iodide. Of these compounds, a thiosulfate, especially, ammonium thiosulfate, can be used in the widest range of applications. In addition, a combination of a thiosulfate with a thiocyanate, a thioether-based compound or thiourea is preferably used. As a preservative of the fixing solution or the bleach-fixing solution, a sulfite, a bisulfite, a carbonyl bisulfite adduct, or a sulfinic acid compound described in European Patent 294,769A is preferred. Further, in order to stabilize the fixing solution or the bleach-fixing solution, various types of aminopolycarboxylic acids or organic phosphonic acids are preferably added to the solution.

In the present invention, 0.1 to 10 moles, per liter, of a compound having a pKa of 6.0 to 9.0 are preferably added to the fixing solution or the bleach-fixing solution in order to adjust the pH. Preferable examples of the compound are imidazoles such as imidazole, 1-methylimidazole, 1-ethylimidazole, and 2-methylimidazole.

The total time of a desilvering step is preferably as short as possible as long as no desilvering defect occurs. A preferable time is one to three minutes, and more preferably, one to two minutes. A processing temperature is 25°C to 50°C, and preferably, 35°C to 45°C. Within the preferable temperature range, a desilvering speed is increased, and generation of a stain after the processing can be effectively prevented.

In the desilvering step, stirring is preferably as strong as possible. Examples of a method of intensifying the stirring are a method of colliding a jet stream of the processing solution against the emulsion surface of the light-sensitive material described in JP-A-62-183460, a method of increasing the stirring effect using rotating means described in JP-A-62-183461, a method of moving the light-sensitive material while the emulsion surface is brought into contact with a wiper blade provided in the solution to cause disturbance on the emulsion surface, thereby improving the stirring effect, and a method of increasing the circulating flow amount in the overall processing solution. Such a stirring improving means is effective in any of the bleaching solution, the bleach-fixing solution, and the fixing solution. It is assumed that the improvement in stirring increases the speed of supply of the bleaching agent and the fixing agent into the emulsion film to lead to an increase in desilvering speed. The above stirring improving means is more effective when the bleaching accelerator is used, i.e., significantly increases the accelerating speed or eliminates fixing interference caused by the bleaching accelerator.

An automatic developing machine for processing the light-sensitive material of the present invention preferably has a light-sensitive material conveyer means described in JP-A-60-191257, JP-A-60-191258, or JP-A-60-191259. As described in JP-A-60-191257, this conveyer means can significantly reduce carry-over of a processing solution from a pre-bath to a post-bath, thereby effectively preventing degradation in performance of the processing solution. This effect significantly shortens especially a processing time in each processing step and reduces the quantity of replenisher of a processing solution.

The photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range in accordance with the properties (e.g., a property determined by the substances used, such as a coupler) of the light-sensitive material, the application of the material, the temperature of the water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineering", Vol. 64, PP. 248 - 253 (May, 1955). In the multi-stage counter-current scheme disclosed in this reference, the amount of water used for washing can be greatly decreased. Since washing water stays in the tanks for a long period of time, however, bacteria multiply and floating substances may be adversely attached to the light-sensitive material. In order to solve this problem in the process of the color photographic light-sensitive material of the present invention, a method of decreasing calcium and magnesium ions can be effectively utilized, as described in JP-A-62-288838. In addition, a germicide such as an isothiazolone compound and a cyabendazole described in JP-A-57-8542, a chlorine-based germicide such as chlorinated sodium isocyanurate, and germicides such as benzotriazole, described in Hiroshi Horiguchi et al., "Chemistry of Antibacterial and Antifungal Agents", (1986), Sankyo Shuppan, Eiseigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", (1982), Kogyogijutsu-Kai, and Nippon Bokin Bobai Gakkai ed., "Dictionary of Antibacterial and Antifungal Agents", (1986), can be used.

The pH of the water for washing the photographic light-sensitive material of the present invention is 4 to 9, and preferably, 5 to 8. The water temperature and the washing time can vary in accordance with the properties and applications of the light-sensitive material. Normally, the washing time is 20 seconds to 10 minutes at a temperature of 15°C to 45°C, and preferably, 30 seconds to 5 minutes at 25°C to 40°C. The light-sensitive material of the present invention can be processed directly by a stabilizing agent in place of water-washing. All known methods described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be used in such stabilizing processing.

In some cases, stabilizing is performed subsequently to washing. An example is a stabilizing bath containing a dye stabilizing agent and a surface-active agent to be used as a final bath of the photographic color light-sensitive material. Examples of the dye stabilizing agent are an aldehyde such as formalin or glutaraldehyde, an N-methylol compound, hexamethylenetetramine, and an adduct of aldehyde sulfite. Various chelating agents and fungicides can be added to the stabilizing bath.

An overflow solution produced upon washing and/or replenishment of the stabilizing solution can be reused in another step such as a desilvering step.

In the processing using an automatic developing machine or the like, if each processing solution described above is concentrated by evaporation, water is preferably added to correct the concentration.

The silver halide color light-sensitive material of the present invention may contain a color developing agent in order to simplify processing and increases a processing speed. For this purpose, various types of precursors of a color developing agent can be preferably used. Examples of the precursor are an indoaniline-based compound described in U.S. Patent 3,342,597, Schiff base compounds described in U.S. Patent 3,342,599 and RD Nos. 14850 and 15159, an aldol compound described in RD No. 13924, a metal salt complex described in U.S. Patent 3,719,492, and a urethane-based compound described in JP-A-53-135628.

The silver halide color light-sensitive material of the present invention may contain various 1-phenyl-3-pyrazolidones in order to accelerate color development, if necessary. Typical examples of the compound are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

Each processing solution in the present invention is used at a temperature of 10 °C to 50 °C. Although a normal processing temperature is 33 °C to 38 °C, processing may be accelerated at a higher temperature to shorten a processing time, or image quality or stability of a processing solution may be improved at a lower temperature.

The present invention will be described in detail below by way of its examples, but the invention is not limited to these examples.

Example 1

Multiple layers having the compositions presented below were coated on a subbed triacetylcellulose film support to make a film sample 11 as a multilayered color light-sensitive material.

(Compositions of layers)

The main materials used in the individual layers are classified as follows.

ExC	Cyan coupler	UV	Ultraviolet absorbent
ExM	Magenta coupler	HBS	High-boiling point organic solvent
ExY	Yellow coupler	H	Gelatin hardener
ExS	Sensitizing dye		

The number corresponding to each component indicates the coating amount in units of g/m^2. The coating amount of a silver halide is represented by the amount of silver. The coating amount of each sensitizing dye is represented in units of mols per mol of silver halide in the same layer.

(Film Sample 11)

1st layer (Antihalation layer)	
Black colloidal silver	silver 0.18
Gelatin	1.40
ExM-1	0.18
ExF-1	2.0×10^{-3}
HBS-1	0.20

2nd layer (Interlayer)	
Emulsion G	silver 0.065
2,5-di-t-pentadecylhydroquinone	0.18
ExC-2	0.020
UV-1	0.060
UV-2	0.080
UV-3	0.10
HBS-1	0.10
HBS-2	0.020
Gelatin	1.04

3rd layer (Low-speed red-sensitive emulsion layer)	
Emulsion A	silver 0.25
Emulsion B	silver 0.25
ExS-1	6.9×10^{-5}
ExS-2	1.8×10^{-5}
ExS-3	3.1×10^{-4}
ExC-1	0.17
ExC-3	0.030
ExC-4	0.10
ExC-5	0.020
ExC-7	0.0050
ExC-8	0.010
Cpd-2	0.025
HBS-1	0.10
Gelatin	0.87

4th layer (Medium-speed red-sensitive emulsion layer)	
Emulsion D	silver 0.70
ExS-1	3.5×10^{-4}
ExS-2	1.6×10^{-5}
ExS-3	5.1×10^{-4}
ExC-1	0.13
ExC-2	0.060
ExC-3	0.0070
ExC-4	0.090
ExC-5	0.025
ExC-7	0.0010
ExC-8	0.0070
Cpd-2	0.023
HBS-1	0.10
Gelatin	0.75

5th layer (High-speed red-sensitive emulsion layer)	
Emulsion E	silver 1.40
ExS-1	2.4×10^{-4}
ExS-2	1.0×10^{-4}
ExS-3	3.4×10^{-4}
ExC-1	0.12
ExC-3	0.045
ExC-6	0.020
ExC-8	0.025
Cpd-2	0.050
HBS-1	0.22
HBS-2	0.10
Gelatin	1.20

6th layer (Interlayer)	
Cpd-1	0.10
HBS-1	0.50
Gelatin	1.10

7th layer (Low-speed green-sensitive emulsion layer)	
Emulsion C	silver 0.35
ExS-4	3.0×10^{-5}
ExS-5	2.1×10^{-4}
ExS-6	8.0×10^{-4}
ExM-1	0.010
ExM-2	0.33
ExM-3	0.086
ExY-1	0.015
HBS-1	0.30
HBS-3	0.010
Gelatin	0.73

8th layer (Medium-speed green-sensitive emulsion layer)	
Emulsion D	silver 0.80
ExS-4	3.2×10^{-5}
ExS-5	2.2×10^{-4}
ExS-6	8.4×10^{-4}
ExM-2	0.13
ExM-3	0.030
ExY-1	0.018
HBS-1	0.16
HBS-3	8.0×10^{-3}
Gelatin	0.90

9th layer (High-speed green-sensitive emulsion layer)	
Emulsion E	silver 1.25
ExS-4	3.7×10^{-5}
ExS-5	8.1×10^{-5}
ExS-6	3.2×10^{-4}
ExC-1	0.010
ExM-1	0.030
ExM-4	0.040
ExM-5	0.019
Cpd-3	0.040
HBS-1	0.25
HBS-2	0.10
Gelatin	1.44

10th layer (Yellow filter layer)	
Yellow colloidal silver	silver 0.030
Cpd-1	0.16
HBS-1	0.60
Gelatin	0.60

11th layer (Low-speed blue-sensitive emulsion layer)	
Emulsion C	silver 0.18
ExS-7	8.6×10^{-4}
ExY-1	0.020
ExY-2	0.22
ExY-3	0.50
ExY-4	0.020
HBS-1	0.28
Gelatin	1.10

12th layer (Medium-speed blue-sensitive emulsion layer)	
Emulsion D	silver 0.40
ExS-7	7.4×10^{-4}
ExC-7	7.0×10^{-3}
ExY-2	0.050
ExY-3	0.10
HBS-1	0.050
Gelatin	0.78

13th layer (High-speed blue-sensitive emulsion layer)	
Emulsion F	silver 1.00
ExS-7	4.0×10^{-4}
ExY-2	0.10
ExY-3	0.10
HBS-1	0.070
Gelatin	0.86

14th layer (1st protective layer)	
Emulsion G	silver 0.20
UV-4	0.11
UV-5	0.17
HBS-1	5.0×10^{-2}
Gelatin	1.00

15th layer (2nd protective layer)	
H-1	0.40
B-1 (diameter 1.7 μm)	5.0×10^{-2}
B-2 (diameter 1.7 μm)	0.10
B-3	0.10
S-1	0.20
Gelatin	1.20

In addition to the above components, to improve shelf stability, processability, a resistance to pressure, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained W-1 to W-3, B-4 to B-6, F-1 to F-17, iron salt, and lead salt.

The emulsions A to G used are shown in Table 1 below, in which:

(1) The emulsions A to F were subjected to reduction sensitization during grain preparation by using thiourea dioxide and thiosulfonic acid in accordance with the Examples in JP-A-2-191938.

(2) The emulsions A to F were subjected to gold sensitization, sulfur sensitization, and selenium sensitization in the presence of the indicated spectral sensitizing dyes described for the respective layers and sodium thiocyanate, in accordance with the Examples in JP-A-3-237450. More specifically, the gold-chalcogen sensitization were performed under the conditions specified in Table 2 below.

(3) Low-molecular weight gelatin was used in preparation of tabular grains in accordance with the Examples in JP-A-1-158426.

(4) In the tabular grains, and regular crystal grains having a grain structure, dislocation lines as described in JP-A-3-237450 under high-voltage electron microscopic observation.

Table 1

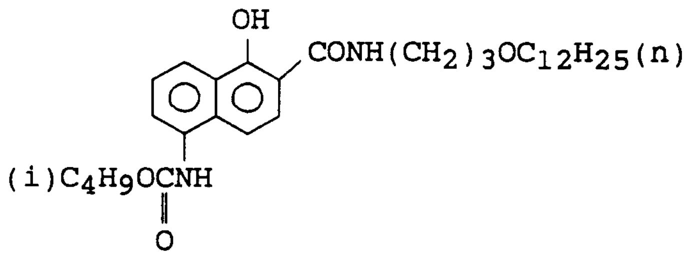
	Average AgI content (%)	Average grain size (µm)	Variation coefficient (%) according to grain size	Diameter/thickness ratio	Silver content ratio [core/intermediate/shell] (AgI content)	Grain structure/shape
Emulsion A	4.0	0.45	27	1	[1/3](13/1)	Double-structure octahedral grain
" B	8.9	0.70	14	1	[3/7](25/2)	Double-structure octahedral grain
" C	2.0	0.55	25	7	-	Uniform-structure tabular grain
" D	9.0	0.65	25	6	[12/59/29](0/11/8)	Triple-structure tabular grain
" E	9.0	0.85	23	5	[8/59/33](0/11/8)	Triple-structure tabular grain
" F	14.5	1.25	25	3	[37/63](34/3)	Double-structure tabular grain
" G	1.0	0.07	15	1	-	Uniform-structure fine grain

Table 2

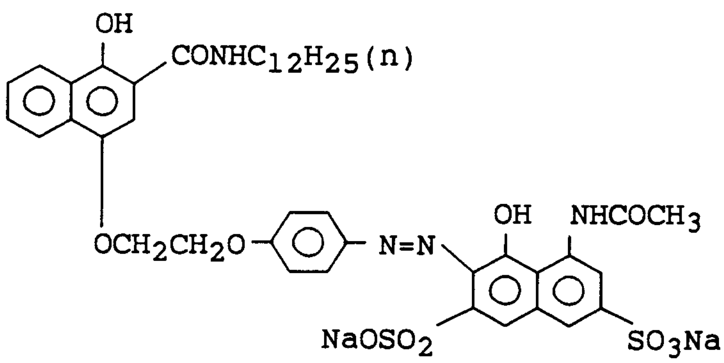
Emulsion	Amount of gold sensitizer (mol/molAg)	Amount of sulfur sensitizer (mol/mogAg)	Amount of selenium sensitizer (mol/mogAg)
A	1.9×10^{-5}	3.2×10^{-5}	3.1×10^{-5}
B	4.3×10^{-6}	1.2×10^{-5}	1.2×10^{-5}
C	4.5×10^{-6}	1.1×10^{-5}	3.9×10^{-6}
D	4.3×10^{-6}	1.2×10^{-5}	3.2×10^{-6}
E	2.0×10^{-6}	8.1×10^{-6}	1.35×10^{-6}
F	8.0×10^{-7}	2.3×10^{-6}	2.2×10^{-7}

The substances used are listed below:

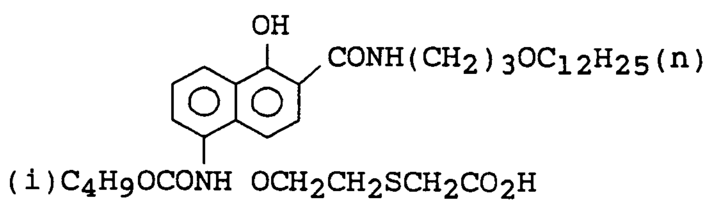
ExC-1



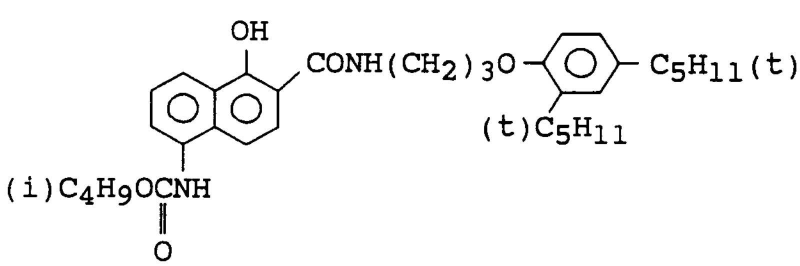
ExC-2



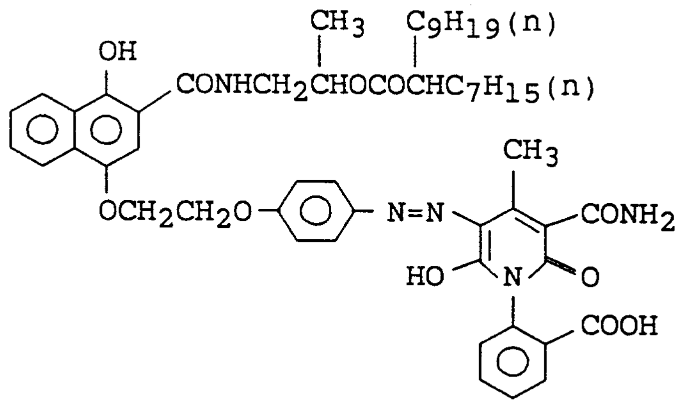
ExC-3



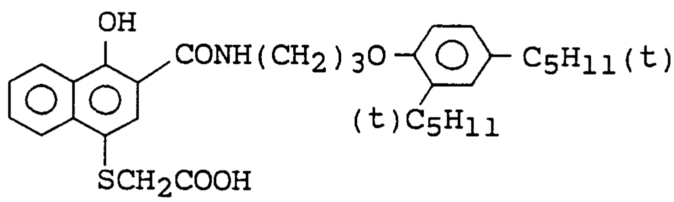
ExC-4



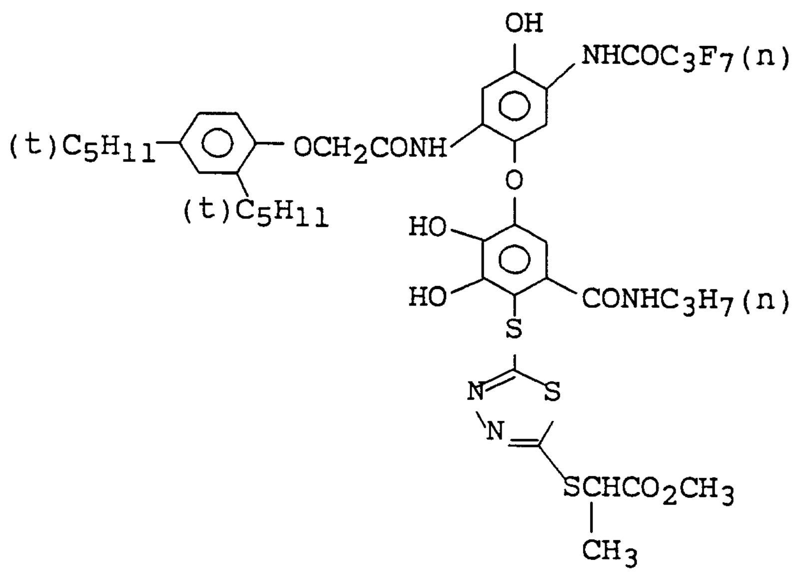
ExC-5



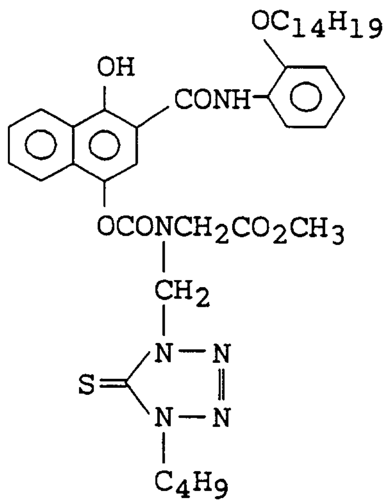
ExC-6



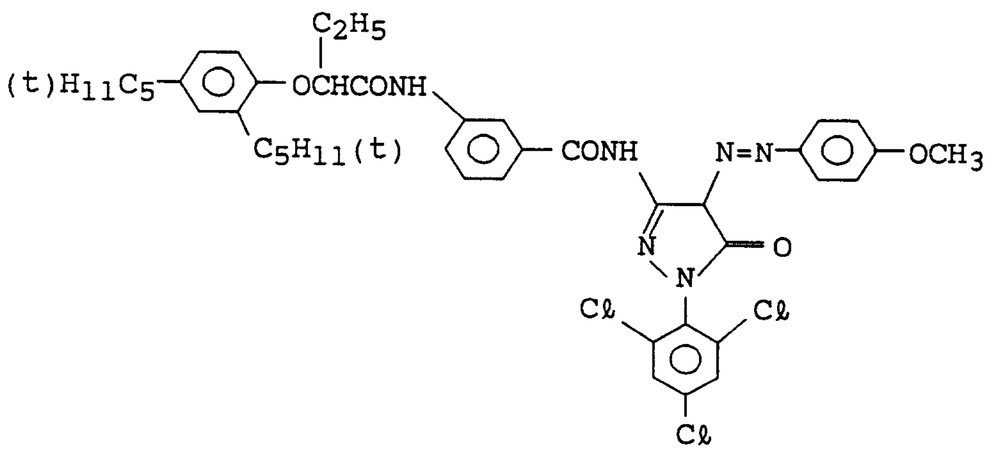
ExC-7



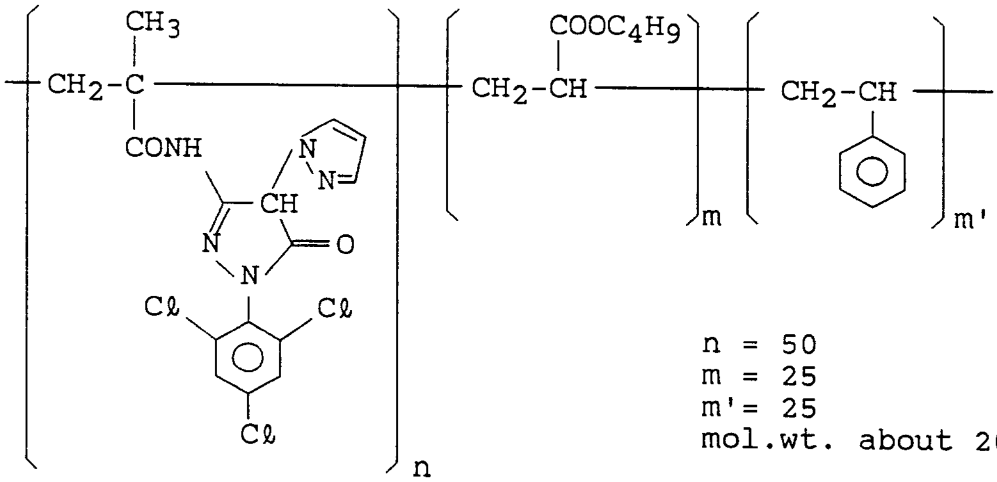
ExC-8



ExM-1

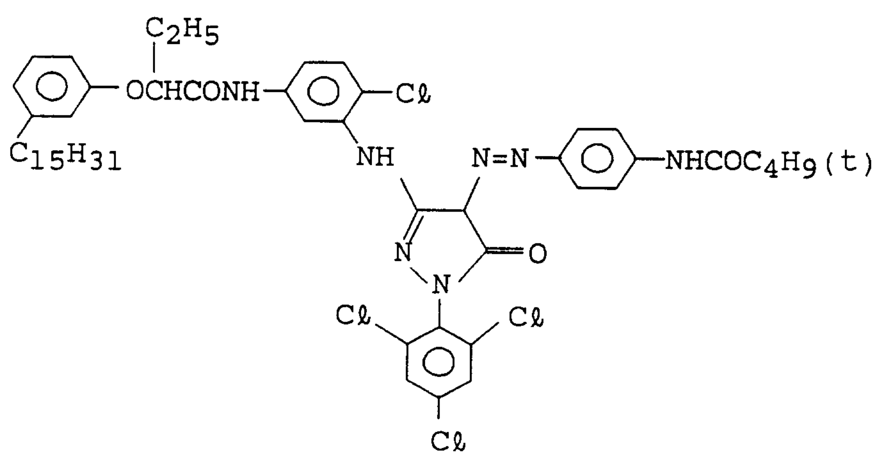


ExM-2

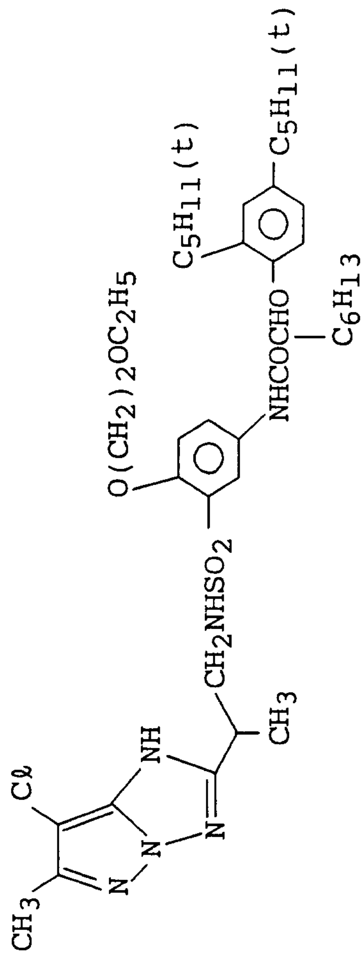


n = 50
m = 25
m' = 25
mol.wt. about 20,000

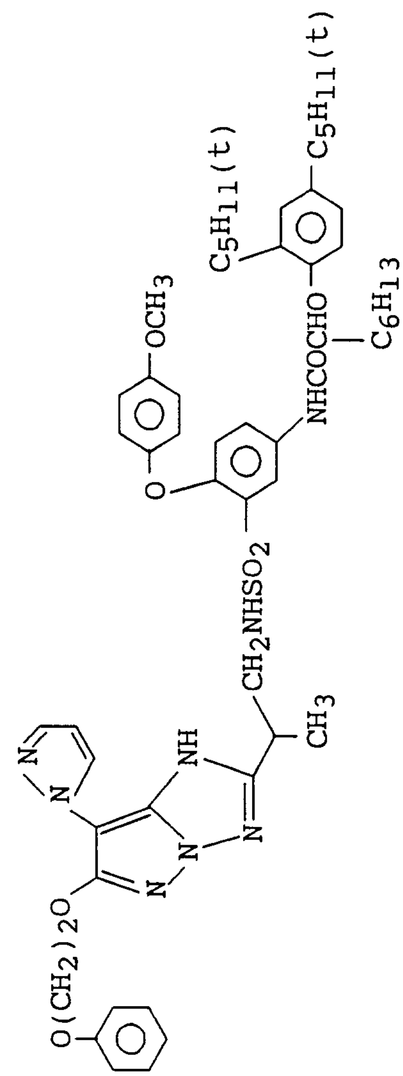
ExM-3



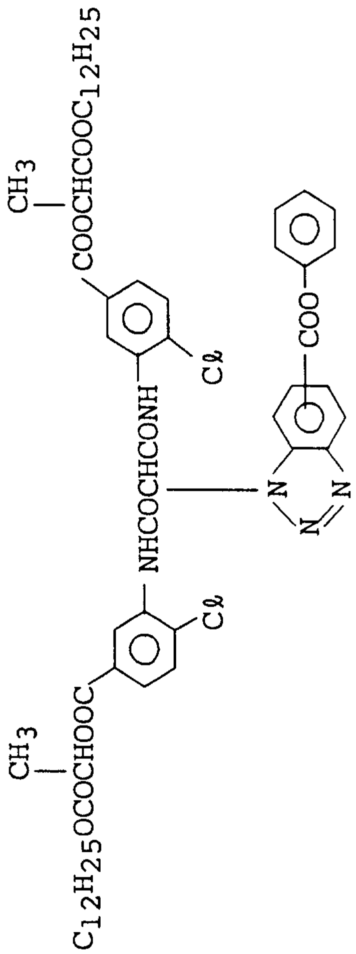
ExM-4



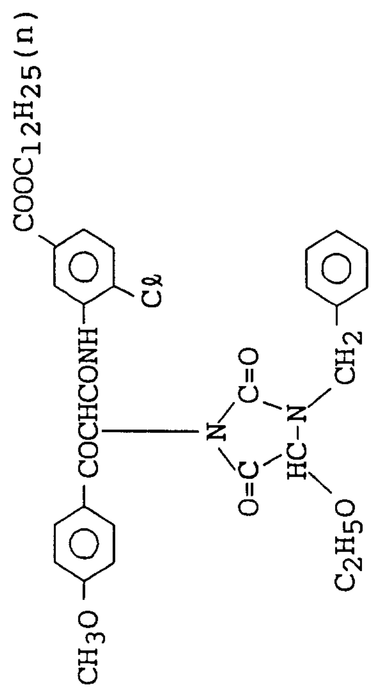
ExM-5



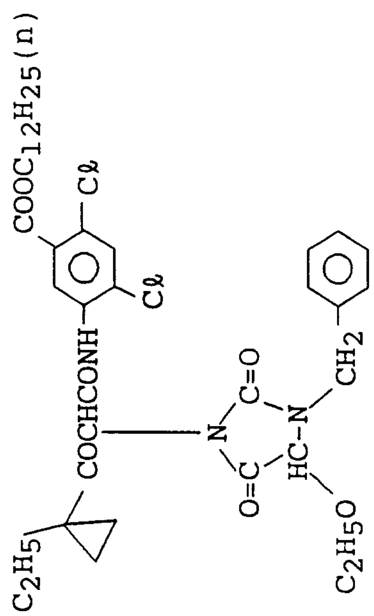
ExY-1



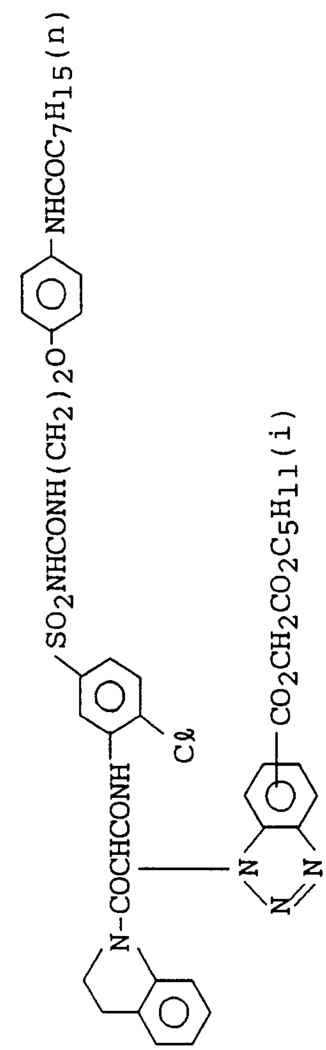
ExY-2



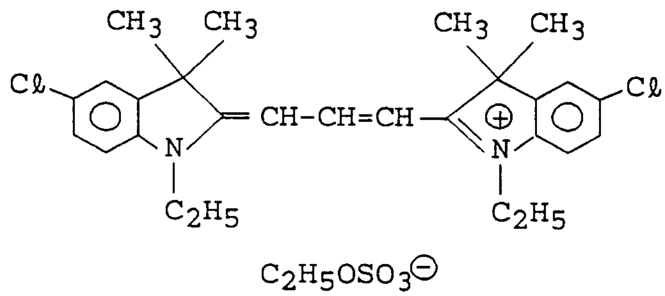
ExY-3


COOC12H25(n)
Cl
Cl
COCHCONH
C2H5
N
C=O
O=C
HC-N
CH2
C2H5O

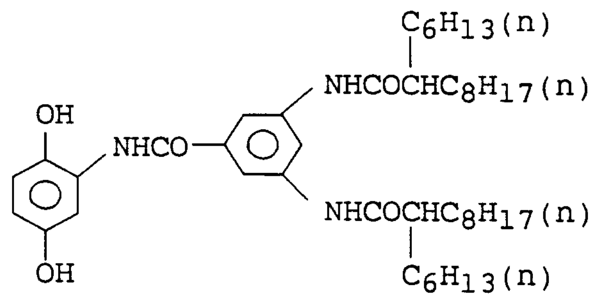
ExY-4


NHCOC7H15(n)
SO2NHCONH(CH2)2O
Cl
N-COCHCONH
CO2CH2CO2C5H11(i)
N
N
N

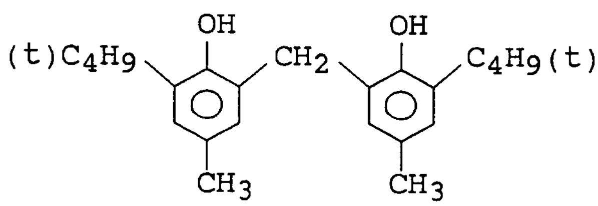
ExF-1



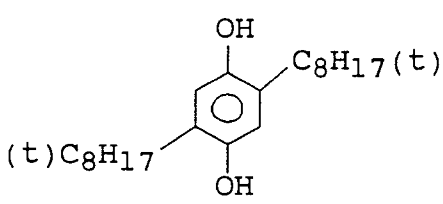
Cpd-1



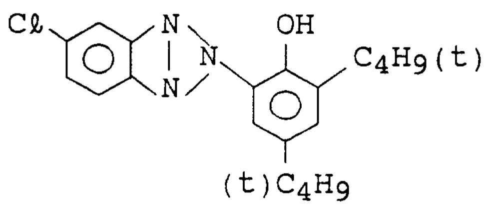
Cpd-2



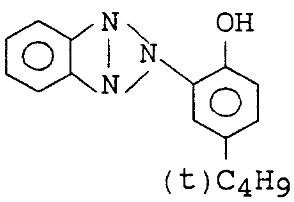
Cpd-3



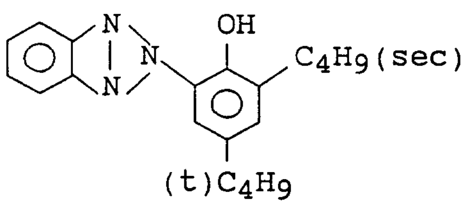
UV-1



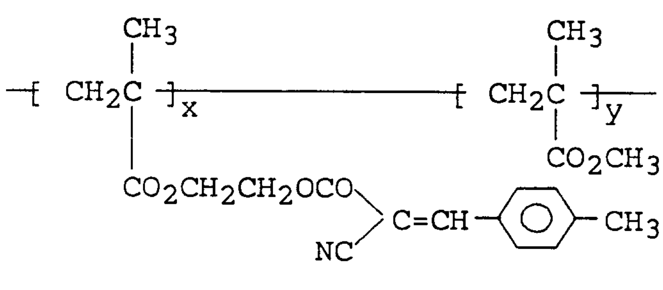
UV-2



UV-3

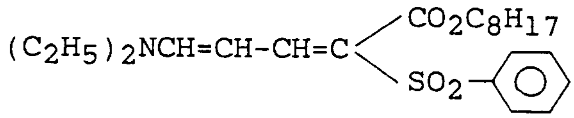


UV-4



x:y = 70:30 (wt%)

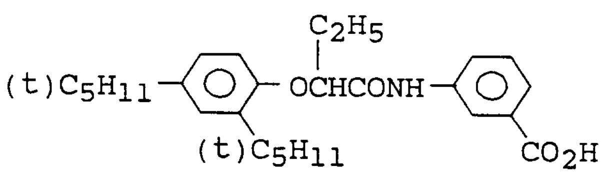
UV-5



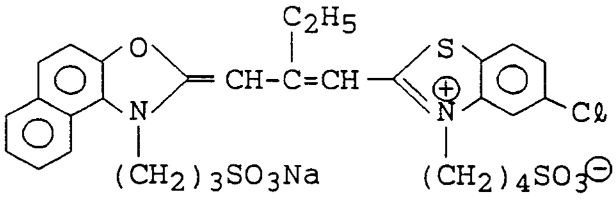
HBS-1 tricresylphosphate

HBS-2 di-n-butylphtalate

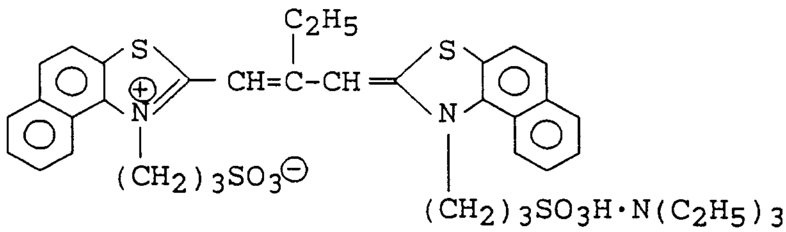
HBS-3



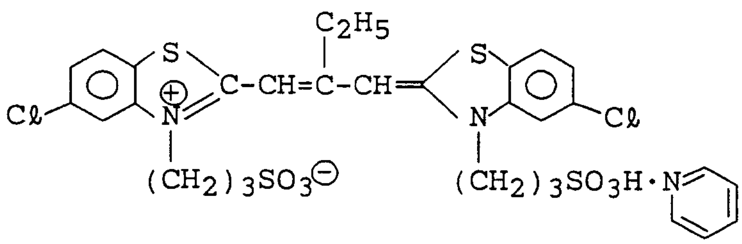
ExS-1



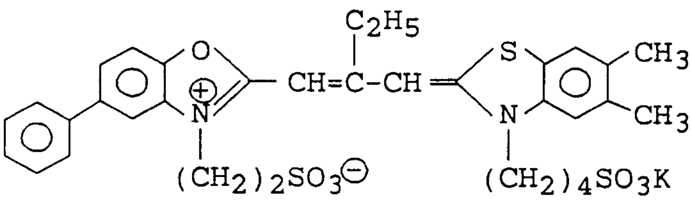
ExS-2



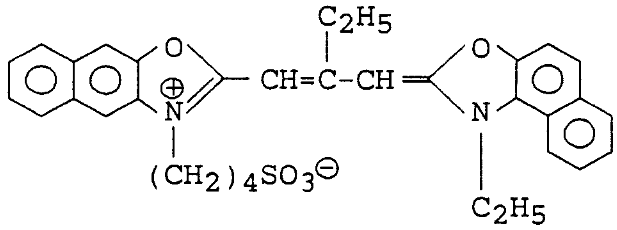
ExS-3



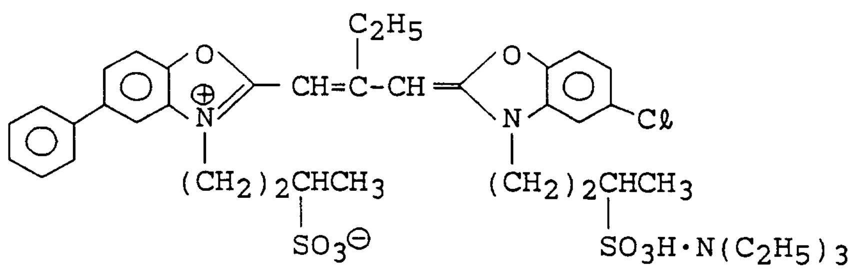
ExS-4



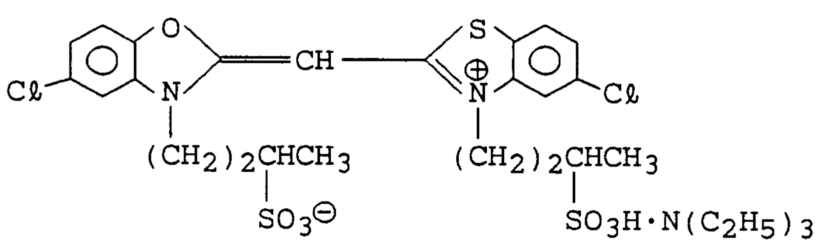
ExS-5



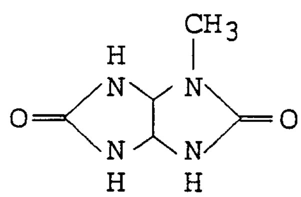
ExS-6



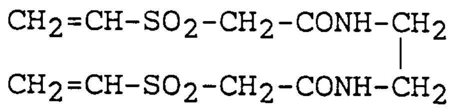
ExS-7



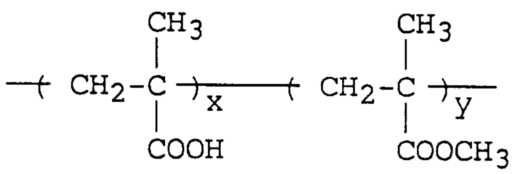
S-1



H-1

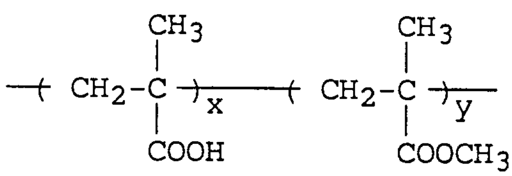


B-1



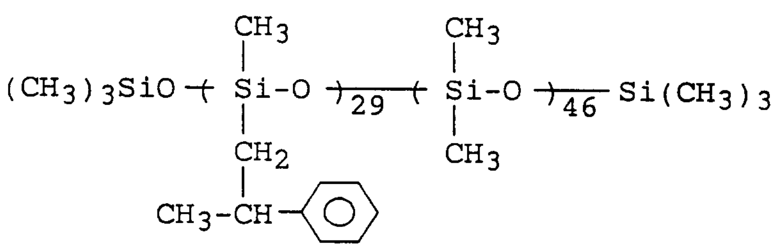
x/y = 10/90

B-2

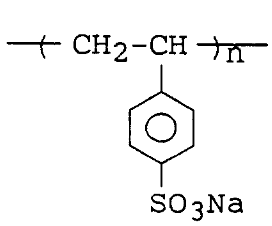


x/y = 40/60

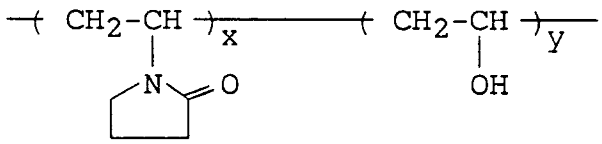
B-3



B-4

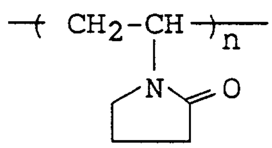


B-5



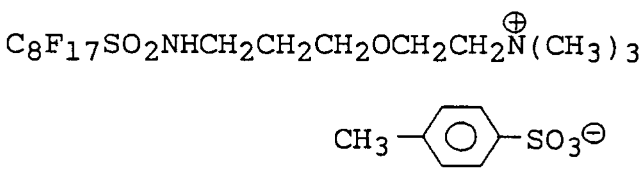
x/y = 70/30

B-6

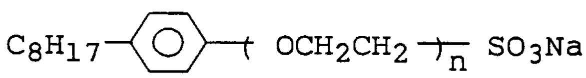


(mol. wt. about 10,000)

W-1

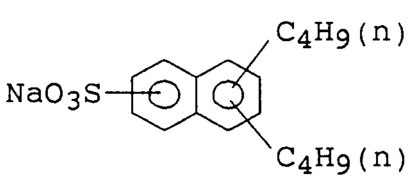


W-2

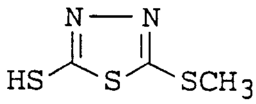


n = 2 - 4

W-3



F-1



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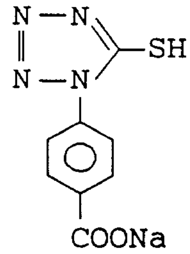

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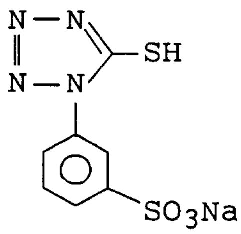

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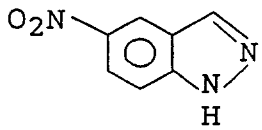

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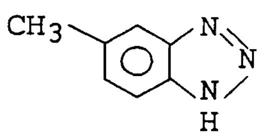

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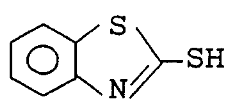

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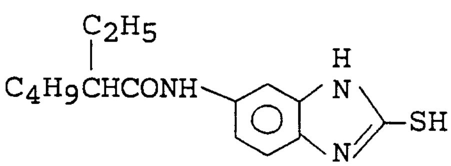

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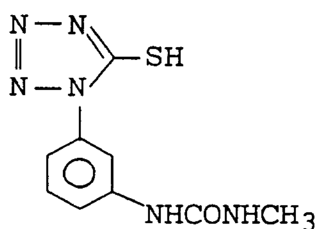

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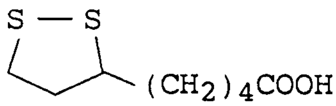

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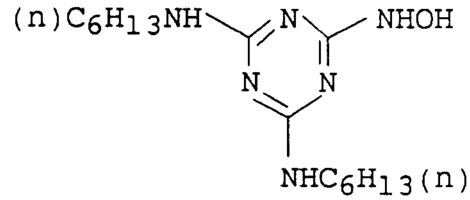

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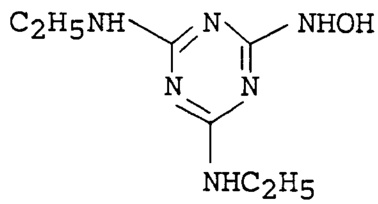

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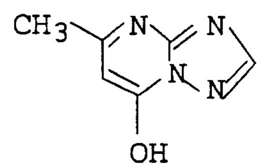

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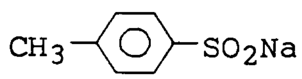

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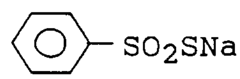
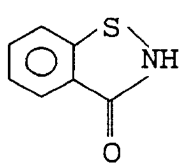
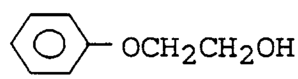


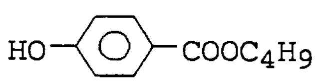
F-15



F-16



F-17



A film sample 12 was made following the same procedures as for the sample 11 except 1×10^{-4} mol/molAg, as a total silver amount, of tetrachloro palladium(II) potassium was added to the sixth layer (interlayer).

Each of the film samples 11 and 12 was formed into a 135-format cartridge of 24 exposures, and moisture-conditioned at a temperature of 25°C and a relative humidity of 60%. Thereafter, these film samples were loaded in perfectly light-shielding cartridges, and then sealed in transparent sealing cases and light-shielding sealing cases, in a dark place, to prepare encased photographic product samples 101 to 108 as shown in Table 3 below.

The ratio of the film area loaded in the cartridge so as to be shielded from light to the film area extracted from a film extraction portion was 1 : 0.05.

One group of these product samples 101 to 108 was irradiated with light of 10,000 lux for 24 hours and preserved, together with the other group not irradiated with light, at 60 °C and a relative humidity of 60% for three days. Thereafter, the films were processed under the following conditions.

The processing steps and the compositions of the processing solutions were as follows.

(Processing Steps)

Step	Time	Temperature
Color development	3 min. 15 sec.	38 °C
Bleaching	3 min. 00 sec.	38 °C
Washing	30 sec.	24 °C
Fixing	3 min. 00 sec.	38 °C
Washing (1)	30 sec.	24 °C
Washing (2)	30 sec.	24 °C
Stabilization	30 sec.	38 °C
Drying	4 min. 20 sec.	55 °C

The compositions of the individual processing solutions are shown below.

(Color developing solution)

	(g)
Diethylenetriaminepentaacetic acid	2.0
1-hydroxyethylidene-1,1 -diphosphonic acid	3.3
Sodium sulfite	4.0
Potassium carbonate	30.0
Potassium bromide	1.4
Potassium iodide	1.5 mg
Hydroxylamine sulfate	2.4
2-methyl-4-[N-ethyl-N-(β-hydroxylethyl)amino]-aniline sulfate	4.5
Water to make	1.0 ℓ
pH	10.05

(Bleaching solution)

	(g)
Ferric sodium ethylenediaminetetraacetate trihydrate	100.0
Disodium ethylenediaminetetraacetated	10.0
3-mercapto-1,2,4-triazole	0.08
Ammonium bromide	140.0
Ammonium nitrate	30.0
Ammonia water (27%)	6.5 mℓ
Water to make	1.0 ℓ
pH	6.0

(Fixing solution)

	(g)
Disodium ethylenediaminetetraacetate	0.5
Ammonium sulfite	20.0
Ammonium thiosulfate aqueous solution (700 g/ℓ)	290.0 mℓ
Water to make	1.0 ℓ
pH	6.7

(Washing solution)

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/ℓ or less. Subsequently, 20 mg/ℓ of isocyanuric acid dichloride sodium salt and 150 mg/ℓ of sodium sulfate were added. The pH of the solution ranged from 6.5 to 7.5.

(Stabilizing solution)

	(g)
Sodium p-toluenesulfinate	0.03
Polyoxyethylene-p-mononony lphenylether (average polymerization degree 10)	0.2
Disodium ethylenediaminetetraacetate	0.05
1,2,4-triazole	1.3
1,4-bis(1,2,4-triazol-1-ylmethyl) piperazine	0.75
Water to make	1.0 ℓ
pH	8.5

The shielded portion of the processed film was cut, and sensitometry was performed.
The results are summarized in Table 3 below.

Table 3

Encased Product Sample	Film Sample	Film Sensitivity	HCN gas scavenger	Humidity inside the case (25°C)	Case	Light irradiation	Fog increase in green-sensitive layer
101	11	435	none	60%	Transparent	yes	0.35
102	11	435	none	60%	Transparent	no	0.06
103	11	435	none	60%	Light-shielding	yes	0.06
104	11	435	none	60%	Light-shielding	no	0.06
105	12	435	Pd	60%	Transparent	yes	0.06
106	12	435	Pd	60%	Transparent	no	0.06
107	12	435	Pd	60%	Light-shielding	yes	0.06
108	12	435	Pd	60%	Light-shielding	no	0.06

It can be seen from Table 3 that only when a film was encased in a transparent case and irradiated with light, abnormally large fog was generated (encased sample 101), which was, however, greatly reduced by the addition of Pd (encased sample 105).

Example 2

A film sample 21 was made following the same procedures as for the film sample 12 except 0.07, 0.015, and 0.02 g/m^2 of Cpd-3 were added to the 11th, 12th, and 13th layers, respectively. Encased product samples 201 and 202 were prepared from the film sample 12 and 21, respectively, following the same procedures as in Example 1, and subjected to the same experiment and processing as in Example 1. The results are shown in Table 4 below.

Table 4

Encased Product Sample	Film Sample	Film Sensitivity	HCN gas scavenger	Humidity inside the case (25°C)	Case	Light irradiation	Fog increase in green-sensitive layer
201	12	435	Pd	60%	Transparent	yes	0.06
202	21	435	Pd	60%	Transparent	yes	0.04

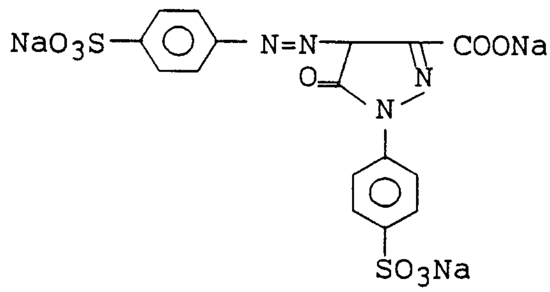
It is apparent from Table 4 that a hydroquinone derivative Cpd-3 know as a halogen gas scavenger further contributes to a reduction in fog.

Example 3

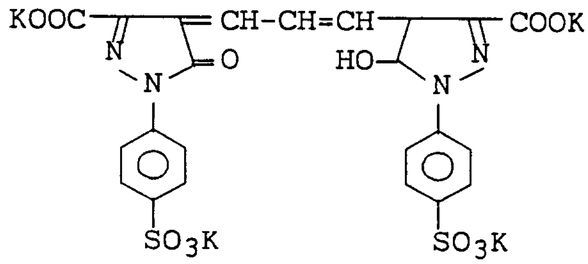
Water-soluble dyes, ExF-1 to ExF-3 indicated below, were added to the 14th layer of the film sample 11 in an amount sufficient to lower the ISO sensitivity of the film sample 11 from 435 to 120, to prepare a film sample 31, and also in an amount sufficient to lower the ISO sensitivity of the film sample 11 from 435 to 50, to prepare a film sample 32.

The same procedures as above were taken for the 14th layer of the film sample 12 to prepare film samples 33 and 34.

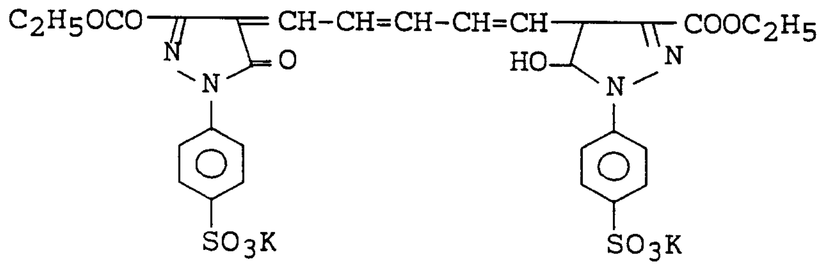
ExF-11



ExF-12



ExF-13



Encased product samples 301 to 306 were prepared from the film samples 11, 12 and 31 to 34, and the same experiment was performed as in Example 1. Results are shown in Table 5.

Table 5

Encased Product Sample	Film Sample	Film Sensitivity	HCN gas scavenger	Humidity inside the case (25°C)	Case	Light irradiation	Fog increase in green-sensitive layer
301	11	435	none	60%	Transparent	yes	0.35
302	31	120	none	60%	Transparent	yes	0.20
303	32	50	none	60%	Transparent	yes	0.12
304	12	435	Pd	60%	Transparent	yes	0.06
305	33	120	Pd	60%	Transparent	yes	0.04
306	34	50	Pd	60%	Transparent	yes	0.04

It can be seen from Table 5 that the higher the sensitivity, the larger the increase in abnormal fog and the higher the effect of the present invention.

Example 4

The sample 101 was subjected to the experiment and the processing following the same procedures as in Example 1 under different humidity conditions. The results are summarized in Table 6 below.

Table 6

Encased Product Sample	Film Sample	Film Sensitivity	HCN gas scavenger	Humidity inside the case (25°C)	Case	Light irradiation	Fog increase in green-sensitive layer
401	11	435	none	60%	Transparent	yes	0.35
402	11	435	none	70%	Transparent	yes	0.50
403	11	435	none	50%	Transparent	yes	0.15
404	11	435	none	40%	Transparent	yes	0.10
405	11	435	none	30%	Transparent	yes	0.07

It is apparent from Table 6 that abnormal fog did not occur so much when a humidity inside the case was lower, and fog increased as the humidity increased. Since the degree of increase in fog largely differed between the encased sample 402 and 403, further similar experiments were conducted wherein the humidity inside the case was changed from 50% to 55%, 60% or 65%. As a result, it was confirmed that the effect of the present invention is remarkable when the humidity is 55% or more.

Example 5

Encased product samples 501 to 508 were prepared, corresponding to the encased product samples 101 to 108 prepared in Example 1, and the same experiment was conducted as in Example 1, except that the samples were processed with the following black-and-white development, using an automatic developing machine.

	Processing solution	Temperature	Time
Development	HPD	26.5 °C	55 sec.
Fixing	Super Fujix DPZ	26.5 °C	76 sec.
Washing	Flowing Water	20 °C	95 sec.
Drying		50 °C	69 sec.

The results are shown in Table 7 below.

Table 7

Encased Product Sample	Film Sample	HCN gas scavenger	Humidity inside the case (25°C)	Case	Light irradiation	Fog increase in green-sensitive layer
501	11	none	60%	Transparent	yes	0.05
502	11	none	60%	Transparent	no	0.03
503	11	none	60%	Light-shielding	yes	0.03
504	11	none	60%	Light-shielding	no	0.03
505	12	Pd	60%	Transparent	yes	0.03
506	12	Pd	60%	Transparent	no	0.03
507	12	Pd	60%	Light-shielding	yes	0.03
508	12	Pd	60%	Light-shielding	no	0.03

It can be seen from Table 7 that abnormal fog did not occur by black-and-white development.

Example 6

Film samples 61 to 64 were prepared by the same procedures as for the film sample 12, except that the amount of tetrachloropalladium (II) potassium was changed as shown in Table 8 below.

Each of the film samples 61 to 64 was formed into a 135-format cartridge of 24 exposures, and moisture-conditioned at a temperature of 25 ° C and a relative humidity of 60%. Then, these samples ware sealed in transparent cases, to prepare encased product samples 601 to 616. The ratio of the extracted film area to the film area loaded in the cartridge was as shown in Table 8.

These encased product samples were irradiated with light of 10,000 lux for 24 hours, and preserved at a temperature of 60 ° C and a relative humidity of 60% for three days. Thereafter, the films were processed as in Example 1, and sensitometry was conducted. The results are shown also in Table 8.

Table 8

Encased Product Sample	Film Sample	HCN gas scavenger	Film Area Ratio	Mols of scavenger/mol of thiocyanate	Case	Fog increase in green-sensitive layer
601	61	none	0	-	Transparent	0.04
602	61	none	0.02	0	Transparent	0.20
603	61	none	0.05	0	Transparent	0.35
604	61	none	0.10	0	Transparent	0.55
605	62	Pd	0	-	Transparent	0.04
606	62	Pd	0.02	1.5	Transparent	0.04
607	62	Pd	0.05	0.6	Transparent	0.06
608	62	Pd	0.10	0.3	Transparent	0.06
609	63	Pd × 1/2	0	-	Transparent	0.04
610	63	Pd × 1/2	0.02	0.8	Transparent	0.05
611	63	Pd × 1/2	0.05	0.3	Transparent	0.06
612	63	Pd × 1/2	0.10	0.2	Transparent	0.08
613	64	Pd × 2	0	-	Transparent	0.04
614	64	Pd × 2	0.02	3.0	Transparent	0.04
615	64	Pd × 2	0.05	1.2	Transparent	0.04
616	64	Pd × 2	0.10	0.6	Transparent	0.06

As can be seen from Table 8, abnormal fog does not occur in the samples having no extracted film portion, and abnormal fog decreases as the amount of hydrogen cyanide gas scavenger increases with respect to thiocyanate salt. Further, it is seen that the degree of increase of fog becomes the same as the sample without an extracted film portion when the amount of hydrogen cyanide gas scavenger is more than 1.0 mol per mol of thiocyanate salt, completely solving the abnormal fog problem.

Example 7

Film samples 71 to 74 were prepared by adding the exemplified compound Y-6 in an amount of 0.01 g/m^2 to the 10th layer of the film sample 12 of Example 1, with the amount of hydrogen cyanide gas scavenger, tetrachloropalladium (II) potassium, varied as shown in Table 9 below.

Each of the film samples 71 to 74 was formed into a 135-format cartridge of 24 exposures, and moisture-conditioned at a temperature of 25 °C and a relative humidity of 60%. Then these samples were sealed in transparent cases to prepare encased product samples 701 to 704. The ratio of the extracted film area to the shielded film area wat set at 0.05.

These encased samples 701 to 704 were irradiated with light of 10,000 lux for 24 hours, and preserved at a temperature of 60 °C and a relative humidity of 60%. Thereafter, the films were processed as in Example 1, the film portions which had been shielded from light within the cartridges were cut, and sensitometry was performed on the cut film portions. The results are shown in Table 9 below.

Table 9

Encased Product Sample	Film Samples	HCN gas scavenger	HCN gas-generating compound	Fog increase in green-sensitive layer
701	12	no	None	0.35
702	71	no	Y-6 0.01 g/m^2	1.00
703	72	Pd × 1/2	Y-6 0.01 g/m^2	0.20
704	73	Pd	Y-6 0.01 g/m^2	0.11
705	74	Pd × 2	Y-6 0.01 g/m^2	0.05

As can be seen from Table 9, fog largely increases in the blue-sensitive layer by the addition of the compound Y6, and the fog is greatly reduced by the addition of the hydrogen cyanide gas scavenger.

Example 8

(Preparation of Emulsion)

Emulsion I:

While one liter of 0.7% aqueous solution of inert bone gelatin containing 0.05 mole per liter was stirred at 60°C, 1.95 M aqueous solution of potassium bromide and 1.9 M aqueous solution of silver nitrate were added (4.4% of the total silver nitrate was consumed). 400 ml of 9% aqueous solution of deionized gelatin was added, and the temperature was raised to 75°C. After 1.52 M aqueous solution of silver nitrate was added to adjust the pBr to 2.25 (3.1% of the total silver nitrate was consumed), 14.2 N aqueous solution of ammonia was added to adjust the pH to 8.3, and physical ripening was performed. Then, 1 N silver nitrate solution was added to adjust the pH to 5.2. With the pBr maintained at 1.56, an aqueous solution containing 1.34 mole of potassium bromide per liter and 0.16 mole of potassium iodide per liter, and 1.9 M aqueous solution of silver nitrate were simultaneously added over 40 minutes while the flow rate was accelerated such that the flow rate at the end was 3.5 times as fast as the flow rate at the start (62.4% of the total silver nitrate was consumed). Further, 250 ml of 0.11 M aqueous solution of potassium iodide was added over five minutes. Ten minutes after the addition of the potassium iodide, 1.34 M aqueous solution of potassium bromide and 1.9 M aqueous solution of silver nitrate were simultaneously added at the constant flow rate, while the pBr was maintained at 2.42 (30.1% of the total silver nitrate was consumed). Then, desalting was performed by the conventional flocculation method, to prepare tabular silver bromide grains (an average silver iodide content of 8.9 mol%) having an average ratio of grain diameter/thickness of 6.0 and an equivalent-sphere diameter of 0.85 μm. These grains were observed by a transmitting electromicroscope to confirm that dislocation lines were introduced mainly at the fringe portion of each grain.

To the thus prepared emulsion I, spectral sensitizing dyes ExS-4, ExS-5 and ExS-6 to be used in the 9th layer of the film sample 81 which will be described later, and optimal chemical sensitization as described below was performed to prepare emulsions 1 and 2. The optimal sensitization means that, after the sensitization, the highest sensitivity is achieved when exposed for 1/100 second.

Emulsion 1 (gold-sulfur sensitization)

Optimal chemical sensitization was performed at 56°C by using 2.2×10^{-3} mole of sodium thiocyanate, 1.5×10^{-6} mole of chloroauric acid and 1.4×10^{-5} mole of sodium thiosulfate, per mole of silver halide.

Emulsion 2 (gold-sulfur-selenium sensitization)

Optimal chemical sensitization was performed at 56°C by using 2.2×10^{-3} mole of sodium thiocyanate, 2.2×10^{-6} mole of chloroauric acid, 1.0×10^{-5} mole of sodium thiosulfate and a selenium sensitizer (the exemplified compound 40), per mole of silver halide.

(Preparation of Film Sample)

Multiple layers having the compositions presented below were coated on a subbed triacetylcellulose film support to make a film sample 81 as a multilayered color light-sensitive material.

(Compositions of layers)

The number corresponding to each component indicates the coating amount in units of g/m^2. The coating amount of a silver halide is represented by the amount of silver. The coating amount of each sensitizing dye is represented in units of mols per mol of silver halide in the same layer.

(Film Sample 81)

1st layer (Antihalation layer)	
Black colloidal silver	silver 0.18
Gelatin	1.40
ExM-1	0.18
ExF-1	2.0×10^{-3}
HBS-1	0.20

2nd layer (Interlayer)	
Emulsion G	silver 0.065
ExC-2	0.020
UV-1	0.060
UV-2	0.080
UV-3	0.10
HBS-1	0.10
HBS-2	0.020
Gelatin	1.04

3rd layer (Low-speed red-sensitive emulsion layer)	
Emulsion A	silver 0.25
Emulsion B	silver 0.25
ExS-1	6.9×10^{-5}
ExS-2	1.8×10^{-5}
ExS-3	3.1×10^{-4}
ExC-1	0.17
ExC-3	0.030
ExC-4	0.10
ExC-5	0.020
ExC-7	0.0050
ExC-8	0.010
Cpd-2	0.025
HBS-1	0.10
Gelatin	0.87

4th layer (Medium-speed red-sensitive emulsion layer)	
Emulsion D	silver 0.70
ExS-1	3.5×10^{-4}
ExS-2	1.6×10^{-5}
ExS-3	5.1×10^{-4}
ExC-1	0.13
ExC-2	0.060
ExC-3	0.0070
ExC-4	0.090
ExC-5	0.025
ExC-7	0.0010
ExC-8	0.0070
Cpd-2	0.023
HBS-1	0.10
Gelatin	0.75

5th layer (High-speed red-sensitive emulsion layer)	
Emulsion E	silver 1.40
ExS-1	2.4×10^{-4}
ExS-2	1.0×10^{-4}
ExS-3	3.4×10^{-4}
ExC-1	0.12
ExC-3	0.045
ExC-6	0.020
ExC-8	0.025
Cpd-2	0.050
HBS-1	0.22
HBS-2	0.10
Gelatin	1.20

6th layer (Interlayer)	
Cpd-1	0.10
HBS-1	0.50
Gelatin	1.10

7th layer (Low-speed green-sensitive emulsion layer)	
Emulsion C	silver 0.35
ExS-4	3.0×10^{-5}
ExS-5	2.1×10^{-4}
ExS-6	8.0×10^{-4}
ExM-1	0.010
ExM-2	0.33
ExM-3	0.086
ExY-1	0.015
HBS-1	0.30
HBS-3	0.010
Gelatin	0.73

8th layer (Medium-speed green-sensitive emulsion layer)	
Emulsion D	silver 0.80
ExS-4	3.2×10^{-5}
ExS-5	2.2×10^{-4}
ExS-6	8.4×10^{-4}
ExM-2	0.13
ExM-3	0.030
ExY-1	0.018
HBS-1	0.16
HBS-3	8.0×10^{-3}
Gelatin	0.90

9th layer (High-speed green-sensitive emulsion layer)	
Emulsion 1 (gold-sulfur sensitized)	silver 1.25
ExS-4	3.7×10^{-5}
ExS-5	8.1×10^{-5}
ExS-6	3.2×10^{-4}
ExC-1	0.010
ExM-1	0.030
ExM-4	0.040
ExM-5	0.019
Cpd-3	0.040
HBS-1	0.25
HBS-2	0.10
Gelatin	1.44

10th layer (Yellow filter layer)	
Yellow colloidal silver	silver 0.030
Cpd-1	0.16
HBS-1	0.60
Gelatin	0.60

11th layer (Low-speed blue-sensitive emulsion layer)	
Emulsion C	silver 0.18
ExS-7	8.6×10^{-4}
ExY-1	0.020
ExY-2	0.22
ExY-3	0.50
ExY-4	0.020
HBS-1	0.28
Gelatin	1.10

12th layer (Medium-speed blue-sensitive emulsion layer)	
Emulsion D	silver 0.40
ExS-7	7.4×10^{-4}
ExC-7	7.0×10^{-3}
ExY-2	0.050
ExY-3	0.10
HBS-1	0.050
Gelatin	0.78

13th layer (High-speed blue-sensitive emulsion layer)	
Emulsion F	silver 1.00
ExS-7	4.0×10^{-4}
ExY-2	0.10
ExY-3	0.10
HBS-1	0.070
Gelatin	0.86

14th layer (1st protective layer)	
UV-4	0.11
UV-5	0.17
HBS-1	5.0×10^{-2}
Gelatin	1.00

15th layer (2nd protective layer)	
Emulsion G	silver 0.10
H-1	0.40
B-1 (diameter 1.7 μm)	5.0×10^{-2}
B-2 (diameter 1.7 μm)	0.10
B-3	0.10
S-1	1.20
Gelatin	1.20

In addition to the above components, to improve shelf stability, processability, a resistance to pressure, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained W-1 to W-3, B-4 to B-6, F-1 to F-17, iron salt, and lead salt.

The emulsions A to G, and the various additives used have already been shown earlier.

A film sample 82 was made following the same procedures as for the film sample 81 except the emulsions 1 in the 9th layer of the film sample 82 was replaced with the emulsion 2.

Each of the film samples 81 and 82 contained 3×10^{-3} mol of thiocyanate salt per mol of silver. The thiocyanate salt had been used in preparing the emulsions A to G, and 1 and 2.

Film samples 83 and 84 were made following the same procedures as for the film samples 81 and 82 except 1×10^{-5} mol/molAg, as a total silver amount, of sodium palladium(II) chloride was added to the sixth layers (interlayer) of the film samples 81 and 82, respectively.

Film samples 85 and 86 were made following the same procedures as for the film samples 81 and 82 except 1×10^{-5} mol/molAg, as a total silver amount, of sodium palladium(II) chloride was added to the sixth layers (interlayer) of the film samples 81 and 82, respectively.

Each of the film samples 81 to 86 was formed into a 135-format cartridge of 24 exposures, and moisture-conditioned at a temperature of 25°C and a relative humidity of 60%. Thereafter, these film samples were placed in transparent cartridge cases and perfectly light-shielding cartridge cases in a dark place, to prepare encased product samples 801 to 812 as shown in Table 10 below.

The ratio of the film area loaded in the cartridge so as to be shielded from light to the film area extracted from a film extraction portion was 1 : 0.05.

Table 10

Encased Product Sample	Film Sample	Silver Halide Emulsion in 9th layer	Amount of Tetrachloropalladium (II) in 6th layer	Cartridge Case
801 (Comparative)	81	Emulsion 1 (gold-sulfur sensitization)	None	Light-shielding
802 (")	"	"	"	Transparent
803 (")	82	Emulsion 2 (gold-sulfur-selenium sensitization)	"	Light-shielding
804 (")	"	"	"	Transparent
805 (")	83	Emulsion 1 (gold-sulfur sensitization)	1×10^{-5} mol/molAg	Light-shielding
806 (The Invention)	"	"	"	Transparent
807 (Comparative)	84	Emulsion 2 (gold-sulfur-selenium sensitization)	"	Light-shielding
808 (The Invention)	"	"	"	Transparent
809 (Comparative)	85	Emulsion 1 (gold-sulfur sensitization)	1×10^{-4} mol/molAg	Light-shielding
810 (The Invention)	"	"	"	Transparent
811 (Comparative)	86	Emulsion 2 (gold-sulfur-selenium sensitization)	"	Light-shielding
812 (The Invention)	"	"	"	Transparent

One group of these encased samples was irradiated with light of 10,000 lux for 24 hours and preserved, together with the other group not irradiated with light, at 25°C or 60°C and at a relative humidity of 60% for three days. The film portions which had been shielded from light in the cartridges were cut from the film samples, exposed through a continuous wedge at a color temperature of 4800°K for 1/100 second, and processed as in Example 1.

The density of the processed samples was measured with a green filter, and an increase in fog and a change in sensitivity were determined for the samples preserved at a temperature of 60°C and a relative humidity of 60%. The results are shown in Table 11 below. The change in sensitivity is expressed as a relative logarithmic value of the exposure amount required to obtain an optical density of fog plus 0.15, with the sensitivity of the encased samples without irradiation of light and preserved at a temperature of 25°C and a relative humidity of 60% taken as 100.

Table 11

Encased Product Sample	Light Irradiation	(1)*	(2)**	(3)***
801 (Comparative)	No	100	0.08	93
	Yes	—	0.08	93
802 (")	No	100	0.08	93
	Yes	—	0.16	71
803 (")	No	128	0.10	98
	Yes	—	0.10	98
804 (")	No	128	0.10	98
	Yes	—	0.43	70
805 (")	No	101	0.07	94
	Yes	—	0.07	94
806 (The invention)	No	101	0.07	94
	Yes	—	0.13	92
807 (Comparative)	No	129	0.10	105
	Yes	—	0.10	105
808 (The invention)	No	129	0.10	105
	Yes	—	0.14	100
809 (Comparative)	No	101	0.06	96
	Yes	—	0.06	96
810 (The invention)	No	101	0.06	96
	Yes	—	0.06	94
811 (Comparative)	No	129	0.06	109
	Yes	—	0.06	109
812 (The inventione)	No	129	0.06	109
	Yes	—	0.07	105

*(1) Relative sensitivity of green-sensitive layer after preserved at a temperature of 25°C and a relative humidity of 60%.

**(2) Increase in fog in green-sensitive layer after preserved at a temperature of 60°C and a relative humidity of 60%.

***(3) Relative sensitivity of green-sensitive layer after preserved at a temperature of 60°C and a relative humidity of 60%.

As apparent from Table 11, abnormal fog occurred in the samples in the transparent cases, irradiated with light and preserved at a temperature of 60°C and a relative humidity of 60%, and the degree of the abnormal fog was remarkable when selenium-sensitized silver halide grains were used. Further, the fog increase and the sensitivity decrease were not suppressed so much in the samples in the transparent cases, irradiated with light, in which palladium salt was added to the sixth layer in an amount of 1/15 mol of palladium salt per mole of thiocyanate salt contained in the extracted film portion. However, the addition of the palladium salt in an amount of 2/3 mole per mole of thiocyanate remarkable suppressed the fog increase and the sensitivity decrease. The effect of the palladium salt added to the samples in the transparent cases, irradiated with light, was particularly remarkable on the samples containing selenium-sensitized silver halide emulsions.

Example 9

To the 11th, 12th and 13th layers of the film sample 86, Cpd-3 was added in an amount of 0.07, 0.015, and 0.02 g/m^2, respectively, to prepare a film sample 87.

An encased product sample 813 was prepared using the film sample 87 in the same procedures as in Example 8. The encased sample 813 was subjected to the same experiment as in Example 8. The results are shown in Table 12.

Table 12

Encased Product Sample	Film Sample	Cartridge Case	Light Irradiation	Fog Increase in Green-sensitive Layer
812 (The invention)	86	Transparent	yes	0.07
813 (The invention)	87	Transparent	yes	0.04

As apparent from Table 12, it was further confirmed that a hydroquinone derivative further contributed to reduction in abnormal fog.

Example 10

Encased product samples 814 to 821 were prepared by the same procedures as in Example 8, except that the moisture-conditioning was performed under different conditions as described in Table 13 below. These product samples were subjected to the same experiment as in Example 8. The results are shown also in Table 13.

Table 13

Encased Product Sample	Film Sample	Moisture-conditioning	Cartridge Case	Light Irradiation	Fog Increase in Green-Sensitive Layer
804 (Comparative)	82	25°C60%	Transparent	yes	0.43
814 (")	"	" 70%	"	"	0.49
815 (")	"	" 50%	"	"	0.18
816 (")	"	" 40%	"	"	0.10
817 (")	"	" 30%	"	"	0.08
812 (The invention)	86	" 60%	"	"	0.07
818 (")	"	" 70%	"	"	0.08
819 (Comparative)	"	" 50%	"	"	0.17
820 (")	"	" 40%	"	"	0.10
821 (")	"	" 30%	"	"	0.08

It was also confirmed from Table 13 that abnormal fog did not occur so much when the humidity in the cartridge case was low, and hence the effect of the present invention was significant when the relative humidity was 55% or more.

Example 11

The same experiment was performed on the encased samples 801 to 812 as in Example 8, except that the samples were processed with the following black-and-white development instead of the color development. As a result, it was confirmed that no remarkable abnormal fog did not occur. Therefore, the effect of the present invention is more significant when the light-sensitive material is processed by color development.

(Black-and-white developer)

Metol	2g
Sodium sulfite	100g
Hydroquinone	5g
Borax-10H_2O	2g
Water to make	1 liter

(Processing)

The samples were developed using the above developer, and stopping, fixing, washing and drying were performed by the conventional method.

Claims

1. An encased photographic material characterized by comprising:
a silver halide light-sensitive material including at least one silver halide emulsion layer on a support, said emulsion layer containing gold- and chalcogen-sensitized silver halide grains and a thiocyanate salt therein;
a lightproof container containing said light-sensitive material such that an end portion of said light-sensitive material is positioned outside said lightproof container, and that a gas can pass between an inside and an outside of said lightproof container;
a light-transmitting case encasing and sealing said lightproof container; and
a hydrogen cyanide gas scavenger present inside said case.

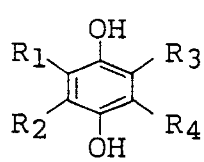
2. The encased photographic material according to claim 1, characterized by further comprising a halogen gas scavenger inside said case.

3. The encased photographic material according to claim 1, characterized in that said hydrogen cyanide gas scavenger is present in said light-sensitive material.

4. The encased photographic material according to claim 2, characterized in that said halogen gas scavenger is present in said light-sensitive material.

5. The encased photographic material according to claim 1, characterized in that said hydrogen cyanide scavenger comprises an organic or inorganic palladium compound.

6. The encased photographic material according to claim 2, characterized in that said halogen gas scavenger comprises a compound represented by Formula (H) below:
Formula (H)



where each of R_1, R_2, R_3 and R_4 is hydrogen or a group substitutable on the benzene ring.

7. The encased photographic material according to claim 1, characterized in that said silver halide light-sensitive material has an ISO sensitivity of 100 or more.

8. The encased photographic material according to claim 1, characterized in that said silver halide light-sensitive material has an ISO sensitivity of 400 or more.

9. The encased photographic material according to claim 1, characterized in that a relative humidity inside said light-transmitting case is 55% or more at 25°C.

10. The encased photographic material according to claim 1, characterized in that said light-sensitive material is a color photographic material.

11. The encased photographic material according to claim 1, characterized in that said hydrogen cyanide gas scavenger is present in an amount of 1/10 mole or more per mole of thiocyanate salt contained in said end portion of said light-sensitive material.

12. The encased photographic material according to claim 1, characterized in that said hydrogen cyanide gas scavenger is present in an amount of 1 mole or more per mole of thiocyanate salt contained in said end portion of said light-sensitive material.

13. The encased photographic material according to claim 4, characterized in that said halogen gas scavenger is present in an amount of 0.05 to 1 g/m^2.

14. The encased photographic material according to claim 1, characterized in that said gold- and chalcogen-sensitized grains are gold- and selenium-sensitized grains.

15. The encased photographic material according to claim 2, characterized in that said gold- and chalcogen-sensitized grains are gold- and selenium-sensitized grains.

16. An encased photographic material characterized by comprising:

a silver halide light-sensitive material including at least one silver halide emulsion layer on a support, said emulsion layer containing gold- and chalcogen-sensitized silver halide grains;

a lightproof container containing said light-sensitive material such that an end portion of said light-sensitive material is positioned outside said lightproof container, and that a gas can pass between an inside and an outside of said lightproof container;

a light-transmitting case encasing and sealing said lightproof container;

a compound which can directly or indirectly generate hydrogen cyanide gas within said light-transmitting case upon irradiation with light; and

a hydrogen cyanide gas scavenger present inside said case.

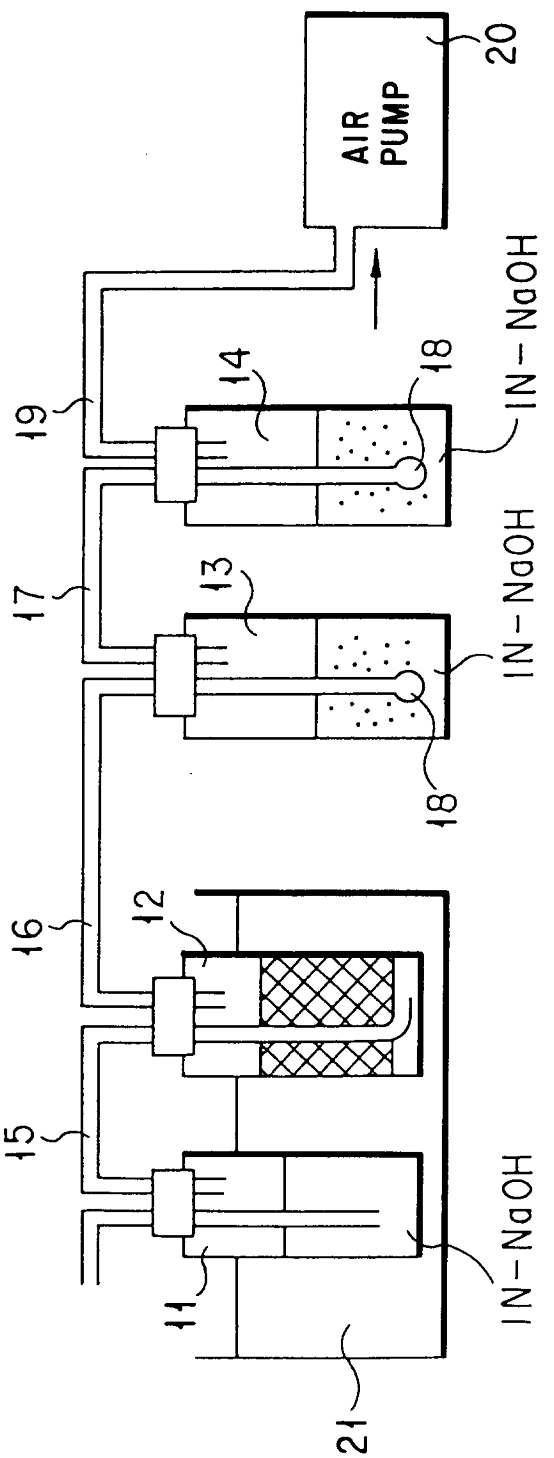
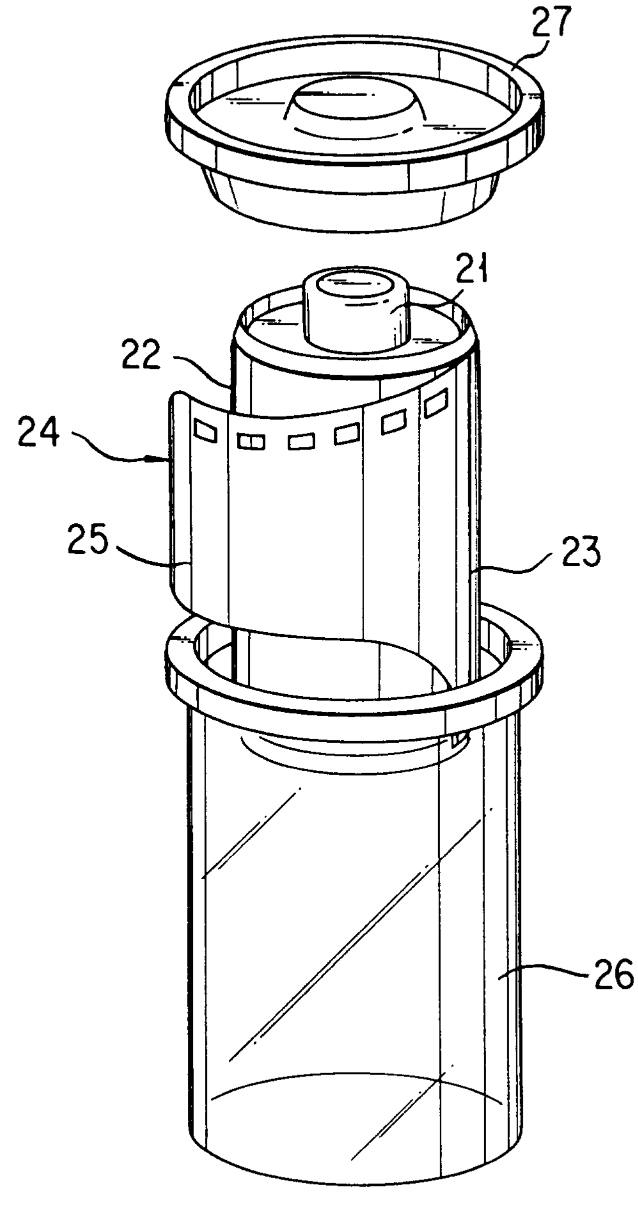


FIG. 1



F I G. 2