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(54) **Heat-developable light-sensitive materials.**

(57) A heat-dvelopable light-sensitive material having a light-sensitive layer containing a silver halide emulsion which comprises multiple-structure silver chlorobromide grains that are gold-sulfur sensitized in the presence of a sensitizing dye and have layers of differing halide composition. The multiple-structure silver chlorobromide grains can have one or more layers of differing halide composition or three or more layers of differing halide composition.

EP 0 420 155 A2

HEAT-DEVELOPABLE LIGHT-SENSITIVE MATERIALS

FIELD OF THE INVENTION

The present invention relates to heat-developable light-sensitive materials, and in particular to heat-developable light-sensitive materials that have an excellent shelf life and high sensitivity.

BACKGROUND OF THE INVENTION

Heat-developable light-sensitive materials are well known. Heat-developable light-sensitive materials and processes thereof are mentioned, for example, in "Fundamentals of Photographic Engineering" Non-Silver Salt Photographic Edition (1982, Corona Co.), pp. 242 to 255; and U.S. Patent 4,500,626.

A method of forming a dye image by a coupling reaction between the oxidation product of a developing agent and a coupler is described in U.S. Patents 3,761,270 and 4,021,240. Further, a method of forming a color positive image using light-sensitive silver dye bleaching process is described in U.S. Patent 4,235,957. Another method of forming a color image involves imagewise releasing or forming diffusible dyes by heat development, and transferring this diffusible dye to a dye fixing element. In this method, by changing the kind of dye providing compound or the kind of silver halide utilized, both a negative dye image and a positive dye image can be obtained. Further details of this are described in U.S. Patents 4,500,626, 4,483,914, 4,503,137, and 4,559,290; JP-A-58-149046, JP-A-60-133449, JP-A-59-218443, and JP-A-61-238056 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"); EP-A-220746; Kokai Giho 87-6199; and EP-A-210660.

Many methods have been proposed for obtaining positive color images by heat development. For example, U.S. Patent 4,559,290 proposes a method in which a DDR compound which has been converted into oxidized form having no dye-releasing ability and a reducing agent or a precursor of a reducing agent are placed together, when this combination is subjected to heat development, the reducing agent is oxidized in proportion to the degree of exposure of the silver halide, and a diffusible dye is released by reduction by the remaining unoxidized reducing agent. In EP-A-220746 and Kokai Giho 87-6199 (Vol. 12, No. 22), a heat-developable color light-sensitive material is described which uses a compound which similarly releases a diffusible dye by the reductive cleavage of a N-X bond (where X represents an oxygen atom, nitrogen atom or sulfur atom).

However, in heat development, unpredictable heat fog frequently arises from conventional wet development.

This heat fog is a major problem in image formation. When obtaining a color image corresponding to latent image in the negative type heat-developable light-sensitive material, heat fog is related to an increase in minimum density. When obtaining a color image counter-corresponding to the latent image in the positive type heat-developable light-sensitive material, heat fog causes a reduction in the maximum density.

In particular, when an emulsion containing large silver halide grains is used to obtain high sensitivity, heat fog is present and a primary factor in achieving higher sensitivities.

In order to prevent heat fog, organic compounds known as antifoggants have generally been utilized. However, because known antifoggants are not very effective at controlling fog, or effectively control fog and simultaneously reduce sensitivity significantly.

The silver halide emulsions in use in heat-developable light-sensitive materials have required the use of large quantities of antifoggants in order to prevent fogging. Further, chemical sensitization in the emulsions is insufficient to give low-fog silver halide grains. For these reasons, increases in sensitivity, decreases in sensitivity, gradation changes, and the like during the time before utilization are much greater than in common conventional light-sensitive materials.

Because of the unpredictable problems, precise guiding principles have not been obtained regarding the design of light-sensitive silver halide emulsions suitable for heat-developable light-sensitive materials. At present various performance features, particularly countermeasures against heat fog and higher sensitivities are pursued by trial and error.

SUMMARY OF THE INVENTION

An object of the present invention is to obtain a heat-developable high-sensitivity light-sensitive material that has an excellent shelf life.

This and other objects of the present invention are achieved by a heat-developable light-sensitive material having a light-sensitive layer containing a silver halide emulsion which comprises multiple-structure silver chlorobromide grains that are gold-sulfur sensitized in the presence of a sensitizing dye and have layers of differing halide composition.

DETAILED DESCRIPTION OF THE INVENTION

The silver halide grains used in the present invention have the following three features:

(1) They are multiple-structure grains possessing one or more layers in the grain interior, where each layer has a different halide composition.

(2) They are silver chlorobromide grains.

(3) They are gold-sulfur sensitized in the presence of a sensitizing dye.

Details are given below of specific preparation methods and preferred forms for these features.

(1) Multiple-structure grains

There have been a number of reports that grains having a multiple structure give excellent performance in heat-developable light-sensitive materials. For example, JP-A-63-261357 describes multiple-structure grains with triple or more layered structure that are used together with an organic compound.

In contrast, the present invention uses double structure, core/shell grains that have only one layer of a different silver halide composition from the composition of the grain's interior; or multiple-structure grains that have more than one different layer.

At present, the mechanism by which these multiple-structure grains yield superior qualities over uniform composition grains is unknown. It is thought, however, that sensitivity specks formed on the surfaces of the grains, by gold-sulfur sensitization in the presence of the sensitizing dye described below effectively form latent images in the presence of the interface between the two layers of differing halide composition in the multiple silver chlorobromide structured grains of the present invention.

The general configuration of the multiple-structure grains of the present invention is a double structure grain. In some cases, however, grains with 3, 4 or more superposed layers give better performance.

In the case of a double structure (sometimes termed a core/shell emulsion), the interior (core) and surface (shell) are preferably in a relative volume ratio of core to shell of from 0.1:99.9 to 99.9:0.1. More preferably, the ratio is from 1:9 to 9:1.

Further, the average grain size of the silver halide grains used in the present invention is from 0.1 μm to 2.0 μm, preferably 0.1 μm to 1.3 μm, and more preferably 0.2 μm to 1.0 μm.

Further, it is preferable for the silver chlorobromide emulsion of the invention to be monodisperse. In the present invention, "an emulsion consisting of monodisperse silver halide grains" refers to an emulsion consisting of silver halide grains, for which the value given by the standard deviation S of the grain diameter divided by the average grain diameter $\bar{r}$ and multiplied by 100 (the "coefficient of variation") is 16% or less as defined by the following formula:

$$\frac{S}{\bar{r}} \times 100 \leqq 16\%$$

Where S is the standard deviation generally in statistics, as expressed by the following formula:

$$S=\sqrt{\Sigma(r_i-\bar{r})^2/n}$$

The term "grain diameter", as used in the invention is the diameter in the case of spherical silver halide grains, or for nonspherical grains it is the diameter of the projected image calculated as the circular image with the same surface area.

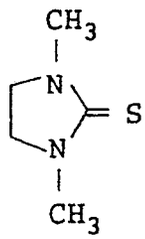
The average grain size $\bar{r}$ is the average value of the grain diameter as defined by the following formula when there are n_i grains of diameter r_i.

$$\bar{r} = \frac{\Sigma n_i r_i}{\Sigma n_i}$$

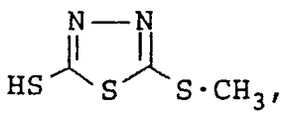
The crystal habit of these silver halide grains may be cubic, octahedral, tetradecahedral, tabular, pebble-like or spherical. The most preferred crystal habit is cubic, consisting of substantially (100) faces.

During the formation of the silver halide grains of the present invention the following can be used as silver halide solvents:

thiocyanates, NH_3,



, HO–S–S–OH,



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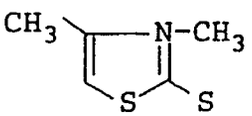
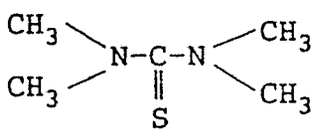




;

organic thioether derivatives as described in JP-B-47-11386 (the term "JP-B" as used herein means an "examined Japanese patent publication"); or sulfur-containing compounds as described in JP-A-53-144319.

The nitrogen-containing compounds, such as those described in JP-B-46-7781, JP-A-60-222842, and JP-A-60-122935, can be added during the formation of the silver halide grains.

It is advantageous to use gelatin as a protective colloid and as a hydrophilic colloid binder during the preparation of the emulsion of the present invention.

In addition, other hydrophilic colloids may be used. For example, it is possible to use various synthetic hydrophilic macromolecular substances such as gelatin derivatives, graft polymers of gelatin and other macromolecules, albumin, casein and similar proteins; hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfate esters and similar cellulose derivatives; sodium alginate, starch derivatives and similar saccharide derivatives; and polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinyl-pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, polyvinylpyrazole and similar homo- or copolymers.

As gelatin, in addition to lime-processed gelatin and acid-processed gelatin, oxygen-processed gelatin as described in Bull. Soc. Sci. Phot. , Japan, No. 16, p. 30 (1966) may also be used as can the hydrolysis

products or enzymolysis products of gelatin.

Soluble salts ate normally eliminated from the emulsion after precipitate formation or physical ripening. This is done, for example, using the noodle washing method in which the gelatin is gelled. It is also possible to use flocculation methods utilizing inorganic salts formed from polyvalent anions (for example, sodium sulfate); anionic surfactants; anionic polymers (for example, polystyrenesulfonic acid); or gelatin derivatives (for example, aliphatic acylated gelatin, aromatic acylated gelatin, and aromatic carbamoylated gelatin).

The process of eliminating the soluble salts may also be omitted.

Other conditions are generally described in the following references: P. Glafkides, Chemie et Physique Photographique , Paul Montel, 1967; G.F. Duffin, Photographic Emulsion Chemistry , The Focal Press, 1966; and V.L. Zelikman et al., Making and Coating Photographic Emulsion , The Focal Press, 1964. These references describe that the known acid methods, neutral methods, or ammonia methods may be used; and to react soluble silver salts and soluble halides generally, single jet processes, double jet processes, and any combinations of these methods may also be used.

The method of forming grains in the presence of excess of silver ions (the reverse mixing method) can also be used. As one form of the double jet method the controlled double jet method to keep the pAg constant in the liquid phase can also be used.

Further, in order to speed up grain growth, the concentration, quantity, or speed of addition of silver salt and halide salt may be increased as disclosed in JP-A-55-142329, JP-A-55-158124, and U.S. Patent 3,650,757.

During grain formation or after grain formation, the silver halide grain surface may be substituted by a halogen that forms a sparingly soluble silver halide grain.

Any conventional stirring method may be used as the reaction liquid stirring method. Further, the temperature and pH of the reaction liquid may be set arbitrarile during silver halide grain formation.

The silver halide emulsion of the present invention may contain iridium, rhodium, platinum, cadmium, zinc, lead, thallium and the like, for the prevention of high-intensity, low-intensity reciprocity law failure, or fogging.

Metals of this kind can be introduced by using iridium salts, rhodium salts, platinum salts, cadmium salts, zinc salts, lead salts or thallium salts together or separately during the grain-formation or the physical-ripening stage.

(2) Silver chlorobromide

The halogen composition of the grains of the present invention involves silver chlorobromide grains consisting of silver chloride and silver bromide. That is, the average halogen composition is substantially silver chlorobromide. Part of the multiple structure can be pure silver bromide or pure silver chloride, and may contain 3 mol% or less of silver iodide.

The preferred average halogen composition is a silver bromide content of from 5 mol% to 98 mol%. More preferably, it is from 25 mol% to 97 mol%. The most preferable range is 35 mol% to 95 mol%.

The preferred range for the halogen composition of the outermost layer of the multiple structure is a silver bromide content of about 25 mol% to 100 mol%. More preferably it is about 35 mol% to 100 mol%, and most preferably about 60 mol% to 100 mol%.

It is desirable that the interior of the multiple structure have a layer with a lower silver bromide content than that of the outermost layer; in this case, the silver bromide content of this interior layer is more desirably about 10 mol% to 35 mol% lower than the outermost layer. However, the present invention is not limited by the silver bromide content of the interior layers.

(3) Gold-sulfur sensitization in the presence of a sensitizing dye

The third characteristic of the present invention is gold-sulfur sensitization in the presence of a sensitizing dye.

Means of including the sensitizing dye

Dyes usable in emulsions of the present invention include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and

hemioxonol dyes.

Such dyes are described in U.S. Patent 4,617,257; JP-A-59-180550; JP-A-60-140335; Research Disclosure (RD) 17029 (Dec., 1978) pp. 12 to 13.

Such sensitizing dyes may be used singly, or in combination. Combinations of sensitizing dyes are frequently used, particularly to achieve super-sensitization.

In addition to sensitizing dyes, the emulsion may contain dyes that show supersensitization, and have no spectral sensitizing action, or compounds that show supersensitization and do not substantially absorb visible light (for example, those described in U.S. Patent 3,615,641, Japanese Patent Application 61-226294 (corresponding to JP-A-63-23145), etc.).

Such sensitizing dyes may be added to the emulsion during chemical sensitization (chemical ripening) or before it; they may be present in the reaction system of soluble silver salt (silver nitrate for example) and a halogen compound (potassium bromide for example) before the formation of silver halide grains (as described in U.S. Patent 4,183,756); or they may be added to this reaction system after the formation of the nucleus of the silver halide grains before completion of the silver halide grain formation process (as described in U.S. Patent 4,225,666). The sensitizing dye may also be present in the reaction solution of this reaction system simultaneously with the mixing of the silver salt and the halogen compound. Light-sensitive material containing an emulsion prepared in this manner shows better gradation and storage properties in a high temperature state.

No matter which addition method is used, the total quantity of dye may be added all at once or in portions over a period of time. Dye may also be added to the reaction system in the form of an admixture with the soluble silver salt and/or the halogen compound.

It is possible to add sensitizing dye to the liquid surface or into the liquid, and any known method of stirring can be used.

Sensitizing dye used in the present invention may be added dissolved in methanol, ethanol, propanol, a fluorinated alcohol, methyl cellosolve, dimethyl-formamide, acetone, and other known organic solvents that are compatible with water, or water (they may be alkaline or acidic), or two or more of the above-mentioned solvents may be used together. Further, sensitizing dye may be added in dispersed form via a water/gelatin dispersion system; in the form of a freeze-dried powder; as a powder dispersed using surfactants; or in the form of a solution.

The quantity of sensitizing dye used is suitably 0.001 g to 20 g, and preferably 0.01 g to 2 g per 100 g of silver used in producing the emulsion.

The concentration of sensitizing dye used in the reaction liquid in silver halide grain formation is suitably about 1 wt% or less, preferably about 0.1 wt% or less.

The silver halide emulsion of the present invention is a gold-sulfur sensitized emulsion.

Useful sulfur sensitizers include active gelatin sulfur-containing compounds that react with silver. Examples of such compounds are thiosulfate, allylthiocarbamide, thiourea, allyl isothiocyanate, cystine, p-toluenethiosulfonate, rhodanine, and mercapto compounds. Such compounds are described in U.S. Patents 1,574,944; 2,410,689; 2,278,947; 2,728,668; and 3,656,955.

Sulfur sensitizer can be used in a quantity of about 10^{-7} to 10^{-2} mol per mol of silver.

Useful gold sensitizers are those with a gold oxidation number of +1 or +3. Examples of these are the chloroaurates, potassium chloroaurate, auric trichloride, potassium auric thiocyanate, potassium iodoaurate, and tetracyanoauric acid.

The amount of gold sensitizer useful is about $1x10^{-7}$ to $1x10^{-2}$ mol per mol of silver.

The temperature during chemical sensitization can be from about 40 to 90 °C, preferably 45 to 75 °C. The pH during chemical sensitization can be from about 3 to 9, preferably 4 to 8, and the pAg can be from about 5 to 11, preferably 7 to 10.

The gold sensitizer may be added simultaneously with the addition of the sulfur sensitizer, before the sulfur sensitizer, or after the sulfur sensitizer.

Other chemical sensitization methods which may be used simultaneously in the present invention and the selenium sensitizatien method; reduction sensitization methods employing reducing substances (for example, stannous salts, amines, hydrazine derivatives, formamidine sulfinic acid, and silane compounds); and noble metal sensitization methods employing noble metal compounds (for example, complex salts of Pt, Ir, Pd, Fe, Os, Co, Rh and other metals of Group VIII of the periodic table).

Useful selenium sensitizers are aliphatic isoselenocyanates such as allyl isoselenocyanate, selenoureas, selenoketones, selenoamides, selenocarboxylic acids and esters, selenophosphates, and selenides such as diethyl selenide and diethyl diselenide. Specific examples of these are described in U.S. Patents 1,574,944; 1,602,592; and 1,623,499.

Selenium sensitizers can be used in a quantity of about 10^{-7} to 10^{-2} mol per mol of silver.

Reduction sensitization methods are described in U.S. Patents 2,983,609, 2,419,974, and 4,054,458; noble metal sensitization methods in U.S. Patents 2,399,083 and 2,448,060, and British Patent 618,061, etc.

In the present invention, chemical sensitizers, notably gold sensitizers, are added to a silver halide photographic emulsion by known methods. For example, water-soluble compounds are added as aqueous solutions, and compounds soluble in organic solvents are added as solutions of organic solvents that are easily miscible with water (for example, methanol or ethanol).

This chemical sensitization can also be performed in the presence of nitrogen-containing heterocyclic compounds as described in British Patent 1,315,755; JP-A-50-63914; JP-A-51-77223; JP-A-58-126526; and JP-A-58-215644.

As mentioned in JP-B-39-22067 and JP-B-39-22068, it is also useful to perform chemical sensitization in the presence of acetylenic compounds, as low-fog silver halide emulsions are obtained.

In addition, it is also effective to perform chemical sensitization in the presence of silver halide solvents. Examples of silver halide solvents are the thiocyanates and the solvents described in JP-A-63-151618.

The heat-developable light-sensitive materials of the present invention are basically light-sensitive silver halide and a binder on a support containing, as required, organic metal salt oxidizing agents or dye providing compounds (as mentioned below that may also act as reducing agents) in the same layer, or if they are in a reactive state in separate layers. For example, when colored dye providing compounds are present in a layer below the silver halide emulsion, a decrease in sensitivity is avoided. It is preferable to incorporate reducing agents into the heat-developable light-sensitive material, but for example, they may be supplied from outside by a method of diffusion from dye fixing materials mentioned as discussed below.

In order to obtain a wide range of colors in the chromaticity chart using yellow, magenta and cyan, at least three silver halide emulsion layers sensitive to the different spectral regions are used in combination. For example, a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer; or a green-sensitive layer, a red-sensitive layer, and an infrared-sensitive layer could be used. Various sequences common in color light-sensitive materials can be used for the various light-sensitive layers. In addition, these light-sensitive layers may be separated into two or more layers as required.

Various auxiliary layers, such as protective layers, undercoating layers, intermediate layers, yellow filter layers, antihalation layers, and backing layers can be provided in the heat-developable light-sensitive materials of the invention.

Well-known silver halides may be used together with silver chlorobromide in the multiple grain structure of the present invention. Any of the following silver halides may be used together: silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver chloroiodide, and silver chloroiodobromide.

The coating quantity of the light-sensitive silver halide utilized in the present invention is about 1 mg to 10 g per m^2, calculated as silver.

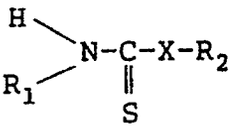
Organic metal salts may be used jointly as oxidizing agents together with light-sensitive silver halide in the present invention. Organic silver salts are particularly preferred.

Organic compounds which may be utilized in forming the organic silver salt oxidizing agents used in the invention are benzotriazoles and fatty acids and other compounds as described in U.S. Patent 4,500,626. Further, silver phenylpropiolate and similar silver salts of carboxylic acids possessing alkinyl groups as described in JP-A-60-113235; and acetylene silver as described in JP-A-61-249044, are also useful. Two or more kinds of organic silver salts may be used together.

Per mol of light-sensitive silver halide, 0.01 to 10 mol, preferably 0.01 to 1 mol, of the organic silver salts described above can be used simultaneously. The total coating amount of the light-sensitive silver halide and the organic silver salts is suitably between about 50 mg and 10 g per m^2, calculated as silver.

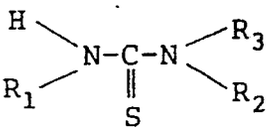
Various antifoggants or photographic stabilizers can be used in the present invention such as the azoles and azaindenes described in RD 17643 (1978), pp. 24 to 25; the nitrogen-containing carboxylic acids and phosphoric acids described in JP-A-59-168442; the mercapto compounds and their metal salts described in JP-A-59-111636; and the acetylenic compounds described in JP-A-62-87957.

It is particularly preferred to utilize as anti-foggants in the present invention the compounds represented by the following general formula (I) or (II).



(I)

(or its tautomers)



(II)

(or its tautomers)

In the formulae, R_1, R_2, R_3 each represents a hydrogen atom; a substituted or unsubstituted aliphatic group; a substituted or unsubstituted aryl group; or a substituted or unsubstituted heterocyclic group. One set or both sets of R_2 and R_3 together and/or R_1 and R_2 together may bond together to form a 5 to 7 membered carbocyclic or heterocyclic ring. X represents a sulfur atom or an oxygen atom.

Non-limiting examples of nitrogen-containing heterocyclic compounds represented by general formula (I) or (II) are given below.

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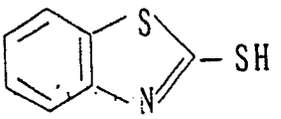

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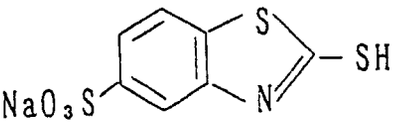

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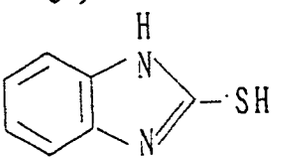

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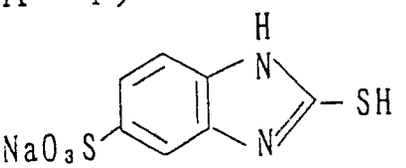

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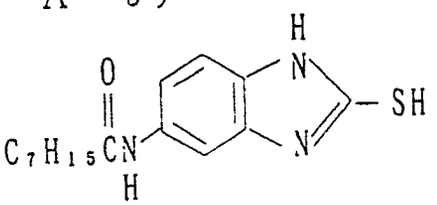

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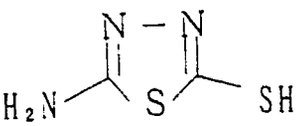

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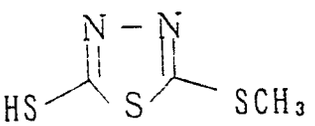

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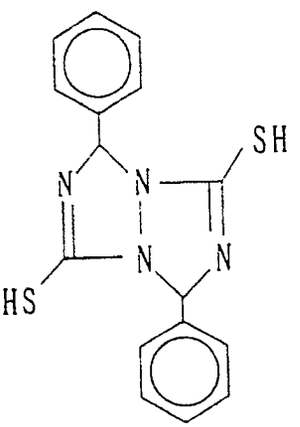

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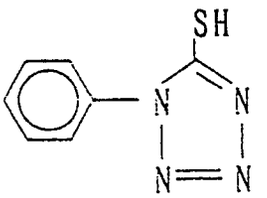

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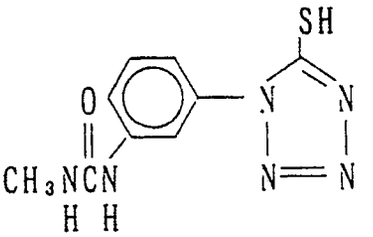

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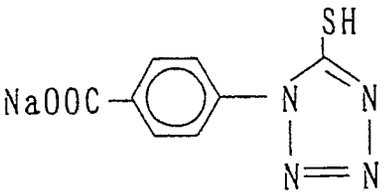

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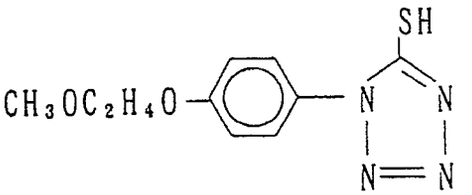

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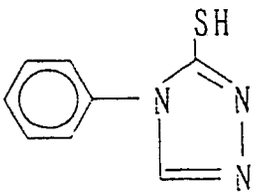

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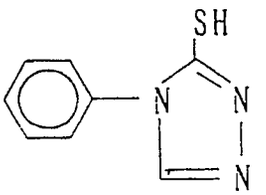

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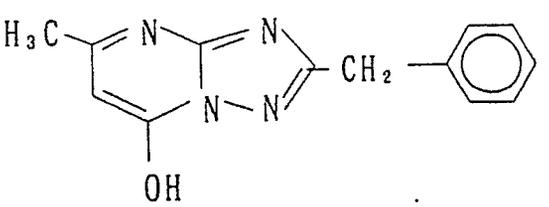

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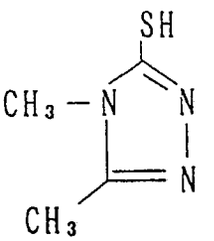

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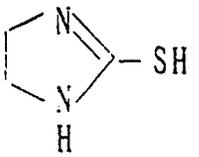

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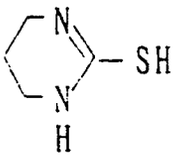

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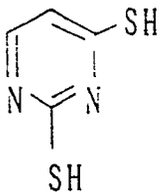

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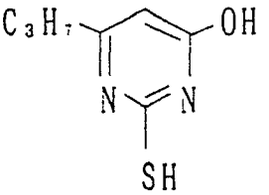

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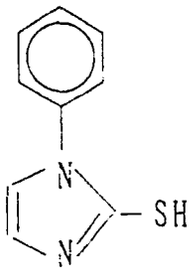

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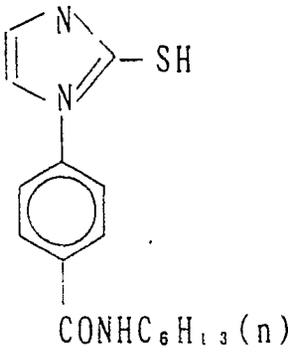

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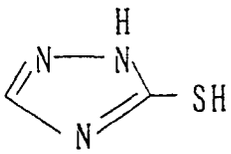

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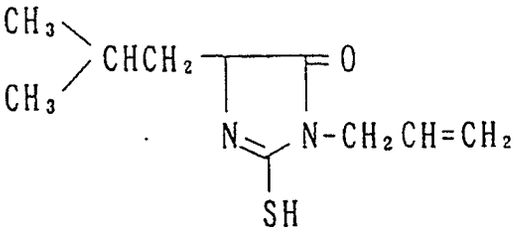


Antifoggants are normally used in the present invention in a quantity of 10^{-7} to 10 mol per mol of silver halide. An advantage of the silver halide emulsions of the present invention is that even when comparatively large amounts of antifoggants are used (for example, 10^{-4} to 1 mol/mol Ag), high sensitivities are still achieved.

Various polymer latexes can be included in the layers constituting the light-sensitive materials or dye fixing materials as well as in the backing layer. Such latexes can be used for dimensional stabilization, curl prevention, adhesion prevention, film cracking prevention, pressure sensitization prevention, and other improvements of film characteristics. In particular, a polymer latex with a low glass transition point (40 °C or less) can be used in a mordant layer to prevent cracking of the mordant layer; and a curl prevention effect is obtained by using a polymer latex with a high glass transition point in the backing layer. Specifically, any of the polymer latexes described in JP-A-62-245258, JP-A-62-136648, JP-A-62-110066 can be utilized.

Known reducing agents in the field of heat-developable light-sensitive materials can be used in the present invention. Dye providing compounds that have reducing properties, described below, can also be used. Such dye providing compounds can be simultaneously with other reducing agents. Reducing agent precursors that manifest reducing properties when activated by nucleophilic reagents or heat can also be used.

Specific examples of reducing agents used in the present invention are the reducing agents and reducing agent precursors described in U.S. Patent 4,500,626, columns 49 to 50; U.S. Patent 4,483,914, columns 30 to 31; U.S. Patent 4,330,617; U.S. Patent 4,590,152; JP-A-60-140335 pages (17) to (18); JP-A-57-40245; JP-A-56-138736; JP-A-59-178458; JP-A-59-53831; JP-A-59-182449; JP-A-59-182450; JP-A-60-119555; JP-A-60-128436 through JP-A-60-128439; JP-A-60-198540; JP-A-60-181742; JP-A-61-259253; JP-A-62-244044; JP-A-62-131253 through JP-A-62-131256; and EP-A-220746 pp. 78 to 96.

Combinations of reducing agents are described, for example in U.S. Patent 3,039,869 can also be used.

When nondiffusible reducing agents are used, electron transfer agents and/or electron transfer agent precursors can be used in combination as required to promote electron transfer between the nondiffusible reducing agent and the developable silver halide.

Electron transfer agents or their precursors can be selected, for example, from the reducing agents or their precursors cited above. The mobility of such electron transfer agents or their precursors is preferably greater than that of the nondiffusible reducing agents (electron donors). Particularly useful electron transfer agents are 1-phenyl-3-pyrazolidones or aminophenols.

Nondiffusible reducing agents (electron donors) useful in combination with electron transfer agents are those which have substantially no mobility in the layers of light-sensitive material. Preferably, these are hydroquinones, sulforamidophenols, sulfonamidonaphthols, the compounds described in JP-A-53-110827 as electron donors, and dye providing compounds possessing nondiffusing reducing properties.

The quantity of reducing agents added in the present invention is 0.001 to 20 mol, preferably 0.01 to 10 mol, per mol of silver.

Silver can be used as the image forming substance in the present invention. Further, when silver ions are reduced to silver at a high temperature state, compounds which can form or release mobile dye corresponding or countercorresponding to this reaction, namely dye providing compounds, can be included.

One example of a type of dye providing compounds of use in the present invention are compounds which form dyes by an oxidative coupling reaction (couplers). These couplers may be 4-equivalent or 2-equivalent couplers. The 2-equivalent couplers that are preferred have a nondiffusible group as an elimination group and form a diffusible dye by an oxidative coupling reaction. This nondiffusible group may form a polymer chain. Specific examples of color developers and couplers are described in detail in T.H. James, "The Theory of the Photographic Process", 4th edition, pp. 291 to 334 and pp. 354 to 361; and in JP-A-58-123533, JP-A-58-149046, JP-A-58-149047, JP-A-59-111148, JP-A-59-124399, JP-A-59-174835, JP-A-59-231539, JP-A-59-231540, JP-A-60-2950, JP-A-60-2951, JP-A-60-14242, JP-A-60-23474, and JP-A-60-66249.

Another example of a useful type of dye providing compounds are compounds having a mechanism of imagewise release or diffusion of diffusible dye. These kinds of compounds can be represented by the following formula (LI).

$$(\underline{\text{Dye}}\text{-Y})_n\text{-Z} \qquad \text{(LI)}$$

Dye represents a dye group, a transiently short-waved dye group, or a dye precursor group. Y represents a single bond or a linking group. Z represents groups possessing properties such that differences in the diffusibility of the compounds represented by $(\underline{\text{Dye}}\text{-Y})_n$-Z are caused to arise, or Dve is released, and differences in the diffusibility between the released Dye and $(\underline{\text{Dye}}\text{-Y})_n$-Z are caused to arise, corresponding or counter-corresponding to a light-sensitive silver salt imagewise possessing a latent image. n represents 1 or 2; when n is 2, each (Dye -Y) may be the same or different.

Specific examples of the dye providing compounds represented by general formula (LI) are compounds (1) to (5), below. Compounds (1) to (3), below, are compounds that form a diffusible dye image (positive dye image) countercorresponding to the development of the silver halide. Compounds (4) and (5) are compounds that form a diffusible dye image (negative dye image) corresponding to the development of the silver halide.

SPECIFIC EAMPLES OF DYE PROVIDING COMPOUNDS

(1) Dye developers with a hydroquinone type developer and dye component bonded together, are

described in U.S. Patents 3,134,764, 3,362,819, 3,597,200, 3,544,545 and 3,482,972. These dye developers are such that they are diffusible in an alkaline environment, but become non-diffusible on reaction with a silver halide.

(2) Nondiffusible compounds as described in U.S. patent 4,503,137 release a diffusible dye in an alkaline environment, but on reaction with silver halide they lose this ability. Examples thereof are compounds described in U.S. Patent 3,980,479 that release a diffusible dyė by intramolecular nucleophilic substitution, and the compounds described in U.S. Patent 4,199,354 that release a diffusible dye by an intramolecular rearrangement reaction of an isoxazolone ring.

(3) Nondiffusible compounds described in U.S. Patent 4,559,290; EP-A-220746; U.S. Patent 4,783,396; and Kokai Giho 87-6199 react with the remaining reducing agent which has not been oxidized by development to release a diffusible dye.

The followings are examples thereof: The compounds described in U.S. Patents 4,139,389 and 4,139,379; JP-A-59-185333 and JP-A-57-84453; that release diffusible dye by an intramolecular substitution reaction after being reduced. The compounds described in U.S. Patent 4,232,107; JP-A-59-101649; and JP-A-61-88257; RD 24025 (April, 1984) that release a diffusible dye by an intramolecular electron transfer reaction after reduction. The compounds described in DF-A-3008588; JP-A-56-142530; U.S. Patents 4,343,893 and 4,619,884 that release a diffusible dye through the opening of a single bond after reduction. The nitro compounds described in U.S. Patent 4,450,223 that release a diffusible dye after accepting an electron; and the compounds described in U.S. Patent 4,609,610 that release diffusible dye after accepting an electron.

The following are prefered compounds: The compounds described in EP-A220746; Kokai Giho 87-6199; U.S. Patent 4,783,396; JP-A-63-201653; and JP-A-63-201654; these compounds possess in one molecule N-X bonds (X represents an oxygen, sulfur or nitrogen atom) and electron attracting groups. The compounds described in Japanese Patent Application 62-106885 (corresponding to JP-A-1-26842) that have in one molecule a SO_2-X bond (X is the same as above) and an electron attracting group. The compounds described in JP-A-63-271344 that have in one molecule a PO-X bond (X is the same as above) and an electron attracting group. The compounds described in JP-A-63-271341 that have in one molecule a C-X′ bond (X′ represents the same as X, or -SO_2-) and an electron attracting group. The compounds described in Japanese Patent Application Nos. 62-319989 and 62-320771 (corresperding to JP-A-1-161237 and JP-A-1-161342, respectively) that release a diffusible dye by opening of a single bond after reduction by means of π-bonds conjugated to an electron accepting group.

Particularly preferred are compounds that, in one molecule, have a N-X bond and an electron attracting group. Specific examples of these are Compounds (1) to (3), (7) to (10), (12), (13), (15), (23) to (26), (31), (32), (35), (36), (40), (41), (44), (53) to (59), (64) and (70) described in EP-A-220746 or U.S. Patent 4,783,396; and Compounds (11) to (23) in Kokai Giho 87-6199.

(4) Compounds that release a diffusible dye by reaction with the oxidation products of reducing agents that are couplers having the diffusible dye in an elimination group (DDR couplers). Specific examples are described in British Patent 1,330,524; JP-B-48-39165; and U.S. Patents 3,443,940, 4,474,867, and 4,483,914.

(5) Compounds that reduce silver halides or organic silver salts, and release a diffusible dye when the counterpart is reduced (DRR compounds). These compounds can be used without other reducing agents and are preferred because there are no image staining problems due to the oxidation decomposition products of such other reducing agents. Representative examples of these are described in U.S. Patents 3,928,312, 4,053,312, 4,055,428 and 4,336,322; JP-A-59-65839; JP-A-59-69839; JP-A-53-3819; JP-A-51-104343; RD 17465 (Oct., 1978); U.S. Patents 3,725,062, 3,728,113 and 3,443,939; JP-A-53-116537; JP-A-57-179840; and U.S. Patent 4,500,626. Also useful are the compounds described in U.S. Patent 4,639,408, columns 37 to 39. Specific preferred examples of DRR compounds are compounds (1) to (3), (10) to (13), (16) to (19), (28) to (30), (33) to (35), (38) to (40), and (42) to (64) described in the U.S. Patent 4,500,626.

Additional dye providing compounds, apart from the couplers and compounds of general formula (LI), are dye silver compounds with organic silver salts and dyes bonded together (Research Disclosure (RD), (May, 1978), pp. 54 to 58); azo dyes used in heat-developable silver dye bleach methods (U.S. Patent 4,235,957, Research Disclosure (RD) (April, 1976), pp. 30 to 32); and leuco dyes (U.S. Patents 3,985,565 and 4,022,617).

Dye providing compounds, nondiffusible reducing agents, and similar hydrophobic additives can be introduced into the light-sensitive material layers using known methods such as those described in U.S. Patent 2,322,027. High-boiling organic solvents such as those described in JP-A-59-83154, JP-A-59-178451, JP-A-59-178452, JP-A-59-178453, JP-A-59-178454, JP-A-59-178455, and JP-A-59-178457 together with

low-boiling organic solvents having a boiling point 50 ° C to 160 ° C can be used as required.

The quantity of high-boiling organic solvent used is 10 g or less per 1 g of dye providing compound, preferably 5 g or less. Preferably 1 cc or less, more preferably 0.5 cc or less, in particular 0.3 cc or less, per gram of binder should be used.

The diffusion method utilizing the polymers described in JP-B-51-39853 and JP-A-51-59943 can also be used.

For compounds that are substantially insoluble in water, they may be dispersed as fine particles in the binder in addition to the methods described above.

For hydrophobic compounds dispersed in a hydrophilic colloid, various surfactants can be used. Such surfactants are mentioned in JP-A-59-157636, at pages (37) to (38).

Compounds can be used in the present invention that simultaneously provide for activation of the development of the light-sensitive material and stabilization of the image. Specific examples of preferred compounds described in U.S. Patent 4,500,626, columns 51 to 52.

In the system in which the image is formed by the diffusion transfer of dye, a dye fixing material can be used together with the light-sensitive material. The dye fixing material may be coated on a separate support from the light-sensitive material, or it may be coated on the same support as the light-sensitive material. The relationship between the light-sensitive material and the dye fixing material, its relationship with the support, and with the white reflecting layer described in U.S. Patent 4,500,626, column 57, are also suitable relationships for the present application.

The dye fixing material used for preference in this invention has at least one layer containing a mordant and a binder. The mordant can be one that is well known in the field of photography. Specific examples of such mordants are described in U.S. Patent 4,500,626, columns 58 to 59; and JP-A-61-88256, pages (32) to (41); and, in particular, those described in JP-A-62-244043 and JP-A-62-244036. The macromolecular dye accepting compounds described in U.S. Patent 4,463,079 can also be used.

The dye fixing material can be provided as required with a protective layer, peelable layer, curl preventing layer, and other kinds of auxiliary layers. A protective layer is particularly useful.

Plasticizers, slip agents, or high-boiling organic solvents, to improve the peeling of the light-sensitive material and the dye fixing material, can be used in the layer constituting the light-sensitive material and the dye fixing material. Specific examples of these are described in JP-A-62-253159, page (25), and JP-A-62-245253. Various kinds of silicone oil (all silicone oils, from dimethylsilicone oil to modified silicone oils in which various organic groups have been introduced into dimethylsiloxane) can also be utilized. Examples of these are the modified silicone oils described in "Modified Silicone Oils" published by Shin'etsu Silicone (Co.) technical data, p. 6-18B, and the silicone oils described in JP-A-62-215953 and JP-A-63-46449. Particularly effective are carboxy-modified silicone (Trade name X-22-3710).

Discoloration inhibitors may be used in the light-sensitive material or the dye fixing material. These can be, for example, antioxidants, ultraviolet absorbers, or certain metal complexes.

Examples of antioxidants are chroman compounds, coumaran compounds, phenolic compounds (for example, hindered phenols), hydroquinone derivatives, hindered amine derivatives, and spiroindan compounds. The compounds described in JP-A-61-159644 are also effective.

Ultraviolet absorbents that are useful are benzotriazole compounds (U.S. Patent 3,533,794), 4-thiazolidone compounds (U.S. Patent 3,352,681), benzophenol compounds (JP-A-46-2784), and the compounds described in JP-A-54-48535, JP-A-62-136641 and JP-A-61-88256, and the ultraviolet-absorbing polymers described in JP-A-62-260152.

Useful metal complexes are described in U.S. Patent 4,241,155, 4,245,018 at columns 3 to 36, and in 4,254,195 at columns 3 to 8; JP-A-62-174741; JP-A-61- 88256 pages (27) to (29); JP-A-63-199248; and Japanese Patent Application Nos. 62-234103 and 62-230595 (corresponding to JP-A-1-75568 and JP-A-1-74272, respectively).

Examples of useful discoloration inhibitors are described in JP-A-62-215272, Pages (125) to (137).

Discoloration inhibitors to prevent the fading of the dye transferred to the dye fixing materials may be included in the dye fixing materials, or supplied to the dye fixing materials from outside, for example from the light-sensitive materials.

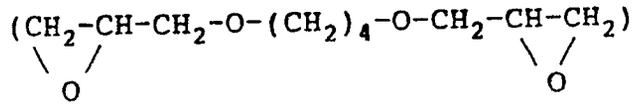
The oxidation inhibitors, ultraviolet absorbents, and metal complexes, described above may be used in combination with each other.

Brightening agents may be used in the light-sensitive materials and dye fixing materials. Brightening agents are preferably incorporated into the dye fixing material, or supplied from outside, for example from the light-sensitive material. Examples of these are described in K. Veenkataraman, "The Chemistry of Synthetic Dyes", Volume V, Chapter 8, and in JP-A-61-143752. More specifically, stilbene-based compounds, coumarin-based compounds, biphenyl-based compounds, benzoxazole-based compounds, naph-

thalimido compounds, pyrazoline-based compounds, carbostyryl compounds can be used.

Brightening agents can be used in combination with discoloration inhibitors.

Hardening agents that can be used in a layer containing the light-sensitive material and dye fixing material are described in U.S. Patent 4,678,739 column 41; JP-A-59-116655; JP-A-62-245261; and JP-A-61-18942. More specifically, the aldehyde-based hardening agents (formaldehyde and the like); azylidene-based hardening agents; epoxy-based hardening agents like



vinylsulfone-based hardening agents (N,N-ethylene-bis(vinylsulfonylacetamido)ethane); N-methylol-based hardening agents (dimethylolurea); and macromolecular hardening agents (compounds described in JP-A-62-234157) are useful.

Various surfactants can be utilized in the layers constituting the light-sensitive material and the dye fixing material as coating aids for separability improvement, slip improvement, static electricity prevention, and development acceleration. Specific examples of surfactants are described in JP-A-62-173463 and JP-A-62-183457.

Organofluorine compounds may be contained in the layers constituting the light-sensitive material and the dye fixing material for slip improvement, static electricity prevention, and separability improvement. Pepresentative examples of organofluorine compounds are the fluorine-based surfactants described in JP-B-57-9053 columns 8 to 17; JP-A-61-20944; JP-A-62-135826; fluorinated oils and oily fluorine compounds; tetra-fluoroethylene resins, solid fluorine compound resins, and the hydrophobic fluorine compounds.

Matting agents can be used in the light-sensitive material and dye fixing material. As matting agents, other than silicon dioxide, polyolefins or polymethacrylates and the like, as described in JP-A-61-88256 page (29), there are the benzoguanamine resin beads, polycarbonate resin beads, AS resin beads the like compounds described in Japanese Patent Applications Nos. 62-110064 and 62-110065 (corresponding to JP-A-63-274944 and JP-A-63-274952, respectively).

Thermal solvents, antifoaming agents, antifungal agents, colloidal silica and other known additive may be included in the layers constituting the light-sensitive material and the dye fixing material. Specific examples of these additives are described in JP-A-61-88256, pages 26 to 32.

Image formation accelerators can be used in the light-sensitive material and/or the dye fixing material in the present invention. The function of image formation accelerators is to accelerate the oxidation-reduction reactions of the silver salt oxidizing agent and the reducing agent; to accelerate the reaction of dye formation, dye decomposition, or release of diffusible dye from dye providing substances; and to accelerate the transfer of dye from the light-sensitive material layer to the dye fixing layer. They are classified according to physicochemical function as bases or base precursors, nucleophilic compounds, high-boiling organic solvents (oils), thermal solvents, surfactants, and compounds that interact with silver or silver ions. These groups of substances generally have more than one function, and usually have some accelerating effect. These accelerators are described, for example, in U.S. Patent 4,678,739, columns 38 to 40.

Useful base precursors are the salts of organic acids and bases from which carbon dioxide is released by heat; and compounds that release an amino group by Rossen rearrangemen, Beckmann rearrangement, or an intramolecular nucleophilic substitution reaction. Specific examples of these are described in U.S. Patent 4,511,493 and JP-A-62-65038.

In a system in which heat development and dye transfer take place simultaneously in the presence of a small amount of water, it is preferable for the base and/or base precursor to be included in the dye fixing material. Such an arrangement gives a light-sensitive material with a long shelf life.

In addition, base precursors can be formed from the combination of sparingly soluble metallic compounds and compounds that react with the metallic ions in these sparingly soluble compounds to form complexes (termed "complex forming compounds"). These are described in EP-A-210660 and U.S. Patent 4,740,445. This method is particularly effective. These sparingly soluble metal compounds and complex forming compounds are advantageously added separately to the light-sensitive material and the dye fixing material. Also useful are compounds that produce bases upon electrolysis as described in JP-A-61-232451.

To change the development processing temperature or processing time, a development stop agent can normally be used in the light-sensitive material and/or in the dye fixing material of the present invention in order to obtain an image.

A development stop agent is a compound that after appropriate development quickly neutralizes or

reacts with the base to reduce the concentration of base in the film and stop development, or a compound which inhibits development by interacting with silver and silver salt. Such agents are acid precursors that liberate acid on heating; electrophilic compounds that initiate a substitution reaction with base that is present on heating; heterocyclic nitrogen-containing compounds; and mercapto compounds and their precursors can be mentioned. These are described in JP-A-62-253159, pages 31 to 32.

Useful supports for the light-sensitive material and dye fixing material of the present invention are materials which can withstand the processing temperature. Generally, paper and synthetic polymers (films) are useful. For example, it is possible to use polyethylene terephthalate; polycarbonate; polyvinyl chloride; polystyrene; polypropylene; polyimides; celluloses (for example, triacetyl cellulose); films with titanium oxide and similar pigments included in them; synthetic papers made by film methods from polypropylene and similar materials; mixed papers made from polyethylene synthetic resin pulp and natural pulp, yankee paper, baryta paper; coated papers (particularly cast coated papers); metals; fabrics; and glass.

These materials can be used independently, or as supports that have been laminated on one or both faces with polyethylene or similar synthetic macromolecules.

The supports described in JP-A-62-253159, pages (29) to (31), can also be used.

Hydrophilic binders and semiconductive metallic oxides such as alumina sol and tin oxide, carbon black, and other antistatic agents may be coated on to the surface of these supports.

The methods of recording an image on the light-sensitive material by direct exposure using a camera; by exposure through reversal film or negative film using a printer or enlarger; by scanning exposure of an original image through a slit using the exposure device of a copying machine; by exposure using a light emitting diode or a laser for image recording via electrical signals; and for recording the image output of a CRT, liquid crystal display, electroluminescent display, or plasma display either directly or via an optical system can be used.

Light sources useful for recording the image on the light-sensitive material are natural light, a tungsten lamp, a light emitting diode, a laser light source, a CRT light source, and the light sources described in U.S. Patent 4,500,626, column 56.

In addition, the image can be exposed using a wavelength conversion element obtained by combining nonlinear optical material and a laser or other coherent light source. The nonlinear optical material is a material which can manifest nonlinearity between the polarization and the electric field appearing when a strong photoelectric field such as laser light has been applied. For the application, it is preferred to use inorganic compounds, such as lithium niobate; potassium dihydrogen phosphate (KDP); lithium iodate and BaB_2O_4; and urea derivatives; nitroaniline derivatives; 3-methyl-4-nitropyridine-N-oxide (POM) and nitropyridine-N-oxide derivatives; and the compounds described in JP-A-61-53462 and JP-A-62-210432. Single crystal photoconductive wave path form and fiber form are known as configurations of wavelength conversion elements that are useful.

An image data can utilize image signal obtained from video cameras, or electronic still cameras, television signals as represented by the Nippon television signal code (NTSC), image signals obtained by dividing an original image into a plurality of pixels in a scanner, or images made using computer graphic or computer-aided design programs.

An electrically conducting layer that generates heat may be used as the heat source for heat development or diffusible dye transfer in the light-sensitive material and/or dye-fixing material. A transparent or non-transparent heat-generating element is described in JP-A-61-145544. Such conductive layers also function as antistatic layers.

Development is possible at about 50 °C to about 250 °C, and about 80 °C to about 180 °C is most useful. The dye diffusion-transfer process may take place simultaneously with heat development, or it may proceed after the end of the heat development process. When dye diffusion follows heat development, transfer is possible from the temperature of the heat development to room temperature. The temperature for transfer is preferably from 50 °C to the temperature about 10 °C lower than the temperature in the heat development process.

The migration of dye can take place due to heat alone, but a solvent may be used to accelerate dye migration.

As mentioned in JP-A-59-218443 and JP-A-61-238056, by heating in the presence of a small quantity of solvent (in particular, water) development and transfer can be done simultaneously or in succession. In these systems, the heating temperature is preferably 50 °C or above, and below the boiling point of the solvent. For example, when the solvent is water the preferred temperature would be 50 °C or above and 100 °C or below.

Useful solvents to accelerate development and/or migration of the diffusible dye to the dye fixing layer are water and a basic aqueous solution containing an inorganic alkali metal salt and one of the organic

bases described in the image-forming accelerator section. Low boiling point solvents; mixed solutions of low-boiling solvents and water or basic aqueous solutions can be utilized. Surfactants, antifoggants, sparingly soluble metallic salts, and complex-forming compounds may be present in the solvent.

These solvents can be used with methods that allow them in the dye fixing material, light-sensitive material, or both the dye fixing material and the light-sensitive material. The amount of solvent utilized may be at most the weight of solvent corresponding to the maximum swelling volume of the whole coated film (in particular, a quantity not more than the difference of the weight of solvent corresponding to the maximum swelling volume of the whole coated film and the weight of the whole coated film). This is, effectively, a small quantity.

A method of providing solvent in the light-sensitive layer or dye fixing layer is described in JP-A-61-147244, page (26). Further, the solvent can be incorporated into the light-sensitive material or the dye fixing material or both beforehand in microcapsules, for example.

In order to accelerate dye migration, a system can be adopted in which a hydrophilic thermal solvent that is solid at normal temperature and melts at a high temperature is incorporated into the light-sensitive material or the dye fixing material. The hydrophilic thermal solvent may be incorporated into either or both of the light-sensitive material or the dye fixing material. Further, it may be incorporated into any emulsion layer, intermediate layer, protective layer, or dye fixing layer. Preferably, it is incorporated into the dye fixing layer and/or a layer adjacent to the dye fixing layer.

Examples of hydrophilic thermal solvents are ureas, pyridines, amides, sulfonamides, amides, alcohols, oximes, and other heterocyclic compounds.

In order to accelerate dye migration, a high-boiling organic solvent may be contained in the light-sensitive material and/or the dye fixing layer.

Examples of heating methods useful in the development and/or transfer process are contact with a heated block or plate; contact with a hot plate, hot press, hot roller; a halogen lamp heater; an infrared or far infrared lamp heater; or passage through a high temperature environment.

An example of the compression conditions and method when the light-sensitive layer and the dye fixing layer are super-posed and in close contact is the method described in JP-A-61-147544, page (27).

In processing the photographic elements of the present invention, any of various known heat development devices may be used. For example, the devices described in JP-A-59-75247, JP-A-59-177547, JP-A-59-181353 and JP-A-60-18951, and JP-A-U-62-25944 are preferably utilized (the term "JP-A-U" as used herein means an "unexamined published Japanese utility model application").

The present invention is now described with reference to the following, non-limiting Examples. Unless otherwise indicated, all percentages and ratios are by weight.

Example 1

An example of a positive heat-developable light-sensitive material which gives a magenta dye image is given below.

(A) Preparation of Emulsions (1) to (5)

Emulsion (1)

Solutions (I) and (II) of Table 2 were mixed simultaneously with an aqueous gelatin solution (Table 1) with good stirring while maintaining the temperature at 50° C. After water wash desalting, 25 g of gelatin were added, the pH and pAg adjusted, and optimum sulfur sensitization performed using 4.5 mg of sodium thiosulfate and 95 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene.

The yield was 630 g of a monodisperse emulsion of cubic silver chlorobromide grains with an average grain size of 0.4 μm. (Uniform structure, sulfur sensitized emulsion).

Table 1 - Composition of aqueous gelatin solution

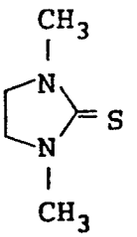
Gelatin	20 g
NaCl	4 g
KBr	0.3 g
H_2O	800 cc
	0.02 g

Table 2

Composition of added solutions		
	(I)	(II)
$AgNO_3$ (g)	100	-
KBr (g)	-	49
NaCl (g)	-	10.4
H_2O was added to total (cc)	450	450

Emulsion (2)

Solutions (I) and (II) or Table 3 were mixed simultaneously with an aqueous gelatin solution (Table 1) with good stirring while maintaining the temperature at 50 ° C. Solutions (III) and (IV) were added simultaneously to this mixture. After water washing, desalting, and chemical sensitization, identical to Emulsion (1), a monodisperse emulsion of cubic silver chlorobromide grains of average grain size 0.4 μm was obtained. The yield was 632 g. (Core/shell structure, sulfur sensitized emulsion).

Table 3

Composition of added solutions				
	(I)	(II)	(III)	(IV)
$AgNO_3$ (g)	50	-	50	-
KBr (g)	-	21	-	28
NaCl (g)	-	6.9	-	3.5
H_2O was added to total (cc)	200	200	200	200

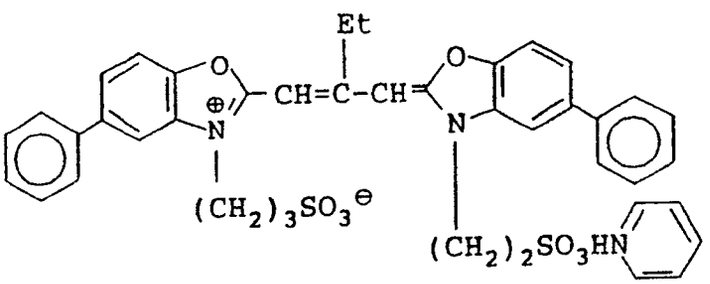
Emulsion (3)

A gold-sulfur sensitized Emulsion (3) was formulated using identical steps to those described in formulating Emulsion (2), except that 3.2 mg of sodium thiosulfate, 155 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, and 0.6 mg of chloroauric acid were used in chemical sensitization. The emulsion obtained was a monodisperse silver chlorobromide emulsion with cubic grains of average grain size 0.4 μm, at a yield of 632 g. (Core/shell structure, gold-sulfur sensitized emulsion).

Emulsion (4)

The preparation of Emulsion (4) was identical to that of Emulsion (2) except at 1 minute after adding solutions (III), (IV), dye solution A of Table 4 was added. The resulting emulsion was a monodisperse silver chlorobromide emulsion with cubic grains of average grain size 0.4 μm, in a yield of 630 g. (Core/shell structure, emulsion sulfur sensitized in the presence of dye).

Table 4 - Composition of dye solution A



0.23 g

Methanol 40 cc

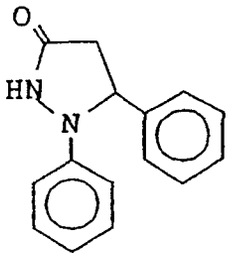
Emulsion (5)

The preparation of Emulsion (5) was identical to the preparation of Emulsion (3) except 1 minute after adding solutions (III), (IV) of Table 3, dye solution A of Table 4 was added. The emulsion obtained was a monodisperse silver chlorobromide emulsion with cubic grains of average grain size 0.4 μm, in a yield of 632 g. (Core/shell structure, emulsion gold-sulfur sensitized in the presence of dye).

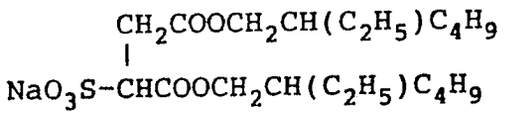
(B) Method of Preparation of Dispersion of an Electron Transfer Agent

Exactly 10 g of Electron Transfer Agent (1) shown below, 0.5 g of polyethylene glycol nonylphenyl ether as a dispersing agent, and 0.5 g of the Anionic Surfactant (1) shown below were added to a 5% aqueous gelatin solution, and comminuted in a mill for 60 minutes with glass beads of average diameter 0.75 mm. The glass beads were separated off, and dispersion of electron transfer agent of average particle size 0.3 μm was obtained.

Electron Transfer Agent (1):



Anionic Surfactant (1):



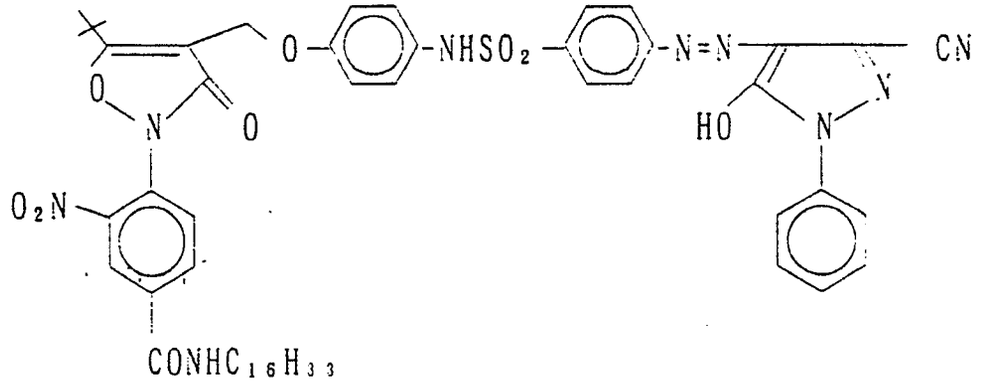
(C) Method of Making Gelatin Dispersion of Dye Providing Compounds (1), (2), and (3)

Yellow, magenta and cyan dyes were each added as shown in the Treatment Method, below, to 50 cc of ethyl acetate and dissolved to a uniform solution by warming to about 60 ° C. This solution and 100 g of a 10% aqueous solution of lime-processed gelatin, 1.5 g of sodium dodecylbenzenesulfonate and 60 cc of water were stirred and mixed, then dispersed in a homogenizer at 10,000 rpm for 10 minutes. These dispersion liquids are termed "gelatin dispersions of dye providing compounds".

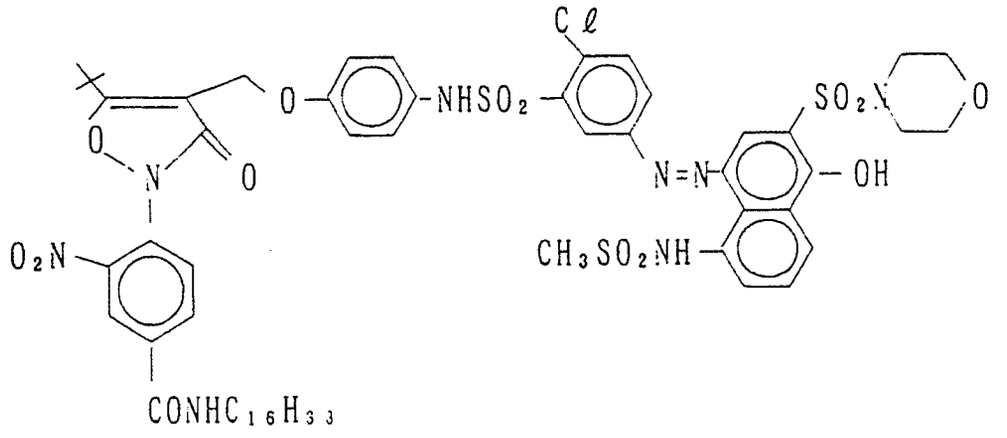
Treatment Method (1):			
	Yellow	Magenta	Cyan
	(g)	(g)	(g)
Dye Providing Compound	(1) 13	(2) 15.5	(3) 16.6
Electron Donor (1)	10.2	8.6	8.1
High-Boiling Solvent (1)	6.5	7.8	8.3
Electron Transfer Agent Precursor (1)	0.9	1.5	1.5

Compounds Used in Treatment Method (1):

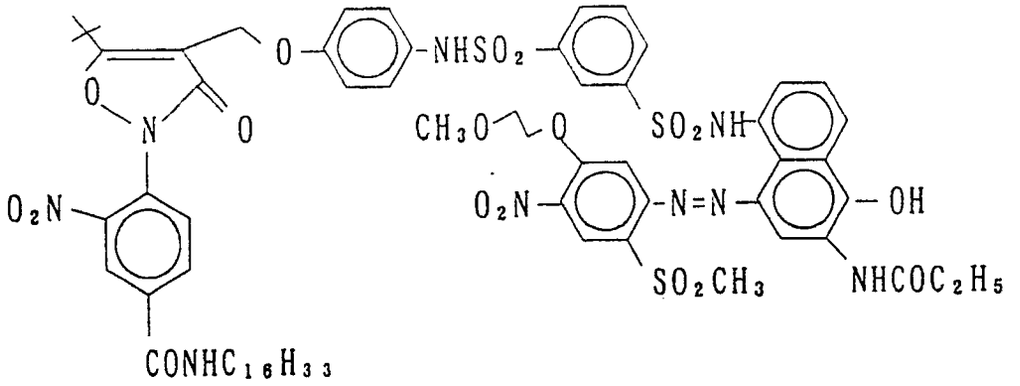
Dye providing compound (1)



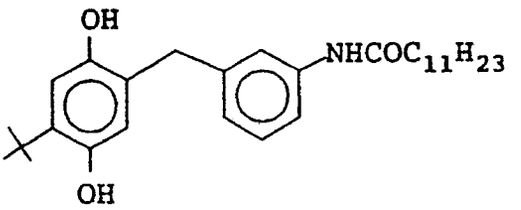
Dye providing compound (2)



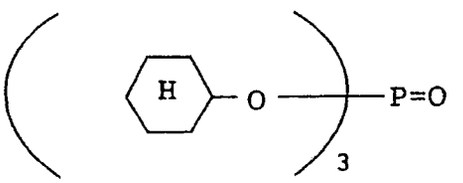
Dye providing compound (3)



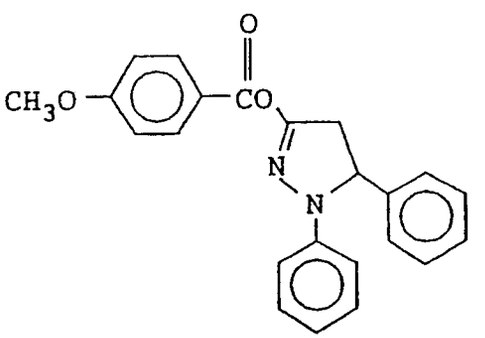
Electron donor (1)



High-boiling solvent (1)



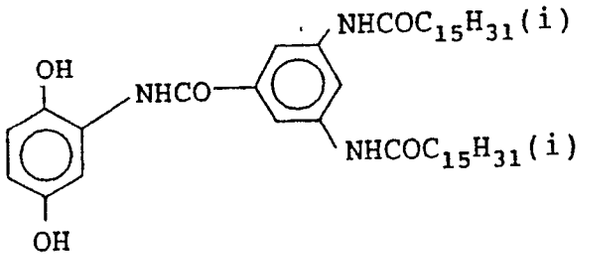
Electron transfer agent precursor (1)



(D) Method of making Gelatin Dispersion of Electron Donor (2) used in Intermediate Layers

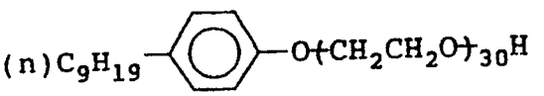
Exactly 23.6 g of Electron Donor (2) shown below, and 8.5 g of High-Boiling Solvent (1) were added to 30 cc of ethyl acetate and uniformly dissolved. This solution and 100 g of a 10% solution of lime-processed gelatin, 0.25 g of sodium hydrogen sulfite, 0.3 g of sodium dodecylbenzenesulfonate, and 30 cc of water were stirred, and then dispersed in a homogenizer at 10,000 rpm for 10 minutes. This dispersion is "Gelatin Dispersion of Electron Donor (2)".

Electron Donor (2)

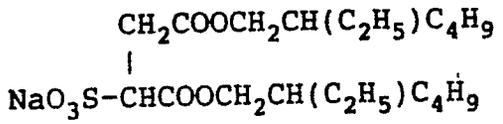


Positive heat-developable color light-sensitive materials were prepared, constituted as shown in Table 5, using these emulsions and dispersions.

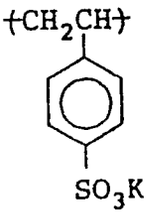
Surfactant (1)



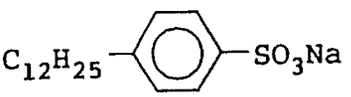
Surfactant (2)



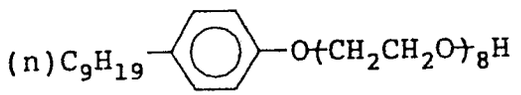
Water-soluble polymer (1)



Surfactant (3)



Surfactant (4)



Hardener (1)

1,2-Bis(vinylsulfonylacetamido)ethane

Antifoggant (1)

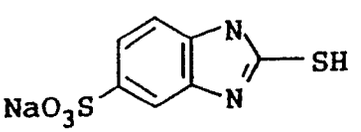


Table 5 - Constitution of Light-sensitive Material

Layer number/name	Quantity coated (mg/m^2)
3: Protective Layer	
Gelatin	900
Silica	40
Zinc Hydroxide	600
Surfactant (1)	130
Surfactant (2)	26
Water-Soluble Polymer (1)	8
2: Emulsion Layer	
Light-sensitive Layer Silver Halide Emulsion (Table 6)	220 (Ag)
Sensitizing Dye (Table 6)	
Dye Providing Compound (2) (Magenta)	348
Gelatin	310
Electron Donor (1)	193
High-Boiling Solvent (1)	175
Electron Transfer Agent Precursor (1)	34
Surfactant (3)	34
Water-Soluble Polymer (1)	11
Antifoggant (1)	0.8
	(About 1.5×10^{-3} mol/mol Ag)

Table 5 - Constitution of Light-sensitive Material (cont'd)

Layer number/name	Quantity coated (mg/m^2)
1: Intermediate Layer	
Gelatin	700
Electron Donor (2)	130
High-Boiling Solvent (1)	48
Surfactant (2)	15
Surfactant (4)	61
Surfactant (3)	2
Electron Transfer Agent (1)	82
Water-Soluble Polymer (1)	19
Hardener (1)	30

The light-sensitive materials prepared in Example 1 are shown in Table 6.

Table 6

Light-sensitive material No.	Emulsion utilized	Sensitizing dye
101	Emulsion (1) (comparison)	Dye Solution (A) 0.8 mg/m^2
102	Emulsion (2) (comparison)	Dye Solution (A) 0.8 mg/m^2
103	Emulsion (3) (comparison)	Dye Solution (A) 0.8 mg/m^2
104	Emulsion (4) (comparison)	-
105	Emulsion (5) (the present invention)	-

Dye fixing materials were prepared, as shown in Table 7.

Table 7 - Constitution of Dye Fixing Materials

Layer No.	Additive	Quantity coated (mg/m^2)
Layer 3	Gelatin	0.05
	Silicone oil (1)	0.04
	Surfactant (5)	0.001
	Surfactant (6)	0.02
	Surfactant (7)	0.10
	Matting agent (1)	0.02
	Guanidine picolinate	0.45
	Water-soluble polymer (1)	0.24
Layer 2	Mordant (1)	2.35
	Water-soluble polymer (2)	0.20
	Gelatin	1.40
	Water-soluble polymer (3)	0.60
	High-boiling solvent (2)	1.40
	Guanidine picolinate	2.25
	Brightening agent (1)	0.05
	Surfactant (9)	0.15

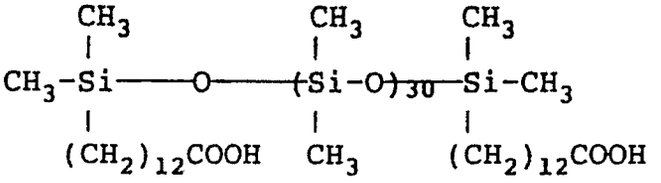
Table 7 - Constitution of Dye Fixing Materials (cont'd)

Layer No.	Additive	Quantity coated (mg/m^2)
Layer 1	Gelatin	0.45
	Surfactant (7)	0.01
	Water-soluble polymer (2)	0.04
	Hardener (2)	0.30
	Support (1)	
Backing Layer 1	Gelatin	3.25
	Hardener (2)	0.25
Backing Layer 2	Gelatin	0.44
	Silicone oil (1)	0.08
	Surfactant (8)	0.04
	Surfactant (9)	0.01
	Matting agent (2)	0.03

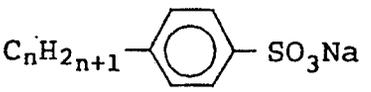
Constitution of Support (1)			
Layer name	Composition		Thickness (μm)
Surface Undercoat	Gelatin		0.1
Surface PE (glossy)	Low density polyethylene (density 0.923): Surface treated TiO_2: Ultramarine:	89.2 parts 10.0 parts 0.8 parts	45.0
Pulp Layer	Fine-quality paper (LBKP/NBKP = 1:1, density 1.080)		92.6
Back Surface PE Layer (matt)	High density polyethylene (density 0.960)		36.0
Back Undercoat Layer	Gelatin		0.05
	Colloidal silica		0.05
		Total	173.8

Values of Properties of Support (1)			
Item	Unit	Value	Measurement Method
Rigidity (long/transverse) Moisture Content Whiteness	g % 	4.40/3.15 5.5 L* 94.20 a* +0.12 b* -2.75	Tabar Rigidometer Dry Weight Method CIE L* a* b*

Silicone oil (1)

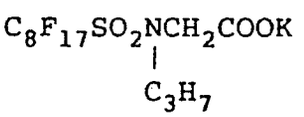


Surfactant (5)

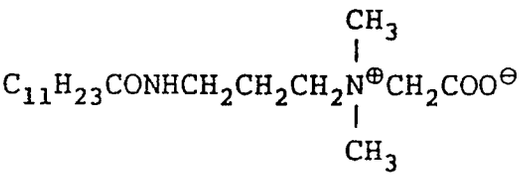


(n ≒ 12.6)

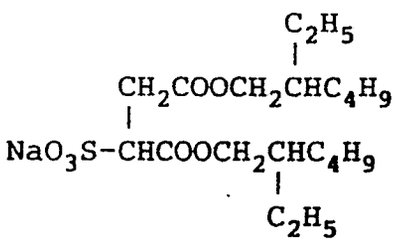
Surfactant (6)



Surfactant (7)



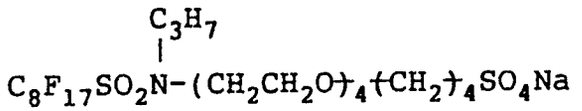
Surfactant (8)



Brightening agent (1)

2,5-bis(5-tertiary butyl benzoxazole (2)) thiophene

Surfactant (9)



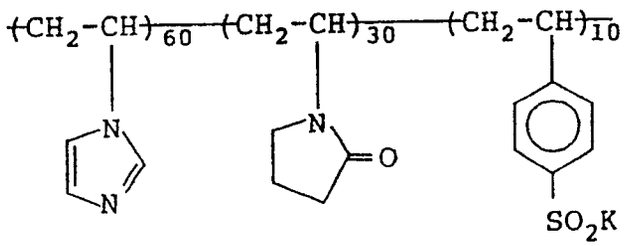
Water-soluble polymer (2)

Sumikagel L 5-H (Sumitomo Chemical Co.)

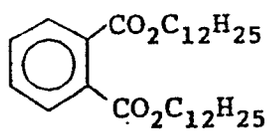
Water-soluble polymer (3)

Dextran (molecular weight 70,000)

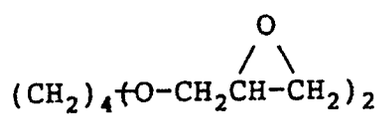
Mordant (1)



High-boiling solvent (2)



Hardener (2)



Matting agent (1) *

Silica

Matting agent (2) *

Benzoguanamine resin (average particle size 15 μm)

Light-sensitive materials 101 to 105 were exposed for 1/10 second at 4000 lux using a tungsten electric lamp through B.G.R and grey color separation filters of continuously varying density.

The emulsion surface of the exposed light-sensitive materials were supplied with 16 ml/m^2 of water (image formation solvent) by wire bar, after which the dye fixing material was superposed on the film surface. After heating for 15 seconds using temperature controlled hot rollers to raise the temperature of the absorbed film to 78 °C, the dye fixing material was stripped off the light-sensitive material, and magenta images corresponding to the B.G.R. and grey color separation filters were obtained without irregularity on the dye fixing material.

Measurements were taken of the density of the magenta dye image corresponding to the green filter (G) on the dye fixing material, and the maximum density, minimum density, and sensitivities compared. The sensitivities are relative values in logarithmic units. The maximum density and sensitivity of these light-sensitive materials was also measured after 3 days of storage in a 45 °C and 80% RH environment. These measurements are also shown in Table 8.

Table 8

No.	Emulsion	Silver halide	Grain structure	Chemical sensitization	Addition period of sensitizing dye	Fresh			After 3 day storage at 45° C, 80% RH		Remarks
						Dmax	Dmin	Sensitivity	Dmax	Sensitivity	
101	(1)	AgBrCl	Uniform	Sulfar	After chemical sensitization	2.21	0.14	0.00	2.02	-0.06	Comparison
102	(2)	AgBrCl	Core/shell	Sulfar	After chemical sensitization	2.13	0.13	+0.07	2.01	+0.03	Comparison
103	(3)	AgBrCl	Core/shell	Gold•sulfur	After chemical sensitization	2.09	0.13	+0.13	2.04	+0.15	Comparison
104	(4)	AgBrCl	Core/shell	Sulfar	Before chemical sensitization	2.21	0.14	+0.16	2.20	+0.13	Comparison
105	(5)	AgBrCl	Core/shell	Gold•sulfur	Before chemical sensitization	2.22	0.13	+0.29	2.20	+0.30	The present invention

Table 8 shows that the light-sensitive materials of the present invention are light-sensitive materials of high sensitivity that have a high maximum density, that is a small degree of fog, in relation to the comparative materials; and even after storage for 3 days at 45° C and 80% RH, the change in sensitivity and the reduction in maximum density is small in relation to the comparative materials.

Example 2

An example of a positive heat-developable light-sensitive material that gives a cyan color image is described below.

(A) Preparation of Emulsions (6) to (10)

Emulsion (6)

Solutions (I) and (II) of Table 9 were added at a constant temperature of 50° C to a well stirred Aqueous Gelatin Solution (Table 1). After addition of solutions (III) and (IV), Dye Solution A of Table 4 was added. Solutions (V) and (VI) of Table 9 were then added. After water wash desalting, chemical sensitization was done exactly as described in Emulsion (3) while controlling the pH and pAg, and a monodisperse emulsion of silver chlorobromide with cubic grains having an average grain size of 0.4 μm was obtained. The yield was 632 g. (Triple structure, emulsion gold-sulfur sensitized in the presence of a dye).

Table 9

Composition of added solutions						
	(I)	(II)	(III)	(IV)	(V)	(VI)
$AgNO_3$ (g)	50	-	20	-	30	-
KBr (g)	-	17.5	-	10.5	-	12.6
NaCl (g)	-	8.7	-	1.8	-	4.2
H_2O added to a total (cc)	200	200	100	100	120	120

Emulsion (7)

Emulsion was prepared exactly as was Emulsion (5) except that the aqueous gelatin solution (Table 1) was kept at 75° C. The emulsion obtained, in a yield of 619 g, was a monodisperse silver chlorobromide emulsion with cubic grains of average grain size 0.9 μm. (Core/shell structure, emulsion gold-sulfur sensitized in the presence of a dye).

Emulsion (8)

Emulsion (8) was prepared exactly as was Emulsion (5), except instead of using the additive of Table 3, solutions (I) and (II) of Table 2 were used. The emulsion obtained was a monodisperse silver chlorobromide cubic emulsion with average grain size 0.4 μm; the yield was 650 g. (Uniform structure, emulsion gold-sulfur sensitized in the presence of a dye).

Emulsion (9)

Emulsion (9) was prepared exactly as was Emulsion (5), except instead of using the additive solutions

of Table 3, solutions (I) and (II) and also (III) and (IV) of Table 10 were added. The emulsion obtained was a monodisperse silver chlorobromide emulsion of cubic grains of average grain size 0.4 μm; the yield was 636 g. (Core/shell structure, emulsion gold-sulfur sensitizei in the presence of a dye).

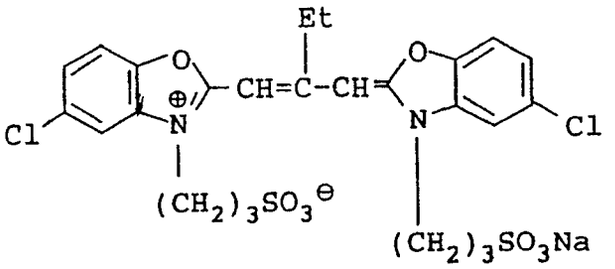
Table 10

Composition of added solutions				
	(I)	(II)	(III)	(IV)
$AgNO_3$ (g)	10	-	90	-
KBr (g)	-	4.2	-	50.4
NaCl (g)	-	1.8	-	6.2
H_2O added to a total (cc)	40	40	360	360

Emulsion (10)

Emulsion (10) was prepared exactly as was Emulsion (5), except instead of dye solution A of Table 4, the dye solution B of Table 11 was used. The resulting emulsion was a monodisperse silver chloro bromide emulsion of cubic grains of average grain size 0.4 μm; the yield was 625 g. (Core/shell structure, emulsion gold-sulfur sensitized in the presence of a dye).

Table 11 - Dye solution B



0.25 g

Methanol 200 cc

Using these emulsions and the dispersions described in Example 1, the light-sensitive materials of Table 12 were prepared.

Table 12 - Constitution of light-sensitive materials

Layer number/name	Quantity coated (mg/m^2)
3: Protective Layer	
Gelatin	900
Silica	40
Zinc Hydroxide	600
Surfactant (1)	130
Surfactant (2)	26
Water-Soluble Polymer (1)	8
2: Emulsion Layer	
Light-sensitive layer silver halide emulsion (Table 13)	220
Dye Providing Compound (3) (Cyan)	373
Gelatin	310
Electron Donor (1)	182
High-Boiling Solvent (1)	186
Electron Transfer Agent Precursor (1)	34
Surfactant (3)	34
Water-soluble Polymer (1)	11
Antifoggant (1)	0.8
1: Intermediate Layer	
Gelatin	700
Electron Donor (2)	130
High-boiling Solvent (1)	48

Table 12 - Constitution of light-sensitive materials (cont'd)

Layer number/name	Quantity coated (mg/m^2)
1: Intermediate Layer	
Surfactant (2)	15
Surfactant (4)	61
Surfactant (3)	2
Electron Transfer Agent (1)	82
Water-soluble Polymer (1)	19
Hardener (1)	30

The light-sensitive materials 201 to 206 were exposed for 1/10 second at 4000 lux using a tungsten electric lamp through B.G.R and grey color separation filters of continuously varying density.

The emulsion surface of these exposed light-sensitive materials were supplied with 16 ml/m^2 of water (image formation solvent) by wire bar, after which dye fixing material as described in Example 1 was superposed on the film surface. After heating for 15 seconds using temperature controlled hot rollers to raise the temperature of the absorbed film to 78° C, the dye fixing material was stripped off the light-sensitive material, and cyan images corresponding to the B.G.R. and grey color separation filters were obtained without irregularity on the dye fixing material.

The light-sensitive materials prepared in Example 2 are described in Table 13.

Table 13

Light-sensitive material No.	Emulsion utilized
201	Emulsion (5)
202	(6)
203	(7)
204	(8)
205	(9)
206	(10)

Density measurements were taken of the cyan dye image corresponding to the green filter (G) on the dye fixing material, and the maximum densities and sensitivities compared. The sensitivities are relative values in logarithmic units. After 5 days at 58° C, the sensitivities of these light-sensitive materials were again measured. These results are shown in Table 14.

Table 14

No.	Emulsion	Silver halide	Grain structure	Chemical sensitization	Addition period of sensitizing dye	Fresh		After 6 day storage at 58° C	Remarks
						Dmax	Sensitivity	Sensitivity	
201	(5)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.09	+0.19	+0.12	The present invention
202	(6)	AgBrCl	Triple	Gold-sulfur	Before chemical sensitization	2.14	+0.21	+0.20	The present invention
203	(7)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.05	+0.34	+0.36	The present invention
204	(8)	AgBrCl	Uniform	Gold-sulfur	Before chemical sensitization	2.01	0.00	-0.16	Comparison
205	(9)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.13	+0.17	+0.15	The present invention
206	(10)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.11	+0.11	+0.07	The present invention

Table 14 shows that the light-sensitive materials of the present invention have high maximum density and high sensitivity. They also exhibit little change in sensitivity when storage.

Example 3

An example of a positive heat-developable light-sensitive material giving a cyan color image is given below.

(A) Preparation of the Emulsions (11) to (14)

Emulsion (11)

Solutions (I) and (II) of Table 16 were simultaneously added at a constant temperature of 60 ° C to a well stirred aqueous gelatin solution (Table 15). Exactly 10 minutes after adding Solution (I), Dye Solution C of Table 17 was added over a period of 25 minutes. After washing desalting, and adding 22 g of gelatin, the pH and pAg were controlled and chemical sensitization optimally performed using 2.5 mg of triethylthiourea and 130 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and 0.3 mg of chloroauric acid.

Table 15

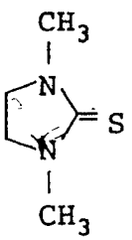
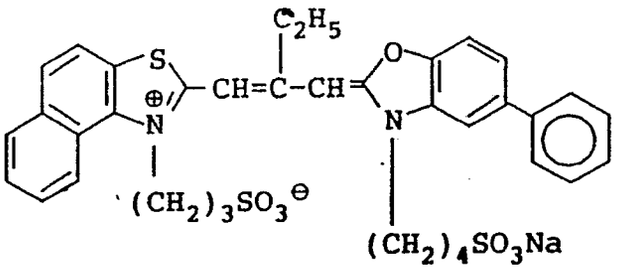
Gelatin	30 g
NaCl	6 g
KBr	0.3 g
	0.02 g
H_2O	750 cc

Table 16

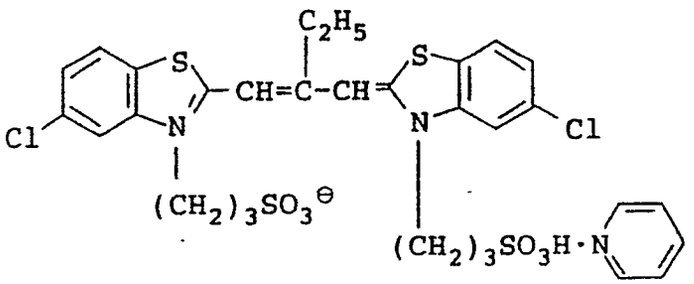
	(I)	(II)
$AgNO_3$ (g)	100	-
KBr (g)	-	70
H_2O added to a total (cc)	450	400

Table 17 - Composition of Dye Solution C



0.04 g

Table 17 - Composition of Dye Solution C (cont'd)



0.08 g

Methanol 60 ml

The emulsion obtained was a monodisperse silver bromide emulsion of pebble-like grains having an average grain size 0.3 μm; the yield was 635 g.

Emulsion (12)

Solutions (I) and (II) of Table 18 were simultaneously added to a well-stirred aqueous gelatin solution while maintaining the temperature at 60 ° C (Table 15). Solutions (III) and (IV) of Table 18 were then added, and Dye Solution C, shown in Table 17, was added starting 5 minutes after the start of addition of solution (III). After water washing and desalting, the emulsion was prepared exactly as outlined for Emulsion (11), above. The emulsion obtained was a monodisperse emulsion with pebble-like grains of average grain size 0.3 μm, with a yield of 631 g.

Table 18

	(I)	(II)	(III)	(IV)
$AgNO_3$ (g)	50	50	-	-
KBr (g)	-	-	21	31.5
NaCl (g)	-	-	6.9	1.8
H_2O added to a total (cc)	200	200	200	200

Emulsion (13)

Emulsion (13) was prepared in exactly the same way as Emulsion (12) except instead of the addition of solutions (I) and (II) of Table 18 in Emulsion (12), solutions (III) and (IV) of Table 18 were added; and instead of solutions (III) and (IV) of Table 18, solutions (I) and (II) were added. In short, Emulsion (13) was prepared with the core and shell halides interchanged vis-a-vis Emulsion (12).

The emulsion obtained was a monodisperse emulsion with pebble-like grains of an average size of 0.3 μm, and a yield of 610 g.

Emulsion (14)

Emulsion (14) was prepared in exactly the same way as Emulsion (12) except instead of adding solutions (I), (II), (III) and (IV) of Table 18 in Emulsion (12), solutions (I), (II), (III) and (IV) of Table 19 were added. The emulsion obtained was a monodisperse emulsion with pebble-like grains having an average size of 0.3 μm, in yield of 623 g.

Table 19

	(I)	(II)	(III)	(IV)
$AgNO_3$ (g)	20	80	-	-
KI (g)	-	-	0.28	-
KBr (g)	-	-	7	39.2
NaCl (g)	-	-	3.5	8.3
Water added to a total of (cc)	200	300	200	250

Light-sensitive materials as described in Table 12, Example 2 were prepared using these emulsions.

Light-sensitive materials 301 to 304 were exposed for 1/10 second at 4000 lux using a tungsten electric lamp through B.G.R and grey color separation filters of continuously varying density.

The emulsion surfaces of these exposed light-sensitive materials were supplied with 16 ml/m^2 of water (image formation solvent) by wire bar, after which dye fixing material as described in Example 1 was superposed on the film surface. After heating for 15 seconds using temperature controlled hot rollers so that the temperature of the absorbed film was raised to 78° C, the dye fixing material was stripped off the light-sensitive material, and cyan images corresponding to the B.G.R. and grey color separation filters were obtained without irregularity on the dye fixing material.

The light-sensitive materials prepared in this Example 3 are described in Table 20.

Table 20

Light-sensitive material No.	Emulsion utilized
301	Emulsion (11)
302	(12)
303	(13)
304	(14)

Measurements were taken of the density of the cyan dye image corresponding to the red filter (R) on the dye fixing material, and the maximum densities and sensitivities compared. The sensitivities are relative values in logarithmic units. The sensitivities of these light-sensitive materials were also measured after they had been stored for 5 days in an environmental test chamber controlled to a temperature of 58° C. These results are shown in Table 21.

Table 21

No.	Emulsion	Silver halide	Grain structure	Chemical sensitization	Addition period of sensitizing dye	Fresh		Sensitivity after 6 day storage at 58°C	Remarks
						Dmax	Sensitivity		
301	(11)	AgBrCl	Uniform	Gold-sulfur	Before chemical sensitization	2.10	0.00	-0.17	Comparison
302	(12)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.21	+0.21	+0.20	The present invention
303	(13)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.18	+0.18	+0.10	The present invention
304	(14)	AgBrCl	Core/shell	Gold-sulfur	Before chemical sensitization	2.20	+0.17	+0.18	The present invention

Table 21 shows that light-sensitive materials of the present invention have high maximum densities and high sensitivities, that exhibit little change in sensitivity when stored.

Example 4

An example of a positive heat-developable light-sensitive material is given below.

(A) Preparation of Emulsions (15) to (18)

Emulsion (15)

Solutions (I) and (II) of Table 23 were simultaneously added at a constant temperature of 55 °C to well stirred aqueous gelatin solution (Table 22). Next, solutions (III) and (IV) of Table 23 were added. At 10 minutes before the addition of Solution (III) was completed, Dye Solution D of Table 24 was added over about 20 minutes. After water wash desalting, and the addition of 20 g of gelatin, the pH and pAg were adjusted and chemical sensitization optimally performed using 6 mg of sodium thiosulfate, 120 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and 0.45 mg of chloroauric acid. The emulsion obtained was a monodisperse cubic emulsion of average grain size 0.43 μm, and a yield of 635 g.

Table 22 - Composition of Gelatin Solutions

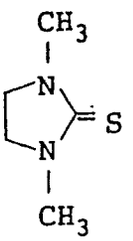
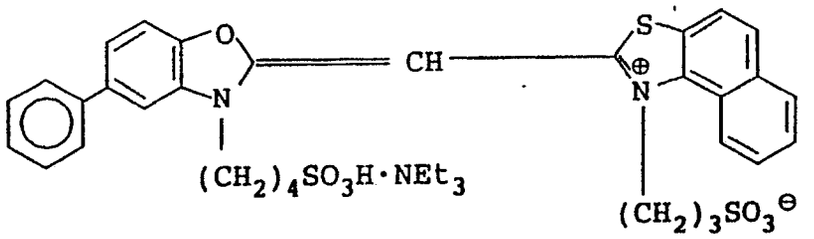
Gelatin	20 g
NaCl	6 g
KBr	0.5 g
	0.015 g
H_2O	810 cc

Table 23

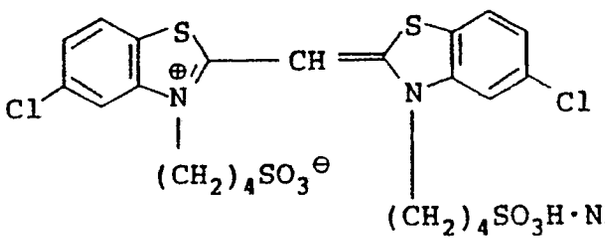
Composition of Added Solutions				
	(I)	(II)	(III)	(IV)
$AgNO_3$ (g)	20	80	-	-
KBr (g)	-	-	9.8	53.2
KaCl (g)	-	-	2.1	1.4
Water added to a total of (cc)	40	160	80	160

Table 24 - Composition of Dye Solution D



0.12 g

Table 24 - Composition of Dye Solution D (cont'd)



0.12 g

Methanol 160 cc

Emulsion (16)

Emulsion (16) was prepared by adding of dye solution D directly before chemical sensitization as described for Emulsicn (15). Other conditions were the same as for Emulsion (15). The average grain size and grain form were the same as for Emulsion (15); the yield was 660 g.

Emulsion (17)

Emulsion (17) was prepared exactly as Emulsion (16) except Dye Solution D was added to the emulsion directly after the addition of the chemical sensitizer. Emulsion (17) had the same grain size and form as for Emulsion (16). The yield was 660 g.

Emulsion (18)

Emulsion (18) was prepared exactly as Emulsion (15) except Dye Solution D in Emulsion (15) was not added. The average grain size and form were the some as for Emulsion (15); the yield was 630 g.

(B) Method of Preparation of a Zinc Hydroxide Dispersion

Exactly 12.5 g of zinc hydroxide having an average particle size of 0.2 μm, 1 g of carboxymethyl

cellulose as dispersant, and 0.1 g of sodium polyacrylate were added to 100 cc of 4% aqueous gelatin solution and comminuted for 30 minutes in a mill, using glass beads of an average diameter 0.75 mm. The glass beads were separated off and a dispersion of zinc hydroxide was obtained.

(C) Method of Preparation of a Dispersion of Active Carbon

Exactly 2.5 g of active carbon powder (Wako Pure Chemical Industries, Ltd.) (reagent, special grade), 1 g of Demol N (Kao Corporation) as dispersant, and 0.25 g of polyethylene glycol nonylphenyl ether were added to 100 cc of a 5% aqueous gelatin solution and comminuted for 120 minutes using glass beads of average diameter 0.75 mm. The glass beads were separated off, and a dispersion of active carbon, of average particle size 0.5 μm, was obtained.

(D) Method of Preparation of a Dispersion of Electron Transfer Agent (1)

The method of preparation of Electron Transfer Agent (1) is described in Example 1, above.

(E) Method of Making a Gelatin Dispersion of Dye Providing Compounds

Yellow, magenta and cyan dyes were each added as shown in the Treatment Method, below, to 50 cc of ethyl acetate and dissolved to a uniform solution by warming to about 60 °C. This solution and 100 g of a 10% aqueous solution of lime-processed gelatin, 0.6 g of sodium dodecylbenzenesulfonate and 50 cc of water were stirred and mixed, then dispersed in a homogenizer at 10,000 rpm for 10 minutes. These dispersion liquids are termed "gelatin dispersions of dye providing compounds".

Treatment Method (2):			
	Yellow	Magenta	Cyan
	(g)	(g)	(g)
Dye Providing Compound	(1) 13	(2) 15.5	(3) 16.6
Electron Donor (1)	10.2	8.6	8.1
High-Boiling Solvent (1)	6.5	7.8	8.3
Electron Transfer Agent Precursor (1)	0.4	0.7	0.7

(F) Method of Making a Gelatin Dispersion of Electron Donor (2)

The method of making a Gelatin Dispersion of Electron Donor (2) is described in Example 1, above.

Using these emulsion dispersions, multi-layer light-sensitive materials as described in Table 25 were prepared. The emulsions for layers 5, 3 and 1 are shown in Table below.

No.	Layer No.	Emulsion	Silver Halide	Grain Structure	Chemical Sensitization	Period of Sensitizing Dye Addition
401	5	(15)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
	3	(5)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
	1	(12)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
402	5	(16)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
	3	(5)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
	1	(12)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
403	5	(17)	AgBrCl	core/shell	Gold-Sulfur	During Chemical Sensitization
	3	(5)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
	1	(12)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
404	5	(18)	AgBrCl	core/shell	Gold-Sulfur	After Chemical Sensitization
	3	(5)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization
	1	(12)	AgBrCl	core/shell	Gold-Sulfur	Before Chemical Sensitization

In light-sensitive material 404, the two sensitizing dyes shown in Table 24 were each coated and added to Layer 5, at 0.65 mg/m^2.

Table 25 - Constitution of Light-sensitive Material

Layer number/name	Quantity Coated (mg/m^2)
6: Protective layer	
Gelatin	900
Silica (particle size 4 µm)	40
Zinc Hydroxide	600
Surfactant (1)	130
Surfactant (2)	26
Water-soluble polymer (1)	8
5: Blue Sensitive Emulsion Layer	
Light-sensitive Silver Halide Emulsion (I)	380 (as Ag)
Yellow Dye Providing Compound (1)	400
Gelatin	600
Electron Donor (1)	308
High-Boiling Solvent (1)	200
Electron Transfer Agent Precursor (1)	15
Zinc Hydroxide	330
Antifoggant (2)	0.6
Surfactant (3)	18

Table 25 (cont'd)

Layer number/name	Quantity Coated (mg/m^2)
5: Blue Sensitive Emulsion Layer	
Water-Soluble Polymer (1)	13
4: Intermediate Layer	
Gelatin	700
Electron Donor (2)	130
High-Boiling Solvent (1)	48
Surfactant (2)	15
Surfactant (4)	61
Surfactant (3)	2
Electron Transfer Agent (1)	27
Electron Transfer Agent (2)	36
Water-Soluble Polymer (1)	19
Hardener (1)	37
3: Green Sensitive Emulsion Layer	
Light-sensitive Silver Halide Emulsion (II)	220 (as Ag)
Magenta Dye Providing Compound (2)	365
Gelatin	310
Electron Donor (1)	158
High-Boiling Solvent (1)	183
Electron Transfer Agent Precursor (1)	15
Electron Transfer Agent (1)	27

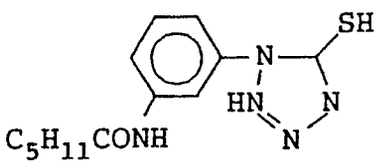
Table 25 (cont'd)

Layer number/name	Quantity Coated (mg/m^2)
3: Green Sensitive Emulsion Layer	
Surfactant (3)	13
Water Soluble Polymer (1)	11
Antifoggant (2)	0.8
2: Intermediate Layer	
Gelatin	790
Zinc Hydroxide	300
Electron Donor (2)	130
High-Boiling Solvent (1)	73
Surfactant (3)	2
Surfactant (4)	100
Surfactant (2)	11
Water-Soluble Polymer (1)	12
Active Carbon	25
1: Red Sensitive Emulsion Layer	
Light-sensitive Silver Halide Emulsion (III)	230 (as Ag)
Cyan Dye providing Compound (3)	343
Gelatin	330
Electron Donor (1)	163
High-Boiling Solvent (1)	172
Electron Transfer Agent Precursor (1)	17

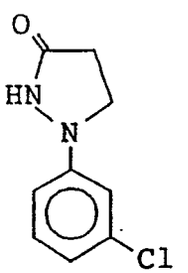
Table 25 (cont'd)

Layer number/name	Quantity Coated (mg/m^2)
1: Red Sensitive Emulsion Layer	
Electron Transfer Agent (1)	28
Surfactant (3)	10
Water-soluble polymer (1)	5
Antifoggant (1)	0.7
Support: Polyethylene terephthalate 96 µm (carbon black coated in the backing layer)	

Antifoggant (2)



Electron transfer agent (3)



Light-sensitive materials 401 to 404 were exposed for 1/10 second at 4000 lux using a tungsten electric lamp through B. G. R and grey color separation filters of continuously varying densities.

The emulsion surface of these exposed light-sensitive materials were supplied with 16 ml/m^2 of water (image formation solvent) by wire bar, after which dye fixing material as described in Example 1 was superposed on the film surface. After heating for 15 seconds using temperature controlled hot rollers to raise the temperature of the absorbed film to 78° C, the dye fixing material was stripped off the light-sensitive material, and blue, green, red and grey images corresponding to the B. G. R. and grey color separation filters were obtained without irregularity on the dye fixing material.

The densities of the grey parts were measured using a reflection densitometer, and the maximum densities and sensitivities of the yellow parts (corresponding to the blue sensitive layer) were measured. In

addition, the sensitivities were measured after 1 week of storage at 35° C and 75% RH.

TABLE 26

Light-sensitive material No.	Sensitivity	Maximum density	Sensitivity, 1 week at 35° C, 70%
401	+0.21	2.31	+0.20
402	+0.17	2.29	+0.18
403	+0.15	2.20	+0.10
404	0	2.11	-0.23

Table 26 shows that higher sensitivities and improved storage properties are achieved by using emulsions of the invention for all the light-sensitive layers in a heat-developable light-sensitive materials with a multi-layer structure.

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

Claims

1. A heat-developable light-sensitive material having a light-sensitive layer containing a silver halide emulsion which comprises:
multiple-structure silver chlorobromide grains that are gold-sulfur sensitized in the presence of a sensitizing dye and have layers of differing halide composition.

2. A heat-developable light-sensitive material as claimed in claim 1, wherein said multiple-structure silver chlorobromide grains have one or more layers of differing halide composition.

3. A heat-developable light-sensitive material as claimed in claim 2, wherein said multiple-structure silver chlorobromide grains have three or more layers of differing halide composition.

4. A heat-developable light-sensitive material as claimed in claim 2, wherein the interior and surface are in a relative volume ratio of 1:9 to 9:1.

5. A heat-developable light-sensitive material as claimed in claim 1, wherein said emulsion consists of monodisperse silver halide grains.

6. A heat-developable light-sensitive material as claimed in claim 1, wherein said multiple-structure silver chlorobromide grains have an average grain size of from 0.1 μm to 2.0 μm.

7. A heat-dvelopable light-sensitive material as claimed in claim 1, wherein said multiple-structure silver chlorobromide grains have an average grain size of from 0.1 μm to 1.0 μm.

8. A heat-dvelopable light-sensitive material as claimed in claim 1, wherein said multiple-structure silver chlorobromide grains are cubic (100) face crystals.

9. A heat-dvelopable light-sensitive material as claimed in claim 1, wherein said chlorobromide grains have an average silver bromide content of from 35 mol% to 95 mol%.