

[54] LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIALS

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[22] Filed: **Mar. 23, 1973**

[21] Appl. No.: **344,401**

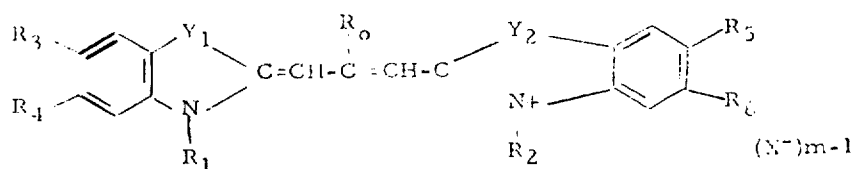
Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 101,233, Dec. 24, 1970, abandoned.

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[57] **ABSTRACT**

There is provided a light-sensitive silver halide photographic material comprising at least one layer on a support which comprises a binder containing (i) light-sensitive silver halide grain particles characterized as exhibiting a high surface-sensitivity; (ii) at least one compound containing a Group VIII metal at a level of from 1×10^{-6} to 1×10^{-3} mol per 1 mol of said silver halide (iii) at least one optical sensitizer selected from the group consisting of compounds of the general formula



[30] **Foreign Application Priority Data**

Dec. 24, 1969 Japan..... 44-104009
Jan. 9, 1970 Japan..... 45-002819

[52] U.S. Cl. 96/125; 96/108; 96/126; 96/137; 96/140

[51] Int. Cl. G03c 1/08

[58] Field of Search 96/125, 126, 137, 140, 96/108

[56] **References Cited**

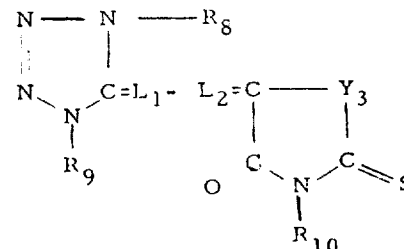
UNITED STATES PATENTS

2,912,329	11/1959	Jones et al.	96/137
3,206,313	9/1965	Porter et al.	96/108
3,672,901	6/1972	Ohkubo et al.	96/108
3,741,767	6/1973	Baylis et al.	96/108
3,761,266	9/1973	Milton	96/108
3,761,267	9/1973	Gilman et al.	96/108
3,782,957	1/1974	Ohkubo et al.	96/125

FOREIGN PATENTS OR APPLICATIONS

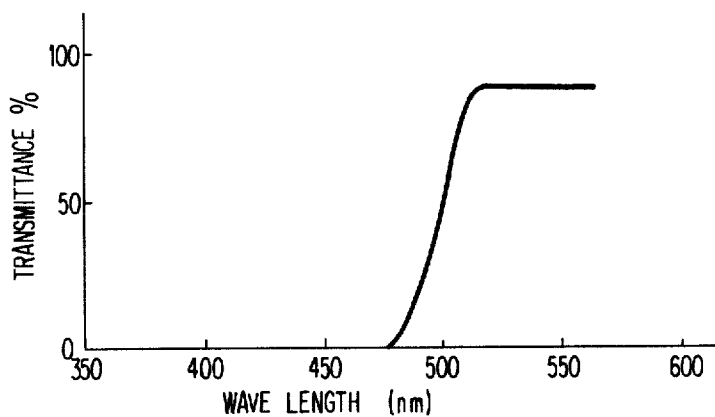
801,275	9/1958	United Kingdom	96/140
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wherein R₀, R₁, R₂, R₃, R₄, R₅, R₆, Y₁, Y₂, X and m are defined hereinafter, and compounds of the general formula



wherein R₈, R₉, R₁₀, L₁, L₂ and Y₃ are defined hereinafter.

23 Claims, 1 Drawing Figure



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LIGHT-SENSITIVE SILVER HALIDE PHOTOGRAPHIC MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application of our earlier co-pending application Ser. No. 101,233 filed Dec. 24, 1970, now abandoned which claims priority from Dec. 24, 1969 and Jan. 9, 1970, respectively, based on Japanese Patent Applications 104009/69 and 2819/70, respectively.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to photographic silver halide light sensitive materials. More particularly, the present invention relates to photographic silver halide light sensitive materials having high sensitivity to green light under flash exposure. The term "flash exposure" is defined hereinafter.

2 Description of the Prior Art

The present age is one of information. Various systems have been developed to promote the speedy transmission of information. For instance, press facsimile systems a speedily transmit press manuscripts to distant places, high speed phototypesetting systems expedite printing and typesetting, and cathode ray tube (CRT) display systems represent speedily in letters of figures the information output of computers. With such equipment used for such rapid information transmitting systems, a short time exposure of less than 1/100,000 of a second or especially about 1/1,000,000 of a second is most often used. The demand for sensitive materials to be used for such equipment has in recent years been particularly high.

There are two types of light sources used in connection with these types of equipment, viz., xenon flash lamps and cathode ray tubes. Of these, the one whose fluorescence has an especially short afterglow known generally to be usable for flying spot, is used as the cathode ray tube. For instance, such fluorescent mate-

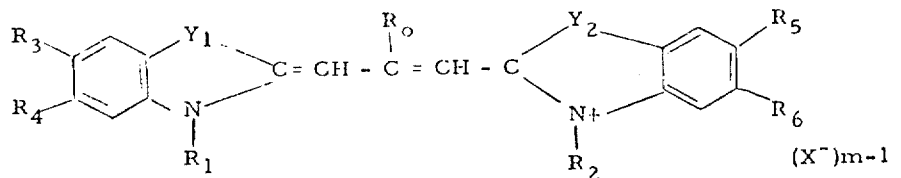
cal system composed of a condenser lens, a negamatrix, a main lens, a prism, a reflector or a deformation lens or other special lenses, or prisms. The light of short wave length is absorbed to a greater extent by the optics in the path. As a result of the light reaching the sensitive material, the shorter wave length component of from ultraviolet to blue diminishes and the longer wave length component from the green becomes richer. For this reason, green sensitization is indispensable in order to enhance the sensitivity of the sensitive material. The above-described afterglow of the fluorescence of a cathode ray tube ranges from 1/10,000,000 to 1/100,000 of a second and with a xenon flash lamp also one of about the same radiation period is used. In the present invention the short time exposure of these two kinds of light sources described above is generically called flash exposure.

The conventional sensitizer for green light shows markedly lower spectro sensitization under a flash exposure of 1/100,000 of a second or less in comparison with the result of a conventional exposure of 1/1,000 of a second or longer. Specifically there is a fair indication of this trend where, in order to expedite after exposure the treatments such as fixing or stabilization, silver halide is partly or wholly composed of silver chloride, i.e., a silver chloride emulsion, a chlorobromide emulsion or a chloriodobromide emulsion.

An object of this invention is to provide photographic sensitive materials having high sensitivity to green light under flash exposure.

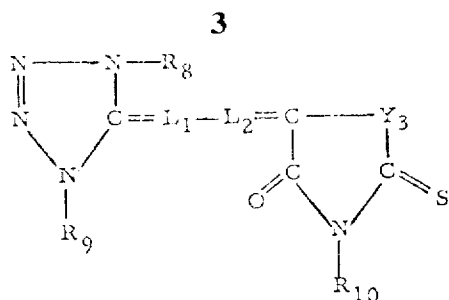
SUMMARY OF THE INVENTION

This invention provides silver halide light sensitive photographic materials comprising a support on which at least one layer having in the binder (such as gelatin and the like) sensitive silver halide grain particles characterized as exhibiting a high surface sensitivity, at least one compound containing a Group VIII metal of the periodic table at the ratio of from 10^{-6} to 10^{-3} mol per 1 mol of silver halide, and at least one optical sensitizer selected from the group consisting of compounds of the general formula:



rials are called "P-11," "P-15," "P-16" and "P-24" and are used as the light source in question. It is known that the luminous distribution of spectral energy reaches a peak when P-11 reaches 460 nm. and when P-16 reaches 385 nm. This peak corresponds to the region of the spectral absorption characteristic of light sensitive silver halides and hence does not need any optical sensitization. On the other hand, it is known that P-15 has its maximum fluorescent spectral energy at 505 nm. and for P-24 at 520 nm. The sensitive materials for recording images on CRT must therefore be given sensitivity to green light. On the other hand, a xenon flash lamp emits light over a comparatively broad spectral region. The light from the light source gives images on the sensitive materials through an opti-

wherein R_0 represents a hydrogen atom or an alkyl group; wherein R_1 and R_2 each represents a hydrogen atom, an alkyl, a substituted alkyl, an allyl, an aryl or an aralkyl group, in which at least one of R_1 and R_2 must be a carboxyalkyl group or a sulfoalkyl group; wherein Y_1 and Y_2 each represents an oxygen atom, a sulfur atom or a $>\text{N}-\text{R}_7$ group in which R_7 is an alkyl group; wherein R_3 , R_4 , R_5 and R_6 each represents a hydrogen atom, a halogen atom, an alkyl, a cyano, an alkoxy or an aryl group, when at least one of R_3 and R_4 is an aryl group, R_5 and R_6 are not an aryl group; wherein X represents an anion, such as a halogen ion or a thiocyanate ion; and wherein m is 1 or 2, in which an intramolecular salt is formed when m is 1, and compounds of the general formula



wherein R_8 , R_9 and R_{10} each represents a hydrogen atom, an alkyl, a substituted alkyl, an allyl, or an aryl group; wherein Y_3 represents an oxygen atom, a sulfur atom or a $>N-R_{11}$ group, in which R_{11} is a hydrogen atom, an alkyl or an aryl group; wherein L_1 and L_2 each represents the atoms of a methine chain.

DESCRIPTION OF THE ACCOMPANYING DRAWINGS

The accompanying drawing shows the light transmittance of a glass filter V-Y50 used in the examples in evaluating the effectiveness of the light sensitive photographic materials.

DETAILED DESCRIPTION OF THE INVENTION

More particularly, the present invention is described in greater detail as follows.

For supports, glass plates, metal plates, wooden plates, baryta papers, photographic papers, cellulose acetate film bases, polyester film bases can be used.

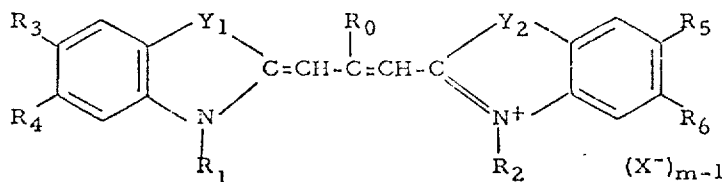
Suitable binders are water soluble, film forming high molecular weight compounds such as gelatin, polyvinyl alcohol, polyvinyl pyrrolidone, sodium alginate, carboxymethyl cellulose. The binders can be used either individually or in combination.

As the light sensitive silver halide, silver chloride, silver bromide, silver chlorobromide, silver iodobromide,

hexacyanoferrate (III) ($K_3[FeCN_6]$); cobalt (II) chloride ($CoCl_2$); cobalt (II) nitrate ($Co[NO_3]_2 \cdot 6H_2O$); potassium hexacyanocobaltate (III) ($K_3[Co(CN)_6]$); nickel (II) chloride ($NiCl_2 \cdot 6H_2O$); nickel (II) nitrate ($Ni[NO_3]_2 \cdot 6H_2O$); ruthenium chloride ($RuCl_3$); potassium hexachlororuthenate (IV) (K_2RuCl_6); rhodium (III) chloride ($RhCl_3 \cdot 4H_2O$); ammonium hexachlororhodate (III) ($[NH_4]_3RhCl_6$); palladium nitrate ($Pd[BO_3]_2$); palladium bromide ($PdBr_2$); potassium hexachloropalladate (IV) (K_2PdCl_6); potassium tetrathiocyanopalladate (II) ($K_2Pd[CNS]_4$); osmium (II) chloride ($OsCl_2$); iridium (III) chloride ($IrCl_3$); iridium (IV) chloride ($IrCl_4$); iridium (III) bromide ($IrBr_3 \cdot 4H_2O$); iridium (IV) bromide ($IrBr_4$); potassium hexachloroiridate (III) (K_3IrCl_6); potassium hexachloroiridate (IV) (K_2IrCl_6); ammonium hexachloroplatinate (IV) ($[NH_4]_2PtCl_6$); potassium hexachloroplatinate (IV) (K_2PtCl_6); ammonium hexabromoplatinate (IV) ($[NH_4]_2PtBr_6$).

These metallic compounds of Group VIII are used either singly or in combinations of two or more compounds together in the silver halide emulsion in a quantity corresponding from 10^{-6} mol to 10^{-3} mol, preferably 10^{-5} to 3×10^{-4} , per 1 mol of silver halide. The addition of these compounds in the emulsion can be made suitably at various stages in the preparation, viz., at the formation of silver halide grain particles in the preparation of silver halide emulsion added either in the halide solution or in the dispersive gelatin solution, or at the beginning of the ripening of the emulsion or at intermediate steps. Also, the compound can be added together with other various prior well known stabilizers, antifogants, antibronzing agents, surface active agents, hardeners, plasticizers, matting agents, development accelerators or brightening agents and the like as desired, prior to the coating of the emulsion.

One of the optical sensitizers in the present invention is the compound having the following general formula:



silver chloriodobromide, can be used. The so-called preparation of the sensitive silver halide emulsion, that is, the preparing of the silver halide crystal grains in the binder in a dispersive state, and making them grow into the proper crystal size thus preparing the silver halide emulsion, can be done by conventional techniques.

With respect to the light sensitive silver halide particles employed in the present invention, it must be emphasized that these particles are characterized as exhibiting a high surface sensitivity. Therefore, the silver halide particles of this invention are quite different from particles of the core-shell type, which exhibit low surface sensitivity and high internal sensitivity.

The metals belonging to Group VIII of the periodic tables are iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum. Examples of the compounds containing these metals desirably used in this invention contain a single salt, or a hexagonal complex, tetragonal complex, or square-plane complex of an alkali metal or ammonium such as ferrous sulfate ($FeSO_4 \cdot 5H_2O$); ferric chloride ($FeCl_3$); potassium hexacyanoferrate (II) ($K_4[Fe(CN)_6] \cdot 3H_2O$); potassium

wherein R_0 represents a hydrogen atom or an alkyl group having from 2 to 3 carbon atoms, such as a methyl group, an ethyl group and the like; wherein R_1 and R_2 each represents hydrogen or an alkyl group having from 1 to 4 carbon atoms, such as a methyl group, an ethyl group or propyl group and the like, a substituted alkyl group of the type usually used as an N-substituent of a cyanine dye such as a hydroxyalkyl group (e.g., β -hydroxyethyl), an acetoxyalkyl group (e.g., β -acetoxyethyl), an alkyl group having a carboxy group such as a carboxy-(alkoxy) $_{n-1}$ -alkyl group wherein n is 1 or 2 (e.g., carboxymethyl, β -carboxyethyl, γ -carboxypropyl, 2-(2-carboxyethoxy) ethyl), an alkyl group having a sulfo group such as a sulfo-(alkoxy) $_{n-1}$ -alkyl group wherein n is 1, 2 or 3, a hydroxysulfo-(alkoxy) $_{n-1}$ -alkyl group wherein n is 1 or 2 or an acyloxysulfoalkyl group (e.g., β -sulfoethyl, γ -sulfopropyl, δ -sulfobutyl, 2-hydroxyl-1-sulfopropyl, 2-(3-sulfopropoxy)ethyl, 2-acetoxy-1-sulfopropyl, 3-methoxy-2-(3-sulfopropoxy)propyl, 2-[2-(3-sulfopropoxy) ethoxy]ethyl, 2-hydroxy-3-(3-sulfopropoxy)propyl, and the like, an aryl group such as phenyl group or an aralkyl group, but at least one of R_1 and R_2 is a carboxyalkyl

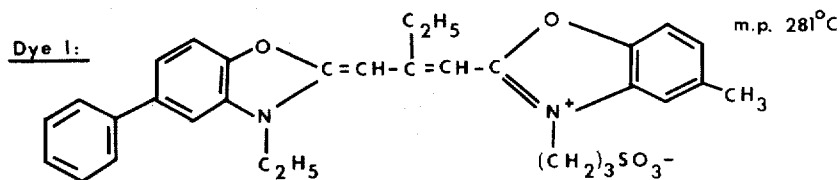
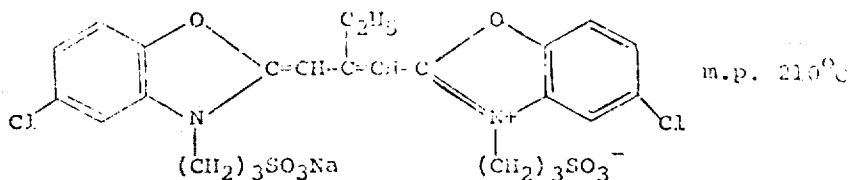
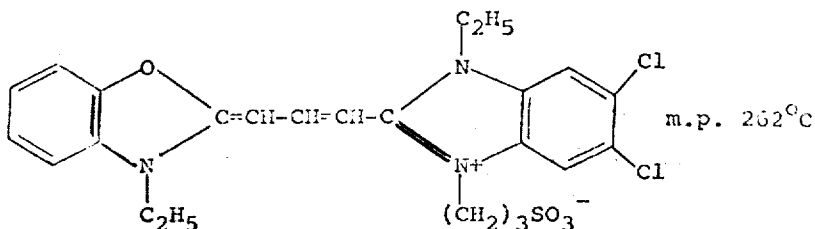
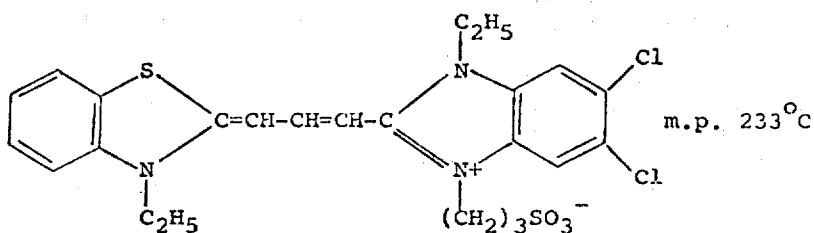
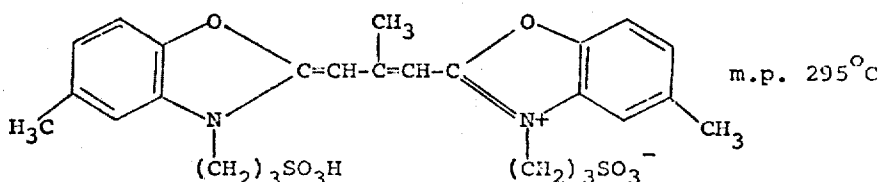
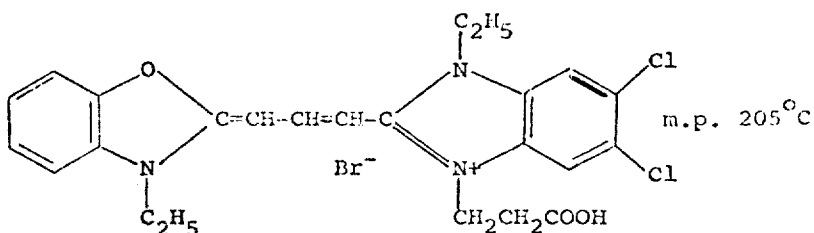
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group or a sulfoalkyl group; wherein Y_1 and Y_2 each are an oxygen atom, a sulfur atom or a $>N-R_7$ group in which R_7 is an alkyl group having from 1 to 3 carbon atoms, such as a methyl group or an ethyl group and the like; wherein R_3 , R_4 , R_5 and R_6 each represents a hydrogen atom, an alkyl group having from 1 to 3 carbon atoms, such as a methyl group or an ethyl group and the like, a halogen atom (such as fluorine, chlorine, bromine), a cyano group, an alkoxy group (such as a methoxy or an ethoxy group) or an aryl such as a phenyl

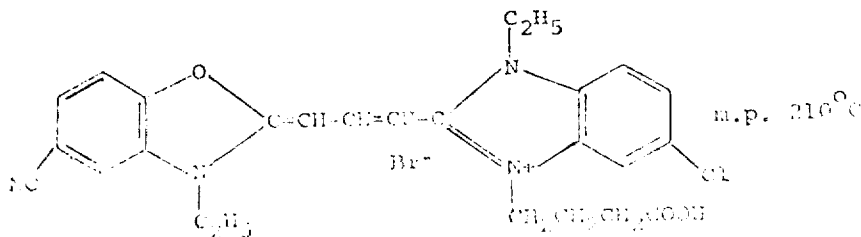
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group but when at least one of R_3 and R_4 is an aryl group then neither R_5 nor R_6 is an aryl group; wherein X is an anion such as a halogen ion, a thiocyanate ion, sulfate ion, sulphamate ion, perchlorate ion, p-toluene sulphate ion, benzenesulphonate ion, ethyl sulphate ion, or methyl sulphate ion, and wherein m represents 1 or 2, in which an intramolecular salt is formed when $m = 1$.

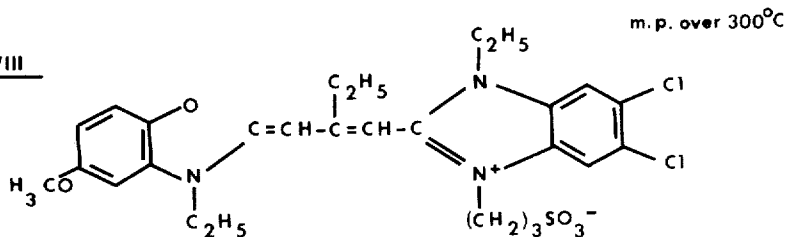
Specific compounds of these optical sensitizers are shown as follows:

Dye IIDye IIIDye IVDye VDye VI

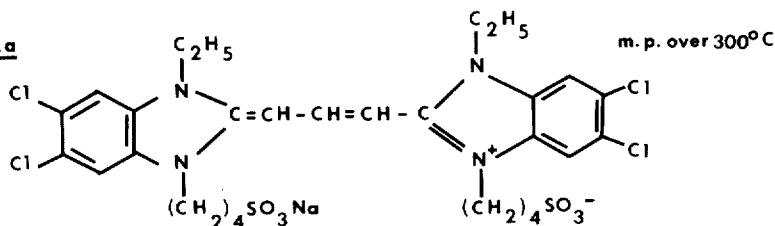
Dye VII



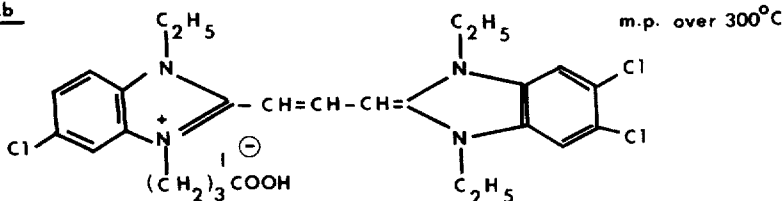
Dye VIII



Dye IXa

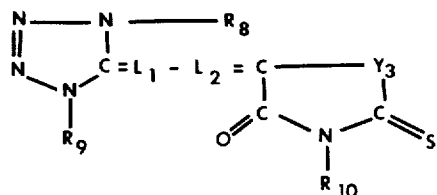


Dye IXb



These sensitizers are described, for example, in U.S. Pat. Nos. 2,503,776; 2,912,329 and 3,397,060, French Pat. No. 1,108,788 and Japanese Patent Publication No. 14030/69, and the synthesis of these sensitizers is well known by reference to the patents cited above and also to the relevant technical literature.

Other sensitizers used in the present invention have the following general formula:

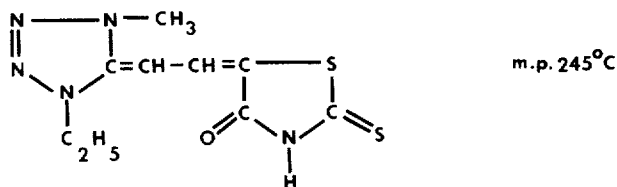


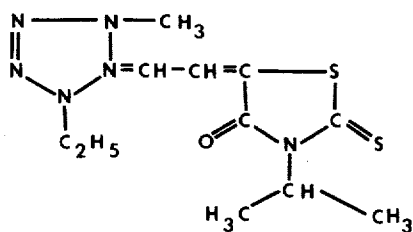
where R₈, R₉ and R₁₀ each represents a hydrogen atom; an alkyl group having from 1 to 8 carbon atoms, such

as a methyl group, an ethyl group, a propyl group, a butyl group; a substituted alkyl group of the type usually used as an N-substituent of a cyanine dye such as a carboxyalkyl group, (e.g., a carboxymethyl group), a hydroxyalkyl group (e.g., a β-hydroxyethyl group), a sulfoalkyl group (e.g., a β-sulfoethyl group, a γ-sulfo-propyl group); an allyl group; or an aryl group such as a phenyl group, a substituted phenyl group (for example, substituted with a halogen atom e.g., a chlorine atom, an alkyl group and the like); wherein Y₃ is an oxygen atom, a sulfur atom or a >N-R₁₁ group, in which R₁₁ is a hydrogen atom, an alkyl group having from 1 to 8 carbon atoms, or an aryl group (e.g., a phenyl group); wherein L₁ and L₂ in each a methine chain (e.g., =CH-, =C(alkyl)-, =C(aryl)-; wherein examples of the alkyl group and the aryl group are a methyl group and a phenyl group, respectively).

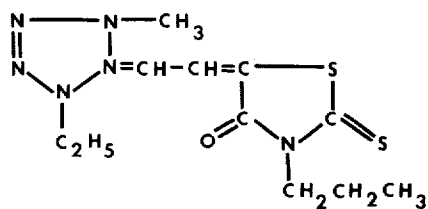
Specific compounds of these sensitizers are as follows:

Dye X

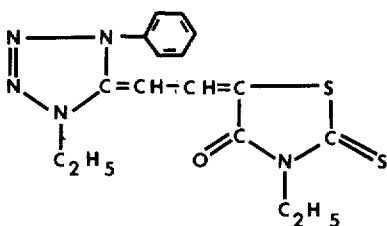


Dye XI

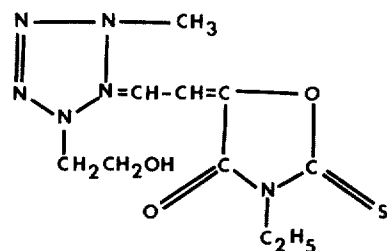
m.p. 232°C

Dye XII

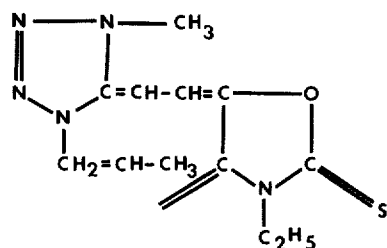
m.p. 190°C

Dye XIII

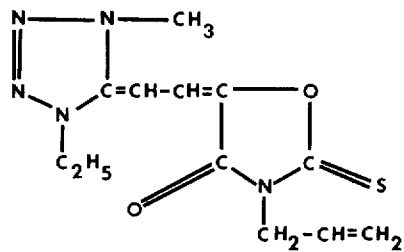
m.p. 201°C

Dye XIV

m.p. 233°C

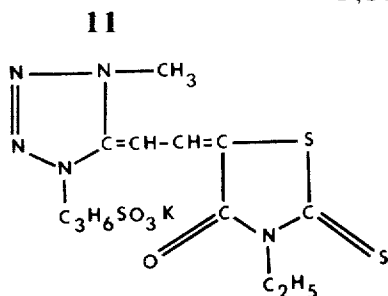
Dye XV

m.p. 240°C

Dye XVI

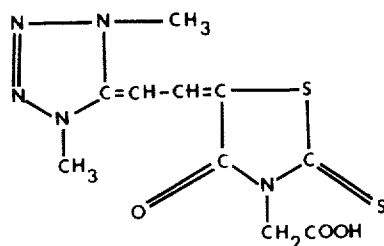
m.p. 230°C

Dye XVII



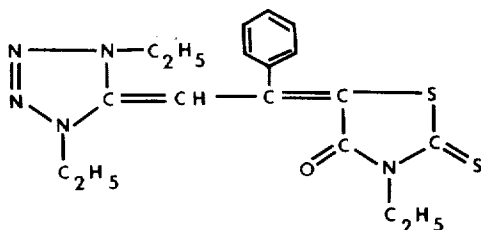
m.p. 290°C

Dye XVIII



m.p. 242°C

Dye XIX



m. p. 250°C

These sensitizers are described, for example, in the British Pat. No. 801,275 and the synthesis of these sensitizers is well known by reference to the patent cited above and also to the relevant technical literature.

These optical sensitizers are applied, either singly or in combination of two or more, at a ratio of from 10^{-6} to 10^{-3} mol, preferably 10^{-15} to 3×10^{-4} mol, per 1 mol of silver halide in the silver halide emulsion. This addition of the optical sensitizer to the emulsion is the same as with the metal compounds above described. The addition into the emulsion can be made either simultaneously with the metal compound, or separately. The sequence of the addition is immaterial.

Thus, it can be seen that the silver halide light-sensitive photographic material can be made essentially in the same manner as usual except that the above metal compound and optical sensitizer are added and the sensitive material thus prepared can, after flash exposure, be developed and fixed in a conventional manner. Also, the material can be treated in a manner known generally as the diffusion transfer process. Or, by adding beforehand an ample quantity of the developing agent in the light-sensitive layer, the development can be treated by the generally known activator development process (a process by which the light-sensitive material containing a developing agent is developed in a solution which does not contain a developing agent and in which only alkaline material is dissolved).

It has been observed that with light-sensitive materials containing the above-described metal compounds but not containing the optical sensitizers, the sensitivity to the green light is not obtained, although, in some cases, their sensitivity to blue light improves. On the other hand, it is recognized that in the case of the sensitive material not containing the metal compounds but containing only the optical sensitizers, the green light

sensitivity is not very high. However, by using these two types of materials simultaneously the green light sensitivity in the flash exposure can be markedly improved.

Specifically, with a silver chloride emulsion, a silver chlorobromide emulsion, or a silver chlorobromiodide emulsion, if the above sensitizer is used alone, a considerable lowering of the efficiency of spectral sensitization in the flash exposure is experienced. For such emulsions the present invention is particularly useful.

It has long been known that the metal compounds described above show various noticeable effects, and as is shown in U.S. Pat. No. 2,448,060, when hexahalogenoruthenium (III) acid salts, hexahalogenohodium (IV) acid salts, hexahalogeno osmium (IV) acid salts, hexahalogenoiridium (IV) acid salts, or hexahalogenoplatinum (IV) acid salts are added to a silver halide emulsion at the time of ripening, the sensitivity of this emulsion increases. And further, as is disclosed in U.S. Pat. No. 2,566,745, when these compounds are added additionally to the silver halide emulsion the stability of the sensitive material under high temperatures and humidity improves, and further, as is disclosed in U.S. Pat. No. 2,517,541, potassium hexacyanocobaltate (III) and in FIAT Report No. 360 rhodium trichloride, when this compound is added to a silver halide emulsion the contrast of the image obtained from this emulsion increases.

We have found that the iron compounds make the contrast of the emulsion higher.

The compounds of Group VIII elements in the periodic table are added solely for the objects of this invention, but they can also be used to obtain various photographic effects as described above at the same time. Also, as is shown in British Pat. No. 570,393, one can apply the method of increasing the sensitivity of the emulsion by adding the metal compounds at the time of ripening. In other words, when used as a sensitizer

or as a stabilizer or as an additive for increasing contrast, the effect of sensitization to green light is displayed if the above dyes are used together. The efficiency which the usual techniques aim at is not hindered.

The present invention will be illustrated in greater detail by the following examples.

EXAMPLE 1

An ordinary acid process silver chlorobromide emulsion was prepared (containing 30 mol % AgBr) not containing the compounds containing metals of Group VIII of the periodic table (hereinafter simply called metal compounds) and by the same method an emulsion was prepared, and at the time of forming the silver halide grains, ammonium hexachlororhodate (III) was added in a quantity equivalent to 7×10^{-6} mol per silver halide 1 mol, and at the after-ripening step, potassium hexachloroplatinate (IV) was added in a quantity corresponding 2×10^{-5} mol per silver halide 1 mol and the thus prepared emulsion was similar in sensitivity to the conventional emulsion. Each of these 2 emulsions was divided into two parts. One part was not dye-sensitized. To the other was added Dye I in a quantity of 4×10^{-3} mol per 1 mol of silver halide in the emulsion. Next, formaldehyde was added to each of these in a quantity of 2.5 per 100 g of gelatin of the emulsion, and then each was applied to a photographic baryta paper.

Using an EG & G Sensitometer Mark VII and through a colored glass filter V-Y50 (made by Tokyo Shibaura Electric Co., Ltd.) and an optical wedge, the above described samples were each given exposures of 1/100 and of 1/1,000,000 of a second. As is shown in the drawing, the colored glass filter V-Y50 (made by Tokyo Shibaura Electric Co., Ltd.) absorbs the light corresponding to the sensitive spectral region of the unsensitized silver halide and transmits only the light corresponding to the optically sensitized region of greater than about 500 nm. The exposed samples were developed at 20°C for 2 seconds in the following developer:

N-Methyl-para-aminophenol	2	g
Sodium Sulfite, Anhydrous	30	g
Hydroquinone	7	g
Sodium Carbonate (Monohydrate)	53	g
Potassium Bromide	1.5	g
Water	up to 1 liter	

After fixing, rinsing and drying, the reflective density of the images were measured.

The reciprocal of the light quantity giving a density of 0.5 was set as the sensitivity value, but, since the absolute light quantity through the filter was not measured, the sensitivity was only relative, but in the following table the sensitivities of the same exposure time could be in the corresponding state. The results obtained are shown in the table below.

	1/100th Second Exposure	1/1,000,000th Second Exposure
Control Emulsion	0	0
Group VIII Metal Only	0	0
Dye I Only	4.9	0.9
Group VIII Metal + Dye I	4.6	3.2

It was observed that by using the rhodate compound, the platinate compound and Dye (I) the green light sensitivity to flash exposure was increased.

EXAMPLE 2

A silver chlorobromide emulsion (containing 50 mol percent AgBr) was prepared in a neutral medium by a well known process and which does not contain the compounds of a Group VIII metal of the periodic table (hereinafter simply called metal compounds), and one was also prepared by adding hexachlororhodate (III) in a quantity of 3×10^{-6} mol per 1 mol of silver halide in the above emulsion at the time of the formation of the silver halide grains, then further after ripening potassium chloroplatinate was added in a quantity of 2×10^{-5} mol per silver halide 1 mol. The thus prepared emulsion had about the sensitive as the above-described emulsion. These two emulsions were each divided in two parts. One was left intact.

To the other part was added the Dye X in a quantity of 6×10^{-3} mol per 1 mol of silver halide in the emulsion. Next, formaldehyde was added to each of these in the quantity of 2.5 g per 100 g of gelatin of the emulsion, and the emulsion was applied to a photographic baryta paper.

The green light sensitivity was measured for the sample thus obtained in the manner as described in Example 1 and the following results were obtained.

	1/100th Second Exposure	1/1,000,000th Second Exposure
Control Emulsion	0	0
Group VIII Metal Only	0	0
Dye X Only	12.0	2.7
Group VIII Metal + Dye X	10.5	7.2

It was observed that by using simultaneously the rhodate salt, the platinate salt and Dye X, the green light sensitivity to the flash exposure was increased.

EXAMPLE 3

A silver chlorobromide emulsion (AgCl 50 mol percent, AgBr 50 mol percent) which does not contain the metal compounds of this invention was prepared in a neutral medium in a conventional manner.

Next, by the same method, at the formation of the silver halide grains, 3×10^{-6} mol per 1 mol of silver halide of ammonium hexachlororhodate was added to the emulsion, and then after ripening, platinum (IV) chloride in the quantity of 2×10^{-5} mol per silver halide 1 mol was added to prepare an emulsion having a sensitivity similar to that of the emulsion without the metal compounds. To each of these emulsions, as in Example 1, Dye IV at a level of 2×10^{-3} mol per 1 mol of silver halide was further added. In addition, 2.5g of formaldehyde was added per 100g of gelatin, and the emulsion was applied to a photographic baryta paper. The optical sensitization of the sample obtained was measured in the same manner as described in Example 1. The results obtained are shown in the following table.

	1/100 Second Exposure	1/1,000,000 Second Exposure
Control Emulsion	0	0
Group VIII Metal Only	0	0
Dye IV Only	12.7	2.9
Group VIII Metal + Dye IV	10.8	7.5

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In this case the effect of using the rhodate compound, the platinate salt and Dye IV together was observed.

EXAMPLE 4

A silver chlorobromide emulsion (AgBr 70 mol percent, AgCl 30 mol percent) which does not contain the metal compounds of this invention was prepared in an ammonium alkali medium in a conventional manner. Next, in the same manner potassium hexacyanoferrate (III) was added in a quantity of 1×10^{-5} mol per 1 mol of silver halide of the emulsion at the formation of silver halide grains. To these two emulsions Dye III was added in quantity of 2×10^{-5} mol per 1 mol of the silver halide.

Further, formaldehyde in a quantity of 2.5g per 100g of gelatin was added and the emulsion was applied to a photographic baryta paper. The sensitivity to green light of the samples thus obtained was measured in the same manner as described in Example 1. The results obtained are shown in the table below.

	1/100th Second Exposure	1/1,000,000th Second Exposure
Control Emulsion	0	0
Group VIII Metal Alone	0	0
Dye III Alone	63	13
Group VIII Metal + Dye III	68	47

In this case the combined effect of a Group VIII metal compound and Dye III was observed.

EXAMPLE 5

A silver chlorobromiodide emulsion (AgBr 70 mol percent, AgCl 29 mol percent, AgI 1 mol percent) which does not contain the metal compounds of this invention was prepared in an ammonium alkali medium using a conventional method. Next, using the same procedure, 4×10^{-6} mol per 1 mol of silver halide of potassium hexacyanoferrate (III), 6×10^{-8} mol per 1 mol of silver halide of potassium hexachloroiridate (IV), 3×10^{-7} mol per 1 mol of silver halide of ammonium hexachlororhodate (III) were added at the time of formation of the silver halide grains, and again at the after-ripening 3×10^{-8} mol per 1 mol of silver halide of chloroauric acid was added, and prepared an emulsion having a sensitivity similar to that of the ordinary sensitivity.

To this emulsion as well as to the emulsion described above, Dye III in a quantity of 6×10^{-3} mol per silver halide 1 mol was added. Further, formaldehyde 2.5g per 100g of gelatin was added and the emulsion was applied to a photographic baryta paper. The green light sensitivity of this sample was then measured in the same manner as in Example 1. The results obtained are shown in the table below.

	1/100th Second Exposure	1/1,000,000th Second Exposure
Control Emulsion	0	0
Group VIII Metal Only	0	0
Dye III Only	177	43
Group VIII Metal + Dye III	111	98

Also, in this case the effect of the joint application of the Group VIII metal salt and Dye III was observed.

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EXAMPLE 6

To the emulsion as used in Example 3 Dye VI was added corresponding to a quantity of 8×10^{-3} mol per silver halide 1 mol, and this sample was tested in the same manner as described in Example 1. The results obtained are shown in the table below.

	1/100th Second Exposure	1/1,000,000th Second Exposure
Control Emulsion	0	0
Group VIII Metal Only	0	0
Dye VI Only	336	77
Group VIII Metal + Dye VI	237	246

In this case also, the effect of the combined treatment of Group VIII metal salt and Dye VI was observed.

EXAMPLE 7

A silver chlorobromide emulsion (AgCl 50 mol percent, AgBr 50 mol percent) which does not contain the metal compounds of this invention was prepared in an ammonium alkali medium in a conventional manner. Next, using the same procedure, at the formation of the silver halide grains, 1×10^{-5} mol per 1 mol of silver halide of potassium hexacyanoferrate (III) was added and the emulsion having a sensitivity similar to that of the emulsion not containing metal compounds was obtained. To each of these emulsions, as described in Example 1, Dye VIII was added in a quantity of 4×10^{-3} mol per 1 mol of silver halide. Further, formaldehyde in a quantity of 2.5g per 100g of gelatin was added, and the emulsion was applied to a photographic baryta paper. The sensitivity to green light of the thus obtained samples was measured using the same method as used in Example 1 and the following results were obtained.

	1/100th Second Exposure	1/1,000,000th Second Exposure
Control Emulsion	0	0
Group VIII Metal Only	0	0
Dye VIII Only	48	11
Group VIII Metal + Dye VIII	49	35

In this case also, the combined effect of the ferrate and the Dye VIII was observed.

EXAMPLE 8

A chloriodobromide silver halide emulsion (AgBr 70 mol percent, AgCl 29 mol percent, AgI 1 mol percent) was prepared not containing metallic compounds of the present invention, using the conventional ammonium method. To an emulsion of the same composition were added at the formation of silver halide grain particles, 4×10^{-6} mol potassium hexacyanoferrate (III) 6×10^{-8} mol potassium hexachloroiridate (IV), 3×10^{-7} ammonium hexachlororhodate (III) per 1 mol silver halide in the emulsion, and then, at the after-ripening, 3×10^{-8} per 1 mol of silver halide of chloroauric acid was added. A sensitivity similar to that of the above-described ordinary emulsion was obtained.

To these emulsions was added Dye VII in a quantity corresponding to 2×10^{-3} mol per silver halide 1 mol. Again, to these emulsions was added formaldehyde in a quantity of 2.5g per 100g of gelatin to prepare a photographic emulsion which was applied to a photo-

tuted phenyl group whose substituents are selected from the group consisting of a halogen atom and an alkyl group.

5. The light-sensitive silver halide photographic material of claim 1, wherein said optical sensitizers are selected from the group consisting of 5,5',6-trichloro-1,1',3-triethyl-3'-(3-carboxypropyl)-benzimidazole-carbocyanine iodide and 3-allyl-5-[2-(1-ethyl-4-methyl-tetrazolylidene)ethylidene]-rhodamine.

6. The light-sensitive silver halide photographic material of claim 1, wherein said sensitizer is used at a level of from 1×10^{-2} to 1×10^{-3} mol per 1 mol of said silver halide.

7. The light-sensitive silver halide photographic material of claim 1, wherein said compound containing a Group VIII metal is potassium hexacyanoferrate (III) and wherein said optical sensitizer is 5,5',6-trichloro-1,1',3-triethyl-3'-(3-carboxypropyl)-benzimidazole-carbocyanine iodide.

8. The light-sensitive silver halide photographic material of claim 1, wherein said compound containing a Group VIII metal is ammonium hexachloro rhodate (III) and wherein said optical sensitizer is 5,5',6-trichloro-1,1',3-triethyl-3'-(3-carboxypropyl)-benzimidazole-carbocyanine iodide.

9. The light-sensitive silver halide photographic material of claim 1, wherein said compound containing a Group VIII metal is potassium hexachloroiridate (IV) and wherein said optical sensitizer is 5,5',6-trichloro-1,1',3-triethyl-3'-(3-carboxypropyl)-benzimidazole-carbocyanine iodide.

10. The light-sensitive silver halide photographic material of claim 1, wherein said compound containing a Group VIII metal is potassium hexacyanoferrate (III) and wherein said optical sensitizer is 3-allyl-5-[2-(1-ethyl-4-methyl-tetrazolylidene)-ethylidene]-rhodamine.

11. The light-sensitive silver halide photographic material of claim 1, wherein said compound containing a Group VIII metal is ammonium hexachlororhodate (III) and wherein said optical sensitizer is 3-allyl-5-[2-(1-ethyl-4-methyl-tetrazolylidene)-ethylidene]-rhodamine.

12. The light-sensitive silver halide photographic material of claim 1, wherein said compound containing a Group VIII metal is potassium hexachloroiridate (IV) and wherein said optical sensitizer is 3-allyl-5-[2-(1-ethyl-4-methyl-tetrazolylidene)-ethylidene]-rhodamine.

13. The light-sensitive silver halide photographic ma-

terial of claim 1, wherein said R_0 represents a member selected from the group consisting of a methyl group and an ethyl group; wherein R_7 represents a member selected from the group consisting of a methyl group and an ethyl group; and wherein R_3 , R_4 , R_5 and R_6 each represents a member selected from the group consisting of a methyl group, an ethyl group, a chlorine atom, a bromine atom, a fluorine atom, a methoxy group, an ethoxy group, and a phenyl group.

14. The light-sensitive silver halide photographic material of claim 1, wherein said complex salt is a member selected from the group consisting of a hexagonal complex salt, a tetragonal complex salt, and a square-plane complex salt.

15. The light-sensitive silver halide photographic material of claim 14, wherein said complex salt is an alkali metal or ammonium salt selected from the group consisting of hexacyanoferrate (II), hexacyanoferrate (III), hexachloroiridate (III).

16. The light-sensitive silver halide photographic material of claim 1, wherein said simple salts are rhodium (III) halide or iridium (IV) halide.

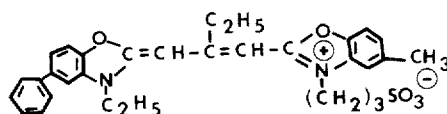
17. The light-sensitive silver halide photographic material of claim 4, wherein the alkyl group having a carboxy group in R_1 and R_2 is a carboxy-(alkoxy) $_{n-1}$ -alkyl group wherein n is 1 or 2; wherein the alkyl group having a sulfo group in R_1 and R_2 is selected from a sulfo-(alkoxy) $_{n-1}$ -alkyl group ($n=1, 2$ or 3), a hydroxy-sulfo-(alkoxy) $_{n-1}$ -alkyl group ($n=1$ or 2) and an acyloxy-sulfo group.

18. The light-sensitive silver halide photographic material of claim 1, wherein the substituted alkyl group in R_1 and R_2 is selected from the group consisting of a beta-hydroxyethyl group, a beta-acetoxyethyl group, a carboxymethyl group, a beta-carboxyethyl group, a gamma-carboxypropyl group, a 2-(2-carboxyethoxy)ethyl group, a beta-sulfoethyl group, a gamma-sulfopropyl group, a delta-sulfobutyl group, a 2-hydroxy-1-sulfopropyl group, a 2-(3-sulfopropoxy)ethyl group, a 2-acetoxy-1-sulfopropyl group, a 3-methoxy-2-(3-sulfopropoxy)propyl group, a 2-[2-(3-sulfopropoxy)ethoxy]ethyl group and a 2-hydroxy-3-(3-sulfopropoxy)-propyl group; wherein the substituted alkyl group in R_8 , R_9 and R_{10} is selected from the group consisting of a carboxymethyl group, a beta-hydroxyethyl group, a beta-sulfoethyl group and a gamma-sulfopropyl group.

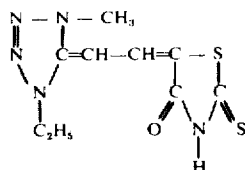
19. The light-sensitive silver halide photographic material of claim 1 wherein the optical sensitizer and the simple or complex salt is selected from the following combination systems:

Combination System No.	The Simple or Complex Salt	The Optical Sensitizer
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1 Ammonium hexachlororhodate (III)
Potassium hexachloroplatinate (IV)



2 do.



- Continued

Combination System No.	The Simple or Complex Salt	The Optical Sensitizer
3	Ammonium hexachlororhodate (III) Platinum (IV) chloride	
4	Potassium hexacyanoferrate (III)	
5	Potassium hexacyanoferrate (III) Potassium hexachloroiridate (IV) Ammonium hexachlororhodate (III)	do.
6	The same as No. 1	
7	Potassium hexacyanoferrate (III)	
8	The same as No. 5	
9	The same as No. 3	

20. The light-sensitive silver halide photographic material of claim 1, wherein flash exposure is exposure to the afterglow of the fluorescence of a cathode ray tube or a xenon flash lamp for time ranging from 1/10,000,000 of a second to 1/100,000 of a second.

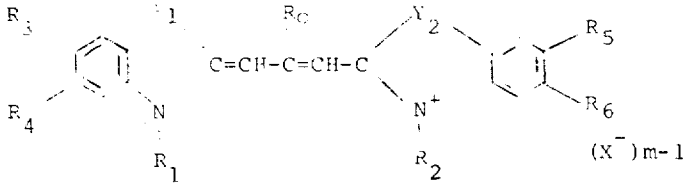
21. A photographic recording process which com-

prises exposing to a flash light the silver halide photographic material comprising at least one layer having high sensitivity to green light under flash exposure on a support which comprises an emulsion consisting essentially of:

1. a binder,

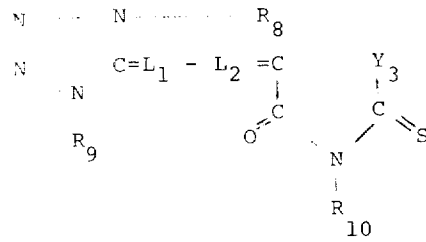
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2. light-sensitive silver halide grain particles of homogeneous structure exhibiting high surface sensitivity, compared to core-shell type particles,
3. at least one simple salt or complex salt of a Group VIII metal selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum, and
4. at least one optical sensitizer selected from the group consisting of compounds of the general formula:



wherein R_0 is a member selected from the group consisting of a hydrogen atom and an alkyl group; wherein R_1 and R_2 each represents a member selected from the group consisting of a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms, a substituted alkyl group selected from the group consisting of a hydroxyalkyl group, and acetoxyalkyl group, an alkyl group having a carboxy group and an alkyl group having a sulfur group, an allyl group, an aryl group, and an aralkyl group, in which at least one of R_1 and R_2 must be selected from the group consisting of a carboxyalkyl group and a sulfoalkyl group; wherein Y_1 and Y_2 each is selected from the group consisting of an oxygen atom, a sulfur atom, and $\text{a}=\text{N}-\text{R}_7$ group, in which R_7 represents an alkyl group wherein R_3 , R_4 , R_5 , and R_6 each is selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group, a cyano group, an alkoxy group, and an aryl group, in which if at least one R_3 and R_4 is an aryl group, then R_5 and R_6 are not an aryl group; wherein X represents an anion selected from the group consisting of a halogen ion and thiocyanate ion, and wherein m represents an integer of 1 or 2, in which an intramolecular salt is formed if m is 1; and compounds of the formula:

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wherein R_8 , R_9 and R_{10} each represents a member selected from the group consisting of a hydrogen atom, an alkyl group of from 1 to 8 carbon atoms, a substituted alkyl group selected from the group consisting of a carboxyalkyl group, a hydroxyalkyl group and a sulfoalkyl group, wherein Y_3 is a member selected from the group consisting of an oxygen atom, a sulfur atom, and $\text{a}=\text{N}-\text{R}_{11}$ group in which R_{11} is a member selected from the group consisting of a hydrogen atom, an alkyl group, and an aryl group; and wherein L_1 and L_2 each represents a methine chain, said exposing being for a time shorter than 1×10^{-5} seconds, and thereafter developing said photographic material.

22. The photographic recording process of claim 20 wherein the photographic material is exposed to a flash light for a time of at most 1×10^{-7} seconds.

23. The photographic recording process as claimed in claim 20 wherein the light-sensitive silver halide particles are formed by a process which comprises forming silver halide precipitates, and further wherein a salt of a Group VIII metal is added at the stage of forming said silver halide precipitate.

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