United States Patent [19]

Kawano et al.

[11] **3,770,450**

[45] **Nov. 6, 1973**

[54] **DIRECT POSITIVE SILVER HALIDE PHOTOGRAPHIC PHOTOSENSITIVE MATERIAL**

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[73] Assignee: **Fuji Photo Film Co., Ltd.,** Kanagawa, Japan

[22] Filed: **Apr. 27, 1971**

[21] Appl. No.: **137,970**

[52] **U.S. Cl.** **96/126,** 96/101, 96/114, 96/132, 96/135, 96/137

[51] **Int. Cl.** **G03c 1/14,** G03c 1/72

[58] **Field of Search** 96/137, 135, 126, 96/140, 114, 64

[56] **References Cited**

UNITED STATES PATENTS

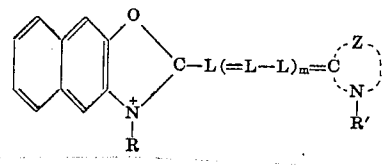
3,567,439 3/1971 Daniel et al. 96/101

Primary Examiner—J. Travis Brown

Attorney—Sughrue, Rothwell, Mion, Zinn and Macpeak

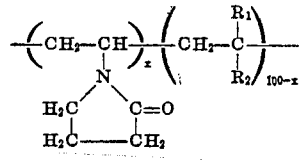
[57] **ABSTRACT**

A direct positive silver halide photosensitive material containing in its silver halide emulsion layer and/or the adjacent layer(s) thereof (1) at least one sensitizing dye represented by the following general formula I:



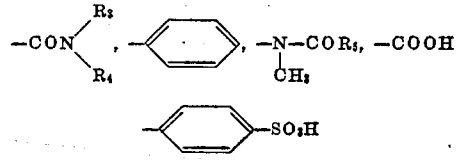
(I)

wherein R and R′ are each an alkyl or a substituted alkyl group, L is a methine chain, Z represents the group of atoms necessary to form a five or six membered nitrogen-containing heterocyclic nucleus, X is an anion and *n* is 0 or 1, and (2) at least one water-soluble (high) polymer having repeating units represented by the following general formula II:



(II)

wherein R_1 is H or CH_3, R_2 is -OH, $-OCOR_3$, $-COOR_3$, -CN, $-CONH_2$, $-CONHR_3$,



or

in which R_3 and R_4 each represents an alkyl group of from one to four carbon atoms and R_5 represents H, CH_3 or C_2H_5, and x is a positive number of from 50 to 100 representing the percentage ratio, is disclosed.

5 Claims, No Drawings

DIRECT POSITIVE SILVER HALIDE PHOTOGRAPHIC PHOTOSENSITIVE MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a direct positive silver halide photographic photosensitive material. More particularly, this invention relates to a silver halide photographic photosensitive material from which a direct positive image having a high sensitivity to reversal and a low minimum density may be obtained using only one exposure and one developing treatment.

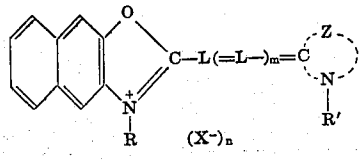
2. Description of the Prior Art

In the art of manufacturing this kind of photographic photosensitive material, it is well known that the sensitivity to reversal is enhanced markedly by adding a desensitizer or a conventional sensitizing cyanine dye into an emulsion which has been previously fogged. As such desensitizers, there are known organic desensitizing dyes such as Pinacriptol Yellow and Pinacriptol Green or metals of the Group VIII of the Periodic Table, for example, as described in U. S. Pat. No. 2,717,833. Furthermore, as the aforesaid sensitizing dyes, conventional cyanine or merocyanine dyes are well known, for example, as described in Japanese Pat. application No. 4,125/68. However, these sensitizing dyes, when added, cause an increase in residual color density together with an increase in the sensitivity to reversal. The degree of the residual color density, of course, depends upon the type of sensitizing dye employed.

An object of the present invention is to prepare a direct positive silver halide photographic photosensitive material having a high sensitivity to reversal and no residual color density.

SUMMARY OF THE INVENTION

We have now found that the above described object may be accomplished by employing a sensitizing dye as described below in combination with a water-soluble polymer of N-vinyl-pyrrolidone or with a water-soluble co-polymer containing more than 50 percent of N-vinyl pyrrolidone. The general formula of the sensitizing dye used is shown below:

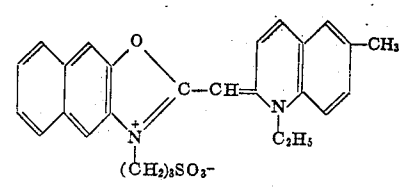


wherein in the above formula R and R′ each represents an alkyl group such as a methyl group, an ethyl group, an n-propyl group and an isobutyl group or a substituted alkyl group such as a β-methoxyethyl group, a β-hydroxy-ethyl group and a carboxymethyl group, L is a methine chain, Z is the group of atoms necessary for forming a five or a six membered nitrogen containing heterocyclic nucleus, X is an anion and *n* is 0 or 1.

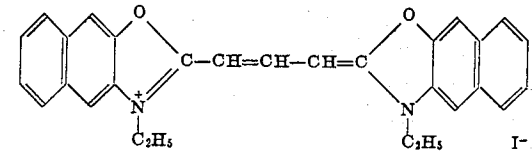
DETAILED DESCRIPTION OF THE INVENTION

Examples of the dyes represented by the above-described general formula include

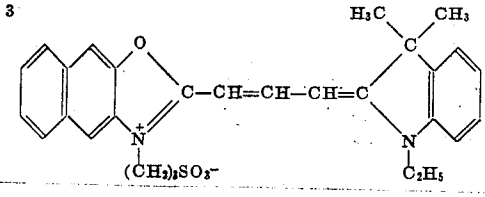
Dye 1



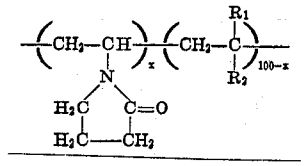
Dye 2



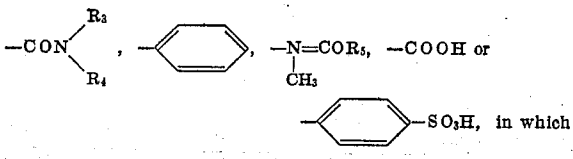
Dye 3



The water-soluble polymer or the water-soluble co-polymer of N-vinylpyrrolidone to be employed together with the above-described dye is a (high) polymer having the repeating unit represented by the following general formula:

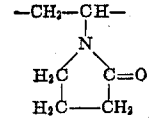


wherein in the above-described formula R_1 is H or CH_3, R_2 is -OH, $-OCOR_3$, $-COOR_3$, -CN, $-CONH_2$, $-CONHR_3$,



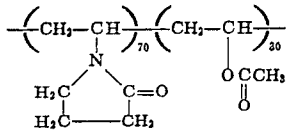
R_3 and R_4 each represent an alkyl group containing from one to four carbon atoms and R_5 represents H, CH_3 or C_2H_5, and *x* stands for a positive percentage number of from 50 to 100. The molecular weight of the water-soluble polymer or copolymer of N-vinylpyrrolidone to be employed according to the present invention may be varied over a wide range, but it is usually within a range of from 5,000 to 500,000, and preferably from 10,000 to 100,000. Examples of such N-vinylpyrrolidone water-soluble polymers or copolymers include:

Compound 1



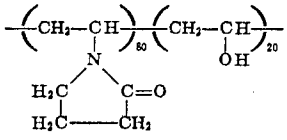
(Average molecular weight: Polyvinylpyrrolidone K-15, manufactured by General Aniline & Film Corp.)

Compound 2



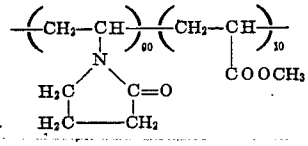
(Average molecular weight: 15,000).

Compound 3



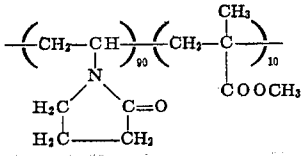
(Average molecular weight: 10,000).

Compound 4



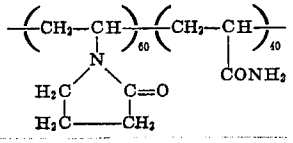
(Average molecular weight: 30,000).

Compound 5



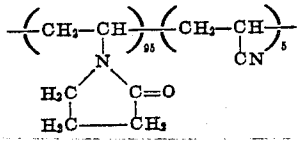
(Average molecular weight: 50,000).

Compound 6



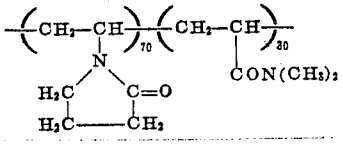
(Average molecular weight: 100,000).

Compound 7



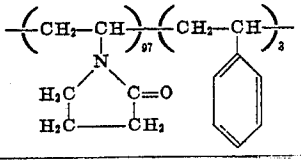
(Average molecular weight: 50,000).

Compound 8



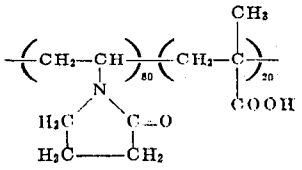
(Average molecular weight: 20,000).

Compound 9



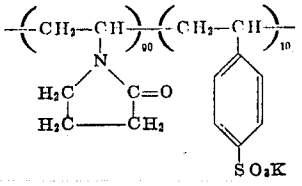
(Average molecular weight: 90,000).

Compound 10



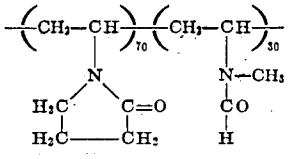
(Average molecular weight: 100,000).

Compound 11



(Average molecular weight: 80,000).

Compound 12



(Average molecular weight: 150,000).

The silver halide photographic emulsion to which these sensitizing dyes and water-soluble (high) polymers are added may be prepared by dispersing silver chloride, silver chlorobromide, silver bromide, silver iodobromide, silver chloroiodide or silver chloroiodobromide into gelatin or a hydrophilic organic colloid as a protective colloid. The addition may be effected at any stage of the emulsion manufacturing process, but preferably from after completion of the formation of fogged nuclei to immediately before coating of the emulsion. The amounts to be employed depend upon the emulsion used, but it is preferred that the sensitizing dye be used in an amount of from 1 mg to 200 mg per mol silver halide and that the water-soluble high polymer be employed in an amount of from 0.5 g to 50 g per mol silver halide. It is also possible to use either one kind of sensitizing dye or water-soluble high polymer, or a mixture of more than one kind of them.

In the present invention, any of known desensitizers such as Pinacriptol yellow and Phenosafranin may be employed together with the above-described compounds.

A direct positive silver halide photographic photosensitive material may be prepared by forming fogged nuclei in a silver halide emulsion obtained by conventional method of precipitation and physical ripening, by irradiation of the emulsion or by addition of a reducing agent such as formaldehyde, hydrazine and thiourea dioxide to the emulsion. Thereafter, the resulting emulsion is coated on a supporting material such as cellulose acetate film, polyethylene terephthalate film, baryta paper and synthetic paper with subsequent drying.

Furthermore conventional photographic additives such as hardening agents and surface active agents may also be added to the silver halide emulsion.

The direct positive silver halide photographic photosensitive materials are extremely excellent in that, as shown in the examples described hereinafter, they have a high sensitivity to reversal and no residual color density.

This invention is illustrated further in detail by reference to the following examples.

EXAMPLE 1

Into a 10 percent aqueous gelatin solution were added simultaneously 500 cc of an aqueous solution containing 100 g of silver nitrate and 500 cc of an aqueous solution containing 6 g of sodium chloride and 70 g of potassium bromide and the reaction was carried out at a temperature of 50° C to form silver halide grains.

After the formation was complete, 1 g of potassium iodide and 40 g of gelatin were added and the pH was adjusted to 9.5 with sodium carbonate. Into this was added 5 cc of 1 percent hydrazine hydrochloride followed by ripening at a temperature of 50° C for 40 minutes to form fogged nuclei. Subsequent to the ripening, the pH was adjusted to 6.0 with 10 percent citric acid. After cooling and washing with water, Dye 2 and High Polymer 1 (Compound 1) were added thereto in the amounts shown in Table 1.

For comparison, a sample using only Pinacriptol Yellow was prepared in the same manner.

TABLE 1

Emulsion No.	Amount of Compounds (g/mol Ag) Pinakryptol Yellow	Dye 2	Compound 1
1	0.5		
2	0.5	0.05	
3	0.5	0.20	
4	0.5	0.05	2.0
5	0.5	0.20	2.0

Each of the above-described emulsions was separately coated on a cellulose triacetate film followed by drying.

The resulting direct positive silver halide photographic photosensitive material was exposed through an optical wedge to a tungsten lamp at 2,660° K and then developed for 3 minutes at 20° C in a developer having the following composition. The sensitivity and residual color density of the resulting samples are summarized in Table 2.

Composition of the Developer	
Monol	3 g
Hydroquinone	12 g
Sodium Sulfite	45 g
Sodium Carbonate	70 g
Potassium Bromide	2 g

Water is added to give the total volume of 1000 cc.

TABLE 2

Emulsion No.	Specific Sensitivity	Residual Color Density (%)
1	100	100
2	200	90
3	350	65
4	380	93
5	700	90

NOTE: The sensitivity was expressed as a specific sensitivity where the sensitivity of the control sample was taken as 100.

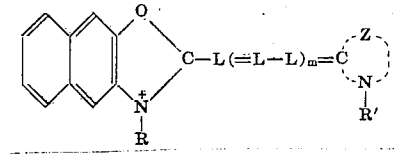
The residual color density was expressed as transmission percentage at a wave length of 550 mμ of the part of the film after treatment having the minimum density, whereby the transmittance percentage of the control sample was taken as 100 percent.

As is evident from the above-described Table 2, Samples No. 4 and 5 containing Dye 2 and Compound 2 of the present invention have markedly high sensitivity but little residual color density.

What is claimed is:

1. A direct positive silver halide photosensitive emulsion containing in its silver halide emulsion layer and/or the adjacent layer(s) thereof

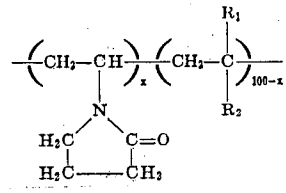
1. at least one sensitizing dye represented by the following general formula I:



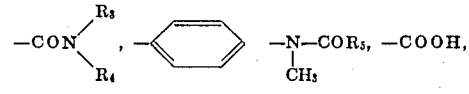
(I)

wherein R and R′ each represents a member selected from the group consisting of an alkyl group, an alkoxyalkyl group, a hydroxyalkyl group, a carboxyalkyl group, and a sulfoalkyl group, L represents a methine chain, Z represents the group of atoms necessary to form a quinoline, a naphthoxazole or an indole nucleus, X is an anion, *m* is 0, or 1, and *n* is 0 or 1, and

2. at least one water soluble high polymer having the repeating unit represented by the following general formula II;



wherein R_1 is selected from the group consisting of a hydrogen atom and a methyl group, R_2 is selected from the group consisting of -OH, $-OCOR_3$, $-COOR_3$, -CN, $-CONH_2$, $-CONHR_3$,

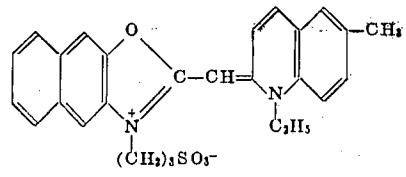


and

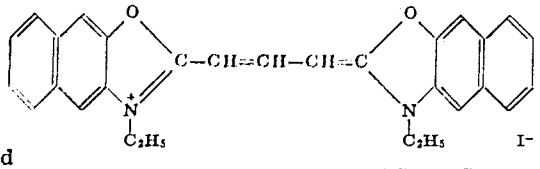


wherein R_3 and R_4 are each an alkyl group having from one to four carbon atoms and wherein R_5 is selected from the group consisting of a hydrogen atom, a methyl group and an ethyl group, and *x* is a positive percentage ranging from 50 to 100, inclusive.

2. The silver halide photosensitive emulsion of claim **1**, wherein said dye is selected from the group consisting of

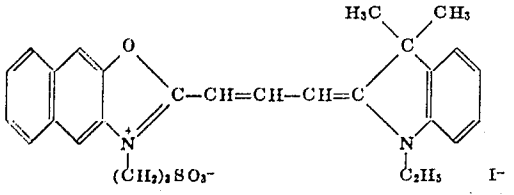


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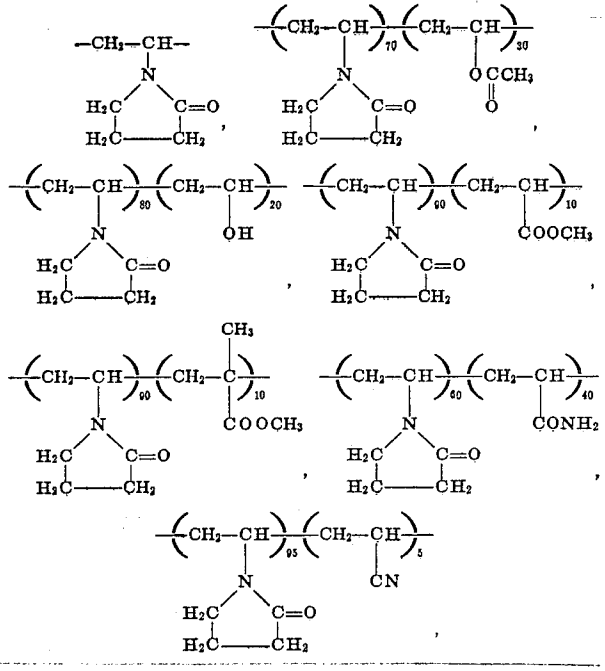
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and

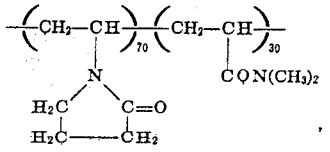


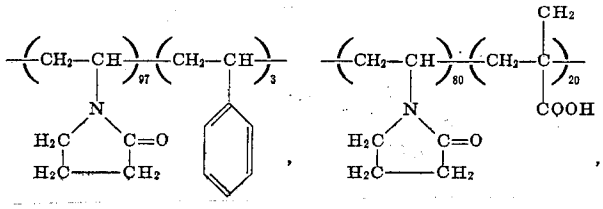
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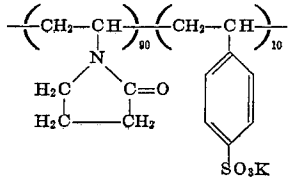
3. The silver halide photosensitive emulsion of claim **2**, wherein said high polymer is selected from the group consisting of:



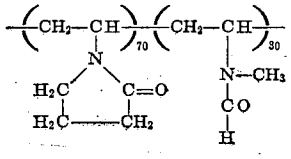
8







and



4. The silver halide photosensitive emulsion of claim **1**, wherein said sensitizing dye is present at a level of from 1 mg to 200 mg per mole of silver halide and wherein said high polymer has a molecular weight ranging from 5,000 to 500,000, and is present at a level of from 0.5 g to 50 g per mole of silver halide.

5. The silver halide photosensitive emulsion of claim **1**, wherein R and R′ are selected from the group consisting of a methyl group, an ethyl group, an n-propyl group, an isobutyl group, a β-sulfoethyl group, a γ-sulfopropyl group, a β-methoxy-ethyl group, a β-hydroxyethyl group, and a carboxymethyl group.

* * * * *