April 27, 1971 KAZUO MATSUI ET AL 3,576,636

LIGHT-SENSITIVE SILVER HALIDE DIRECT-POSITIVE PHOTOGRAPHIC EMULSION

Filed Dec. 16, 1968 2 Sheets-Sheet 1

Fig. 1

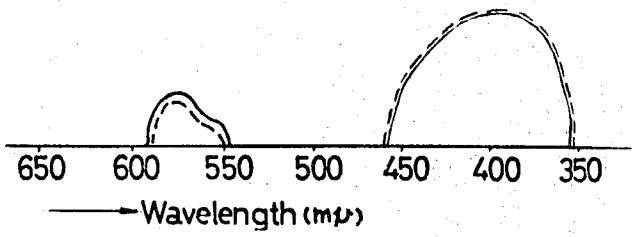


Fig. 2

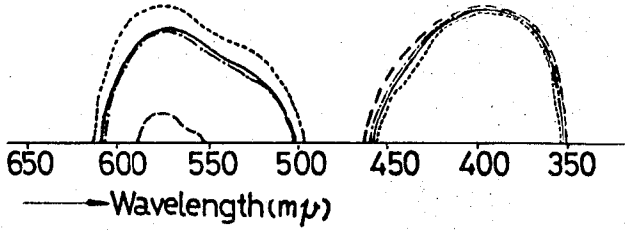


Fig. 3

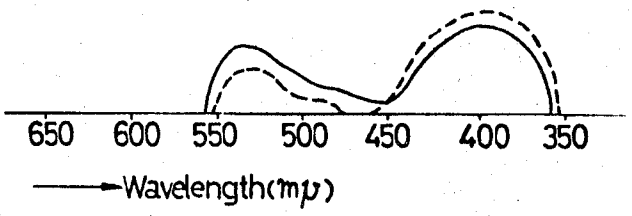


Fig. 4

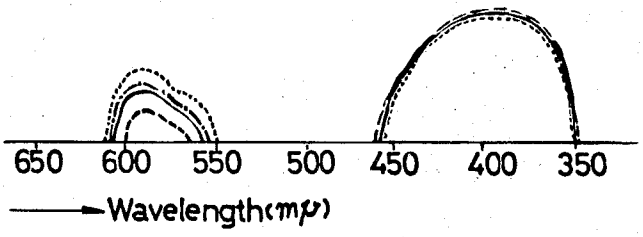
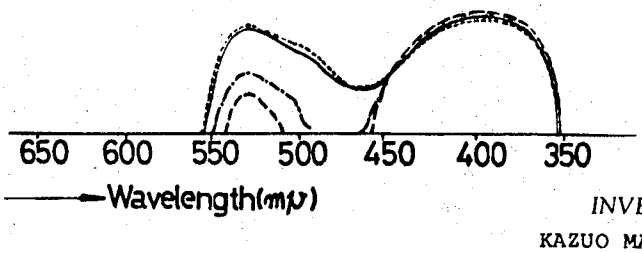


Fig. 5



INVENTORS
KAZUO MATSUI
HAJIME KOMATSU

BY Bierman & Bierman
ATTORNEYS

Fig. 6

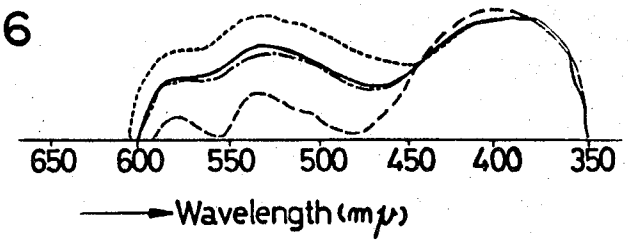


Fig. 7

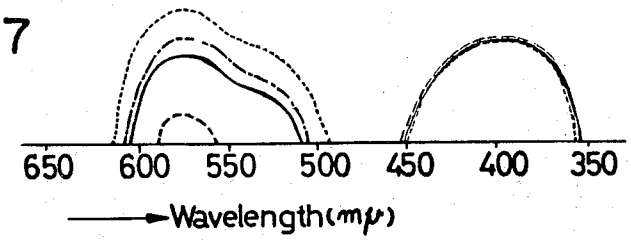


Fig. 8

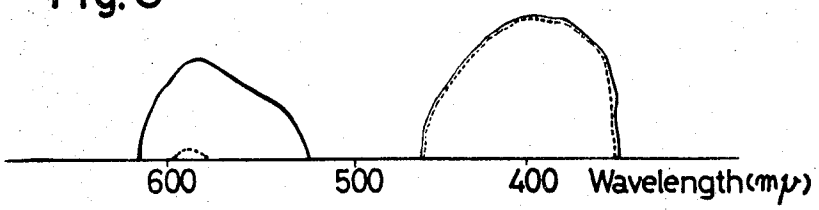
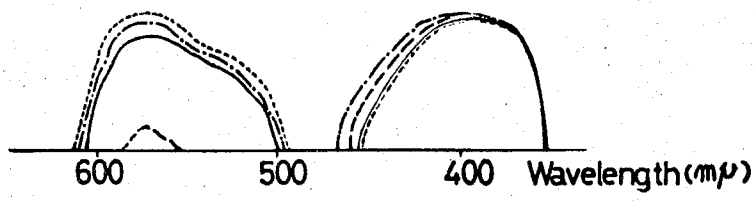


Fig. 9



INVENTORS
KAZUO MATSUI
HAJIME KOMATSU
BY Bierman & Bierman
ATTORNEYS

United States Patent Office

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LIGHT-SENSITIVE SILVER HALIDE DIRECT-POSITIVE PHOTOGRAPHIC EMULSION

Kazuo Matsui, Tokyo, and Hajime Komatsu, Odawara-shi, Japan, assignors to Konishiroku Photo Industry Co., Ltd.

Filed Dec. 16, 1968, Ser. No. 784,103
Claims priority, application Japan, Dec. 23, 1967, 42/82,310
Int. Cl. G03c 1/40
U.S. Cl. 96—100 5 Claims

ABSTRACT OF THE DISCLOSURE

The emulsion contains a sensitizing dye, at least one coupler selected from the group consisting of magenta, yellow and cyan couplers, and a rhodium compound. Fogging is inhibited, sensitivity to light of long wavelength is increased and reversal speed is increased. Additionally, white background dye staining is suppressed.

This invention relates to light-sensitive silver halide direct-positive photographic emulsion which can directly give positive images by single exposure and single development.

An object of the present invention is to provide supersensitized light-sensitive silver halide direct-positive photographic emulsion which has been optically sensitized with sensitizing dyes having sensivity to light of specific wavelength.

Heretofore, there have been known light-sensitive silver halide direct-positive photographic emulsions optically sensitized by incorporation of a cyanine dye as a sensitizing dye or supersensitized by incorporation of a cyanine dye in combniation with an organic desensitizer.

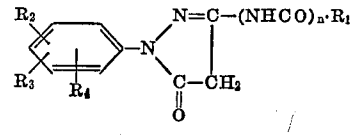
However, the said known photographic emulsions had suck drawbacks that they contained a sensitizing dye at so high concentration that the sensitizing dye stained the white background of photographic materials after development. Further, in the case of the photographic emulsions incorporated with a cyanine dye in combination with an organic desensitizer, there have been observed such drawbacks that the emulsions incorporated with monomethine cyanine dyes were supersensitized, whereas those incorporated with trimethine cyanine dyes were hardly supersensitized. In addition, when rhodium compounds were used as desensitizers in combination with cyanine dyes, the resulting photographic emulsions were increased in fog and were difficultly put into practical use.

Accordingly, in the known light-sensitive silver halide direct-positive photographic emulsions, use of sensitizing dyes providing excellent photographic characteristics, i.e. merocyanine dyes, trimethine-cyanine dyes and the like, was greatly limited. Therefore, it was very difficult to prepare light-sensitive silver halide direct-positive photographic emulsions having light sensitivity to light of long wavelength and less suffering from fogging.

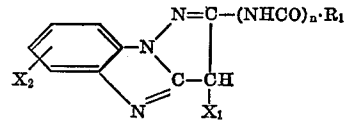
After the investigations, it has been found that light-sensitive silver halide direct-positive photographic emulsions improved in fogging and other photographic properties and supersensitized only in the specific wavelength portions, can be obtained by incorporating into light-sensitive silver halide direct-positive photographic emulsions containing a rhodium compound and a sensitizing dye which is sensitive to light of long wavelength such as merocyanine dye or trimethine cyanine dye one or more of magenta, yellow and cyan couplers.

The magenta couples used in this invention are those

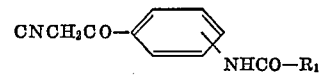
represented by any one of the following general formulas:



(I)



(II)



(III)

in which

R_1 is a higher alkyl, alkoxyaryl or acrylaminoaryl group, whose alkyl portion may have a carboxyl or sulfonic acid group as a substituent;

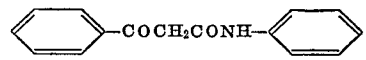
R_2 is hydrogen, halogen, carboxyl group or sulfonic acid group;

R_3 is hydrogen or halogen;

R_4 is hydrogen, halogen or phenoxy or alkylphenoxy group, whose phenyl group may have an alkyl group as a substituent;

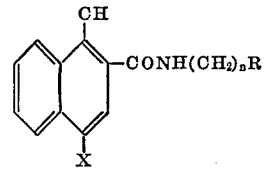
X_1 and X_2 are each hydrogen, sulfonic acid group or its alkali metal salt group; and n is 0 or 1.

The yellow couplers used in this invention are those having the following fundamental structure:



Both phenyl groups may have an appropriate substituent.

The cyan couplers used in this invention are those represented by the following general formula:

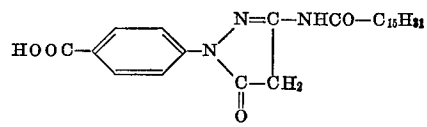


in which R is a higher alkyl, acyl, acylamino, acylaminoaryl, alkylaminoaryl or alkoxy- or aryloxy-aryl group, in which the alkyl portion and/or aryl portion may be substituted by carboxyl or sulfonic acid group, X is hydrogen or sulfonic acid group and n is 0, 1, 2 or 3.

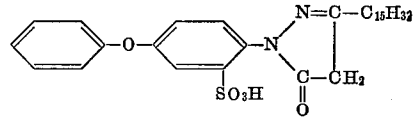
Typical couplers used in this invention are exemplified below, to which the present invention is not limited.

Magenta couplers

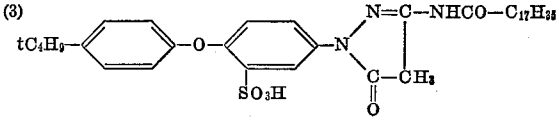
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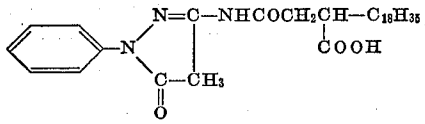
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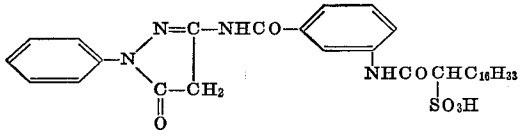
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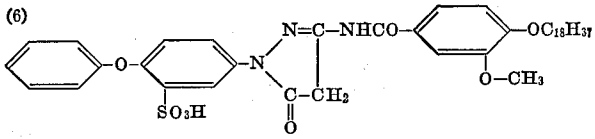
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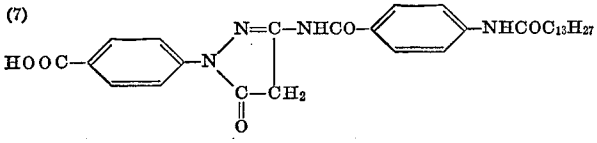
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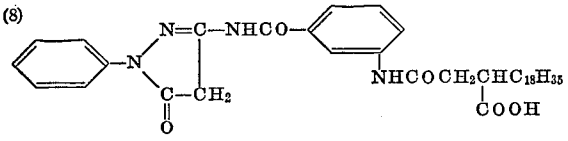
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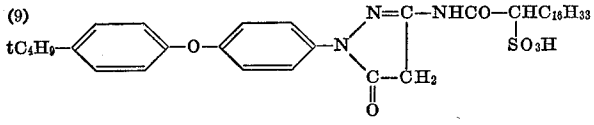
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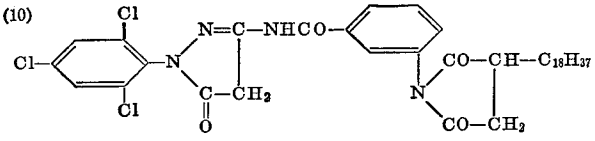
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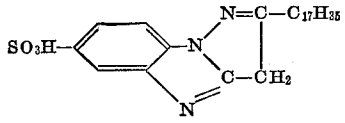
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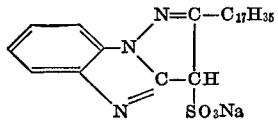
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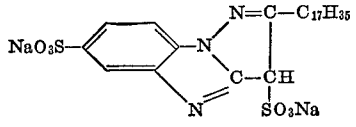
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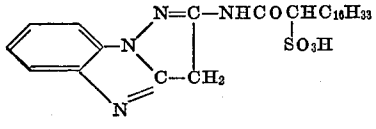
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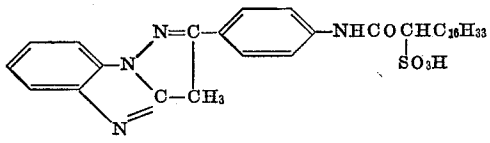
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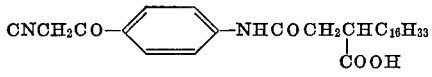
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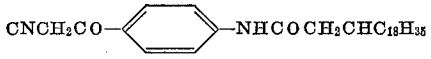
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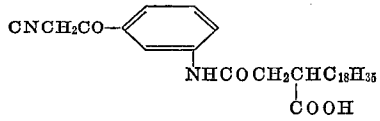
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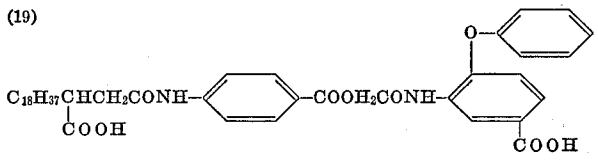


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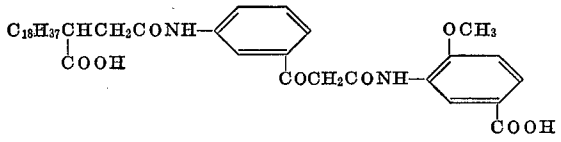


Yellow couplers

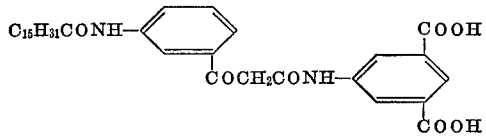
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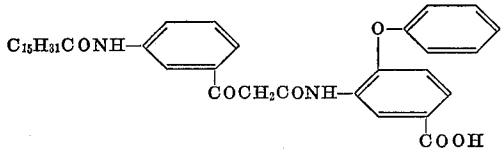
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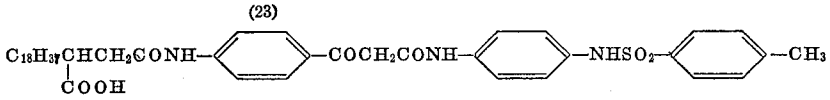
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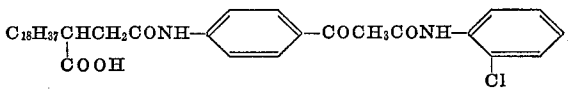
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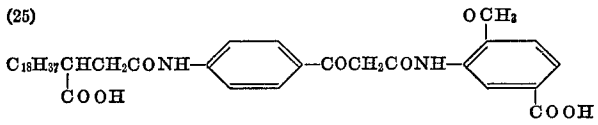
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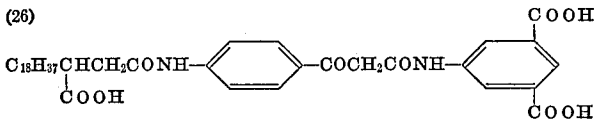
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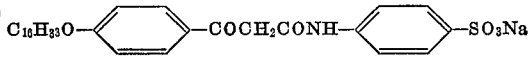
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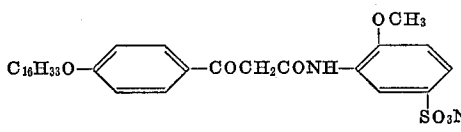
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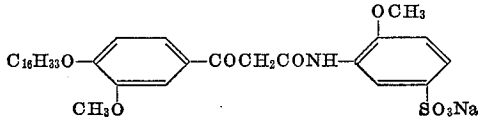
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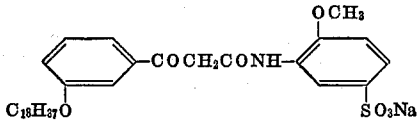
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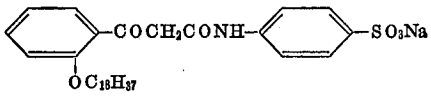
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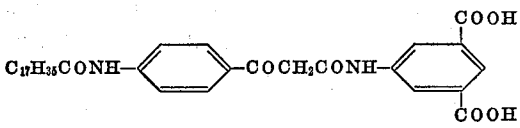
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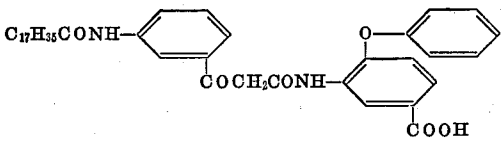
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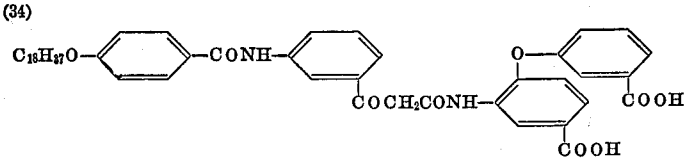
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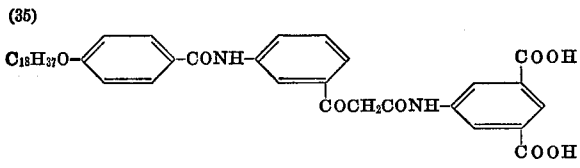
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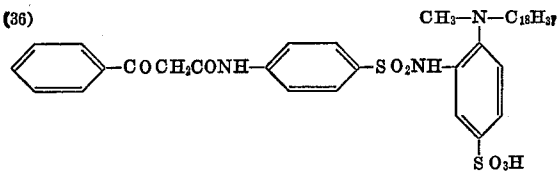
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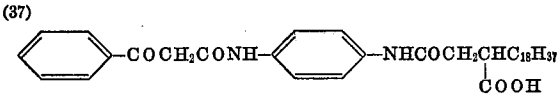
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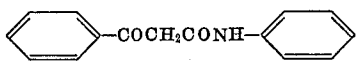
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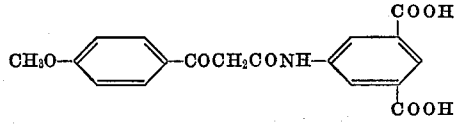
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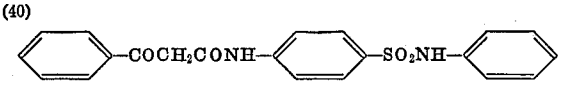
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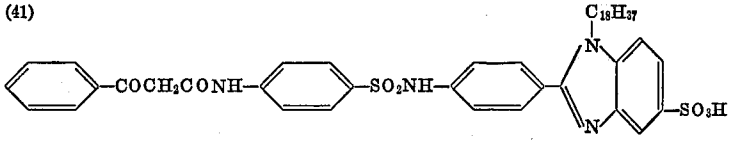
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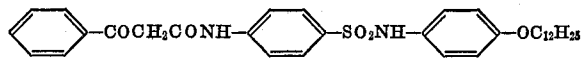
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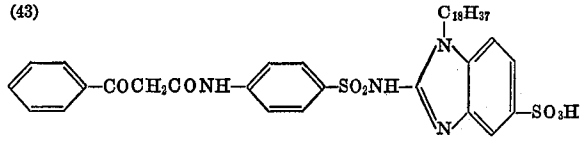
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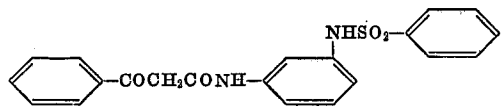
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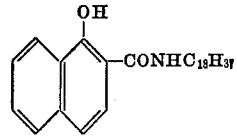
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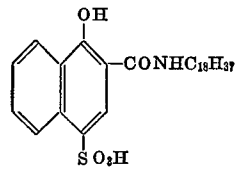
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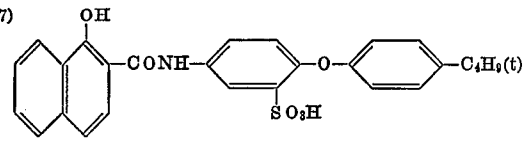
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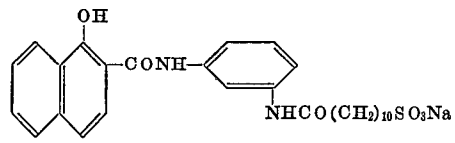
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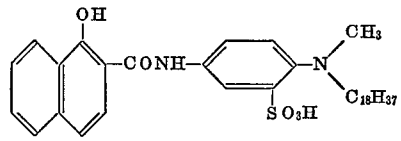
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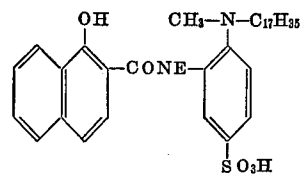
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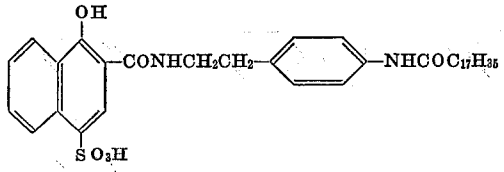


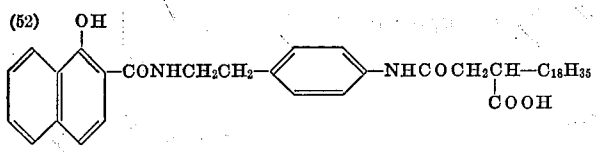
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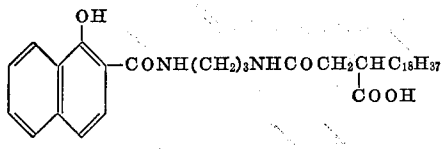


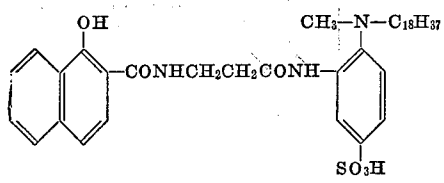
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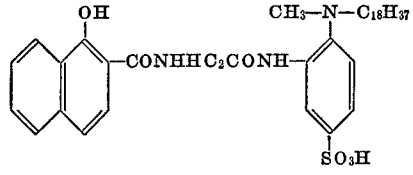


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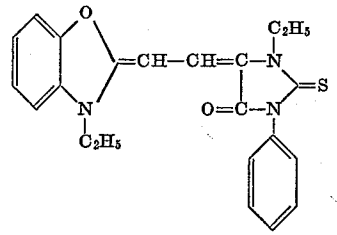
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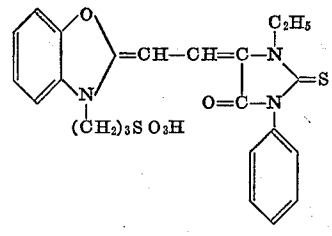
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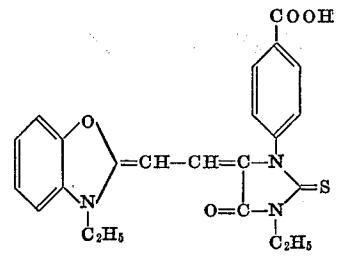
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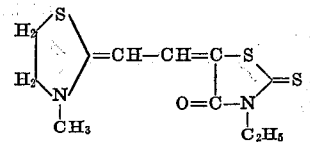
Rhodium compounds employed in the present invention are soluble salts or complex salts of rhodium. Particularly preferable are rhodium halides and hexahalorhodates.

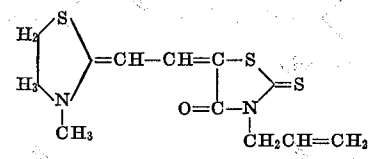
As the sensitizing dyes having sensitivity to light of long wavelength, merocyanine dyes, trimethine cyanine dyes are used and typical compounds of such dyes are exemplified below.

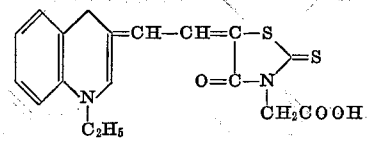
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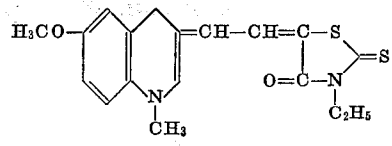
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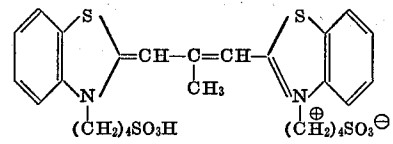
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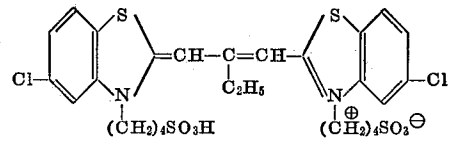
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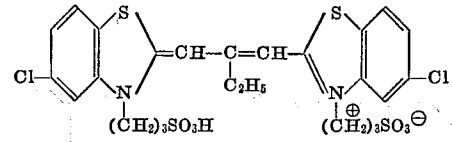
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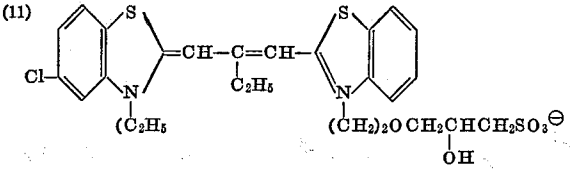
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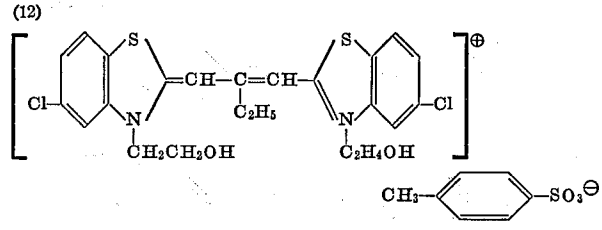
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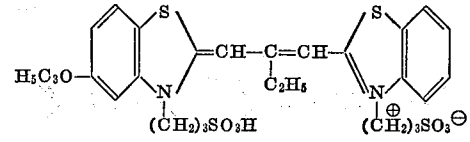
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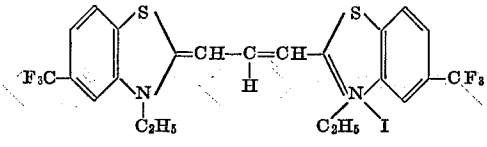
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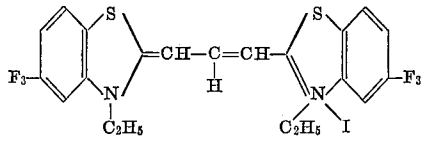
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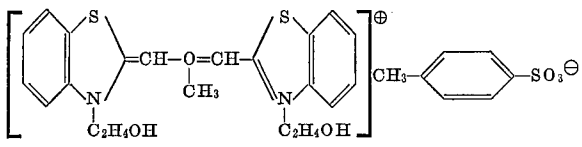
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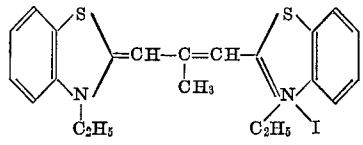
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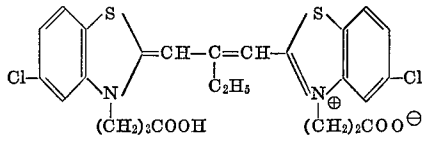
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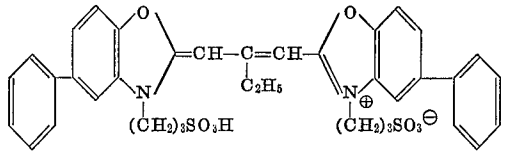
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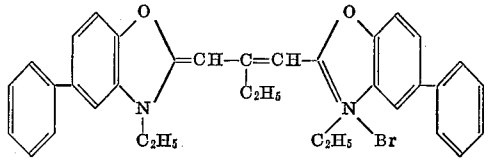
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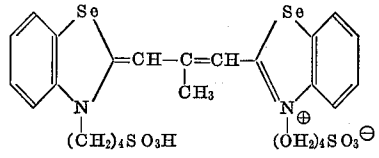
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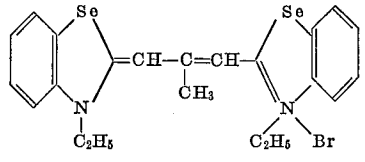
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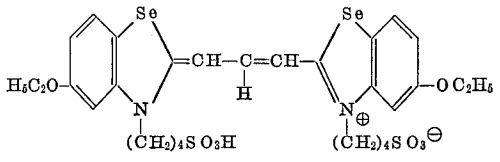
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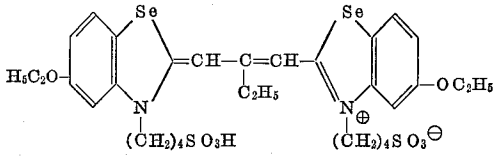
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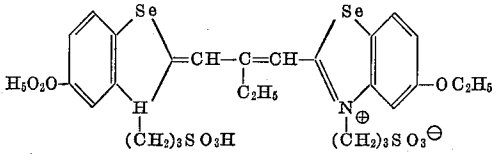
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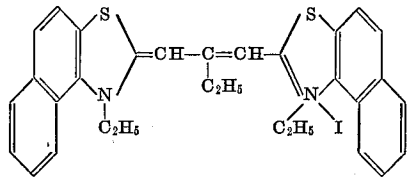
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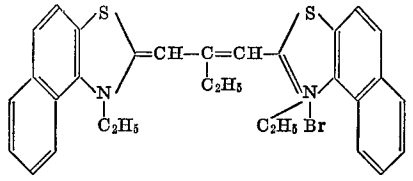
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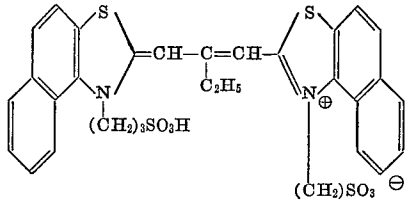
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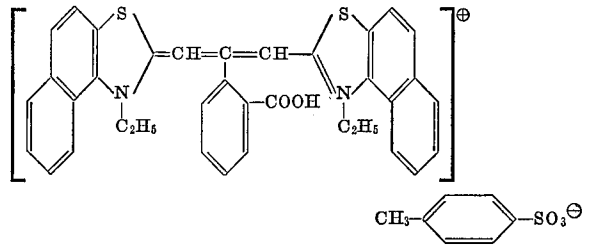
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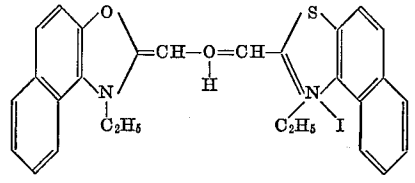
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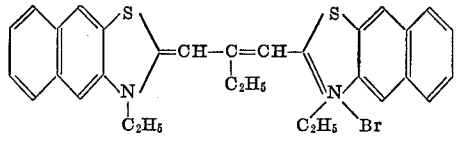
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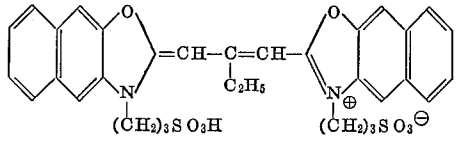
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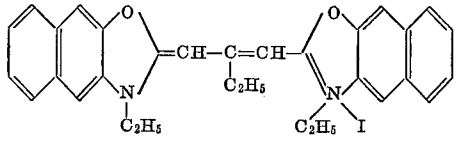
(31)



(32)



(33)



The couplers according to this invention are incorporated preferably in an amount of 7.5–150 g. per mole of silver halide. The amount of coupler may be varied depending on its class. The couplers are added to the emulsion as a solution in an organic solvent such as methanol or ethyl acetate or in an aqueous alkali solvent.

When such coupler is singly added, fogging may somewhat be increased depending on the kind of the sensitizing dyes used. In that case, an organic desensitizer is added in combination with such coupler in order to inhibit the

fogging. Typical organic desensitizers are, for example, pinakryptol yellow, pinakryptol green and phenosafranine. The organic desensitizer is preferably added in an amount of about 100 mg.-1.5 g. per mole of silver halide. The magenta coupler, yellow coupler and cyan coupler may be used in combination.

The rhodium compound is usually added at the stage of emulsification of silver halide or physical ripening in an amount of about 1×10^{-6} to 1×10^{-2} mols per mol of silver halide. The sensitizing dye having sensitivity to light of long wavelength is added in an amount of 10–800 mg. per mole of silver halide. The sensitizing dye may be added singly or in admixture with two or more of them.

The emulsion employed in the present invention may be a silver chloride-, silver bromide-, silver iodide-, silver chlorobromide-, silver chloroiodide-, silver bromoiodide- or silver chlorobromoiodide-emulsion containing gelatine or other hydrophilic organic colloid as a protective colloid. Particularly preferable emulsion is a silver chlorobromoiodide emulsion prepared according to the neutral or acidic method and containing a small amount of silver iodide. Such emulsion has appropriately been fogged by chemical treatment in the preparation thereof. The emulsion may be incorporated with various aids such as stabilizer, hardening agent and matting agent which are ordinarily used in common light-sensitive silver halide photographic emulsions.

As is clear from the above, the conventional light-sensitive silver halide direct-positive photographic emulsions containing rhodium compound and optically sensitized with sensitizing dyes have such drawback that they are increased in fog and are injured in photographic properties. In case an organic desensitizer is added in order to inhibit fogging, the object of inhibiting fogging can be attained but there is brought about such drawback that optical sensitization with a sensitizing dye difficultly takes place due to the organic desensitizer.

The light-sensitive silver halide direct-positive photographic emulsions of the present invention have no such drawbacks. In the emulsions, increase of fogging is inhibited and optical sensitivity is improved. Moreover, in accordance with the present invention, sensitizing dyes having sensitivity to light of optional long wavelength can be selected from a broader scope. Further, the amount of sensitizing dye, which is required to attain the same sensitivity as that of the conventional light-sensitive silver halide direct-positive photographic emulsion, can be made smaller and dye staining on the white background of light-sensitive material after development can be prevented.

The present invention is illustrated in detail below with reference to examples.

EXAMPLE 1

A rhodium compound (rhodium chloride)-containing silver chlorobromiodide emulsion which comprises 3 mole percent of silver iodide and 20 mole percent of silver bromide was adjusted to pH 8.0 with an alkali. Subsequently, the emulsion was charged with 5 cc. of 3% Formalin per kg. of said emulsion and then subjected to the ripening at 50° C. for 20 minutes. After the ripening, pH was adjusted to 6.0 with an acid.

The thus treated emulsion was divided into 2 portions. One portion was added with 10 cc. of 0.05% methanol solution of the sensitizing dye (17), 200 cc. of 0.1% aqueous solution of pinakryptol yellow and 30 cc. of 10% aqueous solution of saponin to prepare a sample (A). To the other portion of said emulsion, in addition to the above-mentioned additives, a solution of 7 g. of the coupler (2) in an alkali which solution had been adjusted to pH 6.0 was added to prepare a sample (B). The samples (A) and (B) were individually coated onto a photographic baryta paper and dried.

The thus obtained light-sensitive materials were individually subjected to stepwise exposure through a yellow filter transmitting a light of wavelength longer than 450 mμ, and treated with the D–72 developer (dope: water=1:1). The results obtained are as shown in Table 1, wherein sensitivity is expressed as relative value to the speed of the sample (A) ratet as 100.

TABLE 1

	Relative speed	Fog
Sample:		
A	100	0.01
B	145	0.01

The spectral sensitivity curves of the two samples are shown in FIG. 1, wherein the solid lines are curves of the sample (B), and the dotted lines are those of the sample (A).

The sample (B) which is a light-sensitive emulsion according to the present invention was not only supersensitized but also inhibited in increase of fogging.

EXAMPLE 2

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion treated in the same manner as in Example 1, the following samples (A) and (B) were prepared:

(A) The emulsion added with 10 cc. of 0.05% methanol solution of the light-sensitive dye (17), 200 cc. of 0.1% aqueous solution of pinakryptol yellow and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with an alkali solution of 8 g. of the coupler (4) which had been adjusted to pH 6.0 besides the additives used in the sample (A).

The samples (A) and (B) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 2, wherein sensitivity is expressed as relative value to the speed of the sample (A) rated as 100.

TABLE 2

	Relative speed	Fog
Sample:		
A	100	0.01
B	165	0.02

The sample (B) which is a light-sensitive emulsion according to the present invention was remarkably supersensitized and increase of fogging was very slight.

EXAMPLE 3

A rhodium compound-containing silver chlorobromide emulsion which comprises 30 mole percent of silver bromide was chemically fogged in the same manner as in Example 1. Using each 1 kg. of the thus obtained silver chlorobromide emulsion, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 12.5 cc. of 0.05% methanol solution of the sensitizing dye (17) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with a solution of 8 g. of the coupler (12) which had been adjusted to pH 6.0, besides additives used in the sample (A).

(C) The emulsion added with the additives used in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 3, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 3

	Relative speed	Fog
Sample:		
A	600	0.04
B	1,040	0.05
C	100	0.01
D	650	0.02

The spectral sensitivity curves of said samples are shown in FIG. 2, in which the sample (A) as referred— sample (B) to - - - -, sample (C) – – –, and sample (D) to –·–·–.

The samples containing the couplers according to the present invention were remarkably supersensitized and increase of fogging was very slight as compared with the samples containing no such couplers.

EXAMPLE 4

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 12.5 cc. of 0.05% methanol solution of the sensitizing dye (**17**) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 8 g. of the coupler (**16**) in which had been adjusted to pH 6.0.

(C) The emulsion added with the additives used in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 4, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 4

	Relative speed	Fog
Sample:		
A	680	0.04
B	530	0.03
C	100	0.01
D	290	0.01

EXAMPLE 5

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A) and (B) were prepared:

(A) The emulsion added with 10 cc. of 0.05% methanol solution of the sensitizing dye (**17**), 200 cc. of 0.1% aqueous solution of pinakryptol yellow and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additions used in the sample (A) and an alkali solution of 8 g. of the coupler (**25**) which had been adjusted to pH 6.0.

The samples (A) and (B) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 6.

TABLE 6

	Relative speed	Fog
Sample:		
A	100	0.01
B	180	0.01

The spectral sensitivity curves of said samples are shown in FIG. 3, in which the curve of sample (A) is represented by the chain line and that of sample (B) by the solid line.

EXAMPLE 6

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 15 cc. of 0.05% methanol solution of the sensitizing dye (**18**) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 8 g. of the coupler (**12**) which had been adjusted to pH 6.0.

(C) The emulsion added with the additives used in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 7, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 7

	Relative speed	Fog
Sample:		
A	240	0.30
B	410	0.32
C	100	0.06
D	308	0.06

The spectral sensitivity curves of said samples are shown in FIG. 4, in which the sample (A) is referred to —, sample (B) to - - - -, sample (C) to – – – –, and sample (D) to –·–·–.

The samples containing the couplers according to the present invention were remarkably supersensitized and increase of fogging was very slight.

EXAMPLE 7

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 15 cc. of 0.05% methanol solution of the sensitizing dye (**20**) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 8 g. of the coupler (**20**) which had been adjusted to pH 6.0.

(C) The emulsion added with the additives used in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 8, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 8

	Relative speed	Fog
Sample:		
A	340	0.20
B	850	0.12
C	100	0.01
D	235	0.01

The spectral sensitivity curves of said samples are shown in FIG. 5, in which the sample (A) is referred to —. sample (B) to - - - -, sample (C) to – – –, and sample (D) to –·–·–.

EXAMPLE 8

Using each 1 kg. of a forged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 10 cc. of 0.05% methanol solution of the sensitizing dye (4), 8 cc. of 0.05% methanol solution of the light-sensitive dye (17) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives use in the sample (A) and an alkali solution of 10 g. of the coupler (12) which had been adjusted to pH 6.0.

(C) The emulsion added with the additives used in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 9, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 9

	Relative speed	Fog
Sample:		
A	420	0.06
B	656	0.07
C	100	0.01
D	380	0.02

The spectral sensitivity curves of said samples are shown in FIG. 6, in which the sample (A) is referred to —, sample (B) to - - - -, sample (C) to – – – –, and sample (D) to –·–·–.

From the above, it is understood that even when two kinds of sensitizing dyes were used together, supersensitization took place.

Likewise, favorable results were obtained even when three kinds or more light-sensitive dyes were used together.

EXAMPLE 9

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A) and (B) were prepared:

(A) The emulsion added with 12 cc., of 0.05% methanol solution of the light-sensitive dye (17), 200 cc. of 0.1% aqueous solution of pinakryptol yellow and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 3 g. of the coupler (4) and 7 g. of the coupler (41) which solution had been adjusted to pH 6.0.

The samples (A) and (B) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 10, wherein sensitivity is expressed as relative value to the speed of the sample (A) rated as 100.

TABLE 10

	Relative speed	Fog
Sample:		
A	100	0.01
B	560	0.01

As seen in the Table 10, the sample (B) containing the coupler according to the present invention was not only greatly sensitized but also free from increased fogging.

EXAMPLE 10

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedures as in Example 1, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 12 cc. of 0.05% methanol solution of the sensitizing dye (17) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 5 g. of the coupler (41) and 5 g. of the coupler (46) which had been adjusted to pH 6.0.

(C) The emulsion added with the additives use in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 11, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 11

	Relative speed	Fog
Sample:		
A	680	0.04
B	1,500	0.04
C	100	0.01
D	820	0.02

The spectral sensitivity curves of said samples are shown in FIG. 7, in which the sample (A) is referred to —, sample (B) to - - - -, sample (C) to – – – –, and sample (D) to –·–·–.

As seen in the Table 11, in the samples containing the yellow and cyan couplers according to the present invention, marked supersensitization is observed and increase of fogging is very slight.

EXAMPLE 11

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion prepared according to the same procedure as in Example 1, the following samples (A) and (B) were prepared:

(A) The emulsion added with 12.5 cc. of 0.05% methanol solution of the sensitizing dye (17), 200 cc. of 0.1% aqueous solution of pinakryptol yellow and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 8 g. of the coupler (46) which had been adjusted to pH 6.0.

The samples (A) and (B) were independently coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 12, wherein sensitivity is expressed as relative value to the speed of the sample (A) rated as 100.

TABLE 12

	Relative speed	Fog
Sample:		
A	100	0.01
B	590	0.01

The spectral sensitivity curves of said samples are shown in FIG. 8, in which the solid lines exhibit the curves obtained by the sample (B) and the dotted lines exhibit the curves obtained by the sample (A).

The sample (B) which is a light-sensitive emulsion according to the present invention was not only supersensitized but also free from increase in fogging.

EXAMPLE 12

Using each 1 kg. of a fogged silver chlorobromoiodide emulsion obtained according to the same procedure as in Example 1, the following samples (A), (B), (C) and (D) were prepared:

(A) The emulsion added with 15 cc. of 0.05% methanol solution of the sensitizing dye (**17**) and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 8 g. of the coupler (**46**) which had been adjusted to pH 6.0.

(C) The emulsion added with the additives used in the sample (A) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

(D) The emulsion added with the additives used in the sample (B) and 200 cc. of 0.1% aqueous solution of pinakryptol yellow.

The samples (A), (B), (C) and (D) were individually coated onto a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 13, wherein sensitivity is expressed as relative value to the speed of the sample (C) rated as 100.

TABLE 13

	Relative speed	Fog
Sample:		
A	690	0.05
B	1,070	0.06
C	100	0.01
D	750	0.02

The spectral sensitivity curves of said samples are shown in FIG. 9, in which the sample (A) is referred to —, sample (B) to - - - -, sample (C) to – – –, and sample (D) to –·–·–.

EXAMPLE 13

Example 121 was repeated using a silver chlorobromide emulsion in place of the silver chlorobromoiodide emulsion. The emulsion according to the present invention gave good results.

EXAMPLE 14

Example 121 was repeated using the light-sensitive dye (**18**) in place of the sensitizing dye used therein. The resulting emulsions were treated in the same manner as in Example 1. The results obtained are as shown in Table 141, wherein the samples (A'), (B'), (C') and (D') correspond to samples (A), (B), (C) and (D) used in Example 121, respectively.

TABLE 14

	Relative speed	Fog
Sample:		
A'	240	0.30
B'	690	0.31
C'	100	0.06
D'	604	0.05

Use of the sensitizing dyes (**5**), (**23**) and (**26**) gave good results.

EXAMPLE 15

Example 121 was repeated using the coupler (**50**) in place of the cyan coupler (**46**) used therein. The results obtained are as shown in Table 15, wherein the samples (A''), (B''), (C'') and (D'') correspond to the samples (A), (B), (C) and D) used in Example 121, respectively.

TABLE 15

	Relative speed	Fog
Sample:		
A''	690	0.05
B''	740	0.05
C''	100	0.01
D''	240	0.02

EXAMPLE 16

Using each 1 kg. of a similar emulsion as used in Example 12, the following samples (A) and (B) were prepared:

(A) The emulsion added with 15 cc. of 0.05% methanol solution of the sensitizing dye (**30**), 200 cc. of 0.1% aqueous solution of pinakryptol yellow and 30 cc. of 10% aqueous solution of saponin.

(B) The emulsion added with the additives used in the sample (A) and an alkali solution of 8 g. of the coupler (**52**) which had been adjusted to pH 6.0.

The samples (A) and (B) were individually coated on a photographic baryta paper and dried. The resulting photographic materials were treated in the same manner as in Example 1. The results obtained are as shown in Table 16.

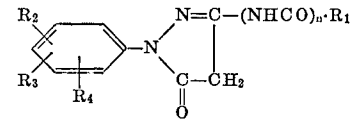
TABLE 16

	Relative speed	Fog
Sample:		
A	100	0.01
B	162	0.02

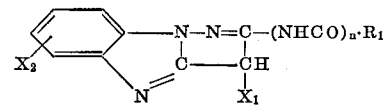
What is claimed is:

1. A light-sensitive silver halide direct-positive photographic emulsion containing a rhodium compound and a sensitizing dye and at least one coupler selected from the group consisting of magenta, yellow and cyan couplers.

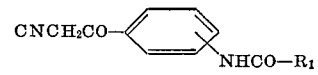
2. An emulsion as claimed in claim **1**, in which as the magenta coupler a compound represented by any one of the following general formulas is used:



(I)



(II)



in which

R_1 is a higher alkyl, alkoxyaryl or acylaminoaryl group, whose alkyl portion may have a carboxyl or sulfonic acid group as a substituent;

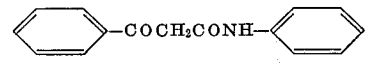
R_2 is hydrogen, halogen, carboxyl group or sulfonic acid group;

R_3 is hydrogen or halogen;

R_4 is hydrogen, halogen or phenoxy or alkylphenoxy group, whose phenyl group may have an alkyl group as a substituent;

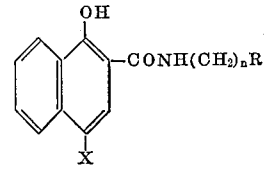
X_1 and X_2 are each hydrogen, sulfonic acid group or its alkali metal salt group; and n is 0 or 1.

3. An emulsion as claimed in claim **1**, in which as the yellow coupler a compound having the following fundamental structure is used:



in which both phenyl group may have an appropriate substituent.

4. An emulsion as claimed in claim **1** in which as the cyan coupler a compound of the following general formula is used:



in which R is a higher alkyl, acyl, acylamino, acylaminoaryl, alkylaminoaryl or alkoxy- or aryloxy-aryl group, in which the alkyl portion, the aryl portion, or the alkyl portion and aryl portion are substituted by a carboxyl or sulfonic acid group, X is hydrogen or a sulfonic acid group and *n* is 0, 1, 2 or 3.

5. An emulsion as claimed in claim 1, in which an organic desensitizer is used in combination with a coupler.

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WILLIAM D. MARTIN, Primary Examiner

B. D. PIANALTO, Assistant Examiner

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