United States Patent

[11] 3,615,637

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

[32] Priority **Dec. 4, 1968**
[33] **Japan**
[31] **43/88768**

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[54] **SPECTRALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS**
7 Claims, No Drawings

[52] **U.S. Cl.** **96/126**
[51] **Int. Cl.** **G03c 1/28**
[50] **Field of Search** 96/126, 124

[56] **References Cited**

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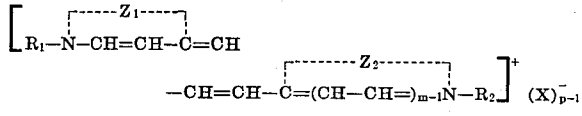
Primary Examiner—J. Travis Brown
Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

ABSTRACT: A supersensitized photographic silver halide emulsion containing a sensitizing dye represented by the following general formula:



and a condensate of formaldehyde and a polyhydroxybenzene, which may be substituted or unsubstituted. The emulsion is supersensitized. The sensitizing dye must contain at least one quinoline nucleus.

SPECTRALLY SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photographic silver halide emulsions, and more particularly, to supersensitized silver halide emulsions.

Description of the Prior Art

It is well known in the technical field of producing photographic silver halide emulsions that by adding a sensitizing dye to a photographic silver halide emulsion the light-sensitive wavelength range is extended and the emulsion is spectrally sensitized.

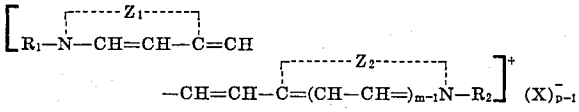
Further, by adding to the photographic silver halide emulsion (together with the sensitizing dye) an additive that does not sensitize the photographic emulsion in the same wavelength range as that of the sensitizing dye, it is sometimes found that at least a part of the wavelength range where the dye sensitizes is more markedly sensitized than when the dye alone is added to the emulsion. This phenomenon is commonly called "supersensitization" and other compounds that do not sensitize the photographic emulsion in the same wavelength ranges as that of the sensitizing dye are called "supersensitizers."

SUMMARY OF THE INVENTION

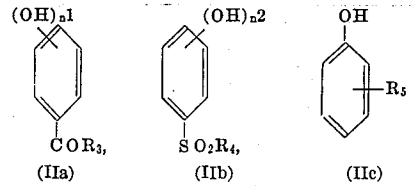
The present invention, essentially, involves the discovery that a supersensitized photographic silver halide emulsion may be formed by a combination of certain sensitizing dyes and a condensate of formaldehyde and a polyhydroxybenzene, which may be substituted or unsubstituted.

More specifically, the photographic silver halide emulsion must contain at least one sensitizing dye represented by the following general formula I:

I



wherein Z_1represents nonmetallic atoms necessary to complete the -quinoline -quinoline nucleus and Z_2 represents nonmetallic atoms necessary to complete 5-6membered heterocyclic rings, R_1 and R_2 are each a member selected from the class consisting of an alkyl group having one to five carbon atoms and an alkyl group substituted by a member selected from the class consisting of hydroxyl, acetoxy, sulfate, carboxyl carboxyalkoxyl, sulpho, hydroxysulpho, alkoxy-sulphoalkoxy, m represents 1 or 2 , X represents an anion, and p represents 1 or 2 , and at least one condensate of formaldehyde and a member selected from the group consisting of a substituted polyhydroxybenzene and an unsubstituted polyhydroxybenzene represented by the following general formulas,



(IIa) (IIb) (IIc)

wherein R_3 and R_4 each represents a member selected from the group consisting of OH, OM, OR_6 , NHR_6 , NH_2 , $N(R_6)_2$, $NHNH_2$, $NHNHR_6$, wherein R_6 is a member selected from the group consisting of an alkyl group having one-eight carbon atoms, an aryl group and an aralkyl group, and M is a member selected from metals consisting of an alkali metal and an alkaline earth metal, R_5 is a member selected from the group consisting of a hydroxyl group and halogen atoms, n^1 and n^2 each represents 1, 2 or 3 .

It is an object of the present invention to provide a supersensitized photographic silver halide emulsion.

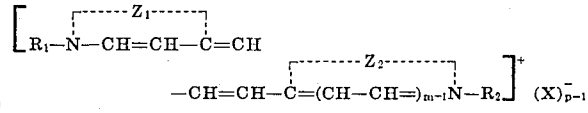
It is a further object to provide a spectrally sensitized photographic silver halide emulsion.

These and other objects will become clear upon a reading of the following detailed description of the preferred embodiments of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The inventors have found that by incorporating in a Photographic silver halide emulsion the sensitizing dye shown in following general formula (I), together with the novalak-type condensate of a substituted or an unsubstituted polyhydroxybenzene and formaldehyde, supersensitization can be obtained. Here the term polyhydroxybenzene means one having one to three hydroxy groups on the benzene nucleus. The novalak-type condensate of a substituted or an unsubstituted polyhydroxybenzene and formaldehyde is hereinafter called simply a "formalin condensate."

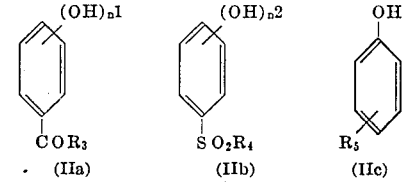
General formula (I) is:



wherein Z_1 represents a nonmetallic atom group necessary to complete the 4-quinoline nucleus; Z_2represents a nonmetallic atom necessary to complete a 5-6membered heterocyclic ring; $R_1$and R_2represent a substituted or an unsubstituted alkyl group; m represents 1 or 2 ; X represents an anion; p represents 1 or 2 , p being 1 when the dye forms an internal salt.

The 4-quinoline nucleus containing Z_1 may also contain such substituted groups as halogen atom, an alkyl group, an alkoxyl group, a hydroxyl group, etc., Z_2 represents nonmetallic groups necessary for completing heterocyclic rings such as e.g., 4-quinoline nucleus, 2-quinoline nucleus, benzothiazole nucleus, naphthothiazole nucleus, benzoselenazole nucleus, naphthoselenazole nucleus, benzoxazole nucleus, naphthoxazole nucleus, thiazole nucleus, oxazole nucleus, benzoimidazole nucleus, 3,3-dialkylindolenine nucleus, etc., R_1 and R_2 each represents a lower alkyl group (e.g., methyl group, ethyl group, propyl group, etc.) or substituted alkyl group such as a β-hydroxyethyl group, β-acetoxyethyl group, ethyl sulfate group ($-C_2H_4SO_4H$), carboxymethyl group, β-carboxyethyl group, γ-carboxypropyl group, 2-(2-carboxyethoxy)ethyl group, β-sulphoethyl γ-sulphopropyl γ-sulphopropyl group, 2-hydroxy- 1-sulphopropyl group, 3-methoxy- 2(3-sulphopropoxyl)propyl group, etc. The basic chemical structural feature of this sensitizing dye is that it contains at least one quinoline nucleus.

The substituted or unsubstituted polyhydroxybenzene used in the present invention is shown by the following general formulas:



(IIa) (IIb) (IIc)

wherein R_3 and R_4 each represents OH, OM OR_6, NH_2, $N(R_6)_2$, $NHNH_2$, NHR_6, or $NHNHR_6$(where R_6 represents an alkyl group having one to eight carbon atoms, an aryl group,

or an aralkyl group, and M represents an alkali metal or an alkaline earth metal), R_5 represents a hydroxyl group or halogen group, and n^1 and n^2 each represents 1, 2, or 3.

Typical examples of compounds shown by the above general formulas are P-dihydroxybenzene, o-dihydroxybenzene, p-hydroxybenzoic acid, p-hydroxybenzenesulphonic acid, m-hydroxybenzoic acid, m-hydroxybenzenesulphonic acid, α-resorcinic acid, β-resorcinic acid, γ-resorcinic acid, 3,5-dihydroxybenzenesulphonic acid, 2,4-dihydroxybenzenesulphonic acid, 2,6-dihydroxybenzenesulphonic acid, 2,5-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 2,5-hydroxybenzenesulphonic acid, pyrogallol carboxylic acid, (5), pyrogallol carboxylic acid (4), pyrogallol sulfonic acid (5), pyrogallol sulfonic acid (4) and their alkali metal salts (Li, Na, K, etc.), and their alkaline earth metal salts (Mg, Ca, etc.). Further examples of materials effectively used in the present invention are the amides or hydrazides of the above-mentioned carboxylic acids or sulfonic acids, and amide compounds or hydrazide compounds of these N-alkyl (one to eight carbon atoms) or N-aralkyl or N-allyl derivatives. The esters of the above-mentioned carboxylic acids or sulfonic acids can also be effectively employed in this invitation.

The condensate of the above-mentioned substituted or unsubstituted polyhydroxybenzene and formaldehyde may be prepared by any conventional method for forming a novolak-type phenol-formaldehyde resin. While the preparation thereof is not particularly critical, such a material is generally prepared as follows. The polysubstituted hydroxybenzene is dispersed in water, and after adding concentrated hydrochloric acid and 37 percent formalin, the dispersion is stirred for 30 to 60 minutes at **100°** C. Thereafter, if necessary, hydrochloric acid is added, followed by the continuation of heating and stirring. After the reaction is finished, the product is poured into cold water and the precipitate is collected and purified to provide the condensate. Another example will now be described in more detail. For example, 415 parts of p-hydroxy-benzoic acid is dispersed in 1,000 parts of water with vigorous stirring and 25 parts of 35 percent (or greater) concentrated hydrochloric acid and 245 parts of 37 percent formalin are added to the dispersion. The reaction mixture is then stirred for 30 minutes at **100°** C. and, after the addition of 20 parts of concentrated hydrochloric acid, the system is reacted for a further 30 minutes.

At the end of the reaction, 20 parts of concentrated hydrochloric acid is added to the reaction product and the system is stirred, whereby the reaction solution becomes turbid and white. After stirring for about 90 minutes, stirring is stopped and the reaction mixture is poured into 3,000 parts of cold water, with stirring. The product thus precipitated is separated by filtration, redissolved in 1,000 parts of methanol while the product is not yet dried, and then reprecipitated by adding water. The product is recovered by filtration and dried to provide the desired condensate. In the cases where other substituted or unsubstituted polyhydroxybenzenes are employed in place of the above-mentioned p-hydroxybenzoic acids, the above-mentioned method or a slightly modified method can be applied to easily obtain the condensate. The condensate obtained by the above-mentioned method has, like the common novolak-resin, about 2–10 units in a condensation unit (degree of polymerization).

A condensate having 2–10 units in its degree of polymerization is effective in the present invention, but a condensate having 2–5 units in its degree of polymerization and having a molecular weight of 300–800 is particularly desirable.

When a formalin condensate of the present invention is added to a silver halide emulsion containing the sensitizing dye of formula (1), excellent supersensitization can be obtained and, moreover, the formation of fog can be remarkably reduced compared with the case where the sensitizing dye alone is added to the emulsion. Some of the sensitizing dyes of formula (1), when incorporated in photographic light-sensitive materials, have the drawback that their sensitivity is lowered during storage, but such a lowering storage can be remarkably prevented by incorporating the dye in the emulsion together with the formalin condensate in accordance with the present invention.

The concentration of the sensitizing dye of the present invention in the silver halide emulsion is preferably 0.002–0.2 g./mol. silver halide, and the concentration of the formalin condensate in the said emulsion is preferably 0.1–5.0 g./mol. silver halide. The most effective concentration ratio of the sensitizing dye to the formalin condensate is preferably from 1:5 to 1:500.

The sensitizing dye may be added into the emulsion by any suitable method known in this field. The formalin condensate may be incorporated in the silver halide emulsion as a solution thereof in water or in an organic solvent such as methanol or ethanol. It is convenient to incorporate the sensitizing dye and the formalin condensate into the emulsion before coating.

The sensitizing dye may be added into the emulsion either before or after the addition of the formalin condensate, or a mixture of the sensitizing dye and the formalin condensate may be added into the emulsion. Further, they may be added into the emulsion not only before coating but also during ripening of the emulsion after washing.

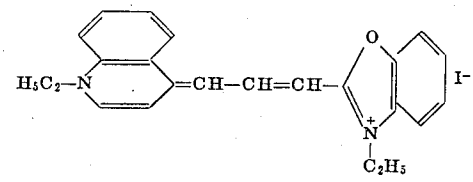
In the present emulsion, gelatin is generally used as a binder for the silver halide emulsion, but other binders such as resinuous material or cellulose derivatives which do not have a bad influence on the photographic light sensitive materials may be used.

The photographic emulsion used in this invention may be a gelatino-silver halide such as gelatino silver-chloride, -bromide,-bromoiodide, -bromochloride or -bromochloroiodide.

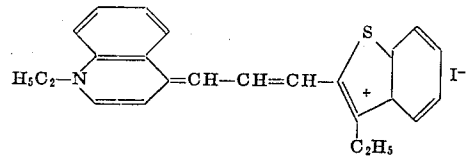
The silver halide emulsion used in this invention may further contain the normal state of the art additives such as a chemical sensitizer, an antifoggant, a stabilizer, a hardening agent, a wetting agent, a plasticizer, a developing accelerator, a toner, a fluorescent whitening agent, an antiairfoggant, a coupler, etc. The silver halide emulsion may be applied by any conventional method to a suitable support such as a glass plate, a cellulose derivative film, a synthetic film or a baryta paper.

The sensitizing dyes of the formula (I) employed in the present invention are should below but it showul be understood that they are not limited to the the following examples.

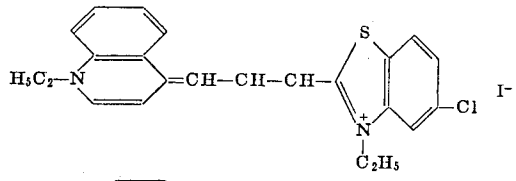
I-1



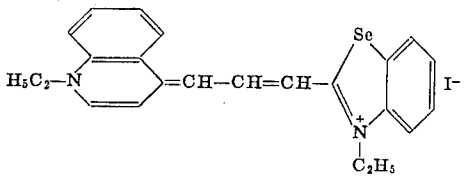
I-2



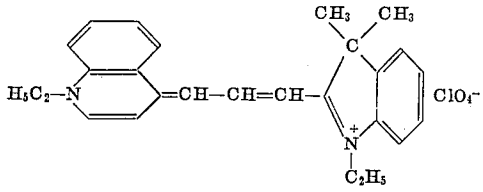
II-3



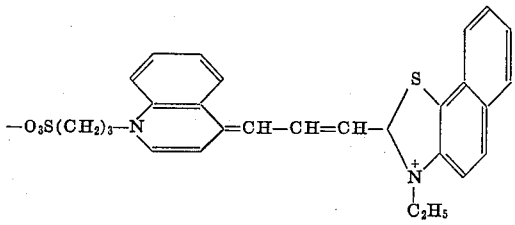
I-4



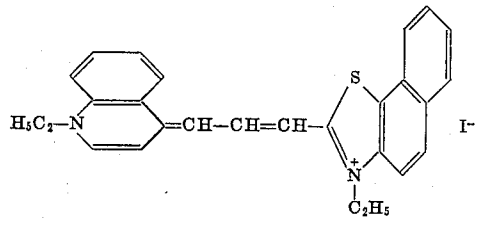
I-5



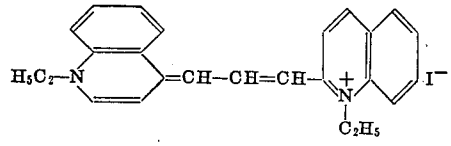
I-6



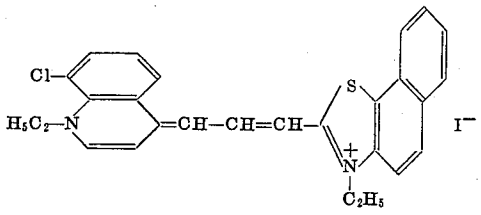
I-7



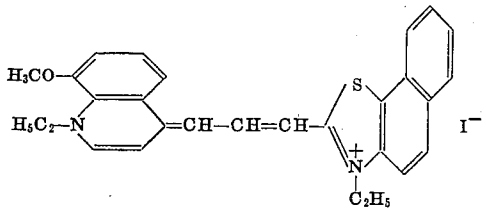
I-8



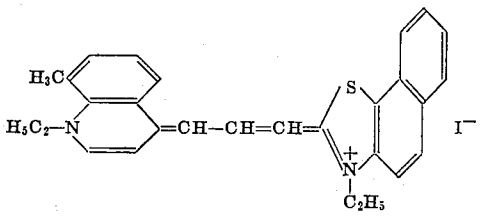
I-9



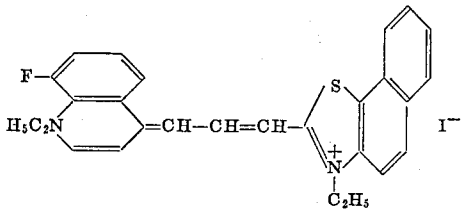
I-10



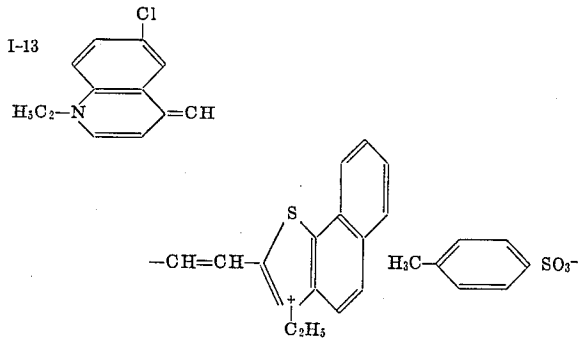
I-11



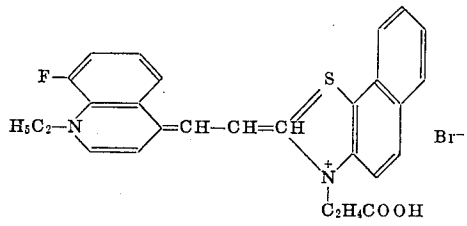
I-12



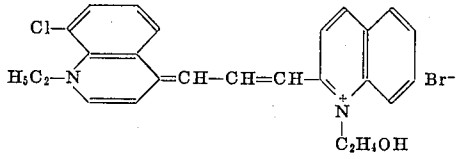
I-13



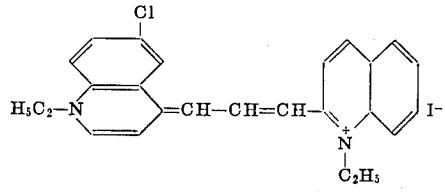
I-14



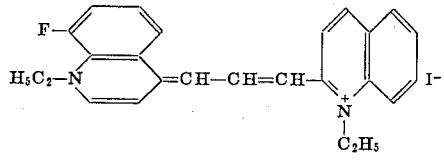
I-15



I-16



I-17



The examples of the present invention are concretely described below, but it should be noted that the present invention is not limited to these examples.

EXAMPLES

To different portions of silver halide emulsions from the same batch were added (1) only a sensitizing dye shown by general formula (I); and (2) a combination of a sensitizing dye shown by general formula (I) and a formalin condensate. Each then was applied to a cellulose acetate base. If the pH was lowered by the addition of the formalin condensate into the emulsion, The pH was adjusted by the addition of an alkali. After drying, the film thus coated was exposed through a Fuji No. 7 Filter (made by Fuji Photo Film Co. LTD., transmitting light having a wavelength longer than 590 millimicrons) and then developed.

The sensitivity of the film is shown by the reciprocal of the exposure necessary to give fog +0.1 in optical density. The sensitivity in the case of incorporating only the sensitizing dye in the emulsion is defined to be 100, and the sensitivity in the case of incorporating the formalin condensate together with the sensitizing dye in the emulsion is shown by a comparison with the defined sensitivity.

In the case of incorporating only novalak-type condensate of substituted or unsubstituted polyhydroxybenzene and formaldehyde in the emulsion, no sensitizing action on the emulsion (or a very low sensitizing action) was produced, so that the the numerical value is not shown. The emulsions used in the comparative formulas were from the same batch, but in

other formulas various emulsions from different batches were used. The results are shown in table **1**, in which a silver chlorobromide emulsion from the same batch was used in examples 1 and 2; a silver bromo-iodide emulsion from the same batch was used in examples 3–10; **and a silver chloro-bromide emulsion from the same batch was used in examples** 11–18. Further, the photographic light sensitive elements prepared as in examples 1–2 and 11–18 were developed for 2 minutes at 20° C. in a developer having the composition shown in table **2**, and Those in examples 3–10 were developed for 4 minutes at 20° C. in a developer having the composition shown in table 3.

TABLE 1

Additives (mg./mol silver halide)	Sensitivity	Fog
1 (a) I-8 (35)	100	0.16
(b) I-8 (35)+Condensation product of β-resorcinic acid and formalin (350)	120	0.06
(c) I-8 (35)+Condensation product of β-resorcinic acid and formalin (1480)	135	0.06
(d) I-8 (35)+Condensation product of 4-Hydroxybenzoic acid hydrazide and formaldehyde C350)	120	0.08
(e) I-8 (35)+Condensation product of 3,5-Dihydroxybenzoic acid hydrazide and formaldehyde (28)	120	0.11
(f) I-8 (35)+Condensation product of p-Chlorophenol and formaldehyde (700)	190	0.08
(g) I-8 (35)+Condensation product of Sodium hydroxybenzene-sulfonic acid and formaldehyde (350)	120	0.12
(h) I-8 (35)+Condensation product of p-Hydroxybenzoic acid and formaldehyde	130	0.06
(i) I-8 (35)+Condensation product of O-Hydroxybenzoic acid and formaldehyde (1400)	250	0.08
2(j) I-6 (40)	100	0.08
(k) I-6 (40)+Condensation product of m-Hydroxybenzoic acid and formaldehyde (2800)	180	0.06
3(j) I-7 (39)	100	0.07
(m) I-7 (39)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (2800)	130	0.04
4(n) I-4 (78)	100	0.06
(o) I-4 (78)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (1400)	140	0.05
5(p) I-2 (72)	100	0.06
(q) I-2 (72)+Condensation product of o-Hydroxybenzoic acid and formaldehyde	150	0.04
6(r) I-3 (38)	100	0.06
(s) I-3 (38)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (2800)	130	0.06
7(t) I-5 (34)	100	0.06
(u) I-5 (34)+Condensation product of Hydroquinone and formaldehyde (1400)	290	0.06
8(v) I-1 (70)	100	0.06
(w) I-1 (70)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (70)	120	0.06
9(x) I-8 (70)	100	0.11
(y) I-8 (70)+Condensation product of Gallic acid and formaldehyde (2800)	150	0.06
10(a') I-9 (42)	100	0.04
(b') I-9 (42)+Condensation product of m-Hydroxybenzoic acid and formaldehyde (2800)	190	0.04
11(c') I-10 (84)	100	0.04
(d') I-10 (84)+Condensation product of m-Hydroxybenzoic acid and formaldehyde (5600)	120	0.04
12(eα) I-11 (41)	100	0.04
(f') I-11 (41)+Condensation product of m-Hydroxybenzoic acid and formaldehyde (2800)	130	0.04

Table 1 – Continued

13(g') I-12 (41)	100	0.04
(h'I-12 (41)+Condensation product of m-Hydroxybenzoic acid and formaldehyde (2800)	140	0.04
14(i') I-13 (45)	100	0.04
(j') I-13 (45)+Condensation product of m-Hydroxybenzoic acid and formaldehyde (1400)	200	0.04
15 (K') I-14 (40)	100	0.04
(l') I-14 (40)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (2800)	170	0.07
16(m') I-15 (38)	170	0.07
(n') I-15 (38)+Condensation product of o-HYdroxybenzoic acid and formaldehyde (2800)	210	0.04
17(o') I-16 (37)	100	0.09
(p') I-16 (37)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (2800)	250	0.04
18) (q') I-17 (35)	100	0.06
(r') I-17 (35)+Condensation product of o-Hydroxybenzoic acid and formaldehyde (2800)	170	0.04

Of course, the numerals in parentheses following the material identification are the amount in mg./mole silver halide.

TABLE 2

N-Methyl-p-aminophenol sulfate	3.1 g.
Sodium sulfite	45.0 g.
Hydroquinone	12.0 g.
Sodium carbonate (anhydrous)	67.5 g.
Potassium bromide	1.9 g.
Water, up to	1.01

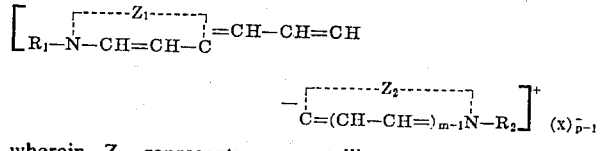
TABLE 3

N-Methyl-p-aminophenol sulfate	2.2 g.
Sodium sulfite	96.0 g.
Hydroquinone	8.8 g.
Sodium carbonate	48.0 g.
Potassium bromide	5.0 g.
Water, up to	1.01

the term "lower alkyl" in this specification means methyl group, ethyl group, propyl group, and butyl group. For R_6, an aralkyl group can have 1–8 carbon atoms. The condensation reaction is further described in "Preparative Methods of Polymer Chemesitry" published by John Wiley and Sons, Inc. in 1961, W. R. Sorenson and P. W. Campbell. Finally, the condensate reaction of the substituted or unsubstituted polyhydroxybenzene and formaldehyde is always carried out in acidic range.

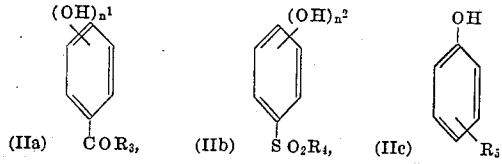
What is claimed is:

1. A photographic silver halide emulsion containing at least one sensitizing dye represented by the following general formula



wherein Z_1 represents nonmetallic atoms necessary to complete the 4-quinoline nucleus and Z_2 represents nonmetallic atoms necessary to complete 5–6 membered heterocyclic rings R_1 and R_2 are each a member selected from the class consisting of an alkyl group having one to five carbon atoms and an alkyl group substituted by a member selected from the class consisting of hydroxyl, acetoxy, sulfate carboxyl, carboxyalkoxyl, sulpho, hydroxysulpho, alkyoxy-sulphoalkoxy, m represents 1 or 2, x represents an anion, and p represents 1 or 2, and at least one condensate of formaldehyde and a member

selected from the group consisting of a substituted polyhydroxybenzene and an unsubstituted polyhydroxybenzene represented by the following general formula,



wherein R_3 and R_4 represents a member selected from the group consisting of OH, OM, OR_6, NHR_6, NH_2, $N(R_6)_2$, $NHNH_2$, $NHNHR_6$, wherein R_6 is a member selected from the group consisting of an alkyl group having one to eight carbon atoms, an aryl group, and an aralkyl group, and M is a member selected from metals consisting of an alkali metal and an alkaline earth metal, R_5 is a member selected from the group consisting of a hydroxyl group and halogen atoms, n^1 and n^2 each represents 1, 2 or 3.

2. The photographic silver halide emulsion claimed in claim 1, wherein said sensitizing dye contains at least one quinoline nucleus, which may also have substituted thereon groups selected from the class consisting of halogen atoms, and alkyl group having one to eight carbon atoms, and alkoxyl group and a hydroxyl group, and said formalin condensate has 2–10 units as a degree of polymerization and a molecular weight of 300–800.

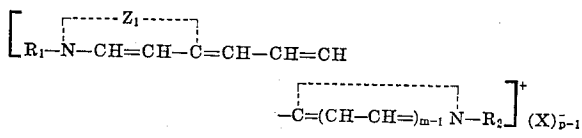
3. The photographic silver halide emulsion claimed in claim 1, wherein the concentration of said sensitizing dye is 0.002–0.2 g./mol. silver halide, and the concentration of said formalin condensate is 0.1–5.0 g./mol. silver halide.

4. The photographic silver halide emulsion claimed in claim 1, wherein the concentration ratio of said sensitizing dye to said formalin concentrate is from 1:5 to 1:500.

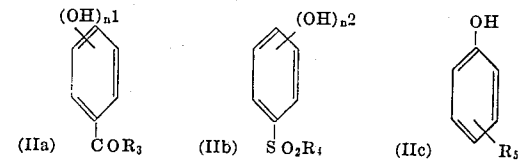
5. The photographic silver halide emulsion claimed in claim 1 wherein said silver halide emulsion is a gelatino silver halide emulsion.

6. The photographic silver halide emulsion claimed in claim 1, wherein said silver halide is from the group consisting of silver chloride, silver bromide, silver bromochloride, silver bromoiodide and silver bromochloroiodide.

7. A photographic silver halide element comprising a support and a photographic silver halide emulsion layer thereon containing at least one sensitizing dye represented by the following general formula:



wherein Z_1 represents nonmetallic atoms necessary to complete the 4-quinoline nucleus and Z_2 represents nonmetallic atoms necessary to complete 5–6 membered heterocyclic rings, R_1 and R_2 are each a member selected from the class consisting an alkyl group having one to five carbon atoms and an alkyl group substituted by a member selected from the group consisting of hydroxyl, acetoxyl, sulfate carboxyl, carboxyalkoxyl, sulpho, hydroxysulpho, alkyoxy-sulphoalkoxy, m represents 1 or 2, X represents an anion, and p represents 1 or 2, and at least one condensate of formaldehyde and a member selected from the group consisting of a substituted polyhydroxybenzene and an unsubstituted polyhydroxybenzene represented by the following general formula



wherein R_3 and R_4 each represents a member selected from the group consisting of OH, OH, OR_6, NHR_6, NH_2,$N(R_6)_2$, $NHNH_2$, $NHNHR_6$ 6wherein R_6 is a member selected from the group consisting of an alkyl group having one to eight carbon atoms, an aryl group and an aralkyl group, and M is a member selected from the group of metals consisting of an alkali metal and an alkaline earth metal, R_5 is a member selected from the consisting of a hydroxyl group and halogen atoms, n^1 and n^2 each represents 1, 2 or 3.