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sulfobutyl, a vinylmethyl, a benzyl, a p-carboxybenzyl, a p-sulfophenethyl or a phenyl group.

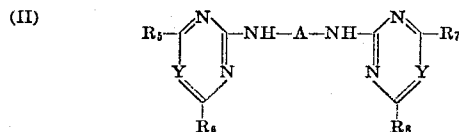
R_2 and R_3 in the general Formula I can be, for example, a methyl, an ethyl, a propyl, a β -hydroxyethyl, a β -acetoxyethyl, a sulfatoethyl, a carboxymethyl, a β -carboxyethyl, a γ -carboxypropyl, a β -sulfoethyl, a γ -sulfo-propyl, a δ -sulfobutyl, a vinylmethyl, a benzyl, a phenyl, a p-carboxybenzyl, and a p-sulfophenethyl group.

R_4 in the general Formula I can be, for example, a hydrogen atom, a methyl, an ethyl or a phenyl group.

Suitable examples of the heterocyclic ring containing Z in the general Formula I are thiazoles, such as thiazole and thiazoles having a methyl or a phenyl group in the ring; benzothiazoles, such as benbothiazole and benzothiazoles having nucleus substituents such as a halogen atom, alkyl, alkoxy and phenyl groups in the benzene ring; naphthothiazoles, such as α -naphthothiazole, β -naphthothiazole, tetrahydronaphthothiazole and naphthothiazoles having nucleus substituents such as an alkoxy group in any of the benzene rings; oxazoles, such as oxazole and oxazoles having substituents such as alkyl and phenyl groups in the ring; benzoxazoles, such as benzoxazole and benzoxazoles having nucleus substituents such as a halogen atom, methyl, ethyl, ethoxy, hydroxy and phenyl groups in the benzene ring; naphthoxazoles such as α -naphthoxazole and β -naphthoxazole; selenazoles, such as 4-methylselenazole and 4-phenylselenazole; benzoselenazoles, such as 5-chlorobenzoselenazole, 5-methylbenzoselenazole, 5-methoxybenzoselenazole and 5-hydroxybenzoselenazole; naphthoselenazoles, such as α -naphthoselenazole and β -naphthoselenazole; thiazolines, such as thiazoline and 4-methylthiazoline; 2-quinolines, such as 2-quinoline and 2-quinolines having nucleus substituents (exclusive of the 2-position) such as a halogen atom, methyl, methoxy and hydroxyl groups in any of the benzene rings; 4-quinolines, such as 4-quinoline and 4-quinolines having nucleus substituents (exclusive of the 4-position) such as methyl and methoxy groups in any of the benzene rings; benzimidazoles, such as 1,3-diethylbenzimidazole, 1,3-diethyl-5-chlorobenzimidazole and 1,3-diethyl-5,6-dichlorobenzimidazole; 3,3'-dialkylindolenines, such as 3,3'-dimethylindolenine, 3,3',5-triethylindolenine and 3,3',7-trimethylindolenine; 2-pyridines, such as 2-pyridine and 2-pyridines having nucleus substituents (exclusive of the 2-position) such as methyl group, and 4-pyridines, such as 4-pyridine.

The sensitizing dye represented by the general Formula I is a dye having four hetero radicals wherein two keto-methylene radicals are directly bonded. The sensitizing dye can sensitize a silver halide emulsion strongly in co-existence with the dye used in the silver-dye bleaching method. Since the dye gives a more excellent sensitivity even in the case of a small quantity of the dye added per g-mole of the silver halide in comparison with conventional basic cyanine dyes, any photographic layer containing the dye substantially is freed from any color remaining after processing.

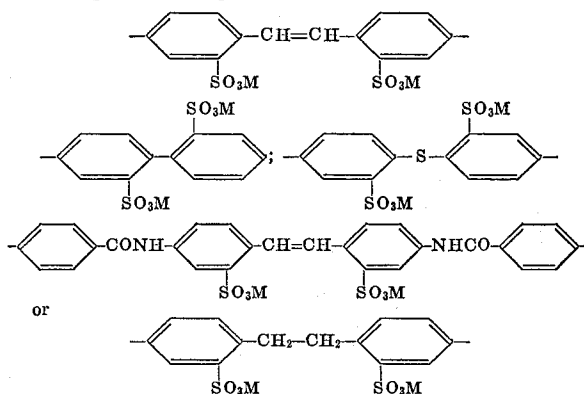
The sensitizing dye represented by the general Formula I can favorably sensitize an emulsion used in the silver-dye bleaching method, containing a dye suitable for the silver-dye bleaching method, without any aid, but the supersensitization thereof by a compound represented by the following general Formula II or III is preferred.



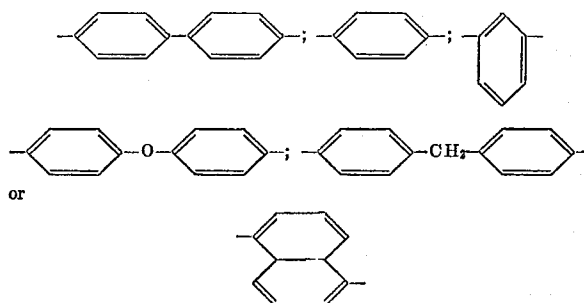
In Formula II, Y represents =CH— or =N—, R_5 , R_6 , R_7 and R_8 , each represents a hydrogen atom, a hydroxyl group, an alkoxy group, an aryloxy group, a substituted aryloxy group such as phenoxy, o-toloxyl or p-sulfo-phenoxy group, a halogen atom such as a chlorine or a bromine atom, a heterocyclic nucleus such as morpholinyl or piperidyl, an alkylthio group such as a methylthio or an

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ethylthio group, a heterocyclic thio group such as a benzothiazylthio group, an arylthio group such as a phenylthio or a tolylthio group, an amino group, an alkylamino group or a substituted alkylamino group such as a methylamino, an ethylamino, a propylamino, a dimethylamino, a diethylamino, a dodecylamino, a cyclohexylamino, a β -hydroxyethylamino, a di- β -hydroxyethylamino or a β -sulfoethylamino group, an arylamino group or a substituted arylamino group such as an anilino, an o-sulfoanilino, a m-sulfoanilino, a p-sulfoanilino, an o-anisilamino, a m-anisilamino, a p-anisilamino, an o-toluidino, a m-toluidino, a p-toluidino, an o-carboxyanilino, a m-carboxyanilino, a p-carboxyanilino, a hydroxyanilino, a naphthylamino or a sulfonaphthylamino group, a heterocyclicamino group such as a 2-benzothiazoleamino or a 2-pyridylamino group, or an aryl group such as a phenyl group, and A represents A_1 or A_2 , in the following, wherein A_1 is:

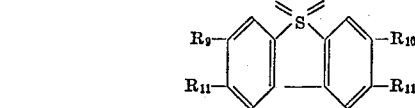


wherein A_2 is:



in particular, at least one of R_5 , R_6 , R_7 and R_8 representing a substituent containing a $-\text{SO}_3\text{M}$ group when A is A_2 .

(III)



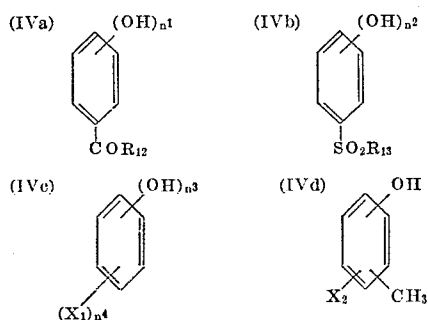
In Formula III, R_9 represents an acylamino group such as an acetamide, a sulfobenzamide, a 4-methoxy-3-sulfobenzamide, a 2-ethoxybenzamide, a 2,4-diethoxybenzamide, a p-toluylamino, a 4-methyl-2-methoxybenzamide, a 1-naphthylamino, a 2-naphthylamino, a 2,4-dimethoxybenzamide, a 2-phenylbenzamide, or a 2-thienylbenzamide group, or a sulfo group, R_{10} represents an acylamino group such as defined for R_9 , R_{11} represents a hydrogen atom or a sulfo group and the general Formula III has at least one sulfo group.

The sensitizing dye represented by the general Formula I is used more advantageously through supersensitization with a novolak type condensate of a polyhydroxybenzene and formaldehyde where the term polyhydroxybenzene is intended to encompass a substituted benzene having from 1 to 3 hydroxyl groups on the benzene nucleus. The "novolak type condensate of the polyhydroxy-

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benzene and formaldehyde" will hereinafter be referred to as the "formalin condensate."

The polyhydroxybenzene is represented by the following general Formulae (IVa, IVb, IVc, IVd,



in which R_{12} and R_{13} each represents $-\text{OH}$, $-\text{OM}$, $-\text{OR}_{14}$, $-\text{NH}_2$, $-\text{NHR}_{14}$, $-(\text{R}_{14})_2$, $-\text{NHNH}_2$ and $-\text{NHNHR}_{14}$, R_{14} represents an alkyl group of from 1 to 8 carbon atoms, an aryl group or an aralkyl group, M represents an alkali metal or an alkaline earth metal, X_1 represents $-\text{OH}$ or a halogen atom, X_2 represents a halogen atom, and n^1 , n^2 , n^3 and n^4 each represents 1, 2 or 3 except that n^3 and n^4 are equal to 3 at the same time.

The sensitizing dye of the invention, represented by the general Formula I is described in British Pats. Nos. 487,051 and 489,335, and in U.S. Pat. No. 2,504,615.

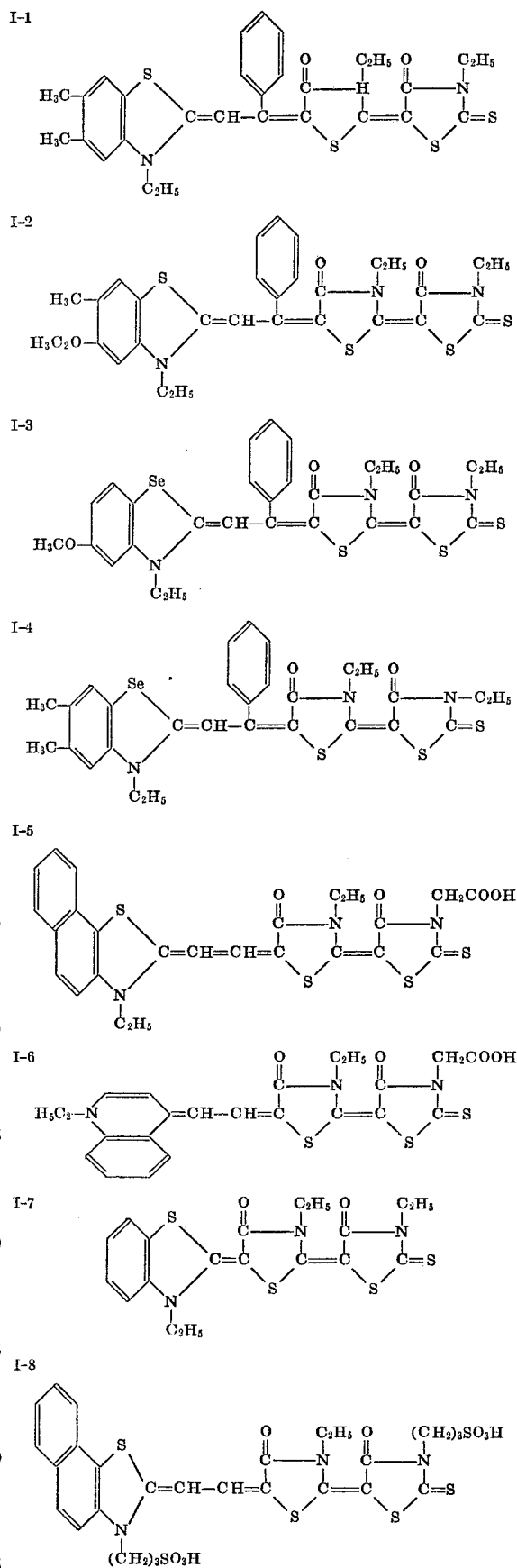
Some of the compounds represented by the general Formula II are described, for example, in U.S. Pats. 2,171,427; 2,660,578 and 2,595,030. A method of synthesis of the "formalin condensate" is illustrated as follows.

The condensate of the polyhydroxybenzene can be synthesized according to the conventional synthesis method for phenol-formaldehyde resins of the novolak type [for example, as described in W. R. Sorenson, T. W. Campbell, Preparative Methods of Polymer Chemistry, John Wiley and Sons, Inc. (1961)]. The poly-substituted hydroxybenzene is dispersed in water, heated after concentrated hydrochloric acid and 37% formalin are added and held at 100°C . for 30 minutes to 1 hour with agitation. Then, if necessary, hydrochloric acid is further added and the heating with agitation is continued. After the reaction, the reaction product is removed into cold water and the resultant precipitate can be purified. As an example, 415 parts of p-hydroxybenzoic acid is dispersed in 1,000 parts of water with vigorous agitation, to which 25 parts of a 35% or more concentrated hydrochloric acid and 245 parts of 37% formalin are added. Then, the reaction mixture is heated at 100°C . with agitation and held as is for 30 minutes, to which 20 parts of concentrated hydrochloric acid is added additionally followed by reaction for 30 minutes. At this point, 20 parts of concentrated hydrochloric acid is further added thereto and the stirring is continued until the reaction solution becomes cloudy. After about 1 hour and 30 minutes, the stirring is stopped and the mixture is removed into 3,000 parts of cold water with stirring. The resulting precipitate is filtered, redissolved in 1,000 parts of methanol without drying, and then reprecipitated with water. The product is obtained by filtering and dried. Other condensates can be obtained readily using other polyhydroxybenzenes in place of the p-hydroxybenzoic acid used in the above-described method. The condensation unit (degree of polymerization) of the condensate obtained by the above-described method is from 2 to 10 as in the usual novolak resins.

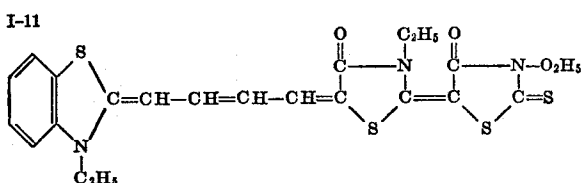
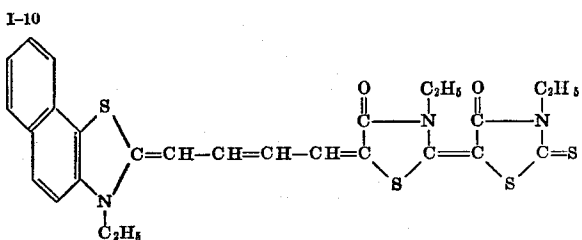
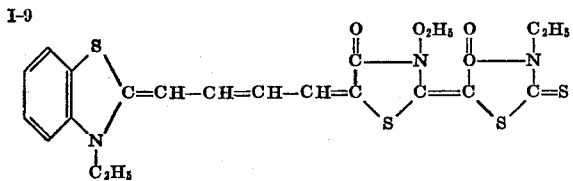
For the purpose of the invention, condensates having a polymerization degree of from 2 to 10, preferably having a polymerization degree of from 2 to 5 and a molecular weight of from 300 to 800 are suitable.

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Examples of the sensitizing dyes used in the invention are given as follows without limiting the invention.



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The sensitizing dye represented by the general Formula I is added to a photographic layer used in the silver-dye bleaching method with a dye suitable for the silver-dye bleaching method. In particular, the sensitizing dye pref-

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erably is added to an emulsion before coating, washed with water, before a dye suitable for the silver dye bleaching method is added.

The method of adding a sensitizing dye to a photographic emulsion is well known in making photographic emulsions. Generally, it is added to a photographic emulsion in the form of a solution in water or an organic solvent such as methanol or ethanol.

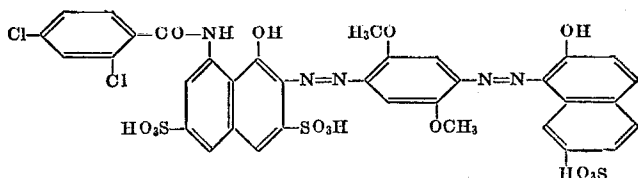
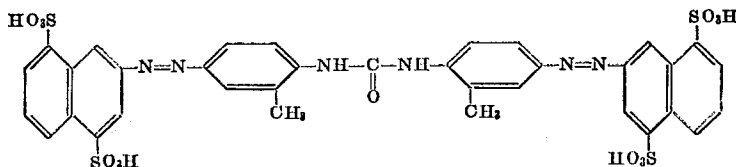
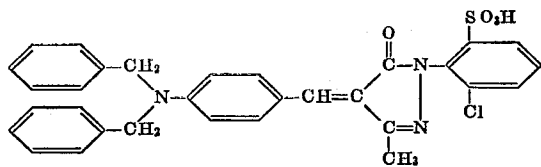
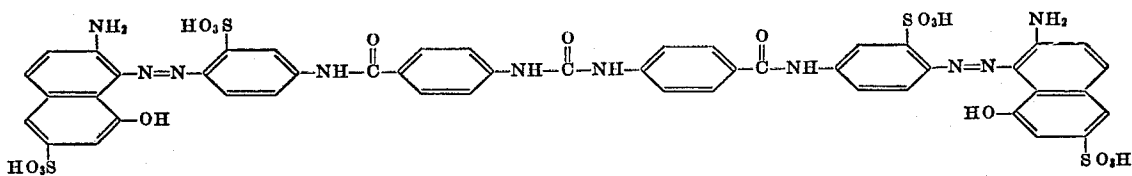
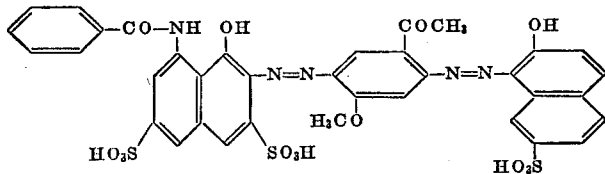
As the emulsion of the invention silver halides such as silver chloride, silver bromide, silver iodobromide, silver chlorobromide or silver chloriodobromide can be used. The usual gelatino-silver halide emulsion is used in the invention, but cellulose derivatives and resinous materials which do not affect the light-sensitive materials can be used in place of gelatin.

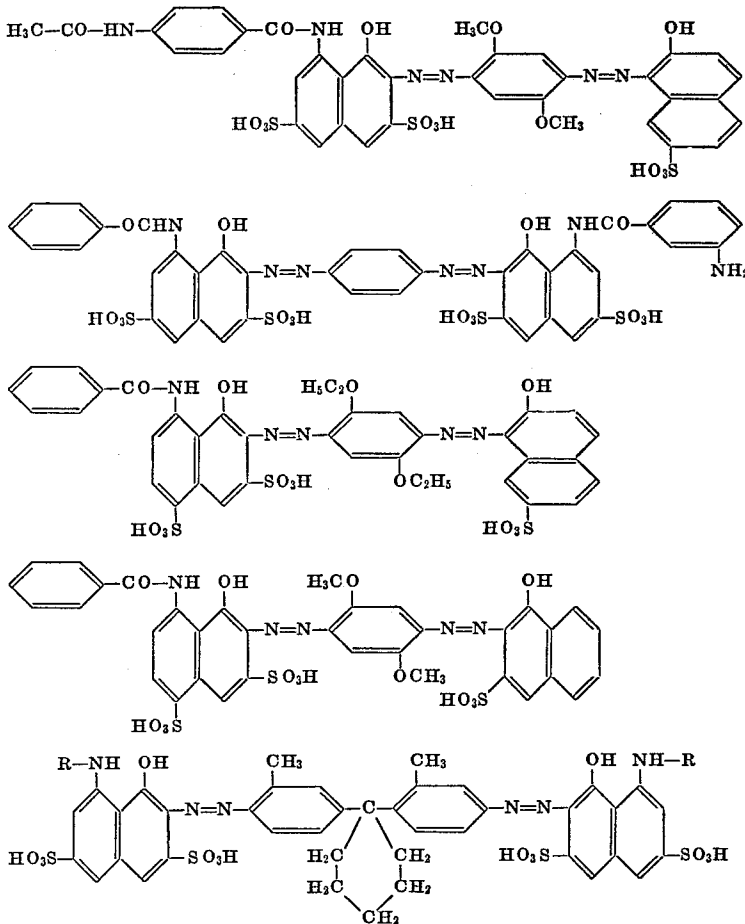
The photographic emulsion used in the invention can contain conventional additives such as chemical sensitizers, fog inhibitors, stabilizers, hardeners, coating aids, plasticizers, development accelerators and air fog inhibitors.

The photographic emulsion can be coated onto a suitable support such as glass, cellulose derivative films, synthetic resin films, laminated papers or synthetic papers in conventional manner.

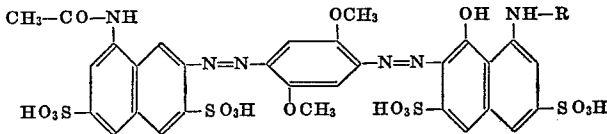
The dye suitable for the silver dye bleaching method and used in combination with the sensitizing dye represented by the general Formula I is a dye used conventionally in the silver-dye bleaching method, preferably containing a phenolic hydroxyl group or a sulfonate group.

Suitable dyes are described in Japanese Patent Publications 10,280/61, 9,587/64, and 25,768/64; U.S. Pats. 3,264,109, 3,454,402, 3,178,291, 3,385,706, 3,455,695, 3,259,498, 3,244,525, 3,304,181, 3,322,543, 3,210,190, 3,454,401, 3,211,554 and 3,223,527. Suitable examples are as follows:





with R being a p-toluenesulfone group or a 4-acetylamino-benzoyl group,



with R being a benzoyl, a 4-acetylamino-benzoyl or a 4-benzoylamino-benzoyl group.

The following examples are given in order to illustrate the invention further without limiting the scope thereof.

EXAMPLE 1

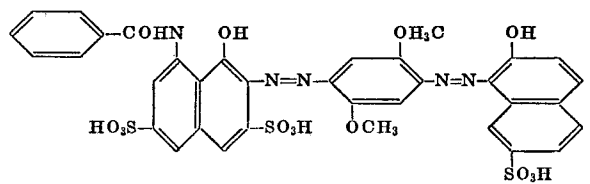
9.68 x 10⁻⁵ g.-mol/g.-mol silver halide of a sensitizing dye was added to a silver chlorobromide emulsion (Br 40 mol percent, Cl 60 mol percent) and stirred adequately for 20 minutes. 24.2 g./g.-mol silver halide of a dye represented by the following structural formula was added thereto, stirred adequately and coated onto a cellulose triacetate base. The coated photographic layer was exposed through a step wedge of a blue light (Latten Filter No. 47B) and a red light (Fuji Filter No. 7), developed and fixed. The development was carried out using the composition of Table 1 at 20° C. for 2 minutes.

The results are shown in Table 2 wherein a larger value means a higher sensitivity.

TABLE 1

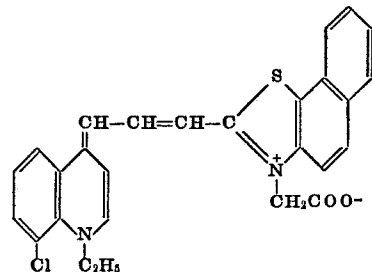
N-methyl-p-aminophenol sulfate -----	3.1	70
Sodium sulfite -----	45	
Hydroquinone -----	12	
Sodium carbonate (anhydrous) -----	67.5	
Potassium bromide -----	1.9	
Water to 1000 ml.		75

STRUCTURAL FORMULA OF DYE USED



STRUCTURAL FORMULA OF COMPARISON SENSITIZING DYE USED

I-a (for comparison)



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I-b (for comparison)

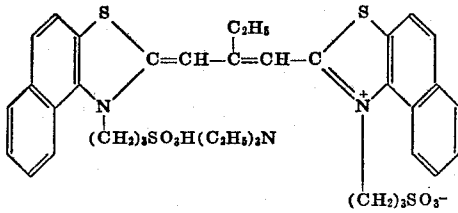


TABLE 2

Sensitizing dye	Relative sensitivity (log)	
	Red sensitivity	Blue sensitivity
I-1	1.14	0.52
I-2	1.04	0.50
I-3	1.10	0.50
I-4	1.18	0.54
I-5	1.10	0.52
I-6	1.09	0.48
I-a	0.81	0.50
I-b	0.80	0.55

EXAMPLE 2

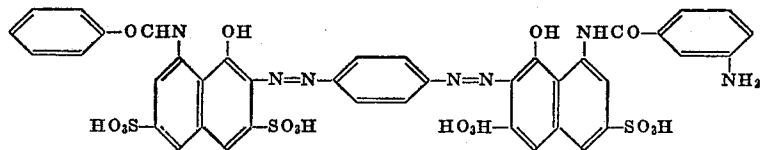
A sensitizing dye or a sensitizing dye and super-sensitizer were added to a silver iodobromide emulsion (iodine 7.0 mol percent) and stirred adequately for 20 minutes. Then, 19.0 g./g.-mol silver halide of a dye represented by the following structural formula was added thereto, stirred adequately, mixed with an ordinary coating aid and hardener and coated onto a baryta paper.

The results obtained are shown in Table 3.

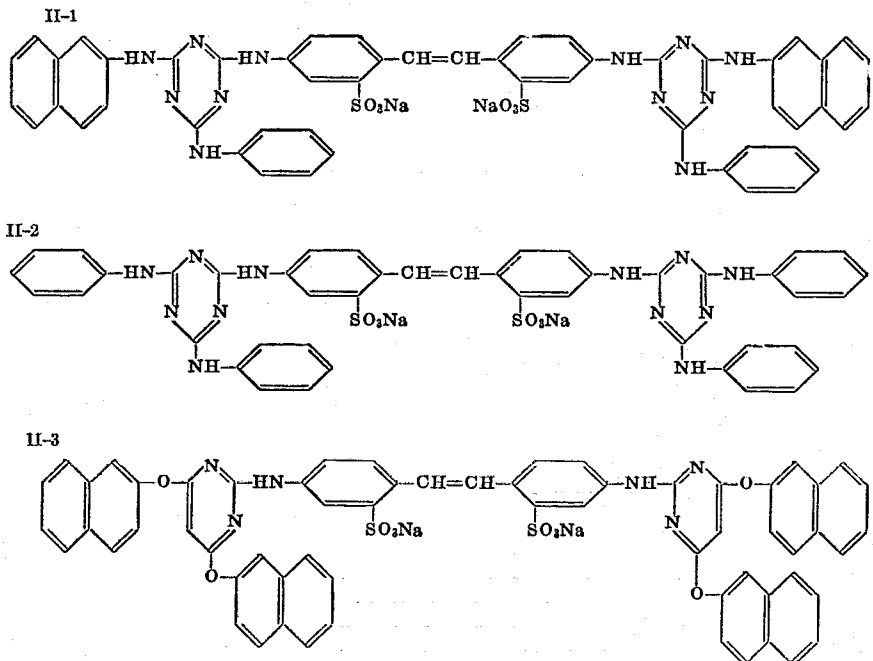
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- (1) Development—5 minutes
- p-Methylaminophenol ----- 1
Hydroquinone ----- 3
Sodium sulfite (anhydrous) ----- 13
Potassium bromide ----- 1
Sodium carbonate (anhydrous) ----- 26
Water to 1000 ml.
- (2) Water washing—5 minutes
- (3) Fixing—5 minutes
- Crystalline sodium thiosulfate ----- G.
Potassium metabisulfite ----- 200
Water to 1000 ml.
- (4) Water washing—5 minutes
- (5) Hardening—5 minutes
- 30% aqueous solution of formaldehyde ...ml... 100
Sodium bicarbonate -----g... 2
Water to 1000 ml.
- (6) Water washing—5 minutes
- (7) Dye bleaching—15 minutes
- Thiourea -----g... 28
Potassium bromide -----g... 18
2-amino-3-hydroxyphenazine -----mg... 3
Concentrated hydrochloric acid -----ml... 200
Water to 1000 ml.
- (8) Water washing—5 minutes
- (9) Bleaching fixing—10 minutes
- Tetrasodium ethylenediaminetetraacetate ----- 26
Anhydrous sodium carbonate ----- 24
Ferric chloride ----- 15
Sodium sulfite (anhydrous) ----- 13
Sodium thiosulfite (crystalline) ----- 200
Water to 800 ml.
- (10) Water washing—20 minutes

Structural Formula of Dye Used



Structural Formula of Supersensitizer Used



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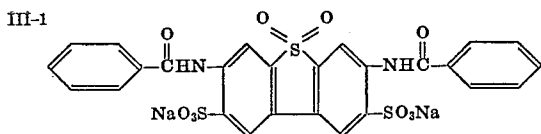


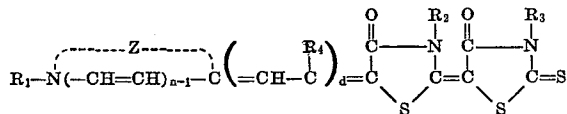
TABLE 3

Sensitizing dye	Supersensitizer and amount	Relative sensitivity (red sensitivity)
I-1	Plus II-1 (950) ¹	1.78
I-1		2.16
I-2		1.70
I-2	Plus II-2 (950)	2.12
I-3		1.50
I-3	Plus II-3 (950)	1.78
I-4		1.56
I-4	Plus III-1 (950)	1.92
I-5		1.70
I-5	Plus condensate of p-chlorophenol and formaldehyde (5,700)	1.95

¹ Mg./g.-mol silver halide.

What is claimed is:

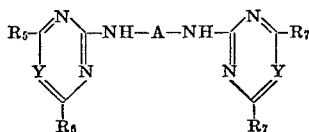
1. A light-sensitive silver halide emulsion containing an azo dye capable of being bleached out in the silver dye bleaching process and at least one sensitizing dye having the following general Formula I



wherein R_1 is selected from the group consisting of an alkyl group, a hydroxyalkyl group, an acetoxyalkyl group, a sulfatoalkyl group, a carboxyalkyl group, a vinylalkyl group, a carboxyarylalkyl group, a sulfoarylalkyl group, a sulfoalkyl group, an aralkyl group, and an aryl group, wherein R_2 and R_3 each is selected from the group consisting of a hydrogen atom, an alkyl group, a hydroxyalkyl group, an acetoxyalkyl group, a sulfatoalkyl group, a carboxyarylalkyl group, an allyl group, carboxyalkyl group, sulfoalkyl group, an aralkyl group, a sulfoarylalkyl group, and an aryl group, wherein R_4 is selected from the group consisting of a hydrogen atom, an alkyl group and an aryl group, wherein Z is a non-metallic atom group necessary to complete a 5- or 6-membered heterocyclic ring ordinarily employed in cyanine dyes, wherein d represents 0, 1 or 2 and n represents 1 or 2.

2. The light-sensitive silver halide emulsion as claimed in claim 1, wherein R_1 , R_2 and R_3 are selected from the group consisting of methyl, ethyl, propyl, β -hydroxyethyl, β -acetovyethyl, sulfatoethyl, carboxymethyl, β -carboxyethyl, γ -carboxypropyl, β -sulfoethyl, γ -sulfoethyl, δ -sulfoethyl, vinylmethyl, benzyl, phenethyl, p-carboxybenzyl, p-sulfophenethyl and phenyl groups; and the heterocyclic ring containing Z is selected from the group consisting of the thiazoles, benzothiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthothiazoles, selenazoles, benzoselenazoles, naphthoselenazoles, thiazolines, 2-quinolines, 4-quinolines, benzimidazoles, 3,3'-dialkylindolenines, 2-pyridines and 4-pyridines.

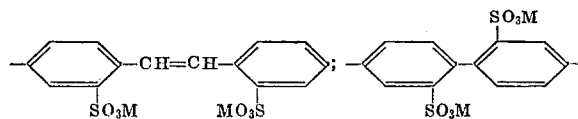
3. A supersensitized photographic emulsion wherein the light-sensitive silver halide emulsion of claim 1 contains additionally at least one compound having the following Formula II.



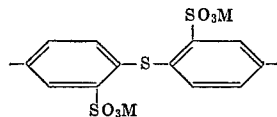
wherein Y is selected from the group consisting of $=\text{CH}-$ and $=\text{N}-$, wherein R_5 , R_6 , R_7 , and R_8 each is selected from the group consisting of a hydrogen atom, a hydroxyl group, an alkoxy group, an aryloxy group,

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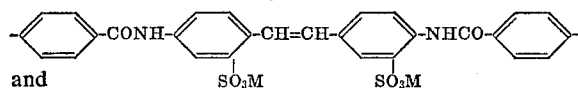
phenoxy group, a toloxy group, a sulfophenoxy group, a halogen atom, a heterocyclic nucleus, an alkylthio group, a heterocyclicthio group, an arylthio group, an amino group, an alkylamino group, a sulfoaryl amino group, a carboxyaryl amino group, an arylamino group, a hydroxy arylamino group, an anisilamino group, a toluidino group, an anilino group, a heterocyclic amino group and an aryl group, and wherein A is selected from the group consisting of A_1 and A_2 , wherein A_1 is selected from the group consisting of



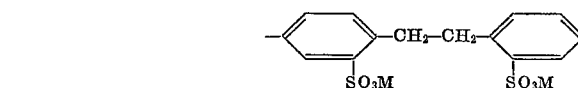
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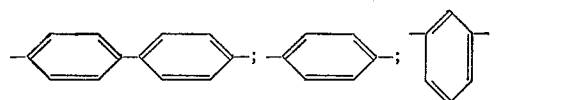
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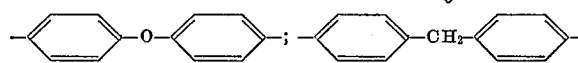
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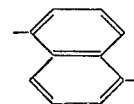
wherein A_2 is selected from the group consisting of

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and



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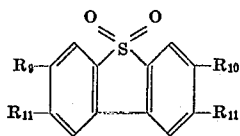
and wherein at least one of R_5 , R_6 , R_7 and R_8 contains a substituent containing a $-\text{SO}_3\text{M}$ group when A is A_2 .

4. The supersensitized photographic emulsion as claimed in claim 3, wherein said toloxy group is an o-toloxyl and said sulfophenoxy group is a p-sulfophenoxy group, wherein the heterocyclic nucleus is selected from the group consisting of a morpholinyl and a piperidyl group; wherein the heterocyclicthio group is a benzothiazylthio group; wherein said hydroxy arylamino group is selected from the group consisting of a β -hydroxyethylamino, and a di- β -hydroxyethylamino, and said alkylamino is a β -sulfoethylamino group; wherein said sulfoaryl amino group is selected from the group consisting of an o-sulfoanilino, a m-sulfoanilino, and a p-sulfoanilino group, said anisilamino is selected from the group consisting of an o-anisilamino a m-anisilamino, and a p-anisilamino group, said toluidino is selected from the group consisting of an o-toluidino, a m-toluidino, and a p-toluidino group, said anilino group is selected from the group consisting of an o-carboxyanilino, a m-carboxyanilino, a p-carboxyanilino, and a hydroxyanilino group, said aryl group is selected from the group consisting of a naphthylamino and a sulfonaphthylamino group; and wherein the heterocyclicamino group is selected from the group consisting of a 2-benzothiazole-amino and a 2-pyridylamino group.

5. The supersensitized photographic emulsion wherein the light-sensitive silver halide emulsion of claim 1,

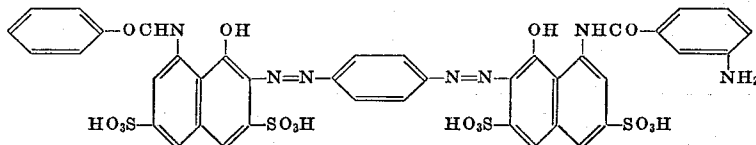
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contains additionally at least one of compound having the following general Formula III



wherein R₉ is selected from the group consisting of an acylamino group and a sulfo group, wherein R₁₀ is an acylamino group and wherein R₁₁ is selected from the group consisting of a hydrogen atom and a sulfo group; and wherein said compound has at least one sulfo group.

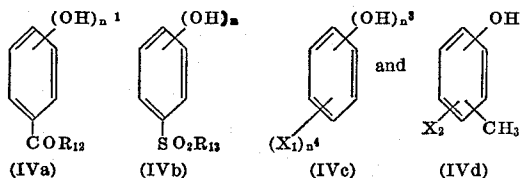
6. The supersensitized photographic emulsion as claimed in claim 5, wherein the acylamino group is



selected from the group consisting of an acetamide, a sulfobenzamide, a 4-methoxy-3-sulfobenzamide, a 2-ethoxybenzamide, a 2,4-diethoxybenzamide, a p-toluylamino, a 4-methyl-2-methoxybenzamide, a 1-naphthylamino, a 2-naphthylamino, a 2,4-dimethoxybenzamide, a 2-phenylbenzamide and a 2-thienylbenzamide group.

7. The supersensitized photographic emulsion wherein the light-sensitive silver halide emulsion of claim 1, contains additionally a condensate of a polyhydroxybenzene having from 1 to 3 hydroxyl groups on the benzene nucleus and formaldehyde.

8. The supersensitized photographic emulsion as claimed in claim 7, wherein the condensate is a novolak type condensate of formaldehyde and a polyhydroxybenzene selected from the group consisting of compounds having the following general formula:



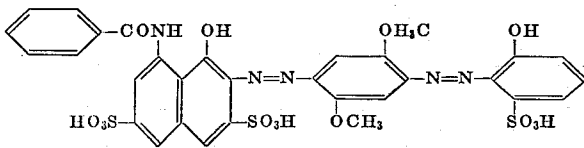
wherein R₁₂ and R₁₃ each is selected from the group consisting of -OH, -OM, -OR₁₂, -NH₂, -NHR₁₄, -N(R₁₄)₂, -NHNH₂ and -NHNHR₁₄, wherein R₁₄ is selected from the group consisting of an alkyl group having from 1 to 8 carbon atoms, an aryl group and an aralkyl group, wherein M is selected from the group consisting of an alkali metal and an alkaline earth metal, wherein X₁ is selected from the group consisting of OH and a halogen atom, wherein X₂ is a halogen atom, wherein n¹, n², n³ and n⁴ each represents 1, 2, 3 except that n³ and n⁴ are equal to 3 simultaneously.

9. The supersensitized photographic emulsion as claimed in claim 8, wherein the condensate has a con-

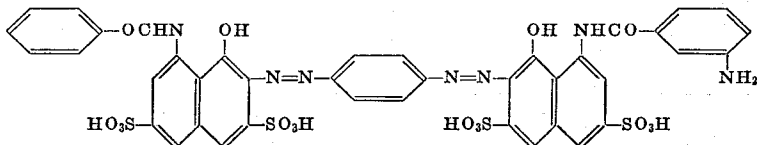
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densation unit of from 2 to 5 and a molecular weight of from 300 to 800.

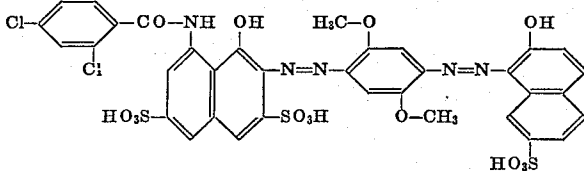
10. The light-sensitive silver halide emulsion as claimed in claim 1, wherein the dye capable of being bleached out in the silver dye bleaching process is



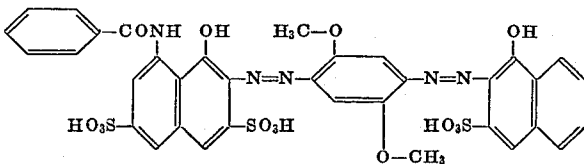
11. The light-sensitive silver halide emulsion as claimed in claim 1, wherein the dye capable of being bleached out in the silver dye bleaching process is



12. The light-sensitive silver halide emulsion as claimed in claim 1, wherein the dye capable of being bleached out in the silver dye bleaching process is



13. The light-sensitive silver halide emulsion as claimed in claim 1, wherein the dye capable of being bleached out in the silver dye bleaching process is



14. A photographic light-sensitive element comprising a support thereon at least a layer containing the light-sensitive silver halide emulsion as claimed in claim 1.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96-123