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3,728,125

PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL SUITABLE FOR SILVER-DYE BLEACHING METHOD

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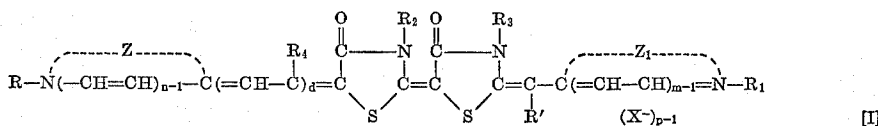
Int. Cl. G03c 1/10

U.S. Cl. 96-99

14 Claims

ABSTRACT OF THE DISCLOSURE

A light-sensitive silver halide emulsion containing a dye capable of being bleached in the silver dye bleaching process and at least one sensitizing dye having the general Formula I



wherein R, R₁, R₂ and R₃ each is selected from the group consisting of an alkyl, a substituted alkyl, an allyl, an aralkyl, a substituted aralkyl and an aryl group; wherein R' is selected from the group consisting of a hydrogen atom, an alkyl group, a substituted alkyl group, and an aliphatic chain to be combined with the N of the heterocyclic ring containing Z₁; wherein R₄ is selected from the group consisting of a hydrogen atom, an alkyl and an aryl group; wherein m, n, and p are 1 or 2, and d represents 0, 1 or 2; wherein X represents an anion, wherein an intramolecular salt is formed when p=1; and wherein Z and Z₁ each is the non-metallic atomic group necessary to complete a 5- or 6-membered heterocyclic ring, is disclosed. The emulsion can be super-sensitized by the addition of a supersensitizing dye to the emulsion.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to the spectral sensitization of a photographic light-sensitive layer containing a dye suitable for use with the silver-dye bleaching method.

(2) Description of the prior art

It is well known that mono- or multi-colored photographic images are obtained by the silver-dye bleaching method based on breakage of a dye depending on the quantity of developed silver. In this method, an image is recorded firstly as a silver image on a light-sensitive layer colored uniformly with a dye using ordinary exposing and developing methods. Then the dye present in this layer is decomposed in proportion to the quantity of silver present sectionally by the silver-dye bleaching bath. Thereafter, the silver is removed to retain a dye layer having a reverse gradation to that of the original silver image. In the silver-dye bleaching method also, as is well known, the use of a multi-layer material having three or more component color layers of sensitivity-differing spectrum regions is advantageous to obtain a multi-colored photograph as in the case of the color developing

method of color forming type using a multi-layer photographic material. For example, such a material comprises on a support member a red-sensitive layer containing a cyan dye, a green-sensitive layer containing a magenta dye, a yellow filter layer capable of decreasing the intrinsic sensitivity of the layers under the filter layer and a blue-sensitive layer containing a yellow dye as an uppermost layer.

One of the disadvantages of the silver-dye bleaching method is that the light-sensitive speed of a dyed photographic layer is considerably decreased, because the maximum wavelength of sensitivity substantially coincides with the adsorption maximum wavelength of the dye. The sensitivity of the light-sensitive layer in the silver-dye bleaching method is lower than that of other color photographic methods. Therefore, one of large difficulties present with the silver-dye bleaching method is to prepare a layer having sufficient sensitivity.

In making silver halide emulsions, a sensitizing dye

is added to silver halide thus to enlarge the spectral region of sensitivity of the silver halide emulsion and to sensitize optically. The sensitizing dye used in a light-sensitive material for the silver-dye bleaching method must satisfy certain necessary conditions. The sensitizing dye should not have adverse influences upon the sensitivity and the stability of the emulsion, in particular, during storage. Furthermore, the sensitizing dye should not result in color remaining after processing of the photographic material. Furthermore, the sensitizing dye should be adsorbed fast on silver halide grains not so as to be substituted by a dye suitable for the silver-dye bleaching method. Otherwise, the sensitizing action is decreased by the presence of the dye suitable for the silver-dye bleaching method. Many of the sensitizing dyes used hitherto in silver halide materials are not suitable for the silver-dye bleaching method.

For example, the basic cyanine tends to be desorbed from the silver halide grains by a dye having a sulfonate group, suitable for the silver-dye bleaching method. Betaine cyanines may be used as the sensitizing dye for a photographic layer in the silver-dye bleaching method, but often a slight coloring is retained therein.

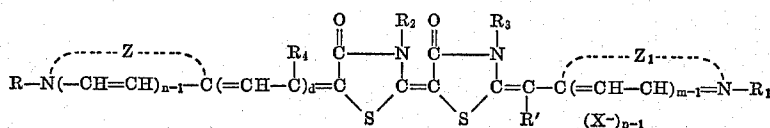
It is an object of this invention to provide a sensitizing dye available for a silver halide emulsion used in the silver-dye bleaching method.

It is another object of this invention provide a photographic material constituted of at least one light-sensitive silver halide emulsion layer optically sensitized and containing a dye suitable for the silver-dye bleaching method.

Other objects will be apparent from the following description and examples.

SUMMARY OF THE INVENTION

A photographic light-sensitive layer suitable for the silver-dye bleaching method and having an extraordinarily high sensitivity is prepared by adding to a silver halide emulsion containing a dye suitable for the silver dye bleaching method, a sensitizing dye, as a sensitizer, represented by the following generally Formula I:



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wherein R, R₁, R₂ and R₃ each represents alkyl, substituted alkyl, allyl, aralkyl, substituted aralkyl and aryl groups; wherein R' represents a hydrogen atom, an alkyl group, a substituted alkyl group or an aliphatic chain to be combined with N in the heterocyclic ring containing Z₁; wherein R₄ represents a hydrogen atom, an alkyl group or an aryl group; wherein m, n and p represent respectively 1 or 2, and d represents 0, 1 or 2; wherein X represents an anion; and wherein Z and Z₁ each represents the non-metallic atom groups necessary to complete a 5- or 6-membered heterocyclic ring. An intramolecular salt is formed when p=1.

R, R₁, R₂ and R₃ in the general Formula I can be, for example, a methyl, an ethyl, a propyl, a β-hydroxyethyl, a β-acetoxyethyl, a sulfato ethyl, a carboxymethyl, a β-carboxyethyl, a γ-carboxypropyl, a β-sulfoethyl, a γ-sulfopropyl, a δ-sulfobutyl, a vinyl-methyl, a benzyl, a phenethyl, a p-carboxybenzyl, a p-sulfophenethyl and a phenyl group.

R₄ in the general Formula I can be, for example, a methyl, an ethyl or a phenyl group. The substituted alkyl group R' in the general Formula I can be, for example, a β-hydroxyethyl, a β-acetoxyethyl or a β-aminoethyl group.

X in the general Formula I can be, for example, a chloride ion, a bromide ion, a perchlorate ion, a p-toluenesulfonate ion, a benzenesulfonate ion, an ethylsulfate ion or a methylsulfate ion.

Examples of the heterocyclic ring containing Z or Z₁ 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 benzothiazole 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 those 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, hydroxyl 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'-trimethylindolenine;

2-pyridine, such as 2-pyridine and 2-pyridines having nucleus substituents (exclusive of the 2-position), such as a methyl group; and 4-pyridines, such as 4-pyridine.

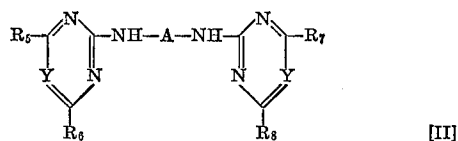
The sensitizing dye represented by the general Formula I is a dye having four hetero radicals wherein two ketomethylene radicals are directly bonded, which can sensitize a silver halide emulsion strongly in the coexistence with the dye used in the silver-dye bleaching method. Since it gives a more excellent sensitivity even in the case of a small quantity of the dye added per g-mole of silver

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halide in comparison with the conventional basic cyanine dyes, any photographic layer containing it is substantially freed from color remaining after processing.

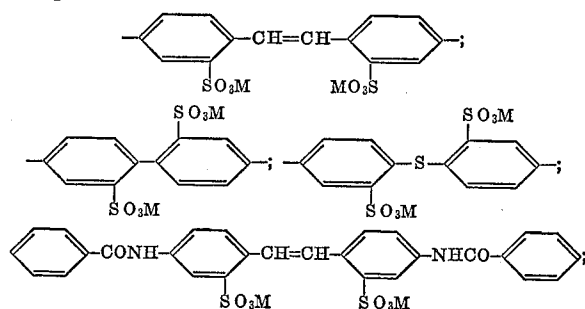
The sensitizing dye represented by the general Formula I can favorably sensitize an emulsion used in the silver-dye bleaching method, containing a dye suitable for the silver-dye bleaching method, without any aid, but super-sensitization of the sensitizing dye by a compound represented by the following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

Compound II has the general formula shown below:

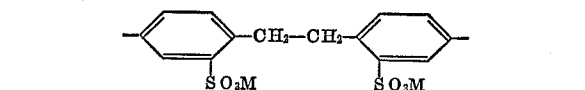


In this formula, Y represents =CH— or =N—; R₅, R₆, R₇ and R₈ each represents a hydrogen atom, a hydroxyl group, an alkoxy group, an aryloxy group, a substituted aryloxy group, such as a phenoxy, an o-toloxyl or a p-sulfophenoxy group, a halogen atom, such as a chlorine or a bromine atom, a heterocyclic nucleus such as morpholinyl or piperidyl, an alkylthio group such as a methylthio or an ethylthio group, a heterocyclic thio group such as a benzothiazylthio group, an arylthio group, an unsubstituted 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 heterocyclic amino group, such as a 2-benzothiazole-amino or a 2-pyridylamino group, or an aryl group, such as a phenyl group; and A represents A₁ or A₂ shown as follows and, in particular, at least one of R₅, R₆, R₇ and R₈ representing a substituent containing a —SO₃M group when A is A₂.

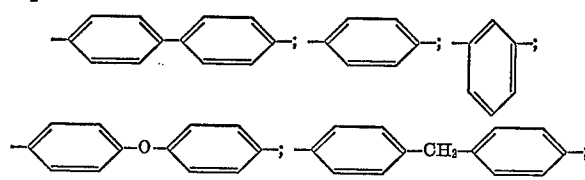
A₁ can be:



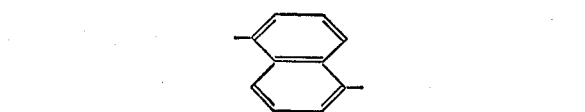
and



A₂ can be:

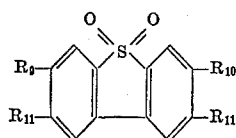


and



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Compound III has the general formula shown below:

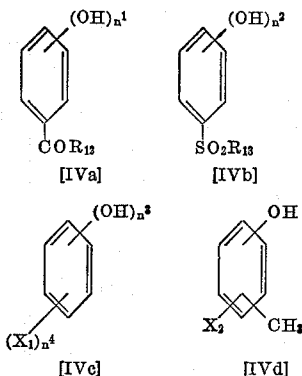


[III]

In this formula, 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 above for R_9 ; and R_{11} represents a hydrogen atom or a sulfo group. The compound having the general Formula III has at least one sulfo group.

The sensitizing dye represented by the general Formula I is used more favorably through supersensitization with a Novolak type condensate of a polyhydroxybenzene and formaldehyde. The term polyhydroxybenzene is intended to cover substituted benzenes having from 1 to 3 hydroxyl groups on the benzene nucleus. The Novolak type condensate of the polyhydroxybenzene and formaldehyde will hereinafter be referred to as the "Formalin condensate."

The polyhydroxybenzenes are represented by the following general Formulae IVa, IVb, IVc, IVd:



wherein R_{12} and R_{13} each represents $-\text{OH}$, $-\text{OM}$, $-\text{OR}_{14}$, $-\text{NH}_2$, $-\text{NHR}_{14}$, $-\text{N}(\text{R}_{14})_2$, $-\text{NHNH}_2$ and $-\text{NHNHR}_{14}$, with R_{14} representing 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 an $-\text{OH}$ group or halogen atom; X_2 represents a halogen atom; n^1 , n^2 , n^3 and n^4 each rep-

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resents 1, 2, or 3, except that n^3 and n^4 are equal to 3 at the same time.

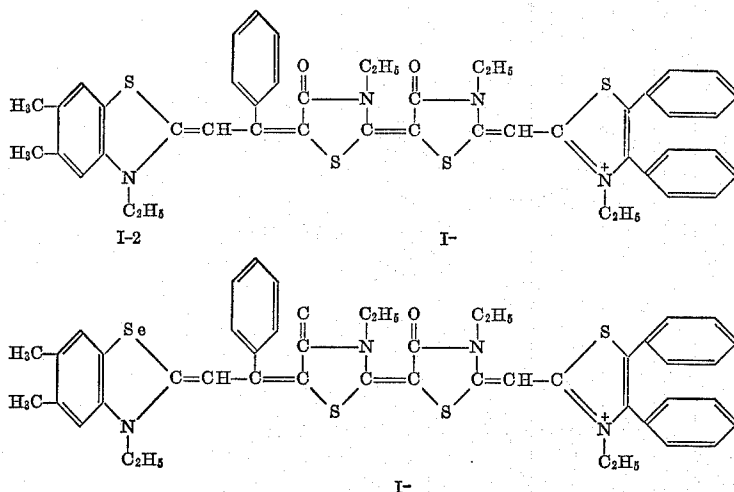
The sensitizing dye of the invention, represented by the general Formula I, is described in F. M. Hamer, Cyanine Dyes and Related Compounds Thereof, Sect. 15, p. 671, Interscience Publishers (1964).

Some of the compounds represented by the general Formula II are mentioned, for example, in U.S. Pats. 2,171,427, 2,660,578 and 2,595,030. One 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 Polymerchemistry, John Wiley and Sons, Inc. (1961)]. The polysubstituted 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 added further 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. More specifically, 415 parts of p-hydroxybenzoic acid is dispersed in 1,000 parts of water with vigorous agitation, to which 25 parts of 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 for 30 minutes as it is, to which 20 parts of concentrated hydrochloric acid is additionally added 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 as it is not dried, and then precipitated with water. The reaction product is filtered and dried to obtain the product. Other condensates can readily be obtained by using other polyhydroxybenzenes in place of the p-hydroxybenzoic acid in the above-described method. The condensation unit (i.e., the degree of polymerization) of the condensate obtained by the above described method is from 2 to 10 as with usual Novolak resins.

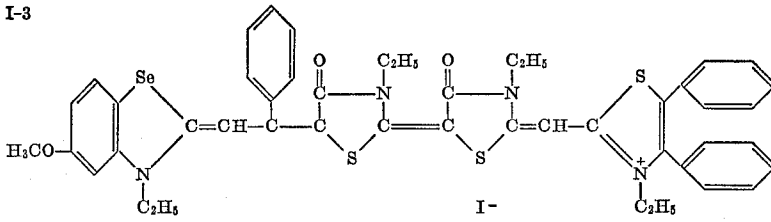
For the purpose of the invention, condensates having a condensation unit of from 2 to 10, preferably having a condensation unit of from 2 to 5 and a molecular weight of from 300 to 800 are suitable.

Examples of the sensitizing dye used in the invention are given as follows, but without limiting the invention.

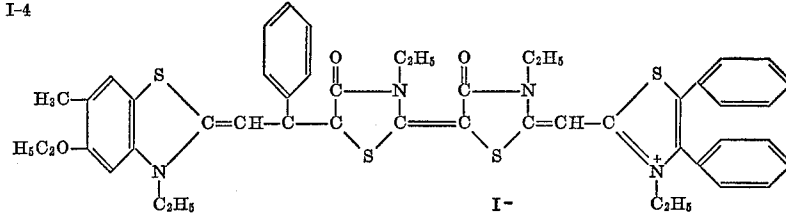


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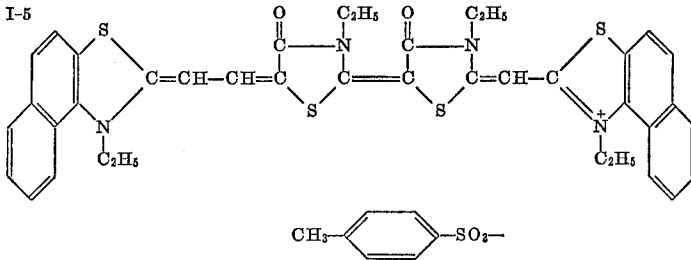
I-3



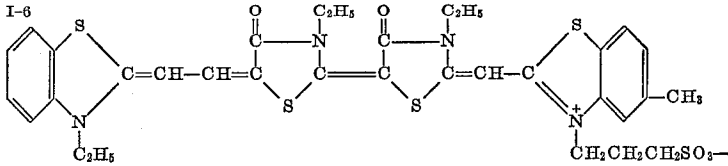
I-4



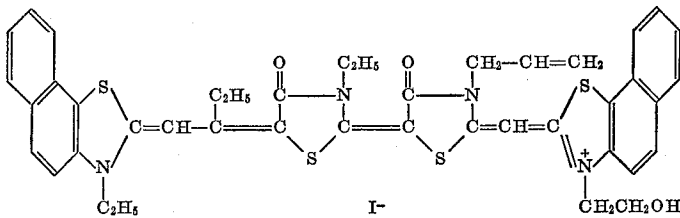
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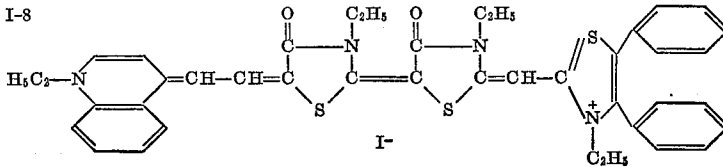
I-6



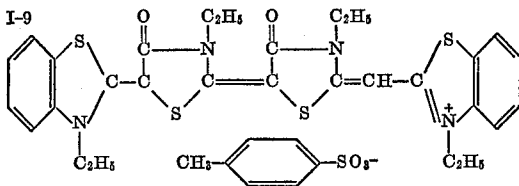
I-7



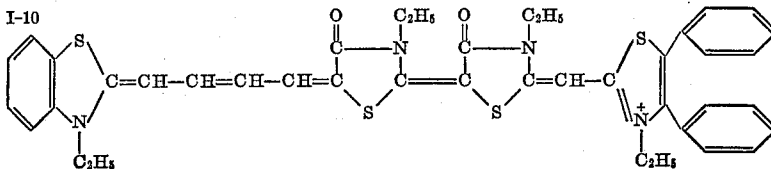
I-8



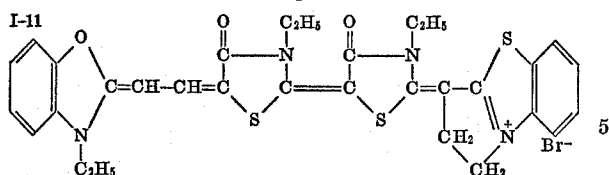
I-9



I-10



9.



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 is preferably added to an emulsion before coating, and washed with water, before an azo dye is added.

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

Suitable emulsions for use in this invention are silver halide, such as silver chloride, silver bromide, silver iodobromide, silver chlorobromide or silver chloriodobromide

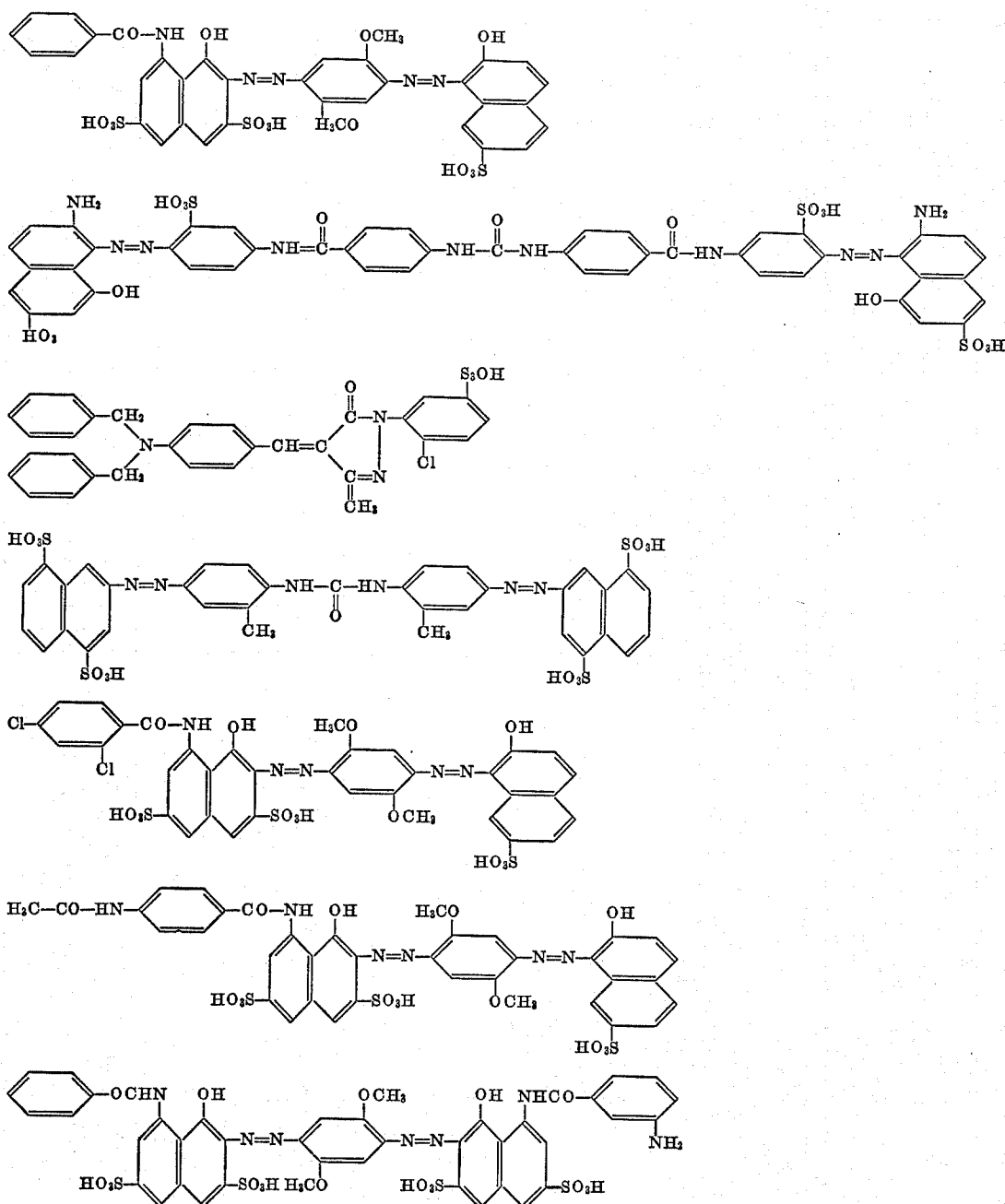
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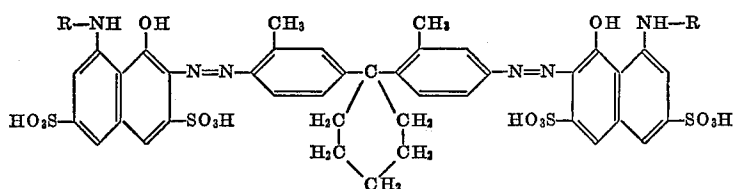
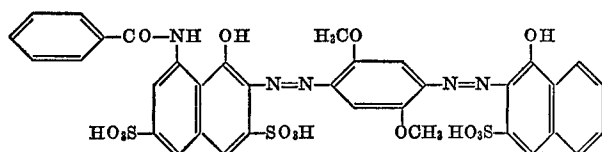
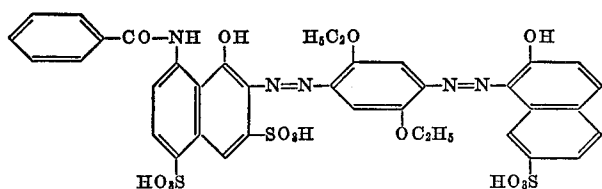
emulsions. The usual gelatino-silver halide emulsion is used in the invention, but cellulose derivatives and resinous materials which do not disturb light-sensitive materials can be used in place of the gelatin.

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

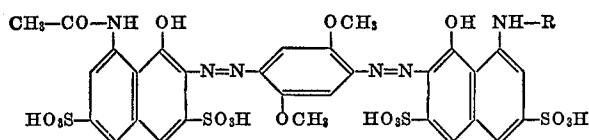
The photographic emulsion can be coated onto a suitable support, such as a glass, a cellulose derivative film, a synthetic resin film, a laminated paper or a synthetic paper in any conventional manner.

The dye used in combination with the sensitizing dye represented by the general Formula I is any dye used conventionally in the silver-dye bleaching method, preferably one 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, and in U.S. Pats. 3,211,554, 3,223,527, 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 and 3,454,401. Suitable dyes are, for example:





with R being a p-tolpenesulfone group or a 4-acetylaminobenzoyl group,



with R being a benzoyl, a 4-acetylaminobenzoyl or a 4-benzoylaminobenzyl group.

The following examples are given to further illustrate the invention without limiting the scope of the invention.

EXAMPLE 1

9.68 $\times 10^{-5}$ g.-mol/g.-mol silver halide of a sensitizing dye described below by Formulae I-1 to I-4 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 having the following structural formula was added thereto, stirred adequately and coated onto a cellulose triacetate base giving rise to four samples. Two additional samples using I-a and I-b were prepared for comparison purposes. For each sample

the coated photographic layer was exposed through a step wedge of blue light (Latten Filter No. 47B) and red light

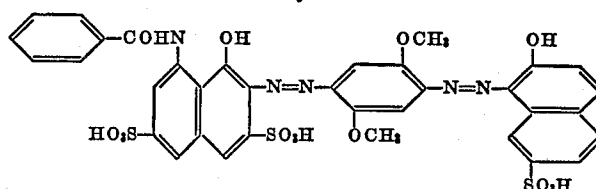
(Fuji Filter No. 7), developed and fixed. The development was carried out with the developer having the composition shown in Table 1 at 20° C. for 2 minutes.

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

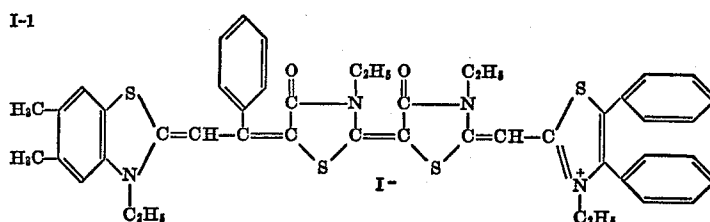
TABLE 1

	G.
N-methyl-p-aminophenyl sulfate	3.1
Sodium Sulfite	45
Hydroquinone	12
Sodium carbonate (anhydrous)	67.5
Potassium bromide	1.9
Water to 1000 ml.	

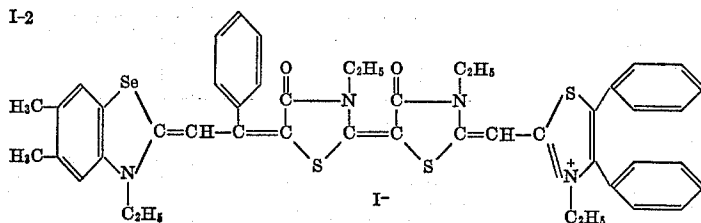
Structural formula of dye used



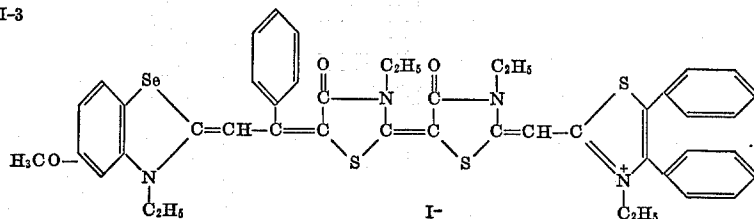
Structural formula of sensitizing dye used



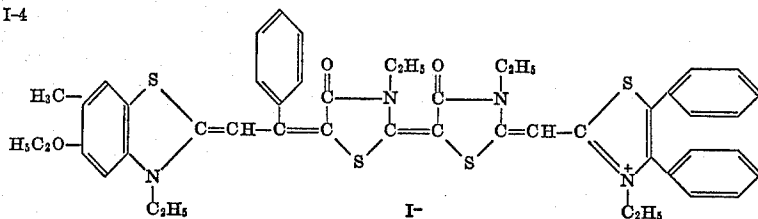
I-2



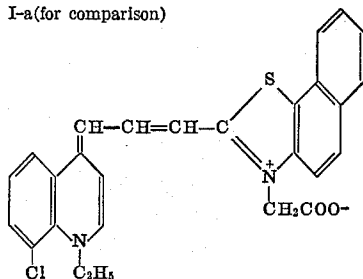
I-3



I-4



I-a (for comparison)



I-b (for comparison)

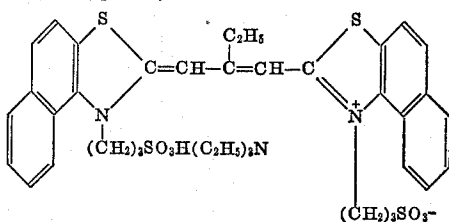


TABLE 2

Sensitizing dye	Relative sensitivity (log)	
	Red sensitivity	Blue sensitivity
I-1	1.35	0.58
I-2	1.37	0.58
I-3	1.27	0.50
I-4	1.10	0.54
I-a (for comparison)	0.81	0.50
I-b (for comparison)	0.80	0.55

EXAMPLE 2

A sensitizing dye or a sensitizing dye and supersensitizer were added to a silver iodobromide emulsion (iodine 7.0 mol percent) and stirred adequately for 20 minutes. Thus, 19.0 g./g.-mole 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 to prepare a number of samples.

The thus coated photographic layer of the samples was exposed through a step wedge and subjected to the following processes.

- (1) Development—5 minutes:

p-Methylaminophenol	g	1
Hydroquinone	g	3
Anhydrous sodium sulfite	g	13
Potassium bromide	g	1
Anhydrous sodium carbonate	g	26
- (2) Water washing—5 minutes.
- (3) Fixing—5 minutes:

Crystalline sodium thiosulfate	g	200
Potassium metasilicate	g	20
Water to 1,000 ml.		
- (4) Water washing—5 minutes.
- (5) Hardening—5 minutes:

30% aqueous formaldehyde solution	ml	100
Sodium dicarbonate	g	2
Water to 1,000 ml.		
- (6) Water washing—5 minutes.

(7) Dye bleaching—15 minutes:

Thiourea	ml	28	
Potassium bromide	g	18	
Thiourea	g	28	
2-amino-3-hydroxyphenazine	mg	3	5
Concentrated hydrochloric acid	ml	200	
Water to 1,000 ml.			

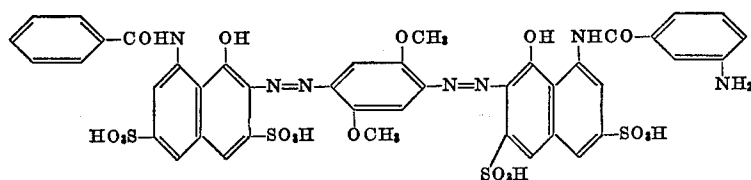
(8) Water washing—5 minutes.

(9) Bleaching fixing—10 minutes:

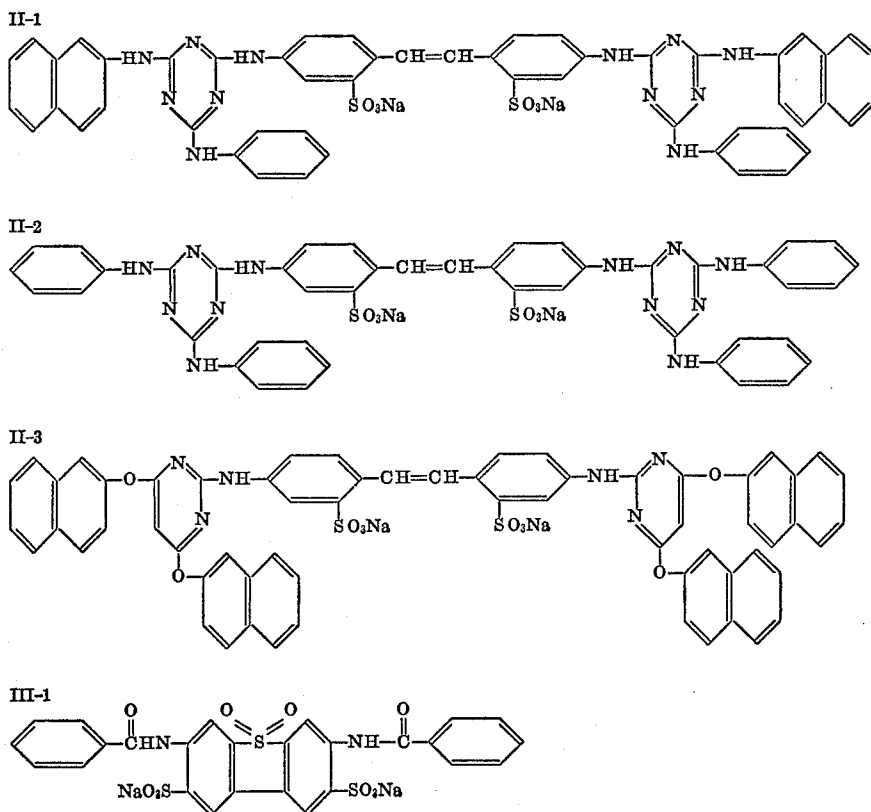
Tetrasodium ethylenediaminetetraacetate	g	26	10
Anhydrous sodium carbonate	g	24	
Ferric chloride	g	15	
Anhydrous sodium sulfite	g	13	
Crystalline sodium thiosulfate	g	200	
Water to 800 ml.			

(10) Water washing—20 minutes.

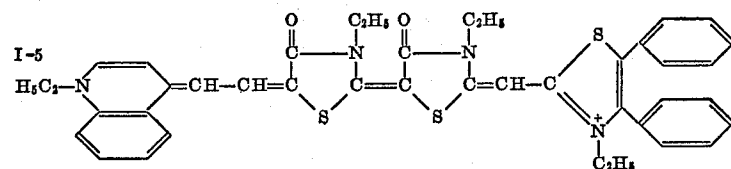
Structural formula of dye used



Structural formula of supersensitizer used



Structural formula of sensitized dye used (I-1, I-2, I-3, and I-4, as shown in Example 1).



The results obtained are showed in Table 3 below:

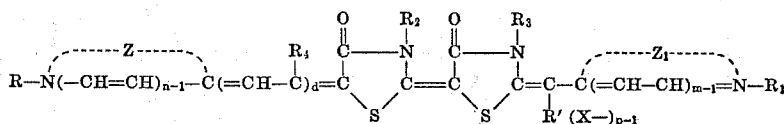
TABLE 3

Sensitizing dye	Supersensitizer	Relative sensitivity (red) sensitivity)
I-1	II-1 (950) ¹	2.02
I-1+		2.42
I-2	II-2 (950)	1.00
I-2+		2.38
I-3	II-3 (950)	2.12
I-3+		2.58
I-4	III-1 (950)	1.88
I-4+		2.17
I-5	(²)	2.02
I-5+		2.50

¹ Milligrams supersensitizer per g.-mol silver halide.² Condensate of p-chlorophenol and formaldehyde (5,700).

What is claimed is:

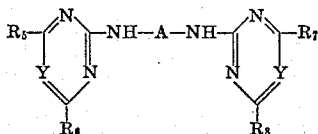
1. A light-sensitive silver halide emulsion containing an azo dye capable of being bleached out in the silver dye bleaching process containing a phenolic hydroxyl or sulfonate group and at least one sensitizing dye having the general Formula I



wherein R, R₁, R₂ and R₃ each is selected from the group consisting of an alkyl group, an allyl group, an aralkyl group, an aryl group, a substituted alkyl group wherein said substituent is selected from the group consisting of hydroxy, acetoxy, sulfato, carboxy, sulfo and vinyl, and a substituted aralkyl group wherein said substituent is selected from the group consisting of sulfo and carboxy, and wherein R' is selected from the group consisting of a hydrogen atom, an alkyl group, a hydroxy alkyl group, an acetoxy alkyl group, and an amino alkyl group, and an aliphatic chain to be combined with the N of the heterocyclic ring containing Z₁; wherein R₄ is selected from the group consisting of a hydrogen atom, an alkyl group, and an aryl group; wherein m, n, and p are 1 or 2, and d represents 0, 1 or 2; wherein X represents an anion wherein an intramolecular salt is formed when p=1; and wherein Z and Z₁ is selected from the group consisting of the thiazoles, benzothiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles, benzoselenazoles, naphthoselenazoles, thiazolines, 2-quinolines, 4-quinolines, benzimidazoles, 3,3'-dialkylindolenines, 2-pyridines and 4-pyridines.

2. The light-sensitive silver halide emulsion as claimed in claim 1, wherein R, R₁, R₂ and R₃ are selected from the group consisting of methyl, ethyl, propyl, β-hydroxyethyl, β-acetoxyethyl, sulfatoethyl, carboxymethyl, β-carboxyethyl, γ-carboxypropyl, β-sulfoethyl, γ-sulfo-propyl, δ-sulfoethyl, vinylmethyl, benzyl, phenethyl, p-carboxybenzyl, p-sulfophenethyl, and phenyl groups; wherein the substituted alkyl group in R' is selected from the group consisting of a β-hydroxyethyl, a β-acetoxyethyl and a β-aminoethyl group; and wherein the heterocyclic ring containing Z or Z₁ is selected from the group consisting of the thiazoles, benzothiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles, benzoselenazoles, naphthoselenazoles, thiazolines, 2-quinolines, 4-quinolines, benzimidazoles, 3,3'-dialkylindolenines, 2-pyridines and 4-pyridines.

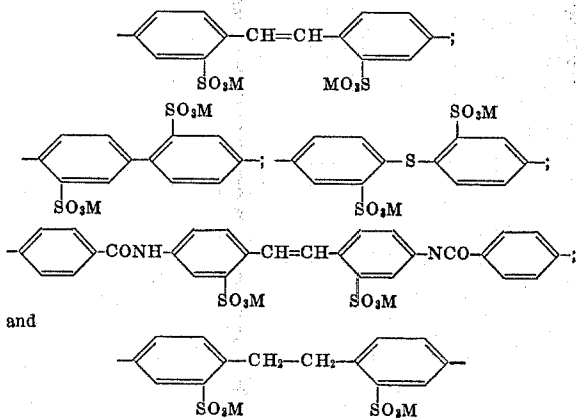
3. A supersensitizing photographic emulsion wherein the light sensitive silver halide emulsion of claim 1 contains additionally at least one compound having the following general Formula II



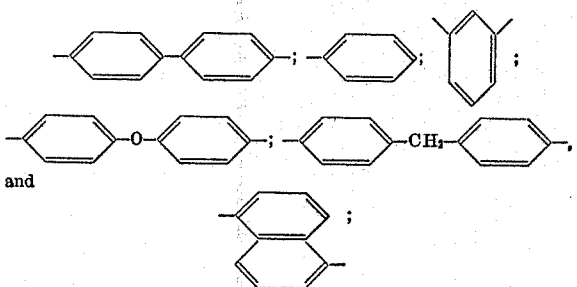
wherein Y represents =CH— or =N—; wherein R₅, R₆, R₇ and R₈ each is selected from the group consisting of a hydrogen atom, a hydroxyl group, an alkoxyl group, an aryloxy group, a substituted aryloxy group selected from the group consisting of an o-toloxyl group and a p-sulfophenoxyl group, a halogen atom, a heterocyclic nucleus selected from the group consisting of a morpholinyl group and a piperidyl group, an alkyl thio group, a benzothiazylthio group, an aryl thio group, an alkyl amino group, a substituted alkyl amino group selected from the group consisting of a β-hydroxyethylamino group, a di-β-hydroxyethylamino group, and a β-sulfoethylamino group, an arylamino group, a substituted arylamino group selected from the group consisting of an o-sulfoanilino group, a m-sulfoanilino group, a p-sulfo-

anilino group, an o-anisilamino group, a m-anisilamino group, a p-anisilamino group, an o-toluidino group, a m-toluidino group, a p-toluidino group, a p-carboxyanilino group, a hydroxyanilino group, a naphthylamino group, and a sulfonaphthylamino group, a heterocyclic amino group selected from the group consisting of a 2-benzo-

thiazoleamino group and a 2-pyridylamino group and an aryl group; and wherein A is selected from the group consisting of A₁ and A₂, wherein A₁ is selected from the group consisting of

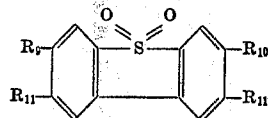


wherein A₂ is selected from the group consisting of



and wherein at least one of R₅, R₆, R₇ and R₈ is a substituent containing a —SO₃M group when A is A₂.

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



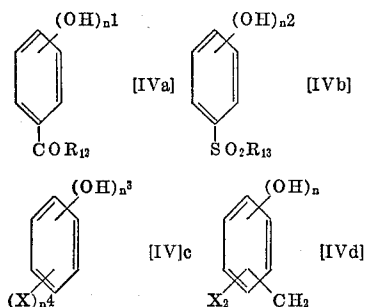
wherein R₉ is selected from the group consisting of an acylamino group and a sulfo group; wherein R₁₀ is an acylamino group; and wherein R₁₁ is selected from the group consisting of a hydrogen atom and a sulfo group; and wherein said compound has at least one sulfo group.

5. The supersensitized photographic emulsion as claimed in claim 4, wherein the acylamino group is selected from the group consisting of an acetamide, a sulfobenzamide, a 4-methoxy-3-sulfobenzamide, a 2-ethoxy-benzamide, a 2,4-diethoxybenzamide, a p-toluidylamino, a 4-methyl-2-methoxybenzamide, a 1-naphthylamino, a 2-naphthylamino, a 2,4-dimethoxybenzamide, a 2-phenylbenzamide and a thienylbenzamide group.

6. A supersensitized photographic emulsion wherein the light-sensitive silver halide emulsion of claim 1 contains additionally a condensate of a polyhydroxy benzene and formaldehyde.

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7. The supersensitized photographic emulsion as claimed in claim 6, wherein the formalin condensate is a Novolak type condensate of formaldehyde and a polyhydroxybenzene having a formula selected from the group consisting of formulas



wherein R_{12} and R_{13} each is selected from the group consisting of $-\text{OH}$, $-\text{OM}$, $-\text{OR}_{12}$, $-\text{NH}_2$, $-\text{NHR}_{14}$, $-\text{N}(\text{R}_{14})_2$, $-\text{NHNH}_2$, and $-\text{NHNHR}_{14}$; wherein R_{14}

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 X_1 is selected from the group consisting of an $-\text{OH}$ and a halogen atom; wherein X_2 is a halogen atom; wherein n^1 , n^2 , n^3 and n^4 each are 1, 2 or 3, except that n^3 and n^4 are equal to 3 at the same time.

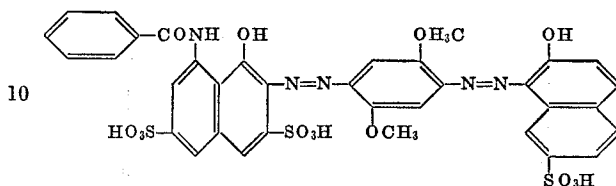
8. The supersensitized photographic emulsion as claimed in claim 7, wherein the condensate has a con-

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

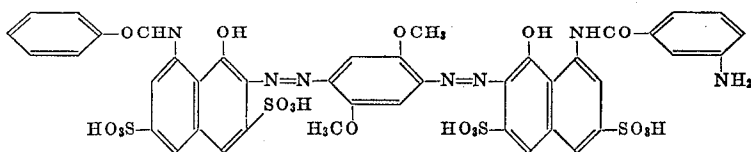
9. The light-sensitive silver halide emulsion as claimed in claim 1 wherein the dye capable of being bleached out in the silver dye bleaching process is

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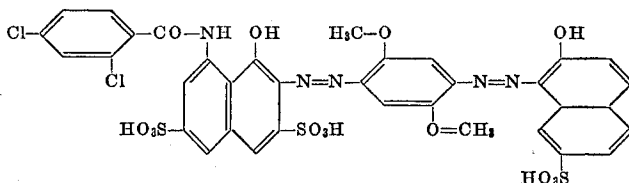


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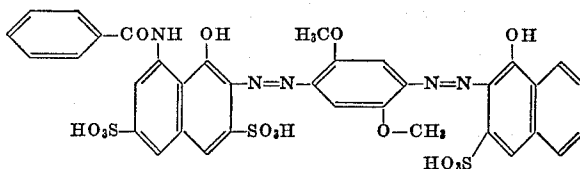
10. The light-sensitive silver halide emulsion as claimed in claim 1, wherein the dye capable of being bleached out in the silver dye bleaching process is



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



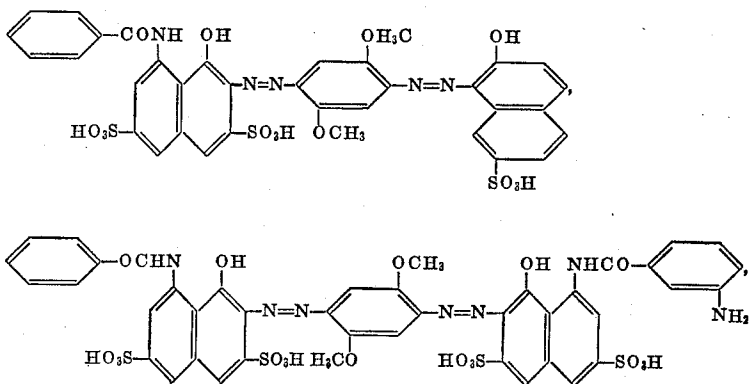
12. The light-sensitive silver halide emulsion as claimed in claim 1, wherein the dye capable of being bleached out in the silver dye bleaching process is

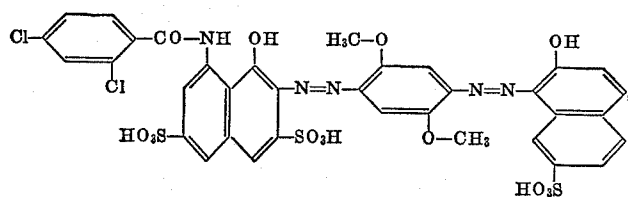


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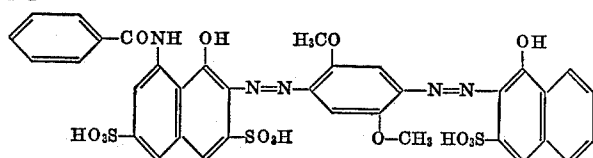
13. A photographic light-sensitive element comprising a support having thereon at least one layer containing the light-sensitive silver halide emulsion as claimed in claim 1.

14. 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 selected from the group consisting of





and



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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—73, 123, 128