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MEROCYANINE DYE-SENSITIZED PHOTOGRAPHIC MATERIALS COMPRISING SILVER HALIDE EMULSION LAYERS CONTAINING AZO-DYES

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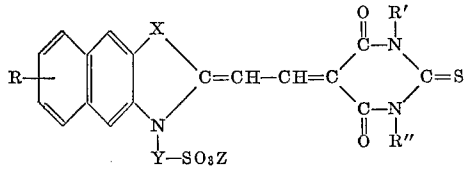
U.S. Cl. 96—99 8 Claims

ABSTRACT OF THE DISCLOSURE

Silver-dye-bleach emulsions are effectively sensitized by merocyanine dyes having the formula



This invention relates to a merocyanine dye-sensitized photographic element comprising at least one silver halide emulsion layer uniformly dyed with an azo-dye for use in the silver dye bleach process.

Colored photographic images can be prepared by the silver dye bleach process in which a negative or a positive silver image is obtained, depending on the processing, by exposure and subsequent development of uniformly colored photographic layers.

After further treatment, such as fixing and subsequent hardening, the azo-dye is bleached, generally in a strongly acidic bleach bath, in accordance with the silver image. In this way, a dye image of the original is obtained. The dye image has a gradation opposite to the gradation of the silver image. The dyes generally employed are azo dyes, both water-soluble dyes and insoluble pigments.

One of the great disadvantages of the silver dye bleach process is that the sensitivity of the dyed photographic layers is very considerably reduced. This occurs in particular if the layers are sensitized in such a way, as is generally the case with color photographic layers, in which the blue-sensitive layer is dyed yellow, the green-sensitive layer magenta and the red-sensitive layer cyan.

The reason for this is that the sensitization maxima coincide with the absorption maxima of the dyes. With respect to the sensitivity of the light-sensitive layers, the silver dye bleach process is inferior to other color photographic processes. Accordingly, one of the great difficulties of the silver dye bleach process is the preparation of sufficiently sensitive layers.

The sensitivity of photographic emulsions can be increased by the addition of suitable sensitizers. Sensitizers which are to be used in materials for the silver dye bleach process have to satisfy several requirements. In addition to good sensitizing properties the sensitizer must not deleteriously effect the stability of the emulsions, particularly in storage and under tropical conditions. Furthermore, the sensitizing dyes have to be sufficiently soluble in the processing baths, so that the dye is readily washed out and no coloring of the support, for example paper, or the binding agent of the layer, for example gelatin, occurs. Furthermore, the sensitizer must adhere sufficiently firmly to the silver halide grains as not to be displaced

by the azo-dyes, because otherwise the sensitizing action is decreased in the presence of azo-dyes. In particular because of the last mentioned requirement many of the sensitizers, operative in conventional silver halide photographic materials, are not suitable for the silver dye bleach process.

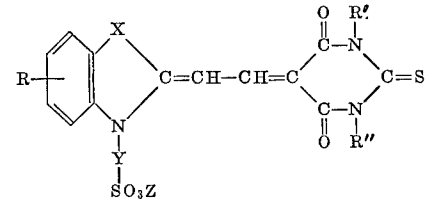
For instance basic cyanines are readily detached or removed from the silver halide grain by azo-dyes containing sulfonic acid groups and, for this reason, are not sufficiently effective in the silver dye bleach process. In some cases even a desensitizing effect can be observed from compounds which act as sensitizers in conventional photographic processes. It is known to employ betaine cyanines as sensitizers for photographic layers for use in the silver bleach process. These sensitizers are, however, of limited utility since they cannot be washed out sufficiently in the processing baths so that the image portions remain slightly colored.

It is an object of the present invention to provide sensitizing dyes for silver halide emulsion layers to be used in the silver dye bleach process. Another object is to provide photographic materials comprising at least one light-hensitive silver halide emulsion layer that is optically sensitized and contains an azo-dye. Other objects will become apparent from a consideration of the following description and examples.

We now have found that a particular class of merocyanine dyes are outstanding in their optical sensitizing properties for silver halide emulsion layers which contain uniformly distributed azo-dyes and which are to be used in the silver dye bleach process.

The merocyanines of the present invention are characterized by the following formula:

(A)



in which

X=S or Se

Y=a bifunctional aliphatic chain such as $-(CH_2)_n-$ in which n is an integer from 2 to 6, preferably 3 or 4, or an unsaturated or hydroxy- or chloro-substituted 2 to 6 carbon aliphatic radical such as

$-CH_2CHOHCH_2-$, $-CH_2-CH=CH-$, or $-CH_2CHClCH_2-$

Z=any monovalent cation such as $Na^{\oplus}$, $Ca/2^{\oplus}$, $[HN(C_2H_5)_3]^{\oplus}$ etc.

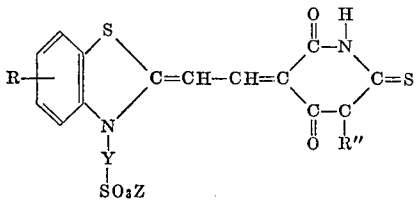
R=(I) H, (II) alkyl, preferably with up to 5 C-atoms, (III) halogen such as Cl, Br, or I, (IV) aryl such as a phenyl, which can in turn be further substituted, anellated aryl preferably phenyl, which in turn can be further substituted such as 4,5-benzo-, (V) cyclo alkyl such as cyclopentyl or cyclohexyl, (VI) aralkyl such as benzyl or phenylalkyl, (VII) heterocyclic groups such as thienyl, (VIII) —O—CH_2O— (in 5,6-position), (IX) alkoxy with preferably up to 5 carbon atoms, (X) aroxy in particular phenoxy, (XI) amino which can be substituted with, for example, alkyl having preferably up to 5 carbon atoms or acyl, preferably acyl groups derived from lower aliphatic carboxylic acids having up to 6 carbon atoms or benzoic acid; (XII) hydroxy etc.

R′=H, alkyl, especially with up to 5 C-atoms, aryl, preferably phenyl, aralkyl such as benzyl or phenylethyl; R′ prferably stands for H;

R″=saturated or olefinically unsaturated aliphatic groups,

especially with up to 5 C-atoms, aralykyl such as benzyl or phenylethyl, aryl, prferably phenyl, R'' preferably stands for alkyl of the formula $—CH_2—CH=CH_2$.

Particular utility is exhibited by compounds of the following formula B

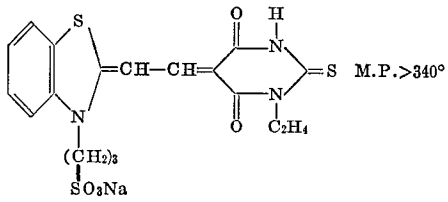


wherein the symbols R, R'', Y and Z have the meanings already defined above.

The merocyanine dyes of the present invention are outstanding in their optically sensitizing action for silver halide emulsion layers containing an azo-dye. Furthermore, they are superior over betain cyanines since the color images obtained by the process of the invention show very clear white portions of the images without any color stain.

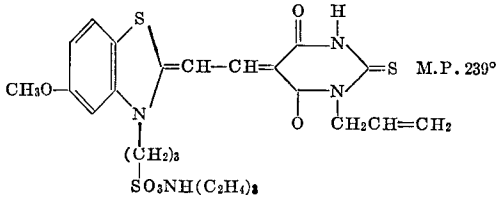
The above merocyanines are substantially inert both to the azo-dyes in the photographic layers for the silver dye bleach process and to other additives, in particular stabilizers, mordants such as biguanides or guanides, wetting agents, agents for influencing the viscosity of azo-dyes in gelatin and/or photographic emulsions, hardening agents such as chrome alum, paraformaldehyde, or plasticizers such as glycerol. The following specific compounds are particularly suitable:

(I)



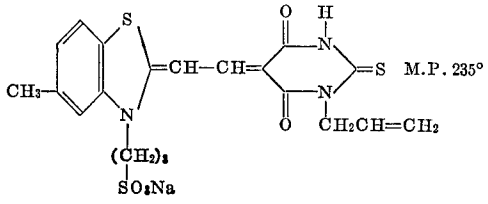
M.P.>340°

(II)



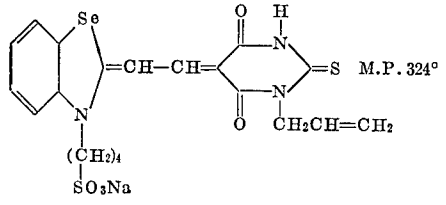
M.P. 239°

(III)



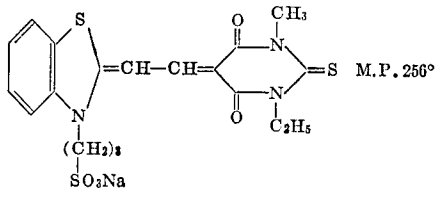
M.P. 235°

(IV)



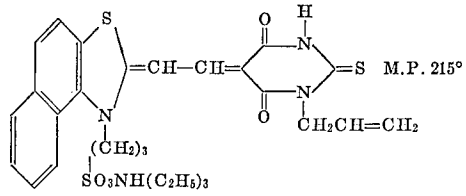
M.P. 324°

(V)



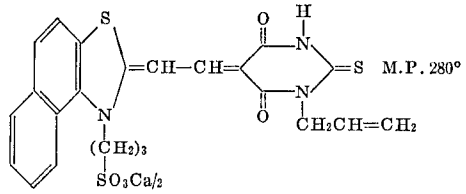
M.P. 256°

(VI)



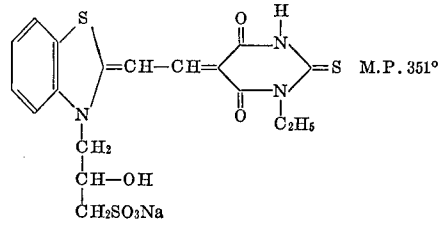
M.P. 215°

(VII)



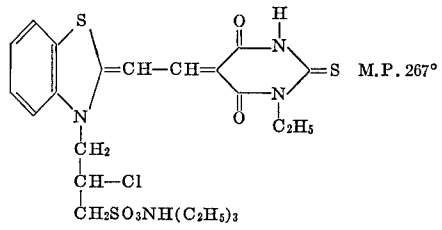
M.P. 280°

(VIII)



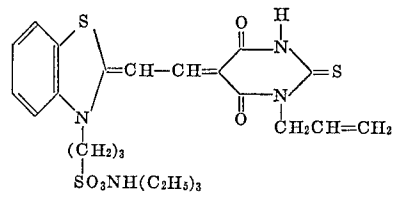
M.P. 351°

(IX)

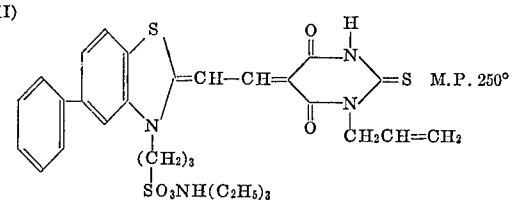


M.P. 267°

(X)

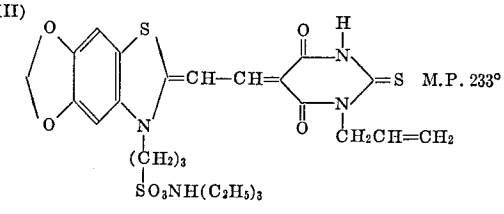


(XI)



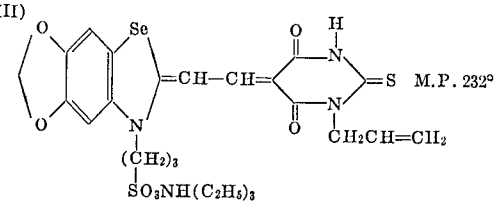
M.P. 250°

(XII)



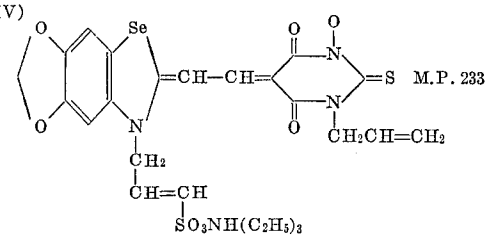
M.P. 233°

(XIII)



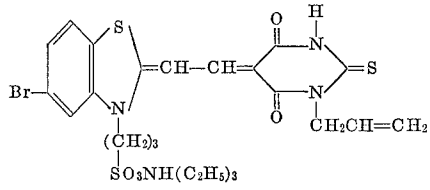
M.P. 232°

(XIV)

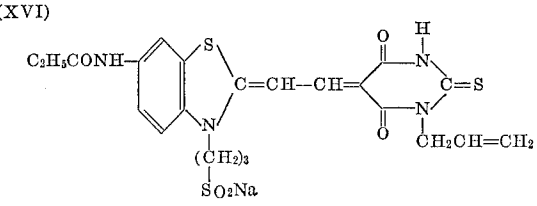


M.P. 233

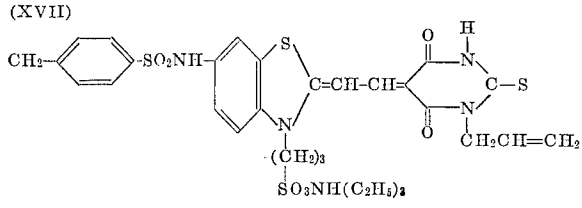
(XV)



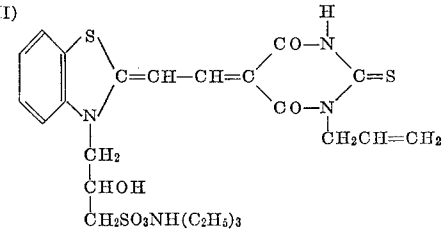
(XVI)



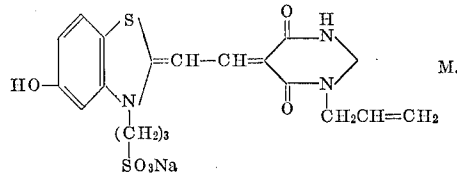
(XVII)



(XVIII)



(XIX)



M.P. >360°

The preparation of the merocyanines to be used according to the invention is known per se and may, for example, be carried out by a procedure analogous to that described by Collins and Kendall in British Patent No. 528,803.

Sensitizing dye No. I of the above table is obtained as follows: 4 g. of 2-methyl-mercaptobenzothiazole-N-propanesulphobetaine and 2.7 g. of the ethylidene compound of N-ethylthiobarbituric acid are dissolved with shaking in 50 ml. of pyridine, 5 ml. of triethylamine are added and the reaction mixture left to stand at room temperature for 24 hours.

The reaction mixture is poured into 250 ml. of water and filtered off from undissolved constituents, and dye I is precipitated from the filtrate with sodium chloride. M.P. above 340° C.

The sensitizing dyes of the present invention preferentially sensitize highly sensitive silver halide gelatin emulsions in the presence of azo dyes to the green region of

the visible spectrum (=500 to 600μ). They are added to the emulsion separately or in admixture in quantities of 20 to 600 mg. per mol of silver halide, preferably 70 to 450 mg. per mol of silver halide. The inventive sensitizers are preferably applied to silver bromide emulsions, more particular to silver bromide emulsions containing up to 10 mol percent of silver iodide.

The compounds according to the present invention are distinguished from known merocyanines such as those disclosed in German Pat. No. 1,213,240, by the fact that they have remarkably steeper sensitization curves in the presence of azo dyes, in particular a steep decay towards the longer wavelength of the green region of the visible spectrum, with the result that the color images produced show improved color separation and an improved reproduction in true colors of the original. Furthermore, the photographic layers containing the sensitizing dyes of the present invention have an improved safety in the dark room, which makes processing much easier.

These advantages are achieved without impairing the known advantageous properties of merocyanines, namely high sensitization with very slight or practically no detectable coloration of the layer, and an excellent keeping quality.

In the preparation of photographic emulsions the merocyanine dyes of the present invention are preferably incorporated in the washed, finished silver halide emulsions before the azo-dyes are added and should be uniformly distributed throughout the emulsion. The methods of incorporating sensitizing dyes in light-sensitive emulsions are well known to those skilled in the art of emulsion making. Generally it is convenient to add the sensitizing dyes from solutions in appropriate solvents that have no deleterious effect on the light-sensitive materials. Lower aliphatic alcohols such as methanol, ethanol or isopropanol, furthermore pyridine and the like, alone or in admixtures, for example with water, have proven satisfactory as solvents.

The type of silver halide emulsions that can be sensitized with the mercocyanines of the present invention include any of those prepared with hydrophilic colloids that are known to be satisfactory for dispersing silver halides. These colloids include preferably gelatin which can be used in admixture with other hydrophilic colloids such as albumin, alginic acids and derivatives thereof, hydrophilic synthetic resins such as polyvinyl alcohol, polyvinyl pyrrolidine and the like.

To prepare a silver halide emuslion sensitized with a merocyanine of the present invention, the following procedure is satisfactory: The desired quantity of the sensitizing dye is dissolved in a suitable solvent and a volume of this solution containing the desired amount of the dye is slowly added to the silver halide emulsion. Thereafter, the azo-dye is added preferably from a solution in a suitable solvent. The photographic emulsions may be coated on any of the photographic supports including, paper, cellulose esters, such as cellulose acetate or nitrate, polystyrene, polyesters in particular of polyethylene terephthalate, polycarbonates, preferably of bishydroxy phenyl alkanes, and the like.

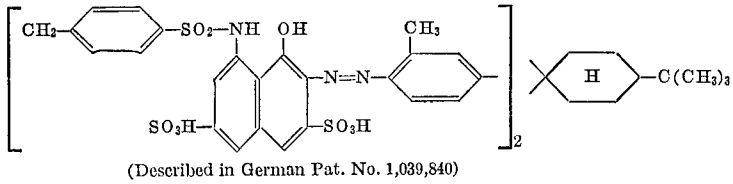
Photographic silver halide emulsions containing the merocyanines of the invention can also contain such addenda as chemical sensitizers, for instance, sulfo sensitizers, noble metal compounds such as gold or palladium compounds, stabilizers such as benzotriazole compounds, heterocyclic mercapto compounds, mercury compounds or azaindenes; hardeners such as glyoxal, formaldehyde, acrolein or the like.

Azo-dyes which can advantageously be used in combination with the merocyanines of the present invention comprise the customarily employed dyes which are known to be satisfactory for the silver dye bleach process. Preferred are those containing phenolic hydroxyl groups and/or sulfinic acid groups. Suitable dyes are described in the book of J. S. Friedman, "History of Color Pho-

tography," published by The American Photographic Publishing Co., Boston, 1947, chapter 24, or for instance in British Pat. Nos. 766,020, 899,758, 953,622, or in German Pat. Nos. 1,039,840 or 1,041,355.

EXAMPLE 1

To 500 g. of a highly sensitive silver bromide gelatin emulsion containing 5 mol percent of silver iodide are added, after it has been melted, 20 parts of a 1% aqueous solution of 5-methyl-7-hydroxy-2,3,4-triazaindolizine as stabilizer and 25 g. of the sensitizing dye of Formula 1 of the above table, 2.9 g. of the dye of the following formula:



(Described in German Pat. No. 1,039,840)

in 250 ml. of a 2% gelatin solution are then added as well as 0.35 g. of saponin and 5 ml. of a 1% aqueous solution of formaldehyde as hardener. 1.2 g. of bis[3-anisidyl-4-biguanide] are added to improve the whites.

The product is applied onto a support of baryta-coated paper or white pigmented cellulose acetate. The final coating contains 0.8 g. of silver in the form of silver halide per square meter.

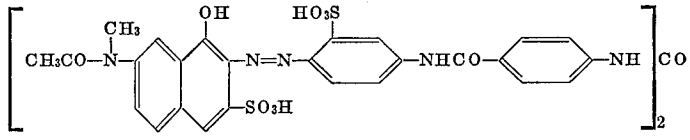
After drying, the sample is exposed behind a grey step wedge through a strict yellow filter. The film is treated according to the silver-dye-bleach process as follows:

(1) 5 minutes development in a solution of 1 g. of p-methylaminophenol, 13 g. of sodium sulfite sicc., 3 g. of hydroquinone, 26 g. of soda sicc. and 1 g. of potassium bromide in 100 ml. of water;
(2) 1 minute washing;
(3) 5 minutes fixing in a solution of 200 g. of sodium thiosulfate cryst. and 20 g. of potassium metabisulfite in 1000 ml. of water;
(4) 5 minutes washing;
(5) 5 minutes hardening in a solution of 60 ml. of formalin (30%) and 15 g. of sodium bicarbonate in 1000 ml. of water;
(6) 5 minutes washing;
(7) 15 minutes dye bleaching in a solution of 100 g. of potassium iodide, 10 g. of sodium hyphosphite, 25 ml. of sulfuric acid conc., 50 ml. of quinoline and 10 mg. of 2,3-dimethylquinoxaline in 1000 ml. of water;
(8) 5 minutes washing;
(9) 5 minutes bleaching in a bath of 25 g. of copper chloride and 5 ml. of conc. hydrochloric acid in 1000 ml. of water;
(10) 10 minutes fixing as under 3;
(11) 20 minutes washing.

The light-sensitive layer is more sensitive by 1:1 logarithmic units than a sample, used for comparison which has not been sensitized. The background is practically free from any coloring in the sensitized sample.

EXAMPLE 2

The procedure is the same as in Example 1, except that the azo dye indicated there is replaced by 2.7 g. of the azo dye of the following formula which is fast to diffusion without mordanting:



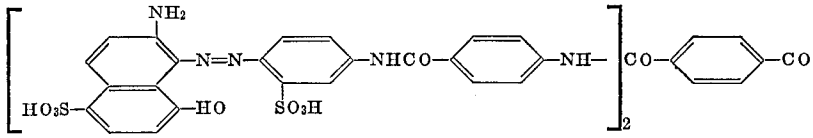
and the sensitizer is replaced by compound III of the above table.

The emulsion is applied onto a white pigmented cellulose acetate support. The dried layer is exposed, and processed as described in Example 1. The sensitivity is increased by 1.2 logarithmic units (log I·t) when compared with a nonsensitized comparison sample. No visible coloration of the background is observed.

EXAMPLE 3

The procedure is the same as described in Example 1 but the sensitizer is replaced by the sensitizer of Formula II of the table.

The sensitizing dye is either used together with the azo dyes indicated in Example 1, Example 2 or with the azo dye of the following formula:



which is described in Belgian Patent No. 683,514. Comparison with non-sensitized samples yields similar results to those in the preceding examples.

In the above examples differences in sensitivity are given in logarithmic units wherein a difference of sensitivity of 0.3 log. units correspond to a factor of 2 and 1.0 log. units correspond to a factor of 10.

As has been mentioned before the essential steps of the processing of silver dye bleach materials consist in development of a silver image, bleaching of the dye according to the silver image and removing residual silver and silver halide by a bleaching and a fixing bath, both of which can be combined in one composition. Between developer and dye bleach bath other steps such as fixing or hardening baths can be included.

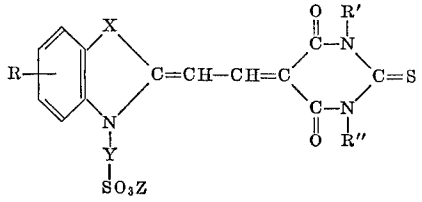
As developer compositions, those containing for instance p-methyl aminophenol and hydroquinone may be used but other systems, especially those containing 1-phenylpyrazolidone, are also useful.

For the purpose of the invention a wide variety of azo-dye bleaching baths can be used. They may contain from 10 to 80 g. of thiourea, 20 to 80 g. of an alkali halide and 10 to 20 g. of a mineral acid per liter such as described in U.S. Pat. No. 2,217,544. Other variations than those indicated are possible, including the omission of halide and the addition of organic solvents. Furthermore, dye bleaching baths on the basis of quinoline, hypophosphite, iodide and mineral acid as described in U.S. Pat. No. 2,629,658 or combinations of iron salts and isothiocyanates are also useful. Besides the basic ingredients mentioned above, the bleaching bath in question normally also contains bleaching catalysts such as 2,3-dimethyl quinoxaline or other quinoxaline derivatives, 2-amino - 3 - hydroxy phenazine, 2,3 - diamino phenazine,

azines, oxazines, thiazines, cinnolines, indophenazines, ferro- or thienoquinoxalines and the like, which are usually added in amounts from 2 to 300 mg. per liter of bleaching solution. Silver bleach baths for use in the process of the present invention may, e.g. consist of copper chloride (10 to 50 g.) and potasium bromide (10–100 g.) together with hydrochloric acid (5 to 20 ml. per liter of solution). In this case an acidic thiosulfate bath containing for instance 200 g. of sodium thiosulfate and 20 g. of potassium metabisulfite per liter of solution, will generally be used as a fixer. Combined bleaching and fixing baths are also very useful, however, and an example of such a composition comprising an Fe(III)-complex of ethylene diamine tetraacetic acid is described hereinbefore.

What is claimed is:

1. In an optically sensitized light-sensitive silver dye-bleach emulsion containing silver halide and a silver dye-bleach azo dye, the improvement wherein the sensitizing dye has the formula:



in which

X represents S or Se;

Y stands for a saturated or olefinically unsaturated bivalent aliphatic grouping having 2 to 6 carbon atoms or a chloro- or hydroxy substituted bivalent aliphatic grouping having 2 to 6 carbon atoms;

Z is a cation;

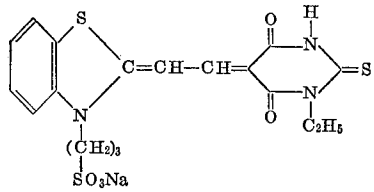
R stands for hydrogen, alkyl having up to 5 carbon atoms, phenyl, anellated phenyl, cyclopentyl or cyclohexyl, benzyl, phenylethyl, thienyl, alkoxy having up to 5 carbon atoms, the grouping —O—CH_2—O—, phenoxy, hydroxy or an amino group;

R′ represents hydrogen, alkyl up to 5 carbon atoms, phenyl, benzyl or phenylethyl;

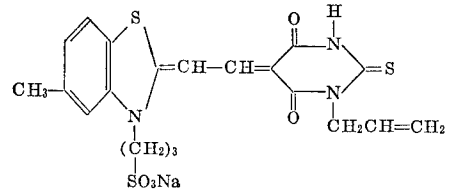
R″ stands for a saturated or olefinically unsaturated aliphatic radical having up to 5 carbon atoms, phenyl, benzyl or phenylethyl.

2. The combination defined in claim **1**, wherein R′ stands for hydrogen.

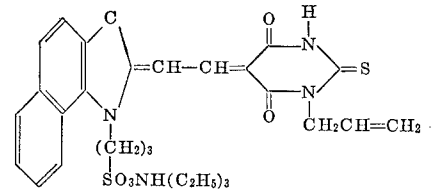
3. The combination defined in claim **1**, wherein the sensitizing dye has the formula:



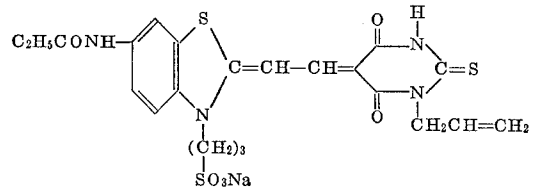
4. The combination defined in claim **1**, wherein the sensitizing dye has the formula:



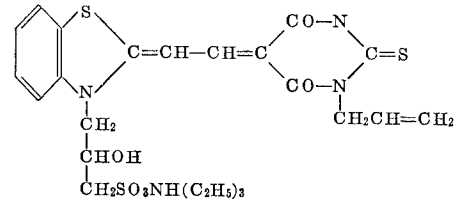
5. The combination defined in claim **1**, wherein the sensitizing dye has the formula:



6. The combination defined in claim **1**, wherein the sensitizing dye has the formula:



7. The combination defined in claim **1**, wherein the sensitizing dye has the formula:



8. The combination defined in claim **1**, in which the emulsion contains 20 to 600 mg. of the sensitizing dye per mol of silver halide.

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J. TRAVIS BROWN, Primary Examiner

U.S. Cl. X.R.

96—102