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SPECTRALLY SENSITIZED SILVER HALIDE PHOTOGRAPHIC MATERIAL SENSITIZED WITH XANTHYLIUM DYES AND ACID MERCAPTO COMPOUNDS

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U.S. Cl. 96—122 6 Claims

ABSTRACT OF THE DISCLOSURE

The sensitization of light-sensitive silver halide emulsions which is brought about by xanthylium, thiaxanthylium or selenaxanthylium dyes is largely increased by using these xanthylium, thiaxanthylium or selenaxanthylium dyes in combination with excessive amounts of an acid isocyclic or heterocyclic aromatic mercapto compound.

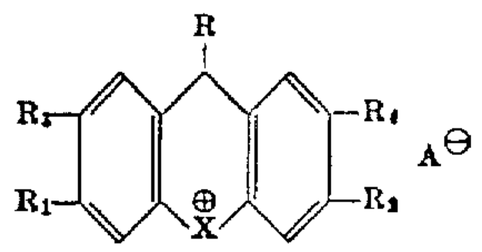
The invention relates to light sensitive photographic layers, in particular to silver halide emulsion layers, which are spectrally sensitized with a mixture of xanthylium dyes and acid mercapto compounds.

Increasing the sensitivity of light sensitive layers, in particular of silver halide emulsion layers, by the addition of substances which increase the spectral range of sensitivity of the light sensitive substances has been known for a long time. Numerous substances, mainly belonging to the class of cyanine dyes, have been described for the sensitization of silver halide emulsion layers. These known substances, however, often have disadvantages, for example their sensitization effect may be insufficient or they may impart an unwanted color to the layer or they may adversely influence the photographic process itself. This applies particularly in the case of special photographic processes or special photographic materials. Their adsorption on the silver halide should be sufficiently strong so that the sensitization effect will be effected as little as possible by other necessary additives such as wetting agents, stabilizers and white toners. The sensitizing effects of most of the sensitizing dyes are particularly impaired by the presence of color forming couplers or of dyes which can be bleached, presumably due to the fact that these additives displace them from the surface of the silver halide particles. Sensitization must be ensured even under extreme conditions such as elevated temperature and moisture. Moreover, the sensitizing dyes must not increase the basic fog as is the case with many basic cyanine dyes. For these reasons, there is considerable interest in finding new possibilities for sensitizing silver halide emulsions.

It is therefore an object of the invention to provide new methods of sensitizing light sensitive photographic materials, especially of silver halide materials. It has been known for a long time that xanthylium dyes are capable of spectrally sensitizing silver halide. The sensitization maximum of these dyes normally lies in the green region of the spectrum. Furthermore, it is also known that the intensity of sensitization of these dyes is only very slight, and these dyes have therefore hitherto not been used in practice for the production of photographic films and papers.

It has now surprisingly been found that the sensitizing effect of dyes belonging to the above mentioned class of dyes, i.e. xanthylium dyes, thiaxanthylium dyes and selenaxanthylium dyes, can be considerably increased by

xanthylium dyes may be represented by the following general formula:



in which

X is an oxygen, sulfur or selenium atom;

R is a hydrogen atom, an alkyl group which may be substituted, an aralkyl group such as a benzyl or phenyl ethyl group, a cycloalkyl group which may be substituted, such as a cyclohexyl group, or an aryl group such as phenyl which may be substituted, e.g. with alkyl, a halogen such as chlorine or bromine, alkoxy, alkylthio, carboxyl, carbalkoxy or sulphamyl groups;

R_1 and R_2 each is an amino group which may be monosubstituted or disubstituted, e.g. with alkyl groups containing up to 6 carbon atoms, cycloalkyl groups such as cyclohexyl, aralkyl groups such as benzyl, or aryl groups such as phenyl; two radicals attached to the same nitrogen atom may together with this nitrogen atom form a 5-membered, 6-membered or 7-membered heterocyclic ring which may contain a further heteroatom, such as pyrrolidine, piperidine, hexamethyleneimine or morpholine;

R_3 and R_4 each is a hydrogen atom, an alkyl group or an alkoxy group containing up to 6 carbon atoms; and

$A^{\ominus}$ is any photographically inert anion, e.g. chloride, bromide perchlorate, sulfate, or p-toluenesulfonate.

Many xanthylium salts of the above formula are known and are available cheaply from the dye chemical industry.

The acid mercapto compounds which are used together with the xanthylium dyes according to the invention may be represented by the following general formula:

acid—Z—SH

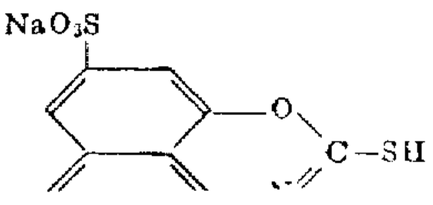
in which

Z is an isocyclic aromatic group such as a benzene or naphthalene group or an unsubstituted or substituted heterocyclic group consisting of a 5-membered or 6-membered heterocyclic ring and, if desired, benzene or naphthalene rings attached thereto by condensation, e.g. benzoxazole, naphtho-[1,2-d]-oxazole, naphtho-[2,1-d]-oxazole, naphtho-[2,3-d]-oxazole, benzo-thiazole naphtho-[1,2-d]-thiazole, naphtho-[2,1-d]-thiazoselenazole, naphtho-[1,2-d]-selenazole, benzimidazole, naphtho-[1,2-d]-imidazole, naphtho-[2,3-d]-imidazole, oxadiazole, thiadiazole, thiadiazolinethione, selenadiazole, triazole, naphtho-[1,8-de]-oxazine, naphtho-[1,8-de]-thiazine, pyrimidine, or pyrimidine; and

"acid" is an acid group which is attached to Z either directly or via one or more vinyl groups, e.g. —SO_3H, —SO_2T, —COOH, —PO_3H_2, —NHS-O_2R or SO_2NH—R in which R denotes an alkyl or aryl group; the acid groups may also be present in the anionic form as metal salts, preferably as alkali metal or alkaline earth metal salts or as salts of organic nitrogen bases.

The acid mercapto compounds are also known. The following compounds, for example, having been found to be suitable for the purpose of the present invention:

I



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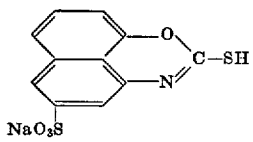

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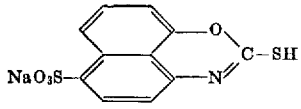

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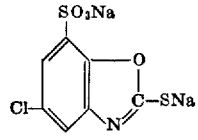

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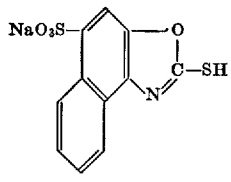

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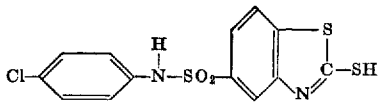

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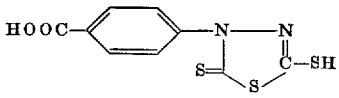

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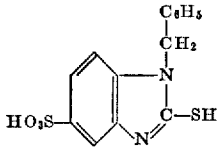

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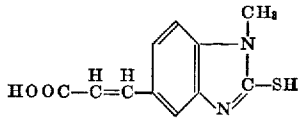
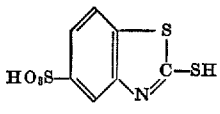


X



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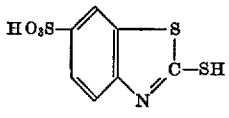
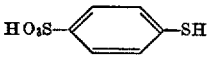


XII



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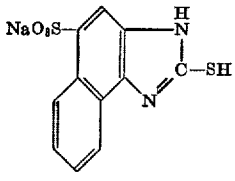
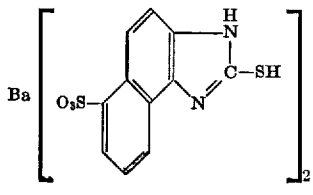


XIV



The use of both the acid mercapto compounds and the xanthylium dyes has the unexpected effect of considerably increasing the sensitizing effect of the xanthylium dyes, so that the mixture of compounds according to the invention is eminently suitable for sensitizing silver halide emulsions in the green region of the spectrum. An increase of up to as much as 40 times the sensitivity which is obtained with xanthylium dyes alone can quite easily be realised. The sensitization maxima lie between 520 and 620 nm., according to the xanthylium dyes used.

The usual silver halide emulsions may be spectrally sensitized by means of the mixtures according to the invention. The silver halide contained in these emulsions is generally silver chloride, silver bromide or a mixture of these, if desired with a small silver iodide content of up to 10 mols percent.

The binder used for the photographic layers is preferably gelatin although it may be partly or completely replaced by other natural or synthetic binders. Suitable natural binders are e.g. alginic acid and its derivatives such as salts, esters or amides, cellulose derivatives such as carboxymethylcellulose, alkyl cellulose such as hydroxyethyl cellulose, starch or derivatives thereof such as ethers or esters or carragheenates. Examples of synthetic binders are polyvinyl alcohol, partly saponified polyvinyl acetate and polyvinyl pyrrolidone.

The sensitizing mixture of xanthylium dye and acid mercapto compound may be added to the emulsions at any stage of their production, e.g. during precipitation of the silver halide, before or after the chemical ripening and preferably before casting. The conventional methods used for this are well known in the art. Both the xanthylium dyes and the mercapto compounds are added to the emulsions in the form of solutions. The solvent must, of course, be compatible with gelatin and must not have any adverse influence on the photographic properties of the emulsion. Water and alcohol are particularly suitable for use as solvents. The quantity of sensitizing xanthylium dye added may vary within wide limits, e.g. between 2 and 100 mg. preferably between 5 and 50 mg./kg. of silver halide emulsion. The quantity of acid mercapto compound added may also vary within wide limits, e.g. between 10 and 2000 mg. and preferably between 50 and 500 mg./kg. of silver halide emulsion. Particularly good results are achieved when the quantity of acid mercapto compound is a multiple of the quantity of xanthylium dye, e.g. 2 to 50 times the quantity of dye. The advantageous effect of the acid mercapto compounds is all the more astonishing in view of the high concentrations used since it is generally known that mercapto compounds act as stabilizers and when used in high concentrations severely impair the general sensitivity of silver halide emulsions. The two components of the sensitizing mixtures according to the invention may be added to the emulsions successively from separate solutions or they may be added simultaneously from a common solution.

The emulsions may also be chemically sensitized, e.g. by adding compounds which contain sulfur at the stage of chemical ripening, for example allylisothiocyanate, allylthiourea, or sodium thiosulfate. Reducing agents, e.g. the tin compounds described in Belgian patent specification Nos. 493,464 and 568,687 polyamines such as diethylene triamine or aminomethanesulfinic acid derivatives, e.g. according to Belgian patent specification No. 547,323, may also be used as chemical sensitizers.

Noble metals and compounds of noble metals such as gold, platinum, palladium, iridium, ruthenium or rhodium are also suitable as chemical sensitizers. This method of chemical sensitization has been described in the article by R. Koslowsky, Z. Wiss. Phot. 46, 65–72 (1951).

The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g. with polyethylene oxide having a molecular weight of between 1,000 and 20,000, or with condensation products of alkylene oxides and aliphatic

alcohols, glycols, cyclic dehydration products of hexitols or with alkyl substituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700 and preferably more then 1,000. These sensitizers may, of course, be combined for achieving special effects, as described in Belgian patent specification No. 537,278 and in British patent specification No. 727,982.

The emulsions may contain the usual stabilizers, e.g. homopolar or salt-type compounds of mercury which have aromatic or heterocyclic rings such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Azaindenes, especially tetra- or penta-azaindenes and especially those which are substituted with hydroxyl or amino groups are also suitable for use as stabilizers. Compounds of this type have been described in the article by Birr. Z. Wiss. Phot. 47, 2–58 (1952). Other suitable stabilizers include heterocyclic mercapto compounds, e.g. phenylmercaptotetrazole, quaternary benzothiazole derivatives, or benzotriazole.

A special advantage of the photographic material which has been senstized according to the invention consists in its insensitivity to the usual additives such as color forming couplers or dyes which can be bleached.

The emulsions may be hardened in the usual manner, for example with formaldehyde or halosubstituted aldehydes which contain a carboxyl group, e.g. mucobromic acid, diketones, methanesulfonic acid esters or dialdehydes.

EXAMPLE 1

A silver chloride emulsion (prepared according to Baker, Photogr. Em. Tech. American Photogr. Publishing Co., Boston, Mass., 1948, page 217) is cast on a layer support and exposed when dry behind a yellow filter GG 435 (made by the firm of Schott) (thickness of glass 3 mm. absorption edge 435 nm.) and a grey wedge with $\sqrt[3]{2}$ steps and is then processed in the usual manner.

Using 6 mg. of Pyronin B (Schultz, No. 855) per kg. of emulsion, a small increase in sensitivity in the green region of the spectrum (sensitization maximum 575 nm.) by two steps is achieved.

The sensitivity is considerably increased by the addition of 2 - mercaptonaphtho-[1,8-de]-oxazine-8-sulfonic acid sodium (I), 2-mercapto-naphtho-[1,8-de]-oxazine-5-sulfonic acid sodium (II) or 2-mercapto-naphtho-[1,8-de]-oxazine-6-sulfonic acid sodium (III) (in each case as a 0.5% aqueous solution), as can be seen from Table I.

TABLE I

	Steps $\sqrt[3]{2}$ Yellow filter GG 435	
	Fresh	After storage under tropical conditions
Standard (no sensitizer)	5	6
6 mg. Pyronin B	7	7
6 mg. Pyronin B plus:		
100 mg. I	16	21
200 mg. I	18	22.5
300 mg. I	18	23
100 mg. II	16	18.5
200 mg. II	17	20
300 mg. II	17	20.5
100 mg. III	16	22
200 mg. III	18.5	23
300 mg. III	19	23.5

Storage under tropical conditions means that the unexposed material was stored for 4 days at 40° C. and 82% relative humidity.

The addition of the acid mercapto compound therefore results in an increase in sensitivity by up to 12 steps (this corresponds to 16 times the sensitivity) compared with an emulsion which has only been sensitized with Pyronin B, and in the case of storage under tropical conditions there is an increase by 16 steps (corresponding to 40 times the sensitivity).

EXAMPLE 2

30 mg. of Rhodamine B (Schultz, No. 864) shows, in 1 kg. of a silver chloride emulsion, a very slight sensitization at about 577 nm. The sensitivity achieved with it and that achieved after the addition of the following mercapto compounds are shown in Table II:

2-mercapto-5-chlorobenzoxazole-7-sulfonic acid sodium (IV),
2-mercapto-naphtho-[1,2-d]-oxazole-8-sulfonic acid sodium (V),
2-mercapto-naphtho-[1,8-de]-oxazine-8-sulfonic acid sodium (I),
2-mercapto-4-phenyl-thiadiazolinethione-(5) (A),
1-phenyl-5-mercaptotetrazole (B),
2-mercaptobenzothiazole (C).

The non-acid mercapto compounds A, B and C used as stabilizers are used here for comparison.

TABLE II

	Steps $\sqrt[3]{2}$ behind yellow filter GG 435 Schott	
30 mg. Rhodamine B	Fresh	After storage under tropical conditions
Alone	6	7.5
+200 mg. IV	10.5	18.5
+200 mg. V	19	20.5
+200 mg. I	19	20
+60 mg. A	8	9
+45 mg. B	7	11
+30 mg. C	8	11

EXAMPLE 3

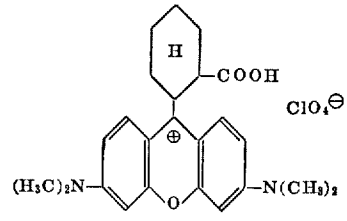
The following results are obtained under the same conditions with 30 mg. of Rhodanin 6 G DN (Schultz No. 866) with a sensitization maximum at 550 nm.:

TABLE III

	$\sqrt[3]{2}$ steps behind yellow filter	
30 mg. of Rhodanin 6 G DN	Fresh	After storage under tropical conditions
Alone	1	3
+200 mg. IV	14.5	13.5
+200 mg. V	17	17.5
+200 mg. I	18	19.5

EXAMPLE 4

20 mg. of a dye of the formula



(prepared, like Rhodamine B, with hexahydrophthalic acid) produces a slight sensitization in the green region of the spectrum with a maximum at 573 nm. on a silver chlorobromide emulsion described in Eder (Rezetpe, Tabellen und Arbeitsvorschriften," editions 20–22, W. Knapp, Halle/Saale, 1948, page 188) and on exposure behind the above mentioned yellow filter and a grey step wedge having the constant 0.1 ($\sqrt[3]{2}$) this sensitization provides a sensitivity of only one step. If 180 mg. of mercapto compound IV are added to the same mixture, 11 steps are obtained, in other words 10 times the spectral sensitivity.

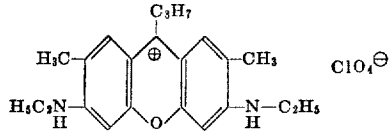
EXAMPLE 5

An "ammonia" emulsion which consists of 98% of AgBr and 2% of AgI and contains 19.3 g. of Ag per kg. of emulsion is used and 10 mg. of Pyronin B produce a sensitivity of 11 steps behind a yellow filter L 489 (Agfa-Gevaert) (absorption edge 489 nm.) and a step wedge of the factor $\sqrt{2}$. If 60 mg. of mercapto Compound IV are also added, the sensitivity rises to 16 steps, in other words to 5.6 times the original value.

This sensitivity increase is also achieved by the addition of 120 mg. of mercapto Compound I.

EXAMPLE 6

In 1 kg. of the silver chloride emulsion mentioned in Example 1 10 mg. of the Pyronin dye having the constitution shown in the following formula



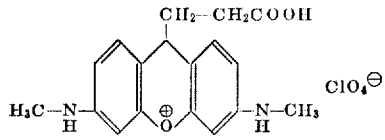
provide a sensitization maximum at 537 nm. The intensity is increased by the addition of mercapto compound IV.

TABLE IV

	Steps $\sqrt[3]{2}$ behind yellow filter
Dye alone	2
Dye+10 mg. IV	4
Dye+30 mg. IV	6
Dye+90 mg. IV	8.5
Dye+270 mg. IV	12

EXAMPLE 7

30 mg. of the Pyronin dye



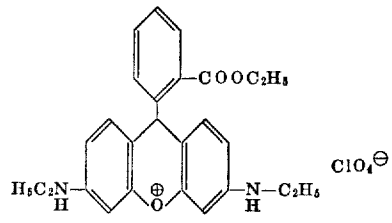
results in a sensitization maximum at 566 nm. The sensitivities achieved in the presence of 10 g. of the color-forming coupler 1-(4'-phenoxy-3'-sulfophenyl)-3'-heptodecylpyrazolone-(5) are as follows:

TABLE V

	Steps $\sqrt[3]{2}$ behind yellow filter
Dye alone	8.5
Dye+120 mg. I	16.5
Dye+120 mg. IV	17

EXAMPLE 8

When 30 mg. of the following dye



are used under the same conditions as in the previous example, the following values are obtained:

TABLE VI

	Steps $\sqrt[3]{2}$ behind yellow filter
Dye alone	5
Dye+120 mg. I	15
Dye+120 mg. VI	16.5

EXAMPLE 9

6 mg. of Pyronin B are introduced into a silver chloride emulsion as in Example 1 and cast on an acetyl cellulose support. The sensitivity behind of the yellow filter described above is two steps $\sqrt[3]{2}$. If in addition 100 mg. of 2-mercapto-4-(p-carboxyphenyl)-thiadiazolinethione-(5) (VII) are added, this sensitivity increases to 13 steps $\sqrt[3]{2}$, in other words to more than 10 times the original value.

EXAMPLE 10

To 1 kg. of an ammonia emulsion (see Example 5) are added: (a) the following dyes, (b) the following dyes and in addition 200 mg. of I. The sensitivity achieved is shown in Table VII.

TABLE VII

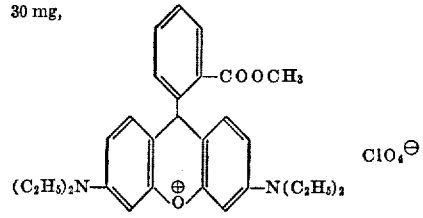
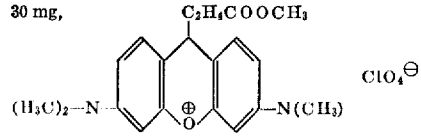
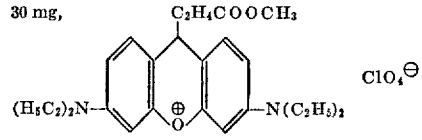
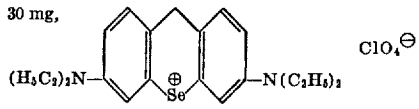
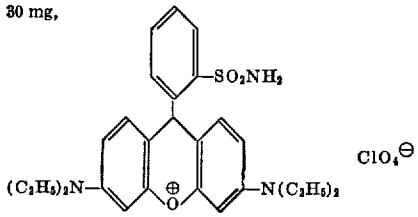
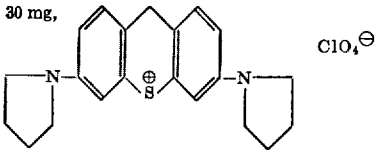
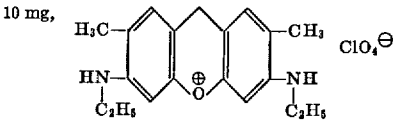
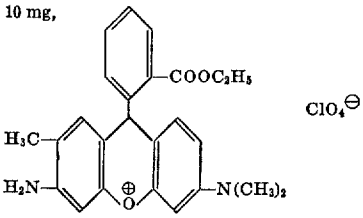
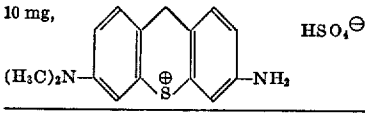
Dyes	Steps $\sqrt[3]{2}$ behind sensitization: Yellow filter	Maximum
30 mg, 	(a) 4 (b) 14	583
30 mg, 	(a) 7 (b) 14	576
30 mg, 	(a) 6 (b) 14	586

TABLE VII—Continued

Dyes	Steps $\sqrt[3]{2}$ behind sensitization: Yellow filter	Maximum
30 mg, 	(a) 5 (b) 13	610
30 mg, 	(a) 11 (b) 13	587
30 mg, 	(a) 5 (b) 10	605
10 mg, 	(a) 10 (b) 12	545
10 mg,  (Rhodamin 3GO)	(a) 10 (b) 13	565
10 mg, 	(a) 8 (b) 9	566

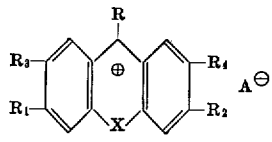
EXAMPLE 11

6 mg. of Pyronin B in methanolic solution (1:2000) are added to 1 kg. of an ammonia emulsion as described in Example 5. The following sensitivities are obtained behind yellow filter L 489:

	Steps $\sqrt{2}$
Dye alone	10
Dye+200 mg. VIII	12
Dye+200 mg. XIX	12
Dye+200 mg. X	13
Dye+200 mg. XI	13.5
Dye+200 mg. XII	15
Dye+200 mg. XIII	14.5
Dye+200 mg. XIV	15

What is claimed is:

1. A photographic material which comprises at least one silver halide emulsion layer that contains both (1) a xanthylium dye of the formula:



in which

X is an oxygen, sulphur or selenium atom,

R is a hydrogen atom or is an alkyl, aralkyl, cycloalkyl or aryl group,

R_1 and R_2, which may be the same or different are an amino group, the nitrogen atom of which may be mono- or di-substituted with alkyl groups containing up to 6 carbon atoms, cycloalkyl, aralkyl or aryl groups; or the nitrogen atom of the amino group may form a 5, 6 or 7 membered heterocyclic ring,

R_3 and R_4, which may be the same or different are a hydrogen atom, an alkyl group or an alkoxy group containing up to 6 carbon atoms,

$A^{\ominus}$ is an anion

and (2) an acid mercapto compound of the formula

acid—Z—SH

in which

Z is phenylene or a heterocyclic ring selected from the group consisting of benzoxazole, naphthoxazole, benzothiazole, naphthothiazole, benzoselenazole, naphthoselenazole, benzimidazole, naphthoimidazole, oxadiazole, thiadiazole, thiadiazolinethione, selenadiazole, triazole, naphthooxazine, naphthothiazine and pyrimidine, and

acid is an acid group selected from the group consisting of —SO_3H, —SO_4H, —COOH, —PO_3H_2,

—$NHSO_2$—R_5

and —SO_2NH—R_5 where R_5 is an alkyl or aryl group, or a salt anion derived from a metal salt or salt of organic nitrogen base; the acid group is attached to Z directly or via one or more vinylene groups.

2. A material as claimed in claim **1** which comprises in the silver halide emulsion layer 2 to 100 mg. of xanthylium dye per kilogram of emulsion.

3. A material as claimed in claim **2** which comprises 5 to 50 mg./kg. of xanthylium dye.

4. A material as claimed in claim **1** which comprises 10 to 2,000 mg. of acid mercapto compound per kg. of emulsion.

5. A material as claimed in claim **4** which comprises 50 to 500 mg./kg. of acid mercapto compound.

6. A material as claimed in claim **1** in which 2 to 50 times the weight of xanthylium dye of the acid mercapto compound is used.

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