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PHOTOGRAPHIC MATERIAL

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11 Claims. (Cl. 95—7)

This invention relates to photographic materials and particularly to photographic materials comprising silver halide emulsions containing de-sensitising agents.

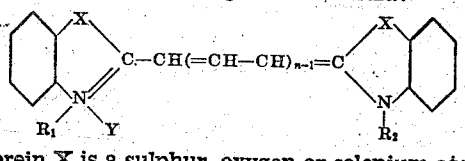
The most common use of photographic de-sensitising agents is in de-sensitising exposed silver halide emulsions, the usual method being to bathe the exposed emulsion in a solution of the de-sensitising agent before development and subsequent processing.

Since the effect of the addition of de-sensitising agents is to reduce the light-sensitivity of silver halide emulsions, the addition of de-sensitising agents to photographic silver halide emulsions during the manufacture of such emulsions, i. e. before exposure of the emulsions, is not usual. However, it is known that for some purposes the addition of certain de-sensitising agents to silver halide emulsions prior to exposure is advantageous. Thus, in the case of emulsions designed to record latent images under the influence of X-rays, the sensitivity of such emulsions to light may be considerably reduced without serious loss of X-ray sensitivity by the addition of a suitable de-sensitising agent to the emulsion during the manufacture of the emulsion. Again, some silver halide emulsions designed for use as positive printing materials tend to become irregularly fogged on development by so-called "sulphite fog" and it is found that the addition of certain desensitising agents during the manufacture of such emulsions reduces or eliminates this fog.

However, my experiments have shown that very many of the known de-sensitising agents are unsuitable for one reason or another for incorporation in silver halide emulsions during the manufacture of the emulsions. Thus, some de-sensitising agents tend to fog the emulsion and others break down and become ineffective.

The present invention is based on the discovery of a specific class of de-sensitising agents which may be incorporated in emulsions for purposes such as those indicated above, without deleterious effect on the emulsions.

According to the present invention, therefore, photographic materials comprising light-sensitive silver halide emulsions that contain a de-sensitising agent are produced by incorporating in silver halide emulsions prior to exposure thereof a de-sensitising agent which is an organic compound of the general formula:



wherein X is a sulphur, oxygen or selenium atom, R_1 and R_2 are alkyl or aralkyl groups, Y is an acid radical, n is 1, 2, 3 or 4 and at least one of the benzene rings contains a nuclear-substituted nitro group.

Preferably, the de-sensitising agents are compounds of the above general formula in which both the atoms X are sulphur atoms and it is also preferred that both benzene nuclei shall contain a nuclear-substituted nitro group. The nitro group or groups may be substituted in any free position in the benzene rings, but the 5 and 5′ positions are preferred. The groups R_1 and R_2 are preferably alkyl groups containing up to 4 carbon atoms, e. g. methyl, ethyl, propyl and butyl, but may be higher alkyl groups and n is preferably 1 or 2.

Specific examples of suitable de-sensitising agents according to the present invention are: 2:2′-diethyl-5:5′-dinitro-thiacarbocyanine-p-toluene sulphonate, 2:2′-dimethyl-5:5′-dinitro-thiacarbocyanine-p-toluene sulphonate and 2:2′-dimethyl-5:5′-dinitro-thiacyanine-p-toluene sulphonate.

The de-sensitising agents of the present invention may be made by any of the known general methods of making cyanine dyes. Thus, for example, the mono-methine cyanine types may be prepared by condensing a nitro-substituted 1-methyl-benzthiazole (or oxazole or selenazole) quaternary salt with a 1-methylthio-benzthiazole (or oxazole or selenazole) which may or may not be nitro-substituted. Symmetrical dyes of the carbocyanine type may be prepared, for example, by condensing the quaternary salt of a nitro-substituted 1-methyl benzthiazole (or oxazole or selenazole) with an alkyl ortho ester, e. g. ethyl ortho formate in pyridine solution. Unsymmetrical dyes of the carbocyanine type may be prepared, for example, by condensing a nitro-substituted 1-methyl benzthiazole (or oxazole or selenazole) quaternary salt with a 1-acetanilido-vinyl derivative of benzthiazole (or oxazole or selenazole) which may or may not be nitro-substituted.

The following examples illustrate the invention:

Example I

A gelatin-silver iodobromide fast negative emulsion containing the equivalent of 300 grams of silver nitrate per gallon of emulsion and suitable for X-ray photography was prepared and to this was added 31 ccs. of a 0.01% solution in ethyl alcohol of 2:2′-diethyl 5:5′-dinitrothiacarbocyanine-p-toluene sulphonate per gallon of emulsion. The emulsion was then coated on a suitable support in the usual way.

The addition of the stated de-sensitising agent caused a reduction in the speed of the emulsion to light rays to less than one-eighth of the speed to light rays of the same emulsion not contain-

ing the de-sensitising agent, but the speed of the emulsion to X-rays was substantially unaffected by the addition of the stated de-sensitising agent.

In consequence the unexposed emulsion could be handled in brighter lighting conditions than would otherwise be necessary, without fear of fogging the emulsion. In addition the emulsion obtained was exceptionally fog-free and had excellent keeping qualities.

Example II

A washed normal silver bromide emulsion of the type employed in development papers as used for enlarging and containing 3.60 grams of silver per 150 cc. of emulsion was prepared and various quantities of a 0.02% solution of 2:2'-diethyl 5:5'-dinitrothiacarbocyanine-p-toluene sulphonate were added to separate portions of such emulsion. The emulsions were then coated on paper in the usual way. Some test pieces of the paper were developed in a metol-hydroquinone developer immediately (without exposure) and others were subjected to incubation at 115° F. and approximately 40% relative humidity for ten days and then developed, without exposure, in a metol-hydroquinone developer.

The density of fog appearing on the developed test pieces was measured in a densitometer and the following results were obtained:

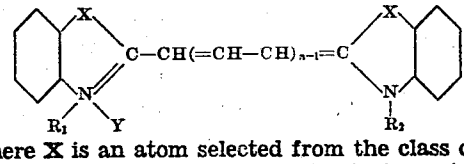
Fog values

Emulsion	Not incubated			Incubated		
	2 mins. devpt. at 65° F.	4 mins. devpt. at 65° F.	2 mins. devpt. at 80° F.	2 mins. devpt. at 65° F.	4 mins. devpt. at 65° F.	2 mins. devpt. at 80° F.
Original emulsion	.02	.18	.24	.06	.30	.40
Emulsion containing 5 ccs. of above solution per pound of emulsion	0	.12	.18	.03	.16	.18
Emulsion containing 10 ccs. of above solution per pound of emulsion	0	.05	.12	.01	.08	.15
Emulsion containing 20 ccs. of above solution per pound of emulsion	0	.02	.06	0	.05	.09

It is apparent from the above table that the addition of the stated de-sensitiser causes a very substantial reduction in the development fog.

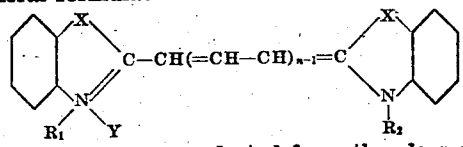
What I claim is:

1. A light sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



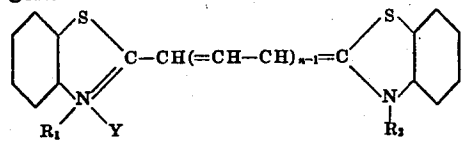
where X is an atom selected from the class consisting of sulphur, oxygen and selenium atoms, R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle, n is a positive integer less than 5 and at least one of the benzene rings contains a nuclear substituted nitro group.

2. A photographic element which includes a light-sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



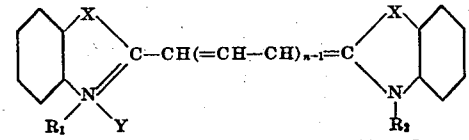
where X is an atom selected from the class consisting of sulphur, oxygen, and selenium atoms, R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle, n is a positive integer less than 5 and at least one of the benzene rings contains a nuclear substituted nitro group.

3. A photographic element which includes a light-sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



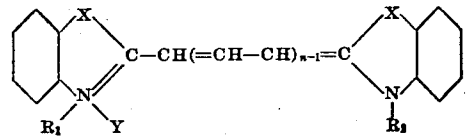
where R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle, n is a positive integer less than 5 and at least one of the benzene rings contains a nuclear-substituted nitro group.

4. A photographic element which includes a light-sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



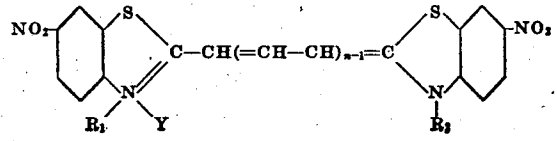
where X is an atom selected from the class consisting of sulphur, oxygen and selenium atoms, R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle, n is a positive integer less than 5 and both benzene rings contain a nuclear-substituted nitro group.

5. A photographic element which includes a light-sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



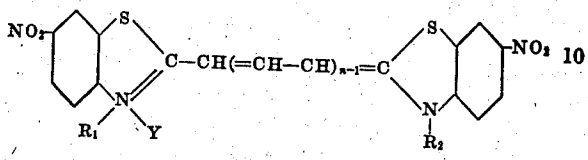
where X is an atom selected from the class consisting of sulphur, oxygen and selenium atoms, R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle, n is a positive integer less than 3 and at least one of the benzene rings contains a nuclear-substituted nitro group.

6. A photographic element which includes a light sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



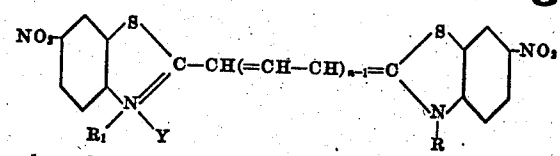
where R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle and n is a positive integer less than 5.

7. A photographic element which includes a light sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



where R_1 and R_2 are selected from the class consisting of alkyl and aralkyl groups, Y is an acid radicle and n is a positive integer less than 3.

8. A photographic element which includes a light sensitive silver halide emulsion containing a de-sensitising agent which is a compound of the general formula:



where R_1 and R_2 are alkyl groups containing up to four carbon atoms, Y is an acid radicle and n is a positive integer less than 3.

9. A photographic element which includes a light sensitive silver halide emulsion containing 2:2'-diethyl -5:5'- dinitro - thiocarbocyanine-p-toluene sulphonate.

10. A photographic element which includes a light sensitive silver halide emulsion containing 2:2'-dimethyl -5:5'- dinitro-thiocarbocyanine-p-toluene sulphonate.

11. A photographic element which includes a light sensitive silver halide emulsion containing 2:2'- dimethyl -5:5'- dinitro-thiocyanine-p-toluene sulphonate.

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