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3,184,313

SILVER HALIDE EMULSION DESENSITIZED WITH A TETRAALKYL THIURAM DISULFIDE

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6 Claims. (Cl. 96—101)

This invention relates to photographic elements for use in radiography, and more particularly, to X-ray sensitive elements which have materially reduced sensitivity to visible radiation.

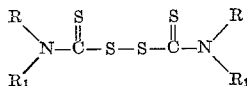
It is known that photographic silver halide emulsions can be usefully employed in radiography, and that these sensitive elements can be provided with an opaque or light impervious overcoat, which is removed during or after processing to a radiographic image. It is obvious that such protective layers have many drawbacks in that they cause contamination of the photographic treating solutions, or they require a separate step to remove them from the surface of the photographic element. Furthermore, it is frequently difficult to disperse uniformly the light reflective or light absorptive pigment throughout the overcoating layer with the result that uniform protection is not always provided.

Other radiographic elements have been suggested which comprise a protective overcoat containing chrome yellow, Venetian red, or the like, and these pigments do have the advantage of allowing the element to be handled in ordinary ordinary daylight or room light, but it is necessary to remove them prior to photographic development, and this development must then necessarily be carried out in a darkroom.

It has also been suggested that photographic silver halide emulsions designed for use in radiography be substantially desensitized to visible radiation without materially affecting their sensitivity to X-rays. However, as a practical matter, it has been difficult to discover desensitizing compounds which effectively reduce the sensitivity of these emulsions to visible radiation without materially reducing the sensitivity of the emulsions to X-ray.

We have now found a class of disulfide compounds which can be effectively employed to reduce the sensitivity of X-ray emulsions to visible radiations so that they can be handled easily under ordinary safelights. These disulfides of our invention have the advantage of only slightly lowering the sensitivity of these emulsions to X-rays.

The disulfide compounds useful in our invention are known as thiuram disulfides and they are characterized by marked desensitizing action toward silver halide emulsions, insofar as their sensitivity to visible radiations is concerned (particularly those beyond the blue region of the spectrum), yet retaining substantially the sensitivity of the emulsions to X-rays. The thiuram disulfide desensitizers which can be effectively employed in our invention include those represented by the following general formula:

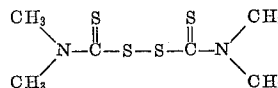


wherein R and R₁ each represents an alkyl group, such as methyl, ethyl, propyl, butyl, isobutyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms), an aryl group, such as phenyl, tolyl, etc., or together R and R₁ represent the atoms necessary to complete an azine ring, such as morpholine, piperidine, etc., or, alternatively, a pyrrolidine ring, for example. The thiuram disulfide

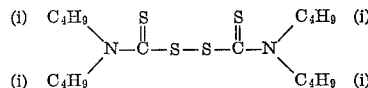
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compounds are characterized in that the nitrogen atoms thereof are tertiary nitrogen atoms. Typical compounds included by the above general formula are, for example, the following:

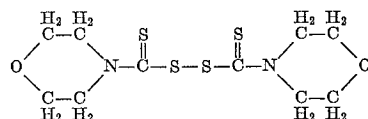
(1) Bis(dimethylthiocarbamyl) disulfide



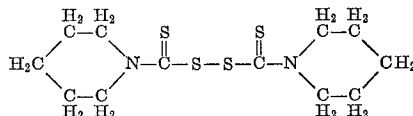
(2) Bis(diisobutylthiocarbamyl) disulfide



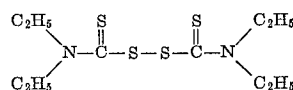
(3) Bis(4-morpholinothiocabonyl) disulfide



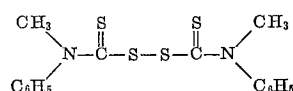
(4) Bis(1-piperidylthiocarbonyl) disulfide



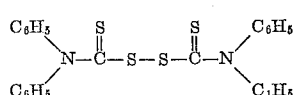
(5) Bis(diethylthiocarbamyl) disulfide



(6) Bis(N-methyl-N-phenylthiocarbamyl) disulfide



(7) Bis(diphenylthiocarbamyl) disulfide



The above compounds can be prepared according to techniques which have been previously described in the prior art, and any of these well known processes can be used to prepare these compounds.

In the copending application of A. H. Herz, Serial No. 147,766, filed October 26, 1961, now Patent No. 3,144,336, there is described a method of sensitizing photographic emulsions by a combination of two sulfur-containing compounds, neither of which is a sensitizer in its own right. As indicated in this application, one of these sulfur-containing compounds can be a thiuram disulfide. However, it is imperative in the sensitizing combinations of U.S. application 147,766, now Patent No. 3,144,336, that a sulfinic acid compound be present. However, in the present invention no sensitization occurs since no reaction occurs between a sulfinic acid compound and the decomposition products of the thiuram disulfide compounds.

The quantity of thiuram disulfide compound employed in our invention can be varied, depending upon the particular silver halide used in the emulsion, the amount of gelatin or other colloid binder, etc. In general, we have found that quite useful results can be obtained at concentrations as low as 2 mg. per mole of silver halide, while amounts as high as 75 mg. per mole of silver halide can be used without affecting the X-ray sensitivity

too seriously. Different types of silver halide, e.g., silver chloride, silver bromide, silver chlorobromide, etc., can be employed, although we have found that iodide-containing emulsions are especially useful. These typically include silver bromoiodide, silver chloroiodide, silver chlorobromoiodide, etc. Emulsions which form the latent image especially within the silver halide grain can be usefully employed in our invention. The preparation of such internal latent image emulsions is described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952. The amount of desensitizer employed will obviously depend somewhat upon the type of silver halide emulsion used.

In order to decrease still further the sensitivity of the silver halide emulsions of our invention to visible radiation, a small amount of a light-absorbing organic dye can be employed either in the emulsion or in an overcoating layer. Since the silver halide emulsions of our invention may retain some sensitivity in the blue region of the spectrum, it has been found that many azo dyes, such as tartrazine, can be usefully employed. Other visible-light absorbing dyes which can be employed in such arrangements are 2-(2'-methoxy styryl)quinoline hydrochloride, the condensation product of two molecular proportions of quinaldine methosulfate and one molecular proportion of 4,4'-diphenyl dialdehyde pyridine, 4,4'-methenyl-bis-(1-naphthyl - 3 - methylpyrazolone - 5), etc. Other light-absorbing dyes are described in Dostes and Pfaff U.S. application Serial No. 83,709, filed January 19, 1961. The amount of light-absorbing dye used to reduce the sensitivity of our photographic elements can vary as described in Serial No. 83,709. Instead of using a dyed silver halide emulsion layer or a dyed overcoating layer to protect further the radiographic sensitive layer, it is possible to use a light-absorbing silver halide emulsion layer which has very low sensitivity to visible radiation. Lippmann-type emulsions can conveniently be employed for this purpose. Silver iodide-containing emulsion layers are also useful for this purpose.

If desired, the silver halide emulsion layers of our invention can be coated on one or both sides of a transparent support, such as cellulose ester film, polyester film, polycarbonate film, polystyrene film, etc.

The silver halide can be dispersed in any of the conventional hydrophilic water-permeable binding materials, such as gelatin, albumin, polyvinyl pyrrolidone, polyvinyl alcohol, hydrolyzed cellulose acetate, etc.

The following examples will serve to illustrate more fully the manner of practicing our invention:

EXAMPLE 1

An ordinary coarse-grained silver bromoiodide emulsion of the type normally used in radiography, which had been chemically sensitized to its optimum speed was then divided into several portions and each portion was then treated with varying amounts of bis(dimethylthiocarbamyl)disulfide at the concentrations indicated in the following table. One portion of emulsion was untreated and this served as a control. Each of the aliquot portions of emulsion was then coated on an ordinary cellulose acetate film base, and the coatings dried. The coated films were then divided in half and one-half was exposed to 80 kilovolt X-rays and the other half was divided into four strips which were separately exposed to a 100-watt bulb equipped with a Kodak Wratten Filter as indicated in the table at a distance of 14 inches. Each section of film was then developed for 5 minutes in an ordinary MQ developer, i.e., a developer containing hydroquinone and N-methyl-p-aminophenol sulfate, such as Kodak Developer D-19b to which had been added a small amount of alkali to increase the pH to about 11.0. After development, the strips were then fixed, washed and dried in the usual manner. The relative speeds of the coatings which had been exposed to 80 kv. X-rays were then measured at a density of 0.85 above fog and the gross density of

the strips which had been exposed through Wratten filters was measured. The following results were obtained:

Table I

Coating	Addenda, mg./mol. AgX	Rel. Speed to X-rays	Gross D (7 mins. Exp.)			
			6B	OC	OA	OO
(a)-----	0	100	>3	>3	>3	>3
(b)-----	5	98	0.28	>3	>3	>3
(c)-----	10	89	0.12	0.00	1.1	>3
(d)-----	20	79	0.12	0.12	0.14	>3
(e)-----	30	71	0.12	0.12	0.12	1.02
(f)-----	50	55	0.12	0.12	0.12	0.48

EXAMPLE 2

An ordinary photographic bromoiodide emulsion of the type described in Example 1 was treated with compounds as identified in the following table at the amount shown and strips of film coated with these emulsions were exposed either to 80 kv. X-rays or to a 15-watt darkroom lamp mounted 4 feet above the film plane and equipped with either a Wratten Series OA or Series OO Filter. The safelight exposure was for 6 minutes. The strips were then developed in an MQ developer, fixed, washed and dried, as described in Example 1. The following results were obtained:

Table II

Coating	Addenda (mg./mole AgX)	80 kv. Direct X-ray Ex- posure, Rel. Spd. at D=0.85 above fog	Safelight Exposure	
			Gross, OA	Density, OO
(g)-----	0	100	0.56	>3.0
(h)-----	25 mg. Compound 1	93	0.12	0.68
(i)-----	25 mg. Compound 2	95	0.18	1.62
(j)-----	40 mg. Compound 2	93	0.14	1.21
(k)-----	75 mg. Compound 2	50	0.12	0.68
(l)-----	25 mg. Compound 3	107	0.12	0.72
(m)-----	35 mg. Compound 3	100	0.12	0.59
(n)-----	50 mg. Compound 3	95	0.12	0.52

Kodak Developer D-19b has the following composition:

	Grams
N-methyl-p-aminophenol sulfate -----	2.2
Hydroquinone -----	8.8
Sodium sulfate anhydrous -----	72.0
Sodium carbonate crystalline -----	130.0
Potassium bromide -----	4.0
Water to make 1 liter.	

For use in the present invention, this developer was found most effective when the pH was raised slightly to 11.0 by the addition of additional alkali.

Kodak Safelight Filter Wratten Series OA transmits visible radiation principally between about 540 and 680 mμ with maximum transmission at about 575 mμ. (Density of about 0.76 at this point.) Kodak Safelight Filter Wratten Series OC transmits radiation principally between about 560 and 660 mμ with maximum transmittance at about 585 mμ. (Density of about 0.92 at this point.) Kodak Safelight Filter Wratten Series OO transmits substantially all wavelengths beyond about 530 mμ. (Density of 0.8 at about 530.) Kodak Safelight Filter Wratten Series 6B transmits radiation between about 565 and 660 mμ with maximum transmittance at about 595 mμ. (Density of 1.7 at this point.)

The amount of desensitizing compound used can be varied considerably as shown in the above examples.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

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What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion which has been substantially desensitized to visible radiation by the addition thereto of from 2 to 75 mg. per mole of silver halide of a tetraalkyl thiuram disulfide.

2. A photographic emulsion according to claim 1 wherein said disulfide is bis(dimethylthiocarbamyl)disulfide.

3. A photographic emulsion as defined in claim 1 wherein said disulfide is bis(diisobutylthiocarbamyl)disulfide.

4. A photographic element comprising a transparent, flexible support having coated thereon a photographic silver halide emulsion having substantially reduced sensitivity to visible light by the addition thereto of from 2 to 75 mg. per mole of silver halide of a tetraalkyl thiuram disulfide.

5. A photographic element comprising a transparent, flexible support having coated thereon a photographic

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silver halide emulsion having substantially reduced sensitivity to visible light by the addition thereto of from 2 to 75 mg. per mole of silver halide of bis(dimethylthiocarbamyl)disulfide.

6. A photographic element comprising a transparent, flexible support having coated thereon a photographic silver halide emulsion having substantially reduced sensitivity to visible light by the addition thereto of from 2 to 75 mg. per mole of silver halide of bis(diisobutylthiocarbamyl)disulfide.

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