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LIGHT-SENSITIVE SILVER COMPOUNDS AND PHOTOGRAPHIC METHODS

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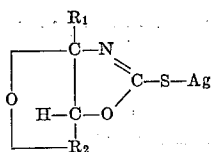
5 Claims. (Cl. 96-63)

This invention relates to light-sensitive silver compounds particularly to certain light-sensitive silver compounds, and to photographic systems and methods that employ such compounds.

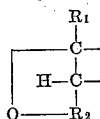
An object of the invention is to provide novel, water-soluble, light-sensitive silver mercaptides and novel photographic systems that employ such compounds. Most of the widely used photographic systems employ one or a mixture of silver halides as the light-sensitive element. A disadvantage with silver halide photographic systems is that in order to permanize a finished photograph a separate bath must be used that contains a silver halide solvent (fixer) for removing water-insoluble silver halides that remain in the film after development. Usually, a further bath is needed to wash residual silver halide solvent from the film. With water-soluble light-sensitive silver compounds of the invention, undeveloped silver that remains in the film after development can be removed simply by washing the film with warm water. This makes the compounds especially suitable for use in diffusion transfer processes.

One specific object of the invention is to provide novel photographic systems comprising water-soluble light-sensitive silver mercaptides that can be developed by known organic silver halide developers and can be permanized after development by using only water, without the need for a special permanizing solvent. Other objects and advantages will appear from consideration of the following detailed description and claims.

According to the present invention photographic systems employ as a light-sensitive element a silver mercaptide having the formula



wherein the radical



represents a 1,2-bivalent or 2,3-bivalent hexose or pentose radical. Compounds having the above formula behave in a photographic emulsion much the same, in some respects, as silver halides behave. The compounds are light-sensitive, and after exposure to actinic light they will respond under certain conditions to the same developers that are used for reduction of exposed silver halides to produce a silver image. A great variety of silver halide developing solutions are described in photographic literature, and these silver halide developers are effective photographic developers for the silver compounds of this invention. The silver mercaptides of the invention are notably different from silver halides in being easily soluble in water.

A convenient method for synthesis of a light-sensitive silver mercaptide of the class described is to react the

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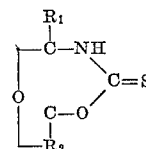
corresponding oxazolidinethione compound with an equimolar portion of a soluble silver salt, such as silver nitrate. The reaction proceeds in aqueous solution. The optimum molar ratio of silver salt reactant to oxazolidinethione reactant in the reaction mixture is 1:1, and this ratio is preferred for optimum results in photographic systems. Excess amounts of silver salt in the solution will produce some fog in a photographic emulsion and excess amounts of the oxazolidinethione will reduce the light sensitivity of a photographic emulsion.

The silver salt for reaction with the oxazolidinethione compound can be an inorganic, water-soluble silver salt such as silver nitrate, silver sulfate, silver acetate, silver perchlorate, and the like, or it can be an organic silver salt such as p-toluenesulfonate silver salt, and other organo-silver complexes having a stability constant less than that of the mercaptide. Organic silver salts can be chosen that will release to the solution, upon reaction with the oxazolidinethione, an organic ion that is useful in a photographic emulsion, such as an acid, dye, hardener, etc. For example, silver p-toluenesulfonate, upon reaction with an oxazolidinethione will release sulfonic acid which contributes necessary acid for a photographic emulsion.

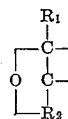
Some specific examples of oxazolidinethione compounds that will react with a silver salt to obtain the light-sensitive mercaptides of the invention are

4,5(2,3-D-fructopyrano)-2-oxazolidinethione,
4,5(1,2-D-galactofurano)-2-oxazolidinethione,
4,5(1,2-D-glucufurano)-2-oxazolidinethione,
4,5(1,2-D-xylofurano)-2-oxazolidinethione,
4,5(1,2-L-arabinofurano)-2-oxazolidinethione,
and the like.

These compounds have the general formula

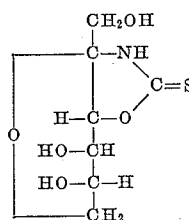


wherein the radical



represents a member selected from the group consisting of 1,2-bivalent or 2,3-bivalent pentose and hexose radicals.

Synthesis of compounds of this class by reaction of hexoses and pentoses with thiocyanic acid is described by Zemlen at 71 Berichte Chemie, 594 A1938. The 4,5(2,3-D-fructopyrano)-2-oxazolidinethione compound can be represented by the formula



Other structures and nomenclature for this compound have been proposed, as by Zemlen, supra.

An emulsion for photographic film comprises an acid solution of the light-sensitive mercaptide and a film-forming binder such as photographic gelatin, polyvinyl

alcohol, and the like. Most conveniently a film-forming binder such as gelatin is included in the same solution in which the silver mercaptide is synthesized by the reaction described above, thereby making an emulsion for coating. Other conventional addenda such as sensitizers, dyes, hardeners, and the like may be included in the emulsion. The emulsion is coated on a film support by one of the conventional emulsion coating methods to produce a light-sensitive film on the support. Of course the light-sensitive mercaptide must be kept from light until photographic exposure. In solution the mercaptide of the invention apparently exists as a complex ion.

A factor that seems necessary for light sensitivity of emulsions containing the silver mercaptide is that the emulsion must be acid. Emulsions having a pH number much above 4 do not exhibit light sensitivity when coated as photographic films. Optimum sensitivity for most of the silver mercaptide emulsions is obtained at about pH 1.5. Inorganic and organic acids may be added to the emulsion to adjust the pH value. Acids such as nitric, sulfuric, taurine, p-toluene sulfonic acid and the like may be employed for this purpose.

It is characteristic of light-sensitive films containing a light-sensitive silver mercaptide described that a silver image can be developed with a reducing agent only in a system that contains an acceptor for the oxazolidinethione compound which is released upon reduction of the silver. This acceptor most conveniently is a cation that is present in the system and that is capable of reacting with the released oxazolidinethione compound to form a mercaptide during the silver development. This acceptor is present in the system as a cation of a soluble salt. In a photographic film the acceptor can be conveniently provided in a water-permeable sub-coating under the light-sensitive emulsion layer. A soluble salt such as barium nitrate, barium sulfate, cadmium nitrate, cadmium sulfate, zinc sulfate, strontium nitrate, magnesium nitrate, calcium nitrate, lead nitrate, stannous chloride, bismuth nitrate, aluminum nitrate and the like may be present, preferably in an undercoat, to provide the acceptor cation. Baryta coated paper provides an excellent support for the light-sensitive emulsion, providing barium ion as an acceptor.

The following examples illustrate preferred embodiments of the invention.

Example 1

On a lightweight paper support an undercoat consisting of

2000 ml. 10% photographic gelatin in water,
100 gm. cadmium nitrate ($x4H_2O$),
20.0 ml. concentrated nitric acid, and
6.25 ml. 40% formaldehyde

was spread to a thickness to give 168 mg. of cadmium per square foot and was dried. A light-sensitive emulsion was prepared as follows. To 500 ml. water was added 55 g. of 4,5(2,3-D-fructopyrano)-2-oxazolidinethione and 1000 ml. of 10% photographic gelatin in water. The mixture was heated at 131° F. until all the oxazolidinethione had dissolved, and then 500 ml. distilled water and 42 grams silver nitrate were added. Acidity of the emulsion increased to about pH 1.5. A layer of the light-sensitive emulsion was applied over the undercoat at a thickness to give 144 mg. of silver per square foot, and was dried. The coated paper had a photographic speed suitable for contact printing, approximately that of Kodak Velox Paper. A sample of the coated paper was exposed to a negative transparency in a contact printer, then a silver image was developed in the film using Kodak Dektol developer, diluted 1:1 with water, for 90 seconds at 70° F. Development was stopped by immersing the sample in cold water for 2 minutes. Undeveloped silver compounds was removed by washing the print for 20 minutes in water at 75° F., then the print was dried. The finished print had a neutral-tone silver

image of good gradation. It contained practically no undeveloped silver.

Example 2

An emulsion was prepared by heating to 55° C. a mixture of 40 ml. distilled water, 2.2 gm. 4,5(2,3-D-fructopyrano)-2-oxazolidinethione and 40 ml. of gelatin. When the oxazolidinethione had completely dissolved, 2.79 gm. of p-toluenesulfonic acid, silver salt was added. Acidity increased to about pH 1.5. Analysis indicated formation of a silver mercaptide.

A photographic paper was prepared by coating the emulsion at .006 inch wet-thickness on Baryta coated paper. After drying, the photographic paper was exposed and developed as in Example 1. Undeveloped silver was removed by washing the print in a warm water bath for 20 minutes.

Because the unexposed silver mercaptide is water-soluble, it is particularly suitable for use in diffusion transfer processes as the light-sensitive compound. Use of this soluble light-sensitive silver compound instead of insoluble silver halides eliminates the need for a silver halide solvent in the diffusion transfer processing solution. Thus ordinary developing solutions can be used for such processing.

Example 3

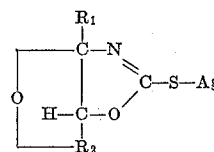
A photographic paper prepared as in Example 1 was exposed to a light pattern on a Processing Control Sensitometer. The exposed paper was immersed for 60 seconds in a 1:1 solution of Kodak Dektol developer in water.

When the paper was removed from the developing solution, and while still wet with developing solution, the emulsion side was pressed for two minutes against a conventional diffusion transfer receiving sheet containing nickel sulfide. When the sheets were separated a positive image of yellowish brown color appeared on the receiving sheet. The experiment was repeated using other conventional diffusion transfer receiving sheets containing silver oxide and lead sulfide nuclei, and positive images were obtained.

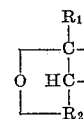
The invention has been described with reference to preferred embodiments but it will be understood that variations and modifications of the invention can be made within the scope of the following claims.

I claim:

1. A light-sensitive compound having the formula



wherein the radical

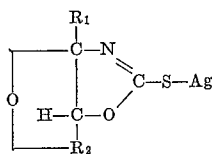


represents a member selected from the group consisting of 1,2-bivalent and 2,3-bivalent pentose and hexose radicals.

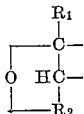
2. A photographic element comprising a support, an undercoat on said support containing a water-soluble salt of a metal that will react to form a mercaptide with the oxazolidinethione compound released upon reduction of silver mercaptide in the overlying layer, and an overlying layer comprising a colloid binder having dispersed therein a photosensitive mercaptide derived from

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an oxazolidinethione compound, said mercaptide having the formula



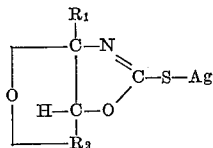
wherein the radical



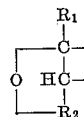
represents a member selected from the group consisting of 1,2-bivalent and 2,3-bivalent pentose and hexose radicals.

3. A photographic element comprising

- (1) a support
- (2) a water-permeable undercoat on said support containing a water-soluble salt whose cation is capable of forming a mercaptide with the oxazolidinethione compound that is released upon reduction of silver in the light-sensitive layer, and
- (3) a water-permeable, light-sensitive layer overlying said undercoat and comprising a light-sensitive silver mercaptide derived from an oxazolidinethione compound dispersed in a colloid binder, said silver mercaptide having the formula



wherein the radical

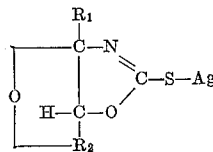


represents a member selected from the group consisting of 1,2-bivalent and 2,3-bivalent pentose and hexose radicals.

4. A photographic film comprising a film-forming binder and dispersed therein a light-sensitive compound

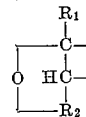
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derived from an oxazolidinethione compound, said compound having the formula



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wherein the radical

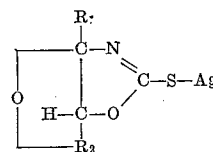


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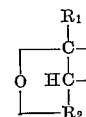
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represents a member selected from the group consisting of 1,2-bivalent and 2,3-bivalent pentose and hexose radicals.

5. A method for producing a photograph comprising
(1) exposing to a pattern of actinic light a film comprising a light-sensitive silver compound having the formula



wherein the radical



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represents a member selected from the group consisting of 1,2-bivalent and 2,3-bivalent pentose and hexose radicals.

- (2) developing a silver image in the exposed areas of said film by selective reduction of exposed mercaptide with a photographic silver halide developer in the presence of a cation that is capable of forming a mercaptide with the oxazolidinethione compound released upon reduction of silver, and
- (3) washing the film with water to dissolve and remove undeveloped silver mercaptide from the film.

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No references cited.

NORMAN G. TORCHIN, *Primary Examiner*.