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PHOTOGRAPHIC EMULSIONS CONTAINING A 1,2-DITHIOLANE

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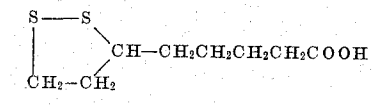
This invention pertains to photography and more particularly to photographic silver halide emulsions of enhanced sensitivity, and to their preparation.

Various sulfur compounds have been added to photographic silver halide emulsions to improve them for diverse purposes. Thus, allyl isothiocyanate, allyl thiocarbimide, allyl diethyl thiourea, phenyl isothiocyanate, sodium thiosulfate, etc., have been added to emulsions to increase their light-sensitiveness. Other compounds including di-o-formylalkylaminodiphenyl disulfides have been added to emulsions as anti-fogging agents. Still other cyclic organic sulfur-containing compounds including the 1-hydrocarbon 5-mercaptotetrazoles have been added to photographic paper silver halide emulsions as anti-plumming or anti-fogging agents.

An object of this invention is to provide new means for improving the sensitivity of photographic silver halide emulsions. Another object is to provide colloid silver halide emulsions of enhanced speed. A further object is to provide such emulsions wherein the added adjuvant does not have an adverse effect on the spectral properties of the emulsion. Still other objects will be apparent from the following description of the invention.

It has been found that photographic emulsions of silver halide in synthetic water-permeable colloid binding agents, which emulsions contain an organic compound containing a 1,2-dithiolane nucleus and more particularly a 5[1,2-dithiolane-3-yl]alkanoic acid and its alkali metal, ammonium, substituted ammonium and amine salts have a marked increase in their light-sensitiveness. Suitable salts include the sodium, potassium, tetramethylammonium, dimethylamine, diethylamine, trimethylamine, triethylamine, and cyclohexylamine salts.

In the preferred aspect of the invention the colloid silver halide emulsions contain a small amount of 5[1,2-dithiolane-3-yl]pentanoic acid. This acid has the formula:



and has been named α-lipoic acid. A method of preparing it has been described in Jour. Am. Chem. Soc., vol. 74, pp. 1868–9 and 3455 (1952). The salts of the above acid can be made by neutralization of the acid with the appropriate base.

The 1,2-dithiolane compound can be incorporated in the silver halide emulsion at various stages in its preparation and in various manners. Thus, it can be added to the fluid silver halide emulsion in crystalline form or from water or a water-miscible solvent, e. g., methanol or ethanol. It can be added in similar manner to the solutions used in making the silver halide emulsion, for example, in the colloid solution. Thus, it can be added to the emulsion at the silver halide precipitation stage or at any later stage prior to coating onto a support, e. g., film or paper as a light-sensitive layer. It preferably is added after the initial preparation of the silver halide emulsion but before the final digestion stage has been concluded.

The 1,2-dithiolane compound confers to the final colloid silver halide emulsion a sensitiveness of the optical type and gives it an overall increase in speed, as distinguished from the extra range of spectral sensitivity conferred by sensitizing dyes. The compound can be used with such dyes, thereby modifying the normal sensitivity and speed of emulsions.

The invention will be further illustrated but is not intended to be limited by the following example.

Example

A dispersion of silver bromide is prepared, in the absence of actinic light, by adding 25 parts of 0.40 N silver nitrate in 100 parts of water to a mixture of 750 parts of water containing 25 parts of 0.44 N ammonium bromide and adjusting the pAg to a value of 8.33. To 150 parts of the silver bromide dispersion is added 50 parts of 2.5% solution of the polyvinyl alcohol made by the complete hydrolysis of polyvinyl acetate as described in U. S. Patent 2,579,016, and 0.1 part of 5[1,2-dithiolane-3-yl]pentanoic acid in 2 parts of ethanol. When a 20 cc. sample of this solution is exposed to light and the exposed silver halide developed with 5 cc. of a 0.1 M solution of p-methylaminophenol buffered with sodium hydrogen phosphate to a pH 7, and excess silver bromide removed by treatment with a fixing solution of sodium thiosulfate, a black deposit of silver remains. When compared with a similar control emulsion free from said 5[1,2-dithiolane-3-yl]pentanoic acid exposed, developed and fixed in like manner the sensitiveness of the first emulsion is 5 to 7 times greater, as indicated by optical density measurements, than that of the latter control emulsion.

The 1,2-dithiolane compound can be used in various amounts, a practical range being from 1 to 250 milligrams and a preferred range being from 5 to 50 milligrams of said compound per mol of silver halide. However, as indicated by the example, up to 40% by weight of the compound, based on the silver halide can be used.

While in the foregoing example the compound was added after precipitation of the halide and there were no digestion, washing, second digestion or ripening steps to bring the emulsion to its maximum sensitivity, these conventional procedures obviously would be used in commercial practice. After adding the 1,2-dithiolane to the emulsion it is desirable to heat the emulsion before coating at temperatures from 60° F. to 120° F. for one-half to four hours.

The invention obviously is not limited to the preparation of colloid silver bromide emulsions as simple and mixed silver halide emulsions of various kinds, e. g., silver chloride, silver chloride bromide, silver bromide iodide, silver chloride iodide, etc., develop a marked increase in speed, without any deleterious effect, by the addition of the 1,2-dithiolane compound.

Various other synthetic water-permeable colloid binding agents for silver halide grains can be used in place of the specific one described in the foregoing example. Among the additional useful colloids are collodion, polyglycuronic acid, polyvinyl acetals containing a large number of intralinear recurring —CH_2— and —CHOH— groups including polyvinyl acetaldehyde acetal, polyvinyl butyraldehyde acetal, polyvinyl o-sulfobenzaldehyde acetal the polyvinyl acetal color formers described in U. S. Patents 2,310,943, 2,320,422, 2,380,032, 2,380,033, 2,397,864, etc., the methacrylamide/acrylic acid, etc. copolymers described in U. S. Patents 2,311,548, 2,592,107, 2,611,763, etc.

Suitable additional 1,2-dithiolane compounds which can be incorporated in the colloid silver halide in like manner and equivalent amount include 1,2-dithiolane, 4-acetyl-

1,2-dithiolane, and the esters and amides of 5[1,2-dithiolane-3-yl]pentanoic acid.

As stated above, the compounds can be used with conventional sensitizing dyes such as the cyanine, carbocyanine, merocyanine, cyazine, neocyanine, pseudocyanine, hemicyanine and styryl dyes and with the usual color formers, etc.

Silver halide emulsions made in accordance with the invention may be used to prepare photographic films and papers for many and various purposes including multicolor films, X-ray film, lithographic film, portrait film, etc.

The invention has the advantage that it provides the art with new means for increasing the speed of photographic silver halide emulsions. Another advantage is that increases in speed can be attained without any new or tedious emulsion techniques. A further advantage is that the increase in speed is not attended by any deleterious disadvantages.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. An emulsion of light-sensitive silver halide in a synthetic, water-permeable colloid, said emulsion containing a 1,2-dithiolane compound.

2. An emulsion of light-sensitive silver halide in a synthetic, water-permeable colloid, said emulsion containing a 1,2-dithiolane compound containing a carboxylic group.

3. An emulsion of light-sensitive silver halide in a synthetic, water-permeable colloid, said emulsion containing from 1 to 250 milligrams of a [1,2-dithiolane-3-yl]alkanoic acid per mole of silver halide.

4. An emulsion of light-sensitive silver halide in a synthetic, water-permeable colloid, said emulsion containing from 1 to 250 milligrams of 5[1,2-dithiolane-3-yl]pentanoic acid per mole of silver halide.

5. A polyvinyl alcohol light-sensitive silver halide emulsion containing from 1 to 250 milligrams of 5[1,2-dithiolane-3-yl]pentanoic acid per mole of silver halide.

6. An emulsion of light-sensitive silver halide in a synthetic water-permeable colloid, said emulsion containing from 1 to 250 milligrams of compound taken from the group consisting of [1,2-dithiolane-3-yl]alkanoic acid and its alkali metal, ammonium, substituted ammonium, and amine salts, per mole of silver halide.

7. An emulsion of light-sensitive silver halide in a synthetic, water-permeable colloid, said emulsion containing from 1 to 250 milligrams, of a compound taken from the group consisting of 5[1,2-dithiolane-3-yl]pentanoic acid and its alkali metal, ammonium, substituted ammonium and amine salts, per mole of silver halide.

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