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SUBSTITUTED DISULFIDES AS ANTIFOGGANTS
FOR SILVER HALIDE EMULSIONS
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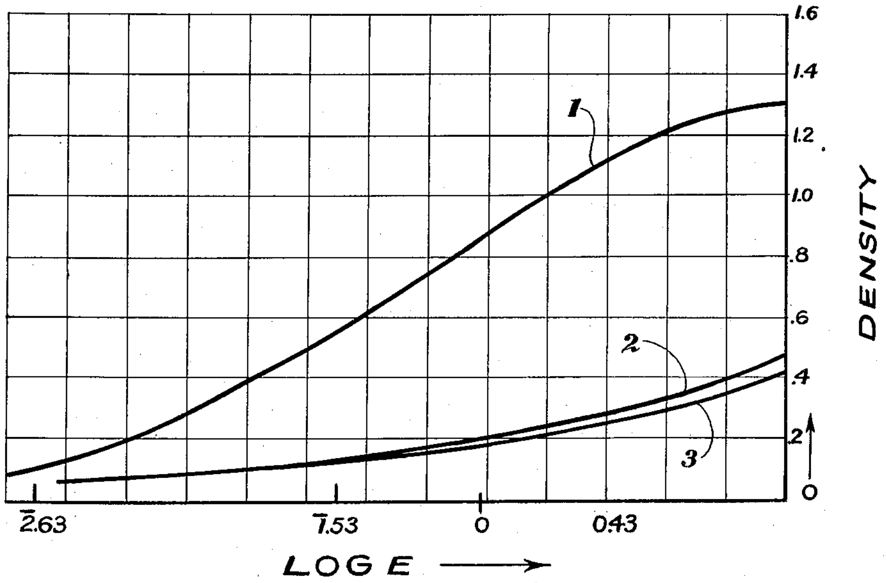

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SUBSTITUTED DISULFIDES AS ANTIFOGGANTS FOR SILVER HALIDE EMULSIONS

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11 Claims. (Cl. 96—108)

This invention relates to the stabilization of photographic silver halide emulsions, and more particularly, to a method of inhibiting development of spontaneous fog without adversely affecting the sensitivity of the photographic silver halide emulsions.

It is well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given; this is commonly called "fog," and sometimes called "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation; in this invention, we are not concerned with the latter.

Fog depends both on the emulsion and the conditions of development; for a given emulsion it increases with the degree of development. With constant development conditions, it tends to increase with time, temperature and relative humidity of storage conditions; it is common practice to make accelerated tests of the stability of photographic emulsions by storage at increased temperature or humidity, or both. It is, of course, desirable to have emulsions as stable as possible under the conditions of high temperature and humidity which may occur in tropical climates, for example. Fog usually appears over the whole area of the sensitive coating, but when severe, it frequently is non-uniform. Fog may also be caused by exposure to chemicals, for example, hydrogen sulfide and other reactive sulfur compounds, hydrogen peroxide vapor, and strongly reducing materials. While antifoggants and stabilizers may protect, to some extent, against such effects, it is normally understood that antifoggants protect against spontaneous growth of fog during prolonged storage or storage at high temperatures and humidities, or during development to maximum contrast and speed, or both.

In emulsion technology, the use of certain organic disulfides as chemical sensitizers and stabilizers against incubation fog has been previously described. Unfortunately, many of these disulfides have properties which place them in more than one of the above categories. For example, cystine is known to exhibit both sensitizing and antifoggant behaviour. In like manner, the disulfides obtained from certain mercapto carboxylic acids, such as those described in Matthies et al., U.S. Patent 1,742,042, issued December 31, 1929, have primarily a sensitizing effect on photographic silver halide emulsions, with a much less marked effect upon the stability of the emulsions.

Because of the above facts, the use of such organic disulfides as antifoggants, offers practical disadvantages. Such disulfides having both sensitizing and some stabilizing activity cannot be employed in unsensitized or undersensitized emulsions. In fully sensitized, high-speed emulsions, the sensitizing or desensitizing disulfides, if they are to act as fog restrainers, must be used at narrow and controlled concentration levels, thus making their introduction into the emulsion, for example, by bathing, impractical.

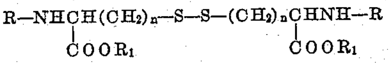
It is, therefore, an object of our invention to provide a method of stabilizing photographic silver halide emulsions. Another object is to provide a method of stabilizing photographic silver halide emulsions without affecting to any material extent the sensitivity of the emulsions. Another object is to provide a method of stabilizing both unsensitized and sensitized emulsions, without introducing any substantial sensitizing or desensitizing effect. Still another object is to provide new organic disulfides and a method of preparation. Other objects will become apparent from a consideration of the following description and examples.

According to our invention, photographic silver halide emulsions can be stabilized and the development of spontaneous fog substantially inhibited by incorporating therein certain organic disulfides.

The advantages of our invention, as compared with the prior art, are illustrated in FIGURE 1 of the accompanying drawing.

The substituted organic disulfides useful in practicing our invention can be represented by the following general formula:

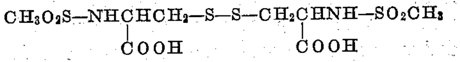
(I)



$$R{-}NH\underset{|\atop COOR_1}{CH}(CH_2)_n{-}S{-}S{-}(CH_2)_n\underset{|\atop COOR_1}{CH}NH{-}R$$

wherein R represents an acyl group, such as acetyl, propionyl, butyryl, benzoyl, toluoyl, methanesulfonyl, ethanesulfonyl, propanesulfonyl, butanesulfonyl, benzenesulfonyl, toluenesulfonyl, etc. (i.e., an acyl group of an aliphatic or aromatic carboxylic acid, or an acyl group of an aliphatic or aromatic sulfonic acid), R_1 represents a hydrogen atom, an alkali metal atom (e.g., sodium, potassium, etc.), an ammonium group (i.e., ammonium or organic ammonium, including pyridinium, triethylammonium, triethanolammonium, etc.), or a lower alkyl group, such as methyl, ethyl, etc., and *n* represents a positive integer of from about 1 to 4. Typical organic disulfides embraced by Formula I above which can be used in practicing our invention include the following, for example:

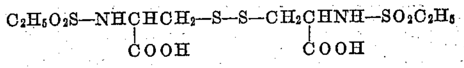
(1)



$$CH_3O_2S{-}NH\underset{|\atop COOH}{C}HCH_2{-}S{-}S{-}CH_2\underset{|\atop COOH}{C}HNH{-}SO_2CH_3$$

α,α'-Di(Methanesulfonamido)-*β,β'*-dithiodipropionic acid

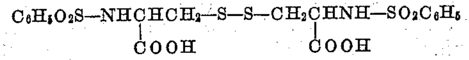
(2)



$$C_2H_5O_2S{-}NH\underset{|\atop COOH}{C}HCH_2{-}S{-}S{-}CH_2\underset{|\atop COOH}{C}HNH{-}SO_2C_2H_5$$

α,α'-Di(ethanesulfonamido)-*β,β'*-dithiodipropionic acid

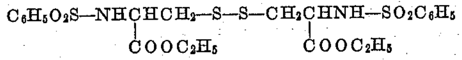
(3)



$$C_6H_5O_2S{-}NH\underset{|\atop COOH}{C}HCH_2{-}S{-}S{-}CH_2\underset{|\atop COOH}{C}HNH{-}SO_2C_6H_5$$

α,α'-Di(benzenesulfonamido)-*β,β'*-dithiodipropionic acid

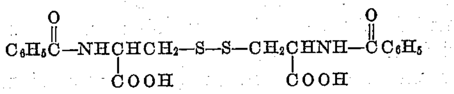
(4)



$$C_6H_5O_2S{-}NH\underset{|\atop COOC_2H_5}{C}HCH_2{-}S{-}S{-}CH_2\underset{|\atop COOC_2H_5}{C}HNH{-}SO_2C_6H_5$$

Ethyl *α,α'*-di(benzenesulfonamido)-*β,β'*-dithiodipropionate

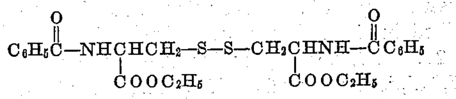
(5)



$$C_6H_5\overset{O\atop \|}{C}{-}NH\underset{|\atop COOH}{C}HCH_2{-}S{-}S{-}CH_2\underset{|\atop COOH}{C}HNH{-}\overset{O\atop \|}{C}C_6H_5$$

α,α'-Dibenzamido-*β,β'*-dithiodipropionic acid

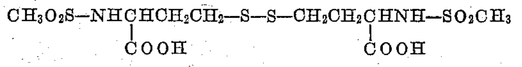
(6)



$$C_6H_5\overset{O\atop \|}{C}{-}NH\underset{|\atop COOC_2H_5}{C}HCH_2{-}S{-}S{-}CH_2\underset{|\atop COOC_2H_5}{C}HNH{-}\overset{O\atop \|}{C}C_6H_5$$

Ethyl *α,α'*-dibenzamido-*β,β'*-dithiodipropionate

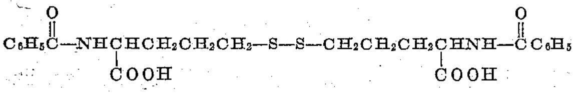
(7)



$$\mathrm{CH_3O_2S{-}NH\underset{\displaystyle COOH}{\underset{|}{C}}HCH_2CH_2{-}S{-}S{-}CH_2CH_2\underset{\displaystyle COOH}{\underset{|}{C}}HNH{-}SO_2CH_3}$$

a,a'-Di(methanesulfonamido)-*γ,γ'*-dithiodibutyric acid

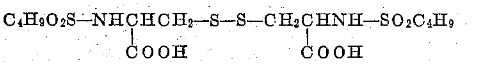
(8)



$$\mathrm{C_6H_5\overset{\overset{O}{\|}}{C}{-}NH\underset{\displaystyle COOH}{\underset{|}{C}}HCH_2CH_2CH_2{-}S{-}S{-}CH_2CH_2CH_2\underset{\displaystyle COOH}{\underset{|}{C}}HNH{-}\overset{\overset{O}{\|}}{C}C_6H_5}$$

a,a'-Dibenzamido-*δ,δ'*-dithiodivaleric acid

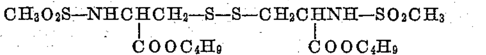
(9)



$$\mathrm{C_4H_9O_2S{-}NH\underset{\displaystyle COOH}{\underset{|}{C}}HCH_2{-}S{-}S{-}CH_2\underset{\displaystyle COOH}{\underset{|}{C}}HNH{-}SO_2C_4H_9}$$

a,a'-Di(butanesulfonamido)-*β,β'*-dithiodipropionic acid

(10)



$$\mathrm{CH_3O_2S{-}NH\underset{\displaystyle COOC_4H_9}{\underset{|}{C}}HCH_2{-}S{-}S{-}CH_2\underset{\displaystyle COOC_4H_9}{\underset{|}{C}}HNH{-}SO_2CH_3}$$

Butyl *a,a'*-di(methanesulfonamido)-*β,β'*-dithiodipropionate

For the purpose of inhibiting fog formation, the disulfides of our invention can be added to the emulsion during the process of manufacture in order to avoid loss of sensitivity and to inhibit the growth of fog with passage of time under non-ideal conditions of storage.

An aqueous or organic solution of the disulfides of our invention when added at suitable concentration to unsensitized, chemically-sensitized, or optically-sensitized photographic emulsions does not appreciably affect the sensitometric values for sensitivity and fog when measurements are made soon after coating. When sensitometric measurements are made at appreciable intervals of time, at elevated temperatures and dry or somewhat humid conditions, the disulfides of our invention do stabilize speed and maintain fog at a low level.

The preparation of silver halide emulsions involves three separate operations: (1) the emulsification and digestion or ripening of the silver halide, (2) the freeing of the emulsion from excess soluble salts, usually by washing, and (3) the second digestion or after-ripening to obtain increased sensitivity. (Mees, "The Theory of the Photographic Process" (1942), Macmillan Co.) We prefer to add the fog-inhibiting agents after the final digestion or after-ripening, although they can advantageously be added prior to digestion.

If desired, the disulfides of our invention can be incorporated in the emulsions without adverse effects by bathing techniques known to those skilled in the art.

The photographic emulsions used in practicing our invention are of the developing-out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951 and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethyl triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(*β*-aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950 and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950 and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patent 2,444,607, issued July 6, 1948 and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or the polymethylene bisbenzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954; (e.g. decamethylene-bis-benzothiazolium perchlorate); or the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955, as well as the thiopolymers of Graham and Sagal U.S. application Serial No. 779,839, filed December 12, 1958, and Dann and Chechak U.S. application Serial No. 779,874, filed December 12, 1958.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956; an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. application Serial No. 662,564, filed May 31, 1957; bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956, or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsions may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenyl-bicyclo (2,2,2)-7-octene-2,3,5,6-tetra-carboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll U.S. Patents 2,725,294, and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methane-sulfonoxy)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxy-methylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness U.S. patent application Serial No. 556,031, filed December 29, 1955; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. patent application Serial No. 599,891, filed July 25, 1956; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959.

The emulsions may contain a coating aid such as saponin; a lauryl or oleyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis, U.S. Patent 2,839,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N- (carbo-p-tert. octyl-phenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg U.S. patent application Serial No. 691,125, filed October 21, 1957.

The addenda which we have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

These may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No. 586,705, filed May 23, 1956. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, granted July 24, 1956, and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed celulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 or an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

The organic disulfides useful in practicing our invention can be added to the photographic emulsions prior to the final digestion, if desired. Generally, these compounds can be added from a substantially neutral solution so that the pH of the emulsion is not disturbed. In the case of compounds containing free carboxylic acid groups, this means that one or more of these carboxylic acid groups may be neutralized. However, where it is desired to stabilize an acidic emulsion, it is obviously not necessary that the antifoggant be added from substantially neutral solutions. Since the disulfides of our invention can be added to the emulsions in such small quantities, it is apparent that they will generally have no adverse effect upon the pH of the emulsions. Many of the organic disulfides useful in practicing our invention can be added to the emulsions in the form of substantially neutral aqueous solutions. If a particular disulfide does not have sufficient solubility in water, addition to the emulsion can be made in the form of a water-miscible organic solvent, such as methanol, ethanol, dioxane, pyridine, etc.

The amount of disulfide compound added to the emulsions of our invention can be varied, depending upon the particular emulsion, the silver halide content of the emulsion, etc. In general, we have found that from about 1.0 to 10.0 grams of disulfide per mole of silver halide can advantageously be employed in our invention. One of the outstanding advantages of the disulfides of our invention, as compared with the disulfides which have been previously described in the prior art, is that they can be used in quite substantial quantities without introducing serious desensitizing effects. Moreover, as indicated above, the disulfides useful in our invention advantageously have little or no sensitizing action of their own, and hence, they can be used to stabilize emulsions which have already been finished to their optimum or near-optimum speeds. Thus, addition of our compounds to such finished emulsions does not result in any substantial desensitizing effect, such as might ordinarily be expected.

The following examples will serve to illustrate the useful stabilizing effect of many of the organic disulfides useful in practicing our invention. A series of coatings was made on ordinary photographic film support, such as cellulose acetate, of an ordinary photographic high-speed bromiodide emulsion, to which had been added one of the organic disulfides of our invention at the concentration shown in the following table. The compounds were added from substatnially neutral solution and comparisons were made with an identical batch of emulsion which contained no antifoggant compound. After coating each series of emulsions on a cellulose acetate support, the emulsions were dried and then exposed on an intensity scale sensitometer (Kodak Type Ib) and developed for about 4 minutes at 68° F. in a developer having the following composition:

Water, about 125° F. (50° C.)	cc	500
N-methyl-p-aminophenol sulfate	grams	2.2
Sodium sulfite, desiccated	do	96.0
Hydroquinone	do	8.8
Sodium carbonate, monohydrated	do	56.0
Potassium bromide	do	5.0

Cold water to make 1.0 liter.

Fresh tests and incubation tests (one week at 120° F., constant relative humidity of about 50%, or for two weeks under the same conditions) were also run for the same emulsion series with development under the same conditions. The relative speed and fog for each of the series coatings were then measured, the speed being determined at a point about 0.3 density above fog.

In the following table, the compound numbers correspond to the numbers used above for the specific disulfides. In each coating series, the same emulsion batch was used, although different emulsion batches were used for some of the coating numbers identified in the coating table. Wherever a different emulsion batch was used, a new control series was run for that batch to show the degree of improvement obtained. The results of these coating series are given in the following table:

Table I

Coating No.	Addendum Compound No. (g./mol. AgX)	Fresh Test		One Week Inc. Test		Two Weeks Inc. Test
		Speed	Fog	Speed	Fog	Fog
1 (*a*)	None	100	.13	87	.31	.66
(*b*)	1 (6.0)	103	.11	94	.18	.36
2 (*c*)	None	100	.11	115	.36	1.0
(*d*)	3 (3.9)	100	.07	105	.18	.34
3 (*e*)	None	100	.11	115	.36	1.0
(*f*)	4 (4.35)	91	.09	100	.20	.42
4 (*g*)	None	100	.11	115	.36	1.0
(*h*)	5 (3.3)	118	.10	141	.28	.63
5 (*i*)	None	100	.11	115	.36	1.0
(*j*)	6 (3.75)	105	.10	115	.27	.65

It has been previously suggested in the literature that certain organic disulfides have the useful property of increasing the speed of photographic silver halide emulsions. It is also known that certain organic disulfides can be used in the presence of various sulfinic or selenic acids or salts to stabilize photographic silver halide emulsions. However, the amount of disulfide which can be employed in these combinations is evidently quite small. (See Mueller U.S. Patent 2,438,716, issued March 30, 1948.) Contrasted with the behavior of the disulfides described in this patent, the disulfides of our invention can be used in gram quantities in order to increase the stability of the emulsions, without having any substantial effect upon the sensitivity or speed of the emulsions. While the compound of our inventions can be employed in relatively large amounts, it has been found that such well-known disulfides as cystine and certain of its derivatives cannot be employed in amounts even approaching those used in the present invention. This adverse effect accompanying the use of cystine, or a derivative thereof, without the use of other addenda to control the adverse effect of these compounds, is illustrated in Table II below. The strong desensitizing effect of cystine is quite evident from the data in this table, which were obtained in the same manner as the data given in Table I above. That is, all of these data were obtained using an ordinary gelatino-silver-bromiodide emulsion.

Table II

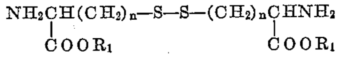
Coating No.	Addendum Compound No. (g./mol. AgX)	Fresh Test		One Week Inc. Test		Two Weeks Inc. Test
		Speed	Fog	Speed	Fog	Fog
6 (*k*)	None	100	.10	159	.14	.36
(*l*)	A (.0015)	21.5	.07	41	.15	.39
(*m*)	A (.045)	13.2	.07	12.6	.40	.90
7 (*n*)	None	100	.10	159	.14	.36
(*o*)	B (.165)	95	.08	174	.14	.38
(*p*)	B (1.65)	76	.08	100	.11	.28
8 (*q*)	None	100	.08	-------	------	.45
(*r*)	C (.036)	95	.08	-------	------	.38
(*s*)	C (.48)	89	.06	-------	------	.42
(*t*)	C (1.92)	57	.09	-------	------	.28
(*u*)	C (3.6)	39	.13	-------	------	.30

A = cystine hydantoin.
B = diguanyl cystine.
C = cystine.

The emulsions used in arriving at the data in Tables I and II above each were sensitized with a labile sulfur compound, such as one of the sulfur compounds described in U.S. Patent 1,574,994, and a gold salt, such as one of the salts described in U.S. Patent 2,399,083. The data in Table II confirm the desensitizing action of cystine in emulsions which have been sensitized by sulfur or gold compounds. (See Mueller U.S. Patent 2,438,716, column 3, line 10.) On the other hand, cystine has the unsatisfactory property of increasing the sensitivity of unsensitized or unfinished emulsions. This effect is illustrated in FIGURE 1 of the accompanying drawings, where curve 1 represents the sensitivity of a photographic gelatino-silver-bromiodide emulsion containing 3.6 g./mole of silver halide of cystine, and curve 2 represents the sensitivity of the same unfinished emulsion containing about 4.5 g./mole of silver halide of Compound 1 above. Curve 3 represents the sensitivity of the same emulsion to which no antifoggant had been added (i.e., "control emulsion").

The disulfides useful in stabilizing emulsions according to our invention can be prepared according to methods which have been previously described in the prior art. For example, the disulfides of Formula I can be obtained by simple acylation of the corresponding aminodisulfides represented by the following general formula:

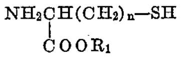
(II)



$$\mathrm{NH_2\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}(CH_2)_n\underset{\substack{|\\ COOR_1}}{C}HNH_2}$$

wherein R_1 and n each have the values given above. Acylation of the depicted amines can be accomplished by simply reacting these amines with an acylhalide, such as acetylchloride, methanesulfonylchloride, benzenesulfonylchloride, etc. The amines of Formula II above can be prepared by simple oxidation of the corresponding mercapto-substituted amines, represented by the following general formula:

(III)



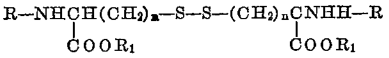
$$\mathrm{NH_2\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}SH}$$

wherein R_1 and n each have the values given above. Oxidation can conveniently be accomplished by simply contacting the mercapto-amine of Formula III with an oxidizing agent, such as hydrogen peroxide, sodium perchlorate, etc.

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.

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

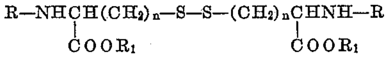
1. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of a compound selected from the class represented by the following general formula:



$$\mathrm{R{-}NH\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}(CH_2)_n\underset{\substack{|\\ COOR_1}}{C}NHH{-}R}$$

wherein R represents an acyl group of an organic acid selected from the class consisting of an aliphatic carboxylic acid, an aromatic carboxylic acid, an aliphatic sulfonic acid and an aromatic sulfonic acid, R_1 represents a member selected from the class consisting of a hydrogen atom, an alkali metal atom, an ammonium group, and an alkyl group, and n represents a positive integer of from about 1 to 4.

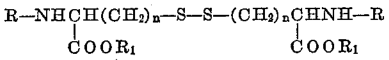
2. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of a compound selected from those represented by the following general formula:



$$\mathrm{R{-}NH\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}(CH_2)_n\underset{\substack{|\\ COOR_1}}{C}HNH{-}R}$$

wherein R represents an acyl group of a carboxylic acid, R_1 represents a hydrogen atom and n represents a positive integer of from about 1 to 4.

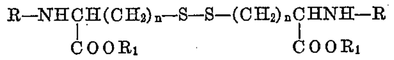
3. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of a compound selected from those represented by the following general formula:



$$\mathrm{R{-}NH\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}(CH_2)_n\underset{\substack{|\\ COOR_1}}{C}HNH{-}R}$$

wherein R represents an acyl group of a sulfonic acid, R_1 represents a hydrogen atom and n represents a positive integer of from about 1 to 4.

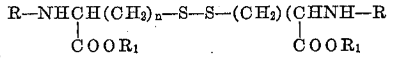
4. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of a compound selected from those represented by the following general formula:



$$\mathrm{R{-}NH\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}(CH_2)_n\underset{\substack{|\\ COOR_1}}{C}HNH{-}R}$$

wherein R represents an acyl group of a carboxylic acid, R_1 represents an alkyl group and n represents a positive integer of from 1 to 4.

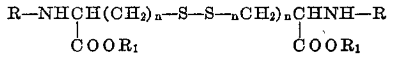
5. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of a compound selected from those represented by the following general formula:



$$\mathrm{R{-}NH\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}(CH_2)(\underset{\substack{|\\ COOR_1}}{C}HNH{-}R}$$

wherein R represents an acyl group of a sulfonic acid, R_1 represents an alkyl group and n represents a positive integer of from 1 to 4.

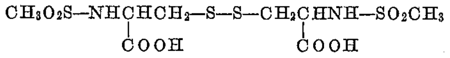
6. A photographic silver halide emulsion sensitized with a labile sulfur compound and a gold compound, said silver halide emulsion being stabilized with from 1.0 to 10.0 g./mol. of silver halide of a compound selected from those represented by the following general formula:



$$\mathrm{R{-}NH\underset{\substack{|\\ COOR_1}}{C}H(CH_2)_n{-}S{-}S{-}_nCH_2)_n\underset{\substack{|\\ COOR_1}}{C}HNH{-}R}$$

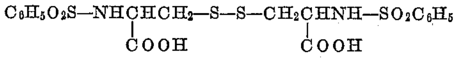
wherein R represents an acyl group of an organic acid selected from the class consisting of an aliphatic carboxylic acid, an aromatic carboxylic acid, an aliphatic sulfonic acid and an aromatic sulfonic acid, R_1 represents a member selected from the class consisting of a hydrogen atom, an alkali metal atom, an ammonium group and an alkyl group, and n represents a positive integer of from about 1 to 4.

7. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of the compound represented by the following formula:



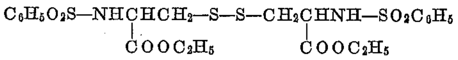
$$\mathrm{CH_3O_2S{-}NH\underset{\substack{|\\ COOH}}{C}HCH_2{-}S{-}S{-}CH_2\underset{\substack{|\\ COOH}}{C}HNH{-}SO_2CH_3}$$

8. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of the compound represented by the following formula:



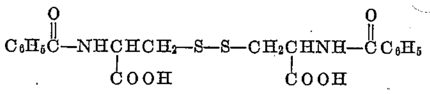
$$\mathrm{C_6H_5O_2S{-}NH\underset{\substack{|\\ COOH}}{C}HCH_2{-}S{-}S{-}CH_2\underset{\substack{|\\ COOH}}{C}HNH{-}SO_2C_6H_5}$$

9. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of the compound represented by the following formula:



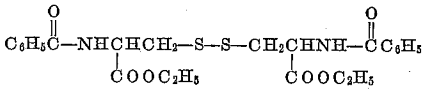
$$\mathrm{C_6H_5O_2S{-}NH\underset{\substack{|\\ COOC_2H_5}}{C}HCH_2{-}S{-}S{-}CH_2\underset{\substack{|\\ COOC_2H_5}}{C}HNH{-}SO_2C_6H_5}$$

10. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of the compound represented by the following formula:



$$\mathrm{C_6H_5\overset{\substack{O\\ \|}}{C}{-}NH\underset{\substack{|\\ COOH}}{C}HCH_2{-}S{-}S{-}CH_2\underset{\substack{|\\ COOH}}{C}HNH{-}\overset{\substack{O\\ \|}}{C}C_6H_5}$$

11. A photographic silver halide emulsion stabilized with from 1.0 to 10.0 g./mol. of silver halide of the compound represented by the following formula:



$$\mathrm{C_6H_5\overset{\substack{O\\ \|}}{C}{-}NH\underset{\substack{|\\ COOC_2H_5}}{C}HCH_2{-}S{-}S{-}CH_2\underset{\substack{|\\ COOC_2H_5}}{C}HNH{-}\overset{\substack{O\\ \|}}{C}C_6H_5}$$

References Cited in the file of this patent

UNITED STATES PATENTS

2,438,716	Mueller	Mar. 30, 1948
2,597,915	Yutzy et al.	May 27, 1952

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

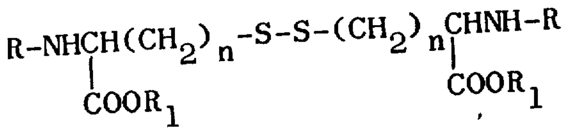
Patent No. 3,043,696

July 10, 1962

Arthur H. Herz et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 9, claim 1, and column 10, claims 5 and 6, the formula, each occurrence, should appear as shown below instead of as in the patent:



$$R\text{-}NH\underset{COOR_1}{CH}(CH_2)_n\text{-}S\text{-}S\text{-}(CH_2)_n\underset{COOR_1}{CH}NH\text{-}R$$

Signed and sealed this 20th day of November 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents