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3,046,134

SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS WITH POLYMERIC COMPOUNDS CONTAINING A PLURALITY OF SULFUR ATOMS

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This invention relates to photographic silver halide emulsions, and more particularly, to an improved means for sensitizing such photographic silver halide emulsions.

A number of methods have been previously described for increasing the sensitivity of photographic silver halide emulsions, other than methods of optical or spectral sensitization which involve the incorporation of certain colored compounds or dyes in the emulsions. The incorporation of such dyes in the emulsions increases the optical range of sensitivity, and for this reason such dyes are commonly referred to as optical or spectral sensitizing dyes. It is also well known to increase the sensitivity of photographic emulsions by addition of sulfur compounds capable of reacting with silver salts to form silver sulfide, or with reducing agents (compounds of these types are also naturally present in gelatin), or with salts of gold or other noble metals, or with combinations of two or more of the aforementioned compounds generally known as chemical sensitizers. Such chemical sensitizers are believed to react with the silver halide to form, on the surface of the silver halide, minute amounts of silver sulfide or of silver or of other noble metals, and these processes are capable of increasing the sensitivity of developing-out emulsions by very large factors. The process of chemical sensitization, however, reaches a definite limit beyond which further addition of sensitizer, or of further digestion with the sensitizer present, merely increases the fog of the photographic emulsion with constant or decreasing speed.

We have now found a means of further increasing the sensitivity of photographic emulsions which may be applied even though the ordinary processes of chemical sensitization have been carried to the effective limit of the photographic emulsion in question. Our process is to be distinguished from hypersensitization, which is produced by bathing a finished coating with water or with solutions of ammonia, amines or silver salts. Such processes act primarily on optically sensitized photographic emulsions and tend to increase the free silver ion concentration of the emulsion and greatly diminish its stability. Our process is also to be distinguished from hypersensitization by mercury vapor, which gives a transitory effect which is lost on storage of the film. The compounds used in our invention do not appear to be chemical sensitizers in the usual sense, since they increase speed by their presence during exposure and processing and require no digestion with the photographic emulsion to produce the increase in speed, nor does their chemistry indicate that they are likely to react with silver halide under normal emulsion conditions.

The novel sensitizers of our invention are quite unique in that the effects produced are additive in photographic emulsions which have already been sensitized to their optimum, or near-optimum, with conventional chemical sensitizers, such as labile sulfur compounds. The novel sensitizers of our invention, however, can be used to sensitize photographic silver halide emulsions containing no other sensitizers, if desired. The novel sensitizers of our invention are not strictly chemical sensitizers, since chemical sensitizers do not generally provide the additive effects of the type mentioned.

It is, therefore, an object of our invention to provide

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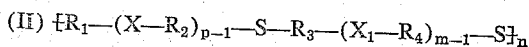
photographic silver halide emulsions which have been sensitized with various polymeric compounds containing a plurality of sulfur atoms. Another object of our invention is to increase the sensitivity of ordinary photographic silver halide emulsions which have already been sensitized with chemical sensitizers, such as compounds containing labile sulfur atoms. Other objects will become apparent from a consideration of the following description and examples.

According to our invention, we have found that the sensitivity of an ordinary photographic silver halide emulsion can be materially increased by incorporating therein polymeric compounds containing a plurality of sulfur atoms. The polymeric compounds useful in our invention contain their sulfur atoms in the form of thioether linkages. By thioether linkage, we mean a linkage wherein the sulfur atom is a divalent atom which is joined to two non-oxocarbonylic carbon atoms. Our invention does not contemplate polymeric compounds containing disulfide linkages, such as those commonly found in vulcanized, rubbery materials. Moreover, the polymeric compounds of our invention are linear polymeric materials wherein the ether-sulfur atoms are present in the polymeric chain, as contrasted with polymeric materials containing their sulfur atoms as substituents attached to carbon atoms of the chain or as parts of a cross-linked arrangement. The polymeric materials used in our invention should have sufficient dispersibility in water (or a dilute alkaline solution), or an organic solvent, such as acetone, the lower alcohols, 1,4-dioxane, ethyl acetate, etc. (directly, or in a colloid mill, or by other means, such as by a dispersing agent, e.g., sodium laurylsulfate, etc.), so that a sensitizing amount of the polymeric materials can be adsorbed by or associated with the silver halide grains. The linear polymers of our invention containing a plurality of ether-sulfur atoms in the chain can be represented by the following general formula:

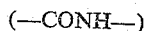


wherein R represents an aliphatic linkage, such as an alkylene group, etc., and n represents a positive integer of at least about 3, i.e., the polymeric compounds of our invention comprise products obtained by condensations or addition-polymerizations involving at least about 3 molecules of reactants. In general, the polymeric materials of our invention have a molecular weight of at least about 250, although polymeric materials having molecular weight from about 500 to 10,000 have been found to be useful in our invention. The terminal groups of our polymers are generally hydrogen atoms, halogen atoms, hydroxyl groups, mercapto groups (or salts thereof, e.g., sodium, potassium, etc.), or combinations of these.

The linear polymers of our invention represented by Formula I above, comprise a well-known class of polymeric materials. Typical of the polymers embraced by Formula I are those polymers represented by the following general formula:



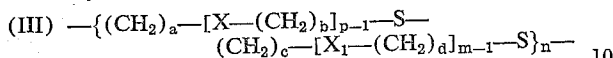
wherein R_1 , R_2 , R_3 and R_4 each represents a hydrocarbon alkylene group containing from about 2 to 20 carbon atoms (e.g., ethylene, trimethylene, 1,2-propylene, tetrabutylene, pentamethylene, octamethylene, decamethylene, dodecamethylene, tetradecamethylene, etc.), X and X_1 each represents an oxygen atom, a sulfur atom, an amino group (substituted or not) such as amino, methylamino, ethylamino, etc., carbamyl ($-\text{NHCO}-$), amido



carbonyl, oxycarbonyloxy, oxycarbonyl ($-\text{OOC}-$), carbonyloxy ($-\text{COO}-$), etc., provided that X does not represent an oxycarbonyl group when X_1 represents a

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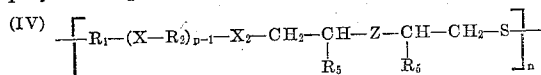
carbonyloxy group and X does not represent an amido group when X_1 represents a carbamyl group, p and m each represents a positive integer of from 1 to 5, and n represents the values given above, i.e., a positive integer of at least 3. An especially useful group of polymers represented by Formula II comprises the polymers represented by the following general formula:



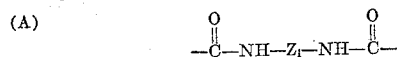
wherein a , b , c and d each represents a positive integer of from 2 to 20, and n , m and p each have the values given above.

See Minsk application Serial No. 779,840, filed on even date herewith, for the photographic application of the polymers of Formula II, wherein X represents an oxy-carbonyl group when X_1 represents a carbonyloxy group. See Beavers application Serial No. 779,875, filed on even date herewith, for the photographic application of the polymers of Formula II, wherein X represents an amido group when X_1 represents a carbamyl group.

Another group of polymers embraced by Formula I above which are useful in our invention comprises the polymers represented by the following general formula:



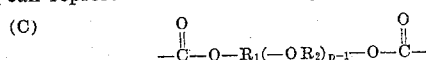
wherein R_1 , R_2 , X , n and p each have the values given above, X_2 represents an oxygen atom or a sulfur atom, R_5 represents a hydrogen atom or a lower alkyl group (e.g., methyl, etc.), Z represents a divalent carbonamide linkage, e.g.,



wherein Z_1 represents an alkylene group, such as that defined above for R_1 , or the group:



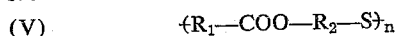
wherein R_7 and R_8 represent a hydrogen atom, a lower alkyl group (e.g., methyl, ethyl, etc.) or a monocyclic aryl group (e.g., phenyl, tolyl, etc.), or alternatively, Z can represent a divalent ester group, such as:



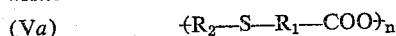
wherein R_1 , R_2 and p each have the values given above, or alternatively, Z can represent an alkylene group, such as:



wherein R_6 represents an alkylene group, such as methylene, ethylene, trimethylene, 1,2-propylene, butylene, pentamethylene, hexamethylene, etc. Another group of polymers embraced by Formula I, which are useful in practicing our invention comprises polymeric linear lactones, such as:

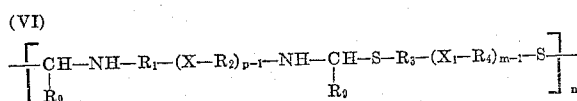


wherein R_1 , R_2 and n each have the values given above. Alternatively, the compounds of Formula V can be written as follows:



wherein R_1 , R_2 and n each have the values given above.

Another group of polymers embraced by Formula I are those represented by the following general formula:

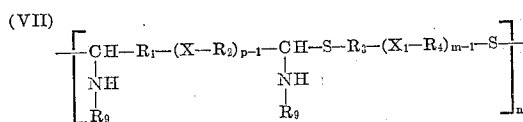


wherein R_1 , R_2 , R_3 , R_4 , X , X_1 , m , n and p , each have the

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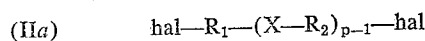
values given above and R_9 represents a hydrogen atom, a lower alkyl group, such as methyl, ethyl, propyl, etc.

Still another group of polymers embraced by Formula I above are those represented by the following general formula:

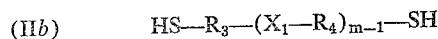


In the above formulas, the symbol groups R_1 , R_2 , R_3 , R_4 , etc., and the integers m , n , p , etc., have the same values throughout.

The compounds of Formula II above can be prepared according to methods which have been previously described in the prior art. For example, these polymers can be prepared by condensing together at least one dihalogenated compound selected from those represented by the following general formula:



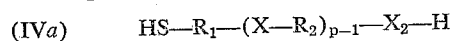
wherein hal represents a halogen atom, such as chlorine, bromine, etc., with approximately a molecularly equivalent amount of at least one dithiol compound selected from those represented by the following general formula:



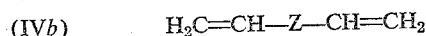
The condensations can advantageously be carried out in the presence of an acid-binding material, such as sodium carbonate, pyridine, sodium acetate, etc. If desired, the condensation can be carried out in the presence of an inert diluent which may be a solvent or non-solvent for the polymeric product obtained.

Alternatively, symmetrical polymers embraced by Formula II above can be prepared by condensing together an intermediate represented by Formula IIa with an alkali metal sulfide, such as sodium sulfide. Such preparations have been previously described in the prior art, such as Lilienfeld U.S. Patent 1,018,329, issued February 20, 1912.

The linear polymers represented by Formula IV above can advantageously be prepared by interacting at least one molecule of at least one compound selected from those represented by the following general formula:

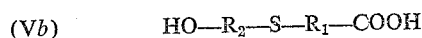


with at least one molecule of at least one diolefinically-unsaturated compound selected from those represented by the following general formula:



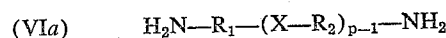
This method has likewise been previously described in the prior art, such as Coffman U.S. Patent 2,347,182, issued April 26, 1944.

The linear polymers represented by Formula V above can advantageously be prepared by self-condensation of at least one hydroxy acid (or alternatively, a lactone of the acid) represented by the following general formula:



The self-condensation of the compounds of Formula Vb occurs spontaneously on standing, although it has been found that the polymers of Formula V can be prepared more rapidly by heating a lactone of the acid of Formula Vb in the presence or absence of an acidic condensation agent, such as zinc chloride, p-toluene sulfonic acid, etc.

The linear polymers represented by Formula VI above can advantageously be prepared by condensing together one molecule of at least one diamine represented by the following general formula:



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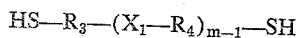
and two molecules of at least one aldehyde represented by the following general formula:

(VIb)



with one molecule of at least one dithiol represented by the following general formula:

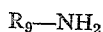
(VIc)



The condensations occur spontaneously on standing, although they can be accelerated by the application of heat, and in some instances, by the use of an inert diluent, such as ethanol, water, etc.

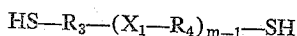
The linear polymers represented by Formula VII above can advantageously be prepared by condensing together two molecules of at least one amine selected from those represented by the following general formula:

(VIIa)



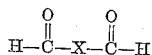
one molecule of at least one dithiol represented by the following general formula:

(VIIb)



and one molecule of at least one dialdehyde selected from those represented by the following general formula:

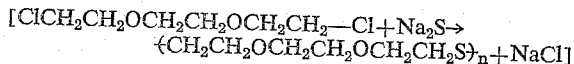
(VIIc)



These condensations also occur spontaneously on standing, but can be accelerated by the application of heat (e.g., 50-150° C.), use of solvents or dispersing agents, or other techniques well-known to those skilled in the art.

The following examples will serve to illustrate the preparation of various linear polymers containing thioether atoms which are useful according to our invention.

EXAMPLE 1

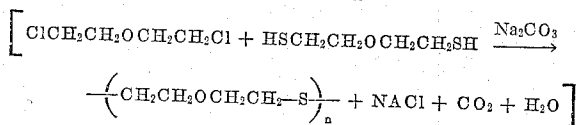


A mixture of 18.7 g. of 1,2-bis(2-chloroethoxy)ethane and 24 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) was heated under reflux for 16 hours with 50 ml. of ethyl alcohol and 50 ml. of distilled water. Removal of the alcohol, water, and NaCl left a syrupy polymer which was insoluble in water but soluble in ethyl acetate.

Analysis.—Calculated: C, 48.6; H, 8.1; S, 21.6%. Found: C, 48.1; H, 8.2; S, 21.2%.

The molecular weight was found by boiling-point elevation to be around 900.

EXAMPLE 2

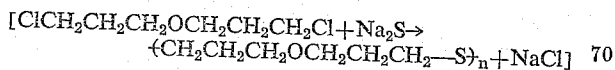


A mixture of 4.14 g. of bis(2-mercaptoethyl)ether and 4.29 g. of bis(2-chloroethyl)ether was placed with 3.18 g. of sodium carbonate in 25 ml. ethyl alcohol and 25 ml. of water. The reaction mixture was left at room temperature overnight and then heated on the steam bath for 3 hours. Removal of the solvent and the NaCl left the desired polymeric material.

Analysis.—Calculated: C, 42.3; H, 7.1. Found: C, 42.0; H, 7.1.

The molecular weight was found to be approximately 434.

EXAMPLE 3



A mixture of 1.71 g. of bis(3-chloro-n-propyl)ether and 2.5 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) was heated under reflux for 16 hours with 5 ml. of ethyl alcohol and 5 ml. of distilled water. Removal of the solvent and

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NaCl left the desired syrupy polymer. It had a molecular weight of about 478.

Analysis.—Calculated: C, 49.6; H, 8.3%. Found: C, 50.5; H, 8.6%.

EXAMPLE 4

A mixture of 14.3 g. of bis(2-chloroethyl)ether and 24 g. of sodium sulfide ($Na_2S \cdot 9H_2O$) was heated under reflux for 16 hours with 50 ml. of ethyl alcohol and 50 ml. of distilled water. Removal of the solvents and the sodium chloride left the syrupy polymer; molecular weight about 474.

Analysis.—Calculated: C, 42.3; H, 7.1; S, 21.2%. Found: C, 45.6; H, 8.2; S, 22.0%.

EXAMPLE 5

In a quartz tube were placed 9.4 g. of ethane-1,2-dithiol and 8.2 g. of biallyl. The tube was stoppered by a glass stopper which was taped down. The tube was irradiated by a Gates U.V. 110-volt mercury quartz arc. A vigorous reaction resulted with the evolution of much heat. The reaction was controlled by removing the tube from before the arc when the heat evolution appeared to become excessive. When the initial reaction had subsided, the tube was irradiated for an additional one-half hour. At the end of this time the reaction mixture had set to a white solid. The solid was triturated repeatedly with absolute ethyl alcohol and dried in a vacuum desiccator under a constantly applied water pump vacuum. The yield of product was 12 g. The polymer was soluble in pyridine, in cyclohexanone at 50° C. and in dimethyl formamide at 60° C.

The polymers in Table A below were prepared in the same manner as the polymer of Example 5, except that a solvent was used in one instance. The results follow:

TABLE A

Example	Dithiol (g.)	Diolefin (g.)	Diluent	Percent Yield
6.....	ethane-1, 2-dithiol (4.1).	biallyl (4.1)....	dioxane.....	2.8 (insol. in dioxane).
7.....	propane-1,3-dithiol (5.4).	-----do-----	none.....	8.0.
8.....	ethane-1,2-dithiol (2.82).	1,9-decadiene (4.2).	-----do-----	4.65.

EXAMPLE 9

A mixture of 33 g. of tetraethyleneglycol dimethacrylate and 7.8 g. of 2-mercaptoethanol was heated for 2 hours on the steam bath with 0.5 ml. of a 35% solution in methanol of benzyl trimethyl ammonium hydroxide. The volatile materials were removed at 3 mm. pressure and temperatures up to 190° C. leaving the formed polymer as a viscous liquid.

Analysis.—Calculated: C, 53.0; H, 7.8; S, 7.8. Found: C, 52.7; H, 7.8; S, 7.9.

EXAMPLE 10

A reaction mixture composed of 15.4 g. (0.1 mole) of N,N'-methylene bis acrylamide, 18.2 g. (0.1 mole) of 1,2-bis(2-mercaptoethoxy)ethane, 500 ml. of ethanol and 10 drops of a 35% solution in methanol of benzyl trimethyl ammonium hydroxide was heated on the steam bath for 2 hours. Upon cooling, a precipitate formed which was recrystallized from N,N-dimethylformamide. M.P. 183-185° C.

Analysis.—Calculated: C, 46.4; H, 7.1; N, 8.6; S, 19.1. Found: C, 46.5; H, 7.1; N, 8.0; S, 18.6.

EXAMPLE 11

The reaction of succindialdehyde, 1,10-dimercaptodecane and ammonia: A solution of 10.3 g. of 1,10-dimercaptodecane and 4.3 g. of succindialdehyde (17 ml. of a 25% aqueous solution) in 25 ml. of ethanol was left at room temperature for 16 hours. A white precipitate

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melting at 90° C. was filtered off. Anal.: C, 58.4; H, 9.7; S, 11.3. This material (5.3 g.) was placed in 50 ml. of cold, concentrated ammonium hydroxide solution and 50 ml. of ethanol and warmed on the steam bath for one-half hour. Fifty ml. more of ammonium hydroxide was then added and the reaction mixture left for 2 days at room temperature. The solid product which was formed was found to contain 4.7% nitrogen, proving that the ammonium hydroxide had reacted with the polymeric material.

EXAMPLE 12

The reaction of formaldehyde ethylenediamine and bis-(2-mercaptoethyl)ether: Formaldehyde (8 ml. of a 30% aqueous solution) was added to a mixture of 4.6 g. of bis-(2-mercaptoethyl)ether and 2 g. of ethylenediamine in 500 ml. of ethanol. The reaction mixture became cloudy, the mercaptan smell disappeared and in a short time a white precipitate was deposited. Analysis showed 10% nitrogen and 29% sulfur, indicating the reaction of all components.

EXAMPLE 13

The reaction of formaldehyde with diethylenetriamine and bis-(2-mercaptoethyl)ether: Formaldehyde (15 ml. of a 30% aqueous solution) was added to a mixture of 6.9 g. of bis-(2-mercaptoethyl)ether and 5.1 g. of diethylenetriamine. A copious white precipitate began to form almost immediately. This material was found to be soluble in dilute hydrochloric acid but insoluble as the pH was raised to 4.5–7.0.

EXAMPLE 14

The reaction of succindialdehyde, bis-(2-mercaptoethyl)ether and ammonia: A mixture of 2.15 g. of succindialdehyde (10 ml. of a 23% aqueous solution) and 3.45 g. of bis-(2-mercaptoethyl)ether in 50 ml. of ethanol was left at room temperature for 20 minutes and 4 ml. of concentrated ammonium hydroxide was then added. The precipitate which formed was found to contain 6% nitrogen and 31% sulfur, indicating the participation of all components in the reaction.

EXAMPLE 15

This polymer was prepared in exactly the manner indicated in Example 14 above, except that the succindialdehyde was replaced by a molecularly-equivalent amount of maleic dialdehyde to give a product of 5.4% nitrogen and 28% sulfur.

The polymers of our invention containing secondary amino groups can be acylated by means of carboxylic acid anhydrides, such as acetic anhydride, etc., and the sulfur atoms of our polymers can also be quaternated by means of alkyl salts, such as methyl-p-toluenesulfonate. The latter is illustrated in the following example.

EXAMPLE 16

Mixed in 1000 cc. of ethanol were 10.6 g. (0.1 mol.) of 1,2-bis-(2-mercaptoethoxy)ethane, 6 g. (0.1 mol.) of ethylenediamine and 0.2 mol. of formaldehyde. The white precipitate which formed was filtered off and dried.

Analysis.—C, 45.2; H, 8.3; S, 24.1; N, 10.4 (calc'd). Found: C, 45.9; H, 7.8; S, 25.4; N, 8.8.

Five grams of this material was placed in 20 g. of methyl p-toluenesulfonate and left at room temperature overnight. An orange wax was formed. This was washed with diethyl ether to remove excess methyl-p-toluenesulfonate.

Analysis.—C, 48.6; H, 7.0; S, 20.0; N, 4.4 (calc'd). Found: C, 47.4; H, 7.0; S, 19.7; N, 3.0.

Two and one-half grams of this material were placed in 20 ml. of acetic anhydride and heated for one hour. Water was added and the solvents were removed in vacuum. The residue was washed with ether and dried.

Analysis.—C, 47.1; H, 7.0; S, 18.6; N, 4.0 (calc'd). Found: C, 47.2; H, 6.8; S, 18.1; N, 3.2.

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EXAMPLE 17

Polymerization of Hydroxymercaptoacetic Lactone at 180° C. With Zinc Chloride

In glass apparatus, under an air condenser, were placed 10 grams of hydroxyethylmercaptoacetic acid lactone and 0.10 gram of anhydrous zinc chloride. The reaction mixture was heated in an oil bath at 180° C. for 115 minutes. The viscous polymer was cooled and dissolved in 70 ml. of acetone, boiled with decolorizing carbon (Norite) and cooled to room temperature. About five volumes of ether were added and the emulsion obtained was chilled in a Dry Ice-acetone bath. A solid polymer deposited. The ether was poured off cold and the residue was extracted at room temperature with several changes of ether. After the last extraction, the residual ether was removed at room temperature under vacuum and the remaining oil was dissolved in acetone to make 100 grams of solution. The solids content was 2.6%. Molecular weight by end-group titration was 7100.

EXAMPLE 18

Polymerization of Hydroxyethylmercaptoacetic Acid Lactone by Chloroacetic Acid

Twenty-seven grams of lactone were heated in an oil bath at 180° C. with 0.270 gram of chloroacetic acid in all-glass reflux outfit for 20¾ hours. After cooling, a viscous, clear, tan dope was obtained. This was thoroughly extracted by kneading with ether. The residual ether in the polymer was removed under vacuum at room temperature. The remaining polymer was then extracted with acetone at room temperature. The acetone filtrates were combined and chilled in a Dry Ice-acetone bath. With chilling, polymer deposited. The cold acetone supernatant was poured off and the remaining polymer was worked with ether until it became friable. It was then dried in a vacuum desiccator under a constantly applied water-pump vacuum. The yield was 3.6 grams. Molecular weight by end-group titration was 5000.

EXAMPLE 19

Polymerization of Hydroxyethylmercaptoacetic Acid Lactone by Toluene Sulfonic Acid

Ten grams of hydroxyethylmercaptoacetic lactone were heated on a steam bath in 90 ml. of benzene with 0.17 gram of toluene sulfonic acid monohydrate. In a short time the solution became turbid. After 15 hours of heating, there was a clear supernatant and viscous second phase. After cooling the benzene phase was poured off and the residue worked with fresh portions of ethyl ether until it became friable. The product was dried in a vacuum desiccator under a constantly applied water-pump vacuum. The yield was 7.1 grams. The molecular weight by end-group titration was 4400.

EXAMPLE 20

Preparation and Polymerization of Hydroxypropylmercaptopropionic Acid Lactone

(1) PREPARATION

In an all-glass reflux outfit were placed 12.5 grams of γ -mercaptoopropanol, 9.8 grams of acrylic acid and 0.136 gram of hydroquinone. The reaction mixture was heated overnight on a steam bath. Volatiles were then removed under vacuum up to a boiling point of 50–53° C. at 0.8 mm. The yield of crude product was 12.4 grams.

(2) POLYMERIZATION

Six grams of the above reaction product were heated on a steam bath with 0.120 gram of anhydrous zinc chloride under an air reflux condenser with a slow stream of nitrogen passing through the reaction mixture. After 44½ hours, a viscous dope was obtained. After cooling, this was extracted repeatedly with 40 ml. portions of ether, pouring off the supernatant liquid. This removed the un-

reacted monomer. The residual ether was removed under vacuum at room temperature and the polymer was repeatedly extracted with water to remove hydroquinone. Residual water was removed under vacuum. A viscous oil remained. In a few days at room temperature, this oil changed to a waxy solid. This was dissolved with warming in 35 ml. of acetone and the solution was chilled in a Dry Ice-acetone bath. White solid polymer deposited. This was filtered onto a chilled Buchner funnel, washed on the funnel with cold acetone, and dried in a vacuum desiccator under a constantly applied water-pump vacuum. The yield was 3.2 grams. Elemental analyses were as follows:

Found: C, 48.6; H, 6.85; S, 21.95. Calculated exclusive of end-groups: C, 49.3; H, 6.9; S, 21.9.

EXAMPLE 20a

Polymerization of β -Hydroxyethylmercaptoacetic Acid Lactone

This polymer was prepared in exactly the manner shown in Example 20 above, using zinc chloride as a catalyst and heating the reaction mixture at 100° C. A white solid polymer was obtained.

EXAMPLE 21

Hydroxyhexylmercaptoacetic Acid Lactone

Mercaptohexanol and acrylic acid were reacted in a manner very similar to the above. Attempts to polymerize with zinc chloride yielded insoluble products. A soluble product was achieved in the following way:

The lactone (about 25 grams) was heated at 150° C. in a flask immersed in an oil bath under a high-vac pump vacuum of 0.07 mm. The viscosity of the melt rose. After 3 hours, the reaction mixture was cooled. There was practically no flow at room temperature. The polymer was dissolved in 50 ml. of acetone. The solution was diluted with 400 ml. of absolute alcohol and the white suspension chilled in a carbon dioxide snow-acetone bath. Gummy polymer deposited. The supernatant liquid was poured off and the residue extracted repeatedly with fresh portions of absolute alcohol. The residual alcohol was then removed under vacuum with gentle warming. The polymer was then dissolved in 30 ml. of acetone and filtered. Thirty-eight and one-half grams of solution with a solids content of 21.2% were obtained.

EXAMPLE 22

Preparation of the Polymer From γ -Hydroxypropylmercaptoacetic Acid

The preparation of γ -hydroxypropylmercaptoacetic acid lactone: Eighty-three and two-tenths grams of sodium hydroxide pellets were dissolved in 200 ml. of distilled water and chilled in an ice bath. To this was added with stirring and continued cooling a solution of 115 g. of 80% mercaptoacetic acid in 100 ml. of water. With the temperature of the above solution maintained at 75° C., 139 g. of chloropropanol was added from a dropping funnel, with stirring, and when addition was completed, the reaction mixture was stirred and heated for an additional hour. The water was then removed under reduced pressure until a heavy slurry was obtained. This was extracted with acetone by triturating with 2 one-liter portions, and after pouring off the supernatant acetone, residual acetone was removed under reduced pressure with mild warming. The solid was suspended in 750 ml. of absolute ethyl alcohol and 90 g. of concentrated hydrochloric acid was added with vigorous stirring. The salt was then removed by filtration, washed with 200 ml. of alcohol, and the combined filtrates were concentrated under reduced pressure. The residue was distilled under high vacuum. The portion boiling between 130°/2 mm. and 168°/12 mm. was redistilled to yield the desired product, boiling at 83°/0.03 mm.-105°/0.05 mm., the major portion at 88°/0.05 to 92°/0.07 mm. The yield was 15 g., M.P. 42.5° C.

Analysis.—Calc'd for $C_5H_8SO_2$: C, 45.5; H, 6.0; S, 24.2. Found: C, 45.7; H, 6.4; S, 24.6.

The polymerization of γ -hydroxypropylmercaptoacetic acid lactone: In an all-glass outfit equipped with an air condenser were placed 10 g. of γ -hydroxypropylmercaptoacetic acid lactone and 0.100 g. of anhydrous zinc chloride. The reaction vessel was placed on a steam bath with a slow stream of nitrogen bubbling through the melt. At the end of 21 hours on the steam bath, the mixture had turned quite dark. After cooling to room temperature under nitrogen, the viscous liquid was dissolved in 20 ml. of acetone, boiled with decolorizing carbon (Norite), and filtered. An additional 40 ml. of acetone was added and the solution was cooled in an acetone-Dry Ice bath. A solid deposited. The supernatant acetone was poured off, replaced by 60 ml. of fresh acetone, and the chilling was repeated. Again, the supernatant was poured off, and the residue was dissolved in 30 ml. of acetone at room temperature. This solution was used for test. The solids content was 10.8%.

EXAMPLE 23

Polymerized β -hydroxyethylmercaptoacetic acid was obtained by placing a quantity of the acid (monomer) in a stoppered bottle and allowing it to stand for several weeks. The polymer formed spontaneously. It had a molecular weight of approximately 1,000.

The following example also illustrates the quaternation of one of the thiopolymers of our invention by means of alkyl salts, such as methyl-p-toluene sulfonate, methyl sulfate, ethyl sulfate, etc. These ternarized compounds can also be used to sensitize photographic silver halide emulsions according to our invention.

EXAMPLE 24

Twelve grams of the polymer obtained by the reaction of sodium sulfide and 1,2-bis(2-chloroethoxy)ethane (Example 1) were mixed with 24 grams of methyl-p-toluene sulfonate and heated under a reflux condenser on the steam bath for 18 hours. After cooling, the reaction mixture was washed with diethyl ether and ethyl acetate. The insoluble residue was then taken up in 50 ml. of hot distilled water and filtered. The aqueous solution was washed with ethyl acetate and the water was then removed to give the product in the form of a clear brown resin.

Analysis.—Calculated: S, 18.2; C, 47.7; H, 6.3%. Found: S, 18.3; C, 46.9; H, 6.4%.

The thiopolymers of our invention can be added to ordinary photographic silver halide emulsions for the purpose of increasing the sensitivity thereof, as has been indicated above. These thiopolymers are non-vulcanizable compounds and are substantially free of disulfide linkages of the type commonly found in vulcanized, rubbery materials. It is known that various sulfur polymers can be added to photographic silver halide emulsions, although the reason for adding such polymeric materials has been for purposes other than increasing the sensitivity of the emulsions. For example, Mueller U.S. Patent 2,699,391 discloses the addition of polypeptides of α -amino acids to photographic silver halide emulsions as anti-sensitizers or restrainers. Among the amino acids disclosed in that patent are those containing disulfide linkages. Such anti-sensitizing materials are not contemplated by the present invention.

The preparation of photographic silver halide emulsions involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, usually by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The sensitizers of our invention can be added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating. Our new

photographic sensitizers require no special final digestion or after-ripening.

The particular quantity of thiopolymer used in a given emulsion can vary, depending upon the effects desired, degree of ripening, silver content of the emulsion, etc. The amount used is also dependent upon the particular stage at which the sensitizer was added during the preparation of the emulsion. We have found that generally from about 50 mg. to about 5 g. of thiopolymer per mole of silver halide are quite adequate to accomplish the desired sensitization.

The linear thiopolymers of our invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the thiopolymers can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. As indicated above, the solvent should be selected so that it has no harmful effect upon the emulsion, and generally solvents or diluents which are miscible with water are to be preferred. Water or dilute alkali is a dispersing medium for some of the thiopolymers of the invention. In a preferred embodiment, the thiopolymer can be dissolved in solvents, such as ethanol, acetone, pyridine, N,N-dimethylformamide, etc., and added to the emulsion in this form. If desired, certain of the thiopolymers can be prepared in finely-divided form and dispersed in water alone, or in the presence of a suitable dispersing agent (such as alkali metal salts of aromatic or aliphatic sulfonic acids) and added to the emulsion in this form. It is quite apparent that the thiopolymers of our invention should have sufficient water-dispersibility so that they can be absorbed to the grains of the silver halide present in the emulsion in sufficient amount to sensitize the emulsion. It is apparent that the optimum amount for each of the thiopolymers will vary somewhat from emulsion to emulsion and from thiopolymer to thiopolymer. The optimum amount for any given thiopolymer can be determined for any particular emulsion by running a series of tests in which the quantity of thiopolymer is varied over a given range. Exposure of the treated emulsion in conventional photographic testing apparatus, such as an intensity scale sensitometer, will reveal the most advantageous concentrations for that thiopolymer in that particular emulsion. Such matters are well understood by those skilled in the art.

The photographic emulsions used in practicing our invention are, of course, 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 and Brigham 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 chloropalladate, 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 chloraurate, potassium aurithiocyanate, potassium chloraurate, auric trichloride and 2-aurosulfo-benzothiazole 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 diethyltriamine (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 2,493,748, issued January 10, 1950; Sprague 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. Patents 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 Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene-bis-benzothiazolium perchlorate); and the zinc and cadmium salts of Jones U.S. patent application Serial No. 493,047, filed March 8, 1955, (now 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.

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 (now U.S. Patent 2,960,404, issued November 15, 1960); 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 (now U.S. Patent 2,904,434, issued September 15, 1959); bis-(ethoxy diethylene glycol) succinate as described in Gray U.S.

application Serial No. 604,333, filed August 16, 1956 (now U.S. Patent 2,940,854, issued June 14, 1960), 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 application Serial No. 311,319, filed September 24, 1952 (now 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-diphenylbicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic 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-(methanesulfonyl)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-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 (now abandoned); 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 (now U.S. Patent 2,950,197, issued August 23, 1960); or 2,3-dihydroxy dioxane as described in Jeffreys U.S. patent application Serial No. 624,968, filed November 29, 1956 (now U.S. Patent 2,870,013, issued January 20, 1959).

The emulsions may contain a coating aid such as saponin; a lauryl or oleoyl 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 2,739,891, 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 application Serial No. 485,812, filed February 2, 1955 (now 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. octylphenoxypentaethoxy)-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 di-sodium 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 bromiodide. 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.

They 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, issued 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 cellulose 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 on an imidized polyacrylamide of like acrylimide 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. application Serial No. 527,872 of Illingsworth,

Dann and Gates, filed August 11, 1954 (now U.S. Patent 2,852,382, 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 following example will serve to illustrate more fully the manner of sensitizing photographic silver halide emulsions according to our invention.

An ordinary photographic silver bromide emulsion containing a sensitizing dye, a sulfur sensitizer of the type mentioned in Sheppard U.S. Patent 1,623,499, mentioned above, and gold sensitized in the manner indicated in U.S. Patent 2,399,083, mentioned above, was divided into several portions. Thiopolymer compounds of the type obtained in the above examples were then added in solutions in an organic solvent, such as ethanol or N,N-dimethylformamide, in the amounts indicated in the table. The various portions of emulsions were then coated on a transparent support, such as cellulose acetate and then dried. The dried coatings were then exposed for about $\frac{1}{25}$ sec. to daylight quality radiation in an Eastman Type 1b Sensitometer. The exposed coatings were then developed for about 5 minutes in a photographic developer having the following composition:

N-methyl-p-aminophenol sulfate-----	G. 2.5
Hydroquinone -----	2.5
Sodium sulfite (dry)-----	30.0
Sodium borate-----	10.0
Potassium bromide-----	0.5
Water to make one liter.	

The relative speed as compared with a portion of the emulsion containing no thiopolymer, gamma and fog for each of the coatings was then measured. The results are given in the following table:

TABLE I

Coating No.	Addenda (g./mol. AgX)	Rel. Speed	Gamma	Fog
I(a)---	None (control)-----	100	1.17	.10
(b)---	Product of Example 1 (0.3)-----	130	1.40	.11
(c)---	do-----	183	1.02	.22
II(d)---	None-----	100	1.30	.11
(e)---	Product of Example 4 (0.3)-----	123	1.27	.13
III(f)---	Product of Example 3 (0.3)-----	110	1.40	.13
IV(g)---	None-----	100	1.40	.13
(h)---	Product of Example 8 (3.0)-----	132	1.14	.12
V(i)---	None-----	100	1.17	.10
(j)---	Product of Example 9 (3.0)-----	127	1.36	.13
VI(k)---	None-----	100	1.50	.14
(l)---	Product of Example 10 (0.3)-----	154	1.03	.13
VII(m)---	None-----	100	-----	.13
(n)---	Product of Example 16 (0.15)-----	150	-----	.18
VIII(o)---	None-----	100	1.46	.14
(p)---	Product of Example 18 (0.3)-----	120	1.38	.15
(q)---	Product of Example 18 (3.0)-----	155	1.35	.20
IX(r)---	None-----	100	1.18	.12
(s)---	Product of Example 22 (0.3)-----	141	1.21	.16
X(t)---	None-----	100	1.51	.12
(u)---	Product of Example 20a (0.3)-----	144	1.24	.22
XI(v)---	None-----	100	1.17	.14
(w)---	Product of Example 20 (0.3)-----	129	1.19	.17
XII(x)---	None-----	100	1.14	.14
(y)---	Product of Example 21 (0.3)-----	129	1.19	.14
(z)---	Product of Example 21 (3.0)-----	162	1.10	.17
XIII(a')---	None-----	100	1.25	.12
(b')---	Product of Example 23 (0.3)-----	177	1.15	.21
XIV(c')---	None-----	100	1.30	.10
(d')---	Product of Example 24 (0.3)-----	160	1.18	.18

The effect of our new thiopolymers has been illustrated above with particular reference to ordinary photographic silver-bromide emulsions, although it is to be understood that other silver halide emulsions can be employed to like advantage. The thiopolymers of our invention can be used in emulsions which are acidic in character or in emulsions which are alkaline. Of course, when adding thiopolymers to such emulsions, it is generally desirable to adjust the pH of the sensitizing solution so that it will not seriously alter the pH of the emulsion to be treated. It is apparent that certain of the thiopolymers may be present in salt form when present in acidic or

alkaline emulsions; and it is to be understood that our invention contemplates these thiopolymers either in their salt or non-salt forms.

As illustrated in Example 16 above, the thiopolymers of our invention can be treated with alkyl salts, such as methyl sulfate, ethyl sulfate, methyl-p-toluenesulfonate, etc., to provide ternarized polymers, which generally have improved water-solubility. From about 10 to substantially 100 percent of the linear thioether atoms can be ternarized by this method, while still retaining many of the valuable photographic properties of the parent polymers.

The intermediates necessary to prepare the polymers of our invention are, of course, well known to those skilled in the art. For example, the intermediates of Formula IIa above can advantageously be prepared according to the general method described in Cox U.S. Patent 2,017,811, issued October 15, 1935. Other alkylene oxides can be employed according to the method of that patent to condense with other glycol chlorhydrins. The intermediates of Formula IIb above can be prepared by condensing the intermediates of Formula IIa together with an alkali metal acid salt of hydrogen sulfide, such as potassium hydrogen sulfide (KSH). See, for example, Marvel U.S. Patent 2,598,407, issued May 27, 1952, which describes certain of these intermediates.

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:

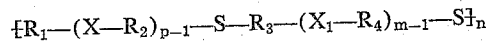
1. A photographic silver halide emulsion containing a sensitizing amount of a member selected from the class consisting of (1) a linear polymer containing at least three linear thioether atoms, said linear polymer being substantially non-vulcanizable and having a molecular weight of at least about 250, and (2) a ternary sulfonium salt of said linear polymer.

2. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer containing a plurality of groups represented by the following general formula:



wherein R represents an aliphatic radical and n represents a positive integer of at least about 3, the depicted sulfur atom in the polymer units of said general formula being attached to a carbon atom of said R radical, said carbon atom having directly attached thereto a hydrogen atom, said linear polymer having a molecular weight of at least about 250.

3. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer containing a plurality of groups represented by the following general formula:

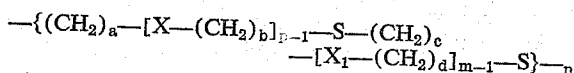


wherein R_1 , R_2 , R_3 and R_4 each represents alkylene containing from about 2 to 20 carbon atoms, X and X_1 each represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, amido, carbonyl, oxycarbonyloxy, oxycarbonyl and carbonyloxy, provided that X does not represent oxycarbonyl when X_1 represents carbonloxy and provided X does not represent amido when X_1 represents carbamyl, p and m each represents a positive integer of from 1 to 5, n represents a positive integer of at least 3, said linear polymer having a molecular weight of at least about 250.

4. A photographic silver halide emulsion as defined in claim 3, wherein the silver halide is silver bromide.

5. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer containing a plu-

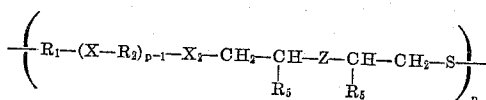
ality of groups represented by the following general formula:



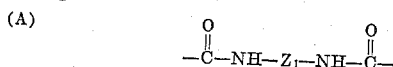
wherein X and X₁ each represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, amido, carbonyl, oxycarbonyloxy, oxycarbonyl and carbonyloxy, provided that X does not represent oxycarbonyl when X₁ represents carbonyloxy and provided that X does not represent amido when X₁ represents carbamyl, a, b, c and d each represents a positive integer of from 2 to 20, m and p each represents a positive integer of from 1 to 5 and n represents a positive integer of at least 3, said linear polymer having a molecular weight of at least about 250.

6. A photographic silver halide emulsion as defined in claim 5, wherein the silver halide is silver bromiodide.

7. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer containing a plurality of groups represented by the following general formula:



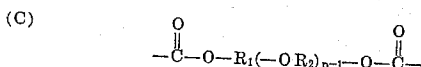
wherein R₁ and R₂ each represents alkylene containing from 2 to 20 carbon atoms, X represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, amido, carbonyl, oxycarbonyloxy, oxycarbonyl and carbonyloxy, X₂ represents a member selected from the class consisting of oxygen and sulfur, R₅ represents a member selected from the class consisting of hydrogen and lower alkyl, n represents a positive integer of at least 3, p represents a positive integer of from 1 to 5, Z represents a member selected from the class consisting of:



wherein Z₁ represents alkylene containing from 2 to 20 carbon atoms,



wherein R₇ and R₈ each represents a member selected from the class consisting of hydrogen, lower alkyl and monocyclic aryl of the benzene series,

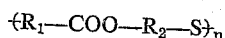


wherein R₁ and R₂ each represents alkylene containing from 2 to 20 carbon atoms and p represents a positive integer of from 1 to 5, and



wherein R₆ represents alkylene containing from 1 to 6 carbon atoms, said linear polymer having a molecular weight of at least about 250.

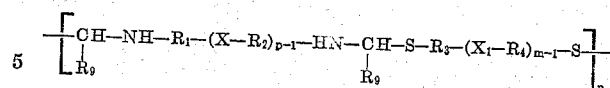
8. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester containing a plurality of groups represented by the following general formula:



wherein R₁ and R₂ each represents alkylene and n represents a positive integer of at least about 3, said linear polyester having a molecular weight of at least about 250.

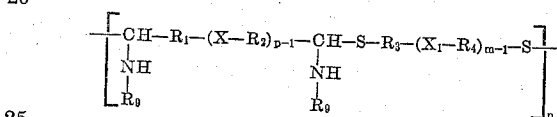
9. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer containing a plu-

ality of groups represented by the following general formula:



wherein R₁, R₂, R₃ and R₄ each represents alkylene containing from 2 to 20 carbon atoms, R₉ represents a member selected from the class consisting of hydrogen and lower alkyl, X and X₁ each represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, amido, carbonyl oxycarbonyloxy, oxycarbonyl and carbonyloxy, m and p each represents a positive integer of from 1 to 5 and n represents a positive integer of at least 3, said linear polymer having a molecular weight of at least about 250.

10. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer having a plurality of groups represented by the following general formula:



wherein R₁, R₂, R₃ and R₄ each represents alkylene containing from 2 to 20 carbon atoms, R₉ represents a member selected from the class consisting of hydrogen and lower alkyl, X and X₁ each represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, amido, carbonyl oxycarbonyloxy, oxycarbonyl and carbonyloxy, m and p each represents a positive integer of from 1 to 5 and n represents a positive integer of at least 3, said linear polymer having a molecular weight of at least about 250.

11. A photographic silver halide emulsion which has been sensitized with a labile sulfur compound and a gold compound, said silver halide emulsion containing a sensitizing amount of a member selected from the class consisting of (1) a linear polymer containing at least three linear thioether atoms, said linear polymer being substantially non-vulcanizable and having a molecular weight of at least about 250 and (2) a ternary sulfonium salt of said linear polymer.

12. A photographic silver halide emulsion sensitized with a labile sulfur compound and a gold compound, said emulsion containing a sensitizing amount of a linear polymer containing a plurality of groups represented by the following general formula:



wherein R represents an aliphatic radical and n represents a positive integer of at least about 3, the depicted sulfur atom in the polymer units of said general formula being attached to a carbon atom of said R radical, said carbon atom having attached thereto a hydrogen atom, said linear polymer having a molecular weight of at least about 250.

13. A photographic gelatino-silver-halide developing-out emulsion, said emulsion containing a sensitizing amount of a member selected from the class consisting of (1) a linear polymer containing at least three linear thioether atoms, said linear polymer being substantially non-vulcanizable, being dispersible in a dispersing medium selected from the group consisting of water and a water-miscible organic solvent, and having a molecular weight of at least about 250, and (2) a ternary sulfonium salt of said linear polymer.

14. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer obtained by heating together 1,2-bis(2-chloroethoxy)ethane and sodium sulfide, said linear polymer having a molecular weight of at least about 250.

15. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer obtained by heating together N,N'-methylene bis acrylamide and 1,2-

bis(2-mercaptoethoxy)ethane in a basic medium, said linear polymer having a molecular weight of at least about 250.

16. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer obtained by condensing together succindialdehyde, 1,10-dimercapto-
 decane and ammonia, said linear polymer having a molecular weight of at least about 250.

17. A photographic silver halide emulsion containing a sensitizing amount of a linear polymer obtained by condensing together formaldehyde, ethylenediamine and bis(2-mercaptoethyl)-ether, said linear polymer having a molecular weight of at least 250.

18. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester obtained by the

self-condensation of a hydroxyalkylmercapto aliphatic carboxylic acid.

19. A photographic silver halide emulsion containing a sensitizing amount of poly(β -hydroxyethyl)mercapto-
 acetic acid.

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