United States Patent Office 3,046,129 Patented July 24, 1962

3,046,129

SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS CONTAINING COLOR-FORMING COMPOUNDS WITH POLYMERIC THIOETHERS

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No Drawing. Filed Dec. 12, 1958, Ser. No. 779,839
16 Claims. (Cl. 96—55)

This invention relates to photographic silver halide emulsions, and more particularly, to an improved means for sensitizing photographic silver halide emulsions containing color-forming compounds, or couplers.

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 photographic silver halide emulsions for color photography which have been sensitized with various polymeric compounds containing a plurality of sulfur atoms. Another object is to provide a method of preparing such sensitized emulsions for color photography. Still another object of our invention is to provide photographic silver halide emulsions for color photography which have increased sensitivity of the type commonly attributed to chemical sensitization, without concomitant increases in fog or poor keeping qualities, to a degree which might seriously affect the usefulness of the emulsions. Other objects of our invention will become apparent from a consideration of the following description and examples.

According to our invention, we have found that the sensitivity of a photographic silver halide emulsion for color photography can be materially increased by incorporating therein polymeric compounds containing a plurality of sulfur atoms, without prohibitively increasing fog in the emulsions. 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 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 in 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., or by dispersing directly in the emulsion in finely-divided form, so that a sensitizing amount of the polymeric materials can be absorbed 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:

(I) $$(R—S)_x$$

wherein R represents an aliphatic linkage, such as an alkylene group, etc., and x 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 should have a molecular weight of about 250 to 10,000, although polymeric materials having molecular weight from about 500 to 3,500 have been found to be particularly useful in our invention. The terminal groups of our polymers are generally hydrogen atoms, halogen atoms, alkenyl groups (e.g., vinyl, allyl, etc.), carboxylic groups (e.g., carboxyl, carboxylic amide, carboxylic ester, such as carbomethoxyl, carbethoxyl, etc.), 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:

(II) $$\left[R_1—(X—R_2)_{p-1}—S—R_3—(X_1—R_4)_{m-1}—S\right]_n$$

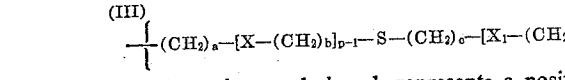
wherein R_1, R_2, R_3 and R_4 each represents a hydrocarbon alkylene group containing from about 2 to 20 carbon

atoms (e.g., ethylene, trimethylene, 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 (—NHCO—), carbonylamido

(—CONH—)

carbonyl, oxycarbonyloxy, oxycarbonyl (—OCO—), carbonyloxy (—COO—), etc., *p* and *m* each represents a positive integer of from 1 to 5, and *n* represents the number of units, e.g., a positive integer of at least 2. An especially useful group of polymers represented by Formula II comprises the polymers represented by the following general formula:

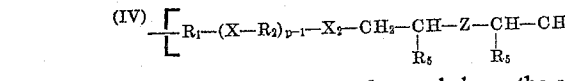
(III)



wherein *a*, *b*, *c* and *d* each represents a positive integer of from 2 to 20, and X, X_1, *n*, *m* and *p* each have the values given above.

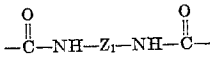
Another group of polymers embraced by Formula I above which are useful in our invention comprise the polymers represented by the following general formula:

(IV)



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.,

(A)



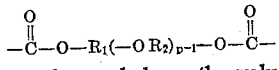
wherein Z_1 represents an alkylene group, such as that defined above for R_1, or the group:

(B)



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:

(C)

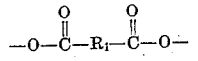


wherein R_1, R_2 and *p* each have the values given above, or alternatively, Z can represent an alkylene group, such as:

(D) —R_6—

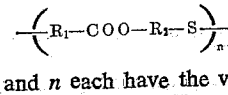
wherein R_6 represents an alkylene group, such as methylene, ethylene, trimethylene, butylene, pentamethylene, hexamethylene, etc., or an acyloxy group of a dicarboxylic acid, such as:

(E)



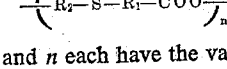
wherein R_1 has the values given above. Another group of polymers embraced by Formula I, which are useful in practicing our invention comprises polylinear lactones, such as:

(V)



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

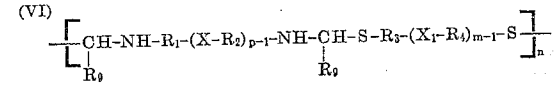
(V*a*)



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:

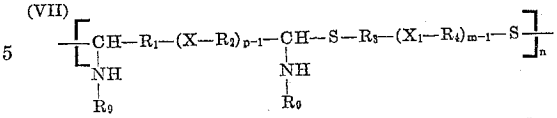
(VI)



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

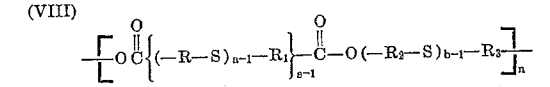
(VII)



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.

Among the linear polymers of our invention represented by Formula I above, are linear polyesters which can advantageously be represented by the following general formula:

(VIII)



wherein R, R_1, R_2, R_3 and *n* each have the values given above, such as a hydrocarbon alkylene group containing from about 1 to about 10 carbon atoms (e.g., methylene, ethylene, trimethylene, tetramethylene, pentamethylene, octamethylene, decamethylene, etc.), *a* and *b* each has the values given above, especially a positive integer of from about 1 to 4 (provided that *a* and *b* do not simultaneously represent 1) and *s* represents a positive integer of from 1 to 2.

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:

(II*a*) hal—R_1—(X—R_2)$_{p-1}$—hal

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

(II*b*) HS—R_3—(X_2—R_4)$_{m-1}$—SH

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 II*a* with an alkali metal sulfide, such as sodium or potassium sulfide. Such preparations have been previously described in the prior art, such as Lilienfeld U.S. Patent 108,329, issued February 20, 1912.

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

(IV*a*) HS—R_1—(X—R_2)$_{p-1}$—X_2—H

wherein R_1, R_2, X, X_2 and *p* each have the values given above, with at least one diolefinically-unsaturated compound selected from those represented by the following general formula:

(IV*b*) H_2C=CH—Z—CH=CH_2

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:

(V*b*) $HO—R_2—S—R_1—COOH$

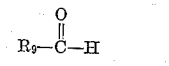
The self-condensation of the compounds of Formula V*b* occurs spontaneously on standing, although it has been found that the polymers of Formula V can be prepared more rapidly by heating a lactone of the acid of Formula V*b* in the presence or absence of an acidic condensation agent, such as zinc chloride,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

(VI*a*) $H_2N—R_1—(X—R_2)_{p-1}—NH_2$

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

(VI*b*)



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

(VI*c*) $HS—R_3—(X_1—R_4)_{m-1}—SH$

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:

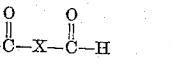
(VII*a*) $R_9—NH_2$

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

(VII*b*) $HS—R_3—(X_1—R_4)_{m-1}—SH$

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

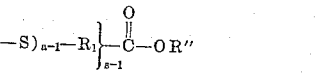
(VII*c*)



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

The linear polyesters of Formula VIII can be prepared according to methods which have been described in the prior art. Among such methods are those comprising the condensation of a carboxylic compound, such as those represented by the following general formula:

(IX)



wherein R, R_1, *a* and *s* each have the values given above, and R′ and R″ each represents a hydrogen atom or a lower alkyl group (e.g., methyl, ethyl, propyl, butyl, etc.), with a glycol compound, such as those represented by the following general formula:

(X) $HO(—R_2—S)_{b-1}—R_3—OH$

wherein R_2, R_3 and *b* each have the values given above. As indicated above, at least one of the reactants, IX and/or X, should contain a thioether linkage. While the carboxylic component represented by Formula IX above has been depicted as either an acid or an ester of a low-boiling alcohol, it is to be understood that acid anhydrides and acid halides can also be employed in such condensations. Moreover, a mixture of two or more dissimilar ingredients, such as two different acids of Formula IX, can simultaneously be employed in the condensations. In like manner, a mixture of glycols can be employed as an ester-forming component in the reaction. Thus, our invention comprises mixed polyester compounds.

It has also been found that linear polyesters of the type represented by Formula VIII above can be prepared by interacting in the presence of ultra-violet radiation a dithiol compound, such as a compound of Formula IV*a*, wherein X_2 represents a sulfur atom, with a compound selected from those represented by the following general formula:

(XI) $CH_2=CH(—CH_2)_{q-1}—CH=CH_{2q-1}—CH=CH_2$

wherein *q* represents a positive integer of from 1 to 2 and Z represents an acyloxyl group of a dicarboxylic acid, such as is represented above by Formula E. Condensations of this type are shown in U.S. Patent 2,347,182, mentioned above.

The following examples will serve to illustrate more fully the preparation of various linear polymers containing thioether atoms which can be effectively used to sensitize photographic emulsions for color photography according to our invention.

EXAMPLE 1

$[ClCH_2CH_2OCH_2CH_2OCH_2CH_2—Cl+Na_2S\rightarrow$
$+CH_2CH_2OCH_2CH_2OCH_2CH_2S+_n+NaCl]$

A mixture of 18.7 g. of 1,2-bis(2-chloroethoxy)ethane and 24 g. of sodium sulfide ($Na_2S·9H_2O$) 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 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

$[ClCH_2CH_2CH_2OCH_2CH_2CH_2Cl+Na_2S\rightarrow$
$+CH_2CH_2CH_2OCH_2CH_2CH_2—S+_n+NaCl]$

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

um 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 (insoluble 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 tetraethylene glycol 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 melting at 90° C. was filtered off. *Analysis.*—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 two 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 succinaldehyde 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 ternarized by means of alkyl salts, such as methyl-p-toluenesulfonate. This 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.—Calculated: C, 45.2; H, 8.3; S, 24.1; N, 10.4. Found: C, 45.9; H, 7.8; S, 25.4; N, 8.8.

Five grams of this material were 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.—Calculated: C, 48.6; H, 7.0; S, 20.0; N, 4.4. 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.—Calculated: C, 47.1; H, 7.0; S, 18.6; N, 4.0. Found: C, 47.2; H, 6.8; S, 18.1; N, 3.2.

EXAMPLE 17

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

In glass apparatus, under an air condenser, were placed 10 g. of hydroxyethylmercaptoacetic acid lactone and 0.100 g. of anhydrous zinc chloride. The reaction mix-

ture 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 g. of solution. The solids content was 2.6 percent. Molecular weight by end-group titration was 7100.

EXAMPLE 18

Polymerization of Hydroxyethylmercaptoacetic Acid Lactone by Chloracetic Acid

Twenty-seven grams of lactone were heated in an oil bath at 180° C. with 0.270 g. of chloracetic acid in an 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 g. 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 steambath in 90 ml. of benzene with 0.17 g. 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 g. 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 g. of mercaptopropanol, 9.8 g. of acrylic acid and 0.136 g. of hydroquinone. The reaction mixture was heated over-night 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 g.

(2) *Polymerization.*—Six grams of the above reaction product were heated on a steam bath with 0.120 g. 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 unreacted 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 Büchner 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 20*a*

Polymerization of β-Hydroxyethylmercaptopropionic 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

Hydroxyhexylmercaptopropionic Acid Lactone

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

The lactone (about 25 g.) 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 were 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 mm. to 92°/0.07 mm. The yield was 15 g., M.P. 42.4° C.

Analysis.—Calculated 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 1000.

The following example also illustrates the ternarization of one of the thiopolymers of our invention by means of alkyl salts, such as methyl p-toluenesulfonate, 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 g. of methyl p-toluenesulfonate 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 produce 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%.

In Examples 25 to 40 of Table B below, are illustrated the preparation of linear polyesters by condensing a dicarboxylic acid or its anhydride with a glycol containing at least one thioether atom. The same general method was employed for preparing each of the polyesters illustrated in Examples 25 to 40, and the yield, melting point and analysis for the resulting polyesters are given in those cases where the polymers were separated from the reaction medium. It has been found that the polyesters could be added to photographic silver halide emulsions without first separating the polyester and re-dissolving it in a suitable organic solvent. It will thus be noted that in some instances, data of the type mentioned above are not given in the table for particular examples, since the polyester was used as obtained without further purification, other than as illustrated in Example 25 which follows.

EXAMPLE 25

In an all-glass outfit equipped with an air-reflux condenser and gas inlet for admitting dry nitrogen below the level of the melt were placed 18.33 g. of 3-thiapentane-1,5-diol and 14.85 g. of succinic anhydride. The reaction flask was immersed in a thermostatically controlled oil bath whose temperature was raised to 150° C. where it was maintained. After the temperature had been at 150° C. for one hour, a slow stream of dry nitrogen was passed through the melt. After 16 hours at 150° C., a water pump vacuum was applied to remove gross water with the reaction vessel still at 150° C. A high vacuum pump, giving a vacuum in the reaction vessel of less than 0.1 mm. was then applied for 3 hours, after which the bath temperature was raised to 170° C. and the pumping continued for an additional 4¾ hours. The melt was then cooled under vacuum. The solidified melt was dissolved by refluxing in 150 g. of acetone. The solution was filtered through paper to remove suspended material and then chilled in a bath of solid carbon dioxide in acetone. The desired product precipitated from solution. This was filtered onto a cold Büchner funnel washed on the funnel with cold acetone, and dried in a vacuum desiccator under a constantly applied water pump vacuum. The yield of product was 24.7 g.

The polyesters of Examples 26 to 40 were obtained in exactly the manner described in Example 25 above, and the results obtained, together with those of Example 25, are summarized in Table B.

TABLE B

Example	Dialcohol (g.)	Dibasic Acid Anhydride or Acid* (g.)	Yield (g.)	M.P., °C.	Analysis		
					C	H	S
25	3-thiapentane-1,5-diol(18.33)	succinic (14.85)	24.7	55–6	47.3	6.2	15.5
					49.2	6.3	14.7
26	3-thiapentane-1, 5-diol (6.1)	glutaric (5.6)	9.0				
27	3-thiapentane-1,5-diol (6.11)	adipic* (7.13)		59–60	57.4	6.9	13.6
28	do	azalaic* (9.32)		54–5	57.2	8.05	10.7
29	do	sebacic* (10.0)		73–5	57.7	8.3	9.7
30	3-thiapentane-1, 5-diol(12.2)	pimelic* (15.86)	11.5	46–8	53.4	7.3	12.3
31	3-thiapentane-1, 5-diol (6.11)	suberic* (8.6)	8.0	62–4	55.1	7.5	12.4
32	3, 6 - dithiaoctane - 1, 8-diol (9.1).	succinic (4.9)	6.5	72			24.2
33	4, 10 - dithiatridecane - 1, 13-diol (3.78).	succinic (1.49)	(left in acetone)				
34	4, 15 - dithiaoctodecane - 1, 18-diol (3.22).	succinic (1.00)	3.4		57.0	8.4	15.6
35	7, 13 - dithianonadecane - 1, 19-diol (6.72).	succinic (2.00)	5.6	40.5–41.5	60.1	9.1	15.3
36	7, 13 - dithiatetracosane - 1, 24-diol (6.09).	succinic (1.50)	6.4	54–5	63.1	9.5	13.1
37	4, 8 - dithiaundecane - 2, 10-diol (6.72).	succinic (6.72)	(left in acetone)				
38	3-thiahexane-1,6-diol (6.8)	succinic (4.95)	A				
39	4-thiaheptane-1, 7-diol (7.5)	succinic (4.05)	B				
40	3-thianonane-1, 9-diol (8.91)	succinic (4.95)	C				
41	ethane-1,2-diol (5.0)	4-thiapimelic* (7.5)	left in acetone				
42	do	3,6-dithiasuberic* (10.5).	do				
43	do	3,7-dithiaazelaic* (11.2).	do				
44	ethanol-1,2-diol (1.50)	3,8-dithiasebaic* (4.76).	do				
45	ethane-1,2-diol (2.05)	3-thiaadipic* (4.92)	crude dissolved in DMF.				

DMF=N,N-dimethylformamide.
A=13.9% solids in 67 g. acetone solution.
B=19.2% solids in 55 g. acetone solution.
C=17.7% solids in 64 g. acetone solution.

In Examples 41 to 45 of Table B above, there are illustrated polyesters obtained from a glycol and a dicarboxylic acid containing at least one thioether sulfur atom as identified above. The same general method was used for preparing the esters of Examples 41 to 45 and this method can be illustrated by the following example.

EXAMPLE 42

[Summarized in Table B above]

In a small, round-bottom flask were placed 5.0 g. of ethane-1,2-diol (ethylene glycol) and 10.5 g. of 3,6-dithiasuberic acid. The flask was placed in an oil bath whose temperature was slowly raised to 170° C .and then maintained at that temperature while a slow stream of dry nitrogen was passed through the melt. After one hour at 170° C., a high vacuum pump was attached, and with the temperature of the reaction was dropped to ca. 100° C., and a vacuum of about one-half millimeter was applied. When the initial evolution of gas had moderated, the temperature of the bath was again raised to 170° C. and there maintained for 5½ hours. The reaction mixture was cooled under vacuum and the viscous oil obtained was dissolved in acetone. The solids content of this solution was 31%.

In preparing the polyesters of Examples 41, 43, 44 and 45, the thiadibasic acid and the glycol, the latter in about 10% excess, were heated in an all-glass reflux outfit with air condenser, in an oil bath at 150° C., while a gentle stream of nitrogen was passed through the melt.

After this preliminary heating, a water aspirator was attached to remove the early accumulation of water to prevent fouling the mechanical pump, and then the mechanical pump was attached to give a vacuum of usually less than 0.10 mm. After the designated time at 150° C., the temperature of the bath was raised to 170° C. and the high vacuum and heating was continued. The melt was cooled, dissolved in a solvent, acetone unless otherwise indicated, boiled with decolorizing carbon (Norite), filtered, and used. The solids content of the solution was calculated from weight of polymer and weight of solution.

HEATING SCHEDULES FOR CONDENSATIONS

Example No.	150°/C. No vac. (hr.)	150°/C. Water Pump vac. (hr.)	150°/C. High vac. (hr.)	170°/C. High vac. (hr.)	(g.) Solution	Percent Solids of Product in Solution
41	2	1½	[1] 3	4½	48	16.7
43	17½	¾	13	-------	62.7	12.7
44	17⅛	⅛	2½	5½	13	[2] 13.8
45	17¼	¼	2⅛	5½	12.6	[3] 17.4

[1] 160°/C.
[2] Acetone-soluble portion. Major portion was not soluble in acetone.
[3] In N,N'-dimethylformamide solution.

It is to be understood that glycols containing at least one thioether sulfur atom can be condensed with dicarboxylic acids containing at least one thioether sulfur atom. For instance, 5.20 grams of 3,6-dithiasuberic acid were condensed with 5.55 grams of 3,6-dithiaoctane-1,8-diol to yield 7.5 grams of a viscous oil, which was soluble in cyclohexanone. Such a polyester provided a speed increase of 50% over an ordinary unsensitized photographic gelatino-silver-bromiodide emulsion, when added at a concentration of 3.0 g. mol. AgX.

As indicated above, the linear polyesters of our invention can be obtained by a conventional ester-interchange reaction by employing a dicarboxylic ester of a low-boiling alcohol. This method of preparation is illustrated in the following example.

EXAMPLE 46

In an all-glass reflux outfit, with a short, air condenser, were placed 14.6 grams (0.1 mole) of diethyl oxalate, 12.2 grams (0.1 mole) of 3-thiapentanediol and 5 drops of titanium butoxide. The flask was immersed in an oil bath whose temperature was raised to 150° C. and

the reaction mixture heated at 150° C. for 22 hours. A water-pump vacuum was then applied to remove easily volatiles and then a high-vacuum pump was applied for 3 hours. At this time the temperature of the oil bath was raised to 170° C. and heating and vacuum continued for an additional 2 hours. The contents of the flask were cooled to room temperature and dissolved in 60 mls. of acetone with warming. The solution was boiled with decolorizing carbon, filtered through paper and a layer of filter aid. Since precipitation through chilling was not easily achieved, the solution was used for test after determination of the solids content.

Other polyesters were obtained in exactly the manner as in Example 46 above, and the physical data for certain of the polyesters thus obtained are given in the following table.

TABLE C

Example	Ester	M.P., °C.	Analysis		
			C	H	S
46	diethyl oxalate				
47	diethyl malonate				
48	diethyl succinate	49–52	46.4	6.4	14.8
49	dimethyl adipate	61.5–63	50.9	6.9	14.6

As indicated above, the linear polyesters of our invention can also be obtained from compounds containing diolefinic unsaturation, such as the compound of Formula IV*b* above. This method of preparation is illustrated in the following example.

EXAMPLE 50

In a quartz tube equipped with a reflux condenser were placed 3.50 g. of a divinyl succinate and 1.88 g. of ethane-1,2-dithiol. The tube was placed before a Gates arc at 5 inches. A vigorous reaction occurred. After two hours of exposure, the tube and contents were cooled to room temperature. A clear, brilliant dope was obtained. Ether was added to this dope and with trituration, a white solid was deposited. This precipitated polymer was thoroughly extracted with ether and dried in a vacuum desiccator under a constantly applied water pump vacuum. The yield of produce was 2.6 g., M.P. 66–67.5° C.

In exactly the manner illustrated in Example 50 above, other polyesters were obtained and the data for such preparation are given in the following table.

TABLE D

Example	Dithiol (g.)	Ester (g.)	Yield (g.)
50	ethane-1,3-dithiol (1.88)	divinyl succinate (3.50)	2.6
51	ethane-1,3-dithiol (5.64)	diallyl adipate (13.44)	5.0
52	ethane-1,3-dithiol (2.82)	diallyl sebacate (8.46)	4.5
53	do	diallyl succinate (6.0)	3.4

The linear thioether polymers of our invention are effectively employed in photographic silver halide emulsions in combination with various color-forming compounds or couplers, which react with the oxidation products of color developers (particularly phenylenediamine developers) to provide subtractively-colored images. The color-forming compounds can be of the customary types employed in color photography, such as pyrazolone couplers for formation of the magenta image, phenolic couplers for formation of the cyan image and open-chain compounds containing a reactive methylene group for formation of the yellow image. Such couplers can be of the type which can be dispersed in a high-boiling, crystalloidal compound, which can be used as a vehicle for incorporating the color-forming compound in the photographic emulsion, or such couplers can be of the "fat-tail" varieties (see, for example, F.I.A.T., Final Report, No. 721 for examples thereof) which can be dispersed in the photographic silver halide emulsions. Both of these types of couplers are characterized by non-diffusing properties

from the particular silver halide emulsions in which they are incorporated. The couplers or color-forming compounds can be incorporated in the silver halide emulsions by any of the common methods known to those skilled in the art.

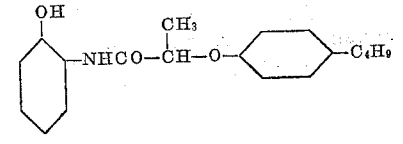
The linear thiopolymers of our invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the thiopolymers can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a finely-divided dispersion, such as described in 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 associated with 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.

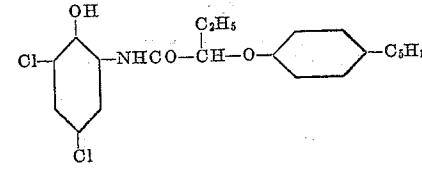
Color-forming compounds or couplers which are useful in practicing our invention include the following:

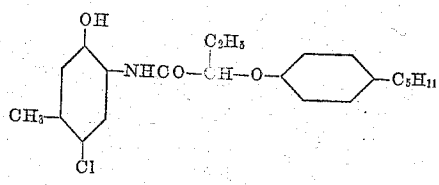
COUPLERS PRODUCING CYAN IMAGES

5-(p-amylphenoxybenzenesulfonamino)-1-naphthol
5-(N-benzyl-N-naphthalenesulfonamino)-1-naphthol
5-(n-benzyl-N-n-valerylamino)-1-naphthol
5-caproylamino-1-naphthol
2-chloro-5-(N-n-valeryl-N-p-isopropylbenzylamino)-1-naphthol
2,4-dichloro-5-(p-nitrobenzoyl-β-o-hydroxyethylamino)-1-naphthol
2,4-dichloro-5-palmithylamino-1-naphthol
2,2'-dihydroxy-5,5'-dibromostilbene
5-diphenylethersulfonamido-1-naphthol
1-hydroxy-2-(N-isoamyl-N-phenyl)naphthamide
1-hydroxy-2-(N-p-sec. amylphenyl)naphthamide
8-hydroxy-1-α-naphthoyl-1,2,3,4-tetrahydroquinoline
2-lauryl-4-chlorophenol
1-naphthol-2-carboxylic-α-naphthalide
1-naphthol-5-sulfo-cyclohexylamide
5-phenoxyacetamino-1-naphthol
5-β-phenylpropionylamino-1-naphthol
Monochlor-5-(N-γ-phenylpropyl-N-p-sec.-amylbenzoylamino)-1-naphthol
2-acetylamino-5-methylphenol
2-benzoylamino-3,5-dimethylphenol
2-α(p-tert. amylphenoxy)-n-butyrylamino-5-methylphenol
6-{γ-{4-[γ-(2,4-di-tert. amylphenoxy)butyramido]phenoxy}acetamido}-2,4-dichloro-3-methylphenol
1-hydroxy-2-[σ-(2,4-di-tert. amylphenoxy-n-butyl]naphthamide
2-α(p-tert. amylphenoxy)-n-butyrylamino-4-chloro-5-methylphenol
2-(p'-tert. amylphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
2-phenylacetylamino-4-chloro-5-methylphenol
2-benzoylamino-4-chloro-5-methylphenol
2-anilinoacetylamino-4-chloro-5-methylphenol
2-{4'-[α-(4''-tert, amylphenoxy)-n-butyrylamino]benzoylamino}-4-chloro-5-methylphenol
2-[4',3''-(4'''-tert. amylphenoxy)benzoylamino]benzoylamino-4-chloro-5-methylphenol
2-p-nitrobenzoylamino-4-chloro-5-methylphenol
2-m-aminobenzoyl-4-chloro-5-methylphenol
2-acetamino-4-chloro-5-methylphenol
2(4'-sec. amylbenzamino)-4-chloro-5-methylphenol
2(4'-n-amyloxybenzamino)-4-chloro-5-methylphenol
2(4'-phenoxybenzoylamino)phenol
2(4''-tert. amyl-3'-phenoxybenzoylamino)phenol
2-[α-(4'-tert. butylphenoxy)propionylamino]phenol
2-[α-(4'-tert. amyl)phenoxypropionylamino]phenol
2-[N-methyl-N-(4''-tert. amyl-3'-phenoxybenzoylamino)]phenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-methyl-1-phenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-6-methyl-1-phenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,6-dimethylphenol
2,6-di(4''-tert. amyl-3'-phenoxybenzoylamino)-1-phenol
2-α-(4'-tert. amylphenoxy)butyrylamino-1-phenol
2(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
2-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-5-methyl-1-phenol
2(4''-tert. amyl-3'-phenoxybenzoylamino)-4-chloro-1-phenol
3-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-6-chlorophenol
3-(4''-tert. amyl-3'-phenoxybenzoylamino)phenol
2-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-6-chlorophenol
3-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-4-chlorophenol
3-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-5-chlorophenol
3-[α-(4'-tert. amylphenoxy)-n-butyrylamino]-2-chlorophenol
2-α-(4'-tert. amylphenoxylbutrylamino)-5-chlorophenol
2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-chlorophenol
5-benzene sulfonamino-1-naphthol
2,4-dichloro-5-benzenesulfonamino-1-naphthol
2,4-dichloro-5-(p-toluenesulfonamino)-1-naphthol
5-(1,2,3,4-tetrahydronaphthalene-6-sulfamino)-1-naphthol
2,4-dichloro-5-(4'-bromodiphenyl-4-sulfonamino)-1-naphthol
5-(quinoline-5-sulfamino)-1-naphthol

Any of the acylaminophenol couplers disclosed in Salminen and Weissberger U. S. Patent 2,423,730, dated July 8, 1947, can be used as couplers for the cyan image, e.g.







etc.

COUPLERS PRODUCING MAGENTA IMAGES

1-p-sec. amylphenyl-3-n-amyl-5-pyrazolone
2-cyanoacetyl-5-(p-sec. amylbenzoylamino)coumarone
2-cyanoacetylcoumarone-5-(n-amyl-p-sec. amylsulfanilide)
2-cyanoacetylcoumarone-5-(N-n-amyl-p-tert. amylsulfanilide)
2-cyanoacetylcoumarone-5-sulfon-N-n-butylanilide
2-cyanoacetyl-5-benzoylamino-coumarone
2-cyanoacetylcoumarone-5-sulfondimethylamide
2-cyanoacetylcoumarone-5-sulfon-N-methylanilide
2-cyanoacetylnaphthalene sulfon-N-methylanilide
2-cyanoacetylcoumarone-5-(N-γ-phenylpropyl)-p-tert. amylsulfonanilide
1-p-laurylphenyl-3-methyl-5-pyrazolone
1-β-naphthyl-3-amyl-5-pyrazolone
1-p-nitrophenyl-3-n-amyl-5-pyrazolone
1-p-phenoxyphenyl-3-n-amyl-5-pyrazolone
1-phenyl-3-n-amyl-5-pyrazolone
1,4-phenylene bis-3-(1-phenyl-5-pyrazolone)
1-phenyl-3-acetylamino-5-pyrazolone
1-phenyl-3-propionylamino-5-pyrazolone
1-phenyl-3-n-valerylamino-5-pyrazolone
1-phenyl-3-chloroacetylamino-5-pyrazolone
1-phenyl-3-dichloroacetylamino-5-pyrazolone
1-phenyl-3-benzoylamino-5-pyrazolone
1-phenyl-3-(m-aminobenzoyl)amino-5-pyrazolone
1-phenyl-3-(p-sec. amylbenzoylamino)-5-pyrazolone
1-phenyl-3-diamylbenzoylamino-5-pyrazolone
1-phenyl-3-β-naphthoylamino-5-pyrazolone
1-phenyl-3-phenylcarbamylamino-5-pyrazolone
1-phenyl-3-palmitylamino-5-pyrazolone
1-phenyl-3-benzenesulfonylamino-5-pyrazolone
1-(p-phenoxyphenyl)-3-(p-tert. amyloxybenzoyl)amino-5-pyrazolone
1-(2',4',6'-tribromophenyl)-3-benzamido-5-pyrazolone
1-(2',4',6'-trichlorophenyl)-3-benzamido-5-pyrazolone
1-(2',4',6'-trichlorophenyl)-3-phenylacetamido-5-pyrazolone
1-(2',4',6'-tribromophenyl)-3-phenylacetamido-5-pyrazolone
1-(2',4'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone
1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone
1-(2',4',6'-tribromophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone
1-(2',4',6'-trichlorophenyl)-3-[β-2''', 4'''-di-tert. amylphenoxy)-propionamido]-5-pyrazolone
1-(2',4',6'-tribromophenyl)-3-[β-2''',4'''-di-tert. amylphenoxy)-propionamido]-5-pyrazolone
1-(2',5'-dichloro)-3-[3''-(4'''-tert. amylphenoxy)benzamido]-5-pyrazolone
1-(2',4',6'-tribromophenyl)-3-[3''-(4'''-tert. amylphenoxy)-benzamido]-5-pyrazolone
1-(2',5'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido)benzamido]-5-pyrazolone

COUPLERS PRODUCING YELLOW IMAGES

N-amyl-p-benzoylacetaminobenzenesulfonate
N-(4-anisoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine

N-(4-benzoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
N-(4-benzoylacetaminobenzenesulfonyl)-N-n-amyl-p-toluidine
N-(4-benzoylacetaminobenzenesulfonyl)-N-benzylaniline
ω-(p-Benzoylbenzoyl)acetanilide
ω-Benzoylacet-2,5-dichloroanilide
ω-Benzoyl-p-sec. amylacetanilide
N,N'-di(ω-benzoylacetyl)-p-phenylenediamine
N,N'-di-(acetoacetamino)diphenyl
α-{3-[α-(2,4-di-tert.-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide
α-{3-[α-(2,4-di-tert.-amylphenoxy)acetamido]benzoyl}-2-methoxyacetanilide
4,4'-di-(acetoacetamino)-3,3'-dimethyldiphenyl
p,p'-Di-(acetoacetamino)diphenylmethane
Ethyl-p-benzoylacetaminobenzenesulfonate
Nonyl-p-benzoylacetaminobenzenesulfonate
N-phenyl-N'-(p-acetoacetaminophenyl)urea
n-Propyl-p-benzoylacetaminobenzenesulfonate
acetoacetpiperidide
ω-Benzoylacetpiperidide
N(ω-benzoylacetyl)1,2,3,4-tetrahydroquinoline
N(ω-benzoylacetyl)morpholine

The above color-forming compounds produce colored images upon development of the exposed emulsions with color developers, such as the phenylenediamine color developers. Especially useful color developers are those derived from p-phenylenediamines containing at least one primary amino group, such as

N,N-dimethyl-p-phenylenediamine,
N,N-diethyl-p-phenylenediamine,
N-carbamidomethyl-N-methyl-p-phenylenediamine,
N^4-carbamidomethyl-N^4-tetrahydrofurfuryl-2-methyl-p-phenylenediamine,
N^4-ethyl-N^4-carboxymethyl-2-methyl-p-phenylenediamine,
N^4-carbamidomethyl-N^4-ethyl-2-methyl-p-phenylenediamine,
N^4-ethyl-N^4-tetrahydrofurfuryl-2-methyl-p-aminophenol,
3-acetylamino-4-aminodimethylaniline,
N-ethyl-N-β-methanesulfonamidoethyl-4-aminoaniline,
N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline,
the sodium salt of N-methyl-N-β-sulfoethyl-p-phenylenediamine, etc.

As can be seen by reference to the large number of thioether polymers included within our invention, as well as the large number of color-forming compounds which can be employed in combination therewith, a number of combinations of sensitizing compounds and color-forming compounds is possible. In order to determine quickly the effectiveness of a particular combination, it has been found that the screening technique described by Pontius and Thompson in "Phot. Sci. Eng.," vol. 1, pages 4–51, can be used to get an idea of the potential effectiveness of a given combination for use in a photographic color element containing a coupler. This technique does not necessitate the preparation of any coupler dispersions, but the sensitizers can be added to ordinary photographic silver halide emulsions of the type used in black-and-white photography, such as gelatino-silver-bromiodide emulsions, and the emulsions exposed in an intensity scale sensitometer to daylight quality radiation for a fraction of a second (usually $\frac{1}{25}$) and processed for about 15 minutes in a phenylenediamine color developer, to which has been added 10 g. per liter of H-acid. The pH of this developer is usually adjusted to 10.8 by adding sodium

hydroxide. A suitable developer composition for this screening technique is as follows.

Benzyl alcohol	cc	10
Sodium hexametaphosphate	g	2.0
Sodium sulfite	g	2.0
Sodium hydroxide	g	3.4
H-acid (1-amino-8-naphthol-3,6-disulfonic acid)	g	10.0
4-amino-3-methyl-N-ethyl-N-(β-methyl sulfonamidoethyl)aniline sulfate	g	8.0
Sodium carbonate monohydrate	g	40.0
Sodium bromide	g	1.5
Sodium thiocyanate	g	0.2
Benzotriazole	g	.03

Water total to 1 liter, pH 10.8±.1

The relative speed, gamma and fog for coating processed in this manner are given in Table E below.

Coating No. Test	Addenda (g./mol. AgX)	Relative Speed	Gamma	Fog
1(a)	none	100	1.21	.12
(b)	Product of Example 1 (.03)	120	1.27	.13
(c)	Product of Example 1 (0.3)	183	1.35	.39
2(d)	none	100	1.24	.16
(e)	Product of Example 4 (.03)	123	1.55	.18
3(f)	none	100	1.66	.18
(g)	Product of Example 10 (.03)	118	1.60	.15
(h)	Product of Example 10 (0.3)	203	1.49	.24
4(i)	none	100	----------	.17
(j)	Product of Example 16 (.15)	135	----------	.30
5(k)	none	100	1.27	.19
(l)	Product of Example 8 (3.0)	123	1.30	.16
6(m)	none	100	1.16	.30
(n)	Product of Example 18 (.3)	148	1.12	.30
7(o)	none	100	1.30	.21
(p)	Product of Example 20 (.3)	120	1.20	.30
8(q)	none	100	1.47	.18
(r)	Product of Example 20a (.3)	151	1.77	.27
9(s)	none	100	1.18	.20
(t)	Product of Example 21 (.3)	123	1.23	.22
10(u)	none	100	1.10	.17
(v)	Product of Example 22 (.3)	135	1.22	.26
11(w)	none	100	1.23	.13
(x)	Product of Example 23 (.15)	197	1.55	.28
12(y)	none	100	1.24	.16
(z)	Product of Example 24 (.3)	182	1.22	.34
13(a')	none	100	1.44	.20
(b')	Product of Example 25 (1.5)	132	2.08	.20
14(c')	none	100	1.30	.21
(d')	Product of Example 26 (3.0)	141	1.57	.24
15(e')	none	100	----------	.15
(f')	Product of Example 27 (3.0)	144	----------	.15
16(g')	none	100	----------	.15
(h')	Product of Example 28 (3.0)	132	----------	.17
17(i')	none	100	1.35	.20
(j')	Product of Example 32 (.3)	148	1.49	.23
18(k')	none	100	1.30	.26
(l')	Product of Example 33 (3.0)	158	2.08	.28
19(m')	none	100	1.30	.26
(n')	Product of Example 34 (3.0)	115	1.45	.16
20(o')	none	100	1.25	.14
(p')	Product of Example 35 (3.0)	117	1.59	.16
21(q')	none	100	1.25	.14
(r')	Product of Example 37 (3.0)	126	1.62	.17
22(s')	none	100	1.25	.26
(t')	Product of Example 41 (.3)	115	1.30	.24
23(u')	none	100	1.54	.20
(v')	Product of Example 42 (3.0)	186	2.14	.26
24(w')	none	100	1.35	.20
(x')	Product of Example 43 (3.0)	155	1.67	.28
25(y')	none	100	1.38	.16
(z')	Product of Example 44 (3.0)	170	1.68	.27
26(a'')	none	100	1.27	.19
(b'')	Product of Example 53 (3.0)	129	1.40	.26
27(c'')	none	100	1.18	.20
(d'')	Product of Example 51 (3.0)	132	1.06	.67
28(e'')	none	100	1.54	.20
(f'')	Product of Example 50 (.3)	144	1.80	.24
29(g'')	none	100	1.25	.14
(h'')	Product of Example 54 (3.0)	117	2.06	.16
30(i'')	none	100	.94	.13
(k'')	Product of Example 55 (.3)	107	.99	.12

As indicated above, the thiopolymer compounds of our invention can be used to increase further the sensitivity of photographic color emulsions which have already been sensitized to their optimum, or near-optimum, with known chemical sensitizers and spectral sensitizing compounds.

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 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 2,339,083, 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. 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); 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), etc.

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 2,904,854, 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-(methane-sulfonoxy)-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 Canadian Patent 588,451, issued December 8, 1959; 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 Know 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 disodium sulfosuccinamate as described in Knox and Stenberg U.S. patent application Serial No. 691,125, filed October 21, 1957.

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 thiopolymers of our invention 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 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 polyacrylamine 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 cyanoacetyl 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 examples will serve to illustrated the effect produced by the thiopolymer compounds of our invention in photographic silver halide emulsions which contain a coupler or a color-forming compound.

In Table F below, is shown the effect produced by the thiopolymer compound in an ordinary negative speed silver bromiodide emulsion which had been digested to optimum sensitivity with a mixture of a labile sulfur compound of the type shown in Sheppard U.S. Patent 1,623,499, mentioned above, and a gold compound of the type shown, for example, in U.S. Patent 2,399,083, mentioned above, and which had been red-sensitized (ca. 600–700 mμ) with a spectral sensitizing dye. The emulsions contained a thiopolymer compound in the amount indicated in the table, and also contained a coupler dispersion of one of the color-forming compounds for producing the cyan image upon color development, as identified further below. Two series of coatings were prepared for each of the emulsions, one for processing in the color negative process and another series for processing in a reversal color process. Each of the emulsions was coated on a transparent support, such as cellulose acetate film, dried, and then exposed in an Eastman Type Ib Sensitometer to daylight quality radiation for approximately 1/50 second. Samples of each were then processed through the color negative process or the reversal color process. A typical negative color process is described in detail by W. T. Hanson, Jr. and W. I. Kisner in an article in the "Journal of the Society of Motion Picture and Television Engineers," vol. 61 (1953), pages 667–701. The reversal color process was as follows:

The exposed film was developed in a developer having the following composition:

		G.
Sodium hexametaphosphate	g	2.0
N-methyl-p-aminophenol sulfate	g	6.0
Sodium sulfite, anhydrous	g	50.0
Hydroquinone	g	6.0
Sodium carbonate monohydrate	g	35.0
Potassium bromide	g	2.0
Sodium thiocyanate	g	1.5
0.5% solution of 6-nitrobenzimidazole nitrate	cc	12.0
0.1% solution of potassium iodide	cc	10.0

Water to make 1 liter.

The element was then thoroughly washed with water and treated in a hardening bath having the following composition:

	G.
Potassium chrome alum crystals	30.0

Water to make 1 liter.

The element was then thoroughly washed with water and treated for 30 seconds in a solution having the following composition:

	G.
Sodium borohydride	0.25
Sodium hydroxide	4.0

Water to make 1 liter.

The element was then treated in a color developer having the following composition:

Benzyl alcohol	cc	6.0
Sodium hexametaphosphate	g	2.0
Sodium sulfite, anhydrous	g	5.0
Trisodium phosphate	g	40.0
Potassium bromide	g	0.25
0.1% solution of potassium iodide	cc	10.0
Sodium hydroxide	g	6.5
Color developer [1]	g	11.33
Ethylenediamine sulfate	g	7.8
Citrazinic acid	g	1.5

Water to make 1 liter.

[1] 4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

The element was then thoroughly washed with water and treated in a clearing and fixing bath having the following composition:

	G.
Sodium thiosulfate	150.0
Sodium bisulfite	20.0

Water to make 1 liter.

The element was then treated in a bleach bath having the following composition:

	G.
Potassium dichromate	5.0
Potassium ferricyanide	70.0
Potassium bromide	20.0

Water to make 1 liter.

The element was again washed and treated once again with the clearing and fixing bath identified above. The element was again washed and treated in a stabilizing bath having the following composition:

Formaldehyde (37% by weight)	cc	7.0
Dispersing agent [1]	g	0.5

Water to make 1 liter.

[1] Such as Triton X–100, i.e., an alkylaryl polyether alcohol (octylphenoxy polyethoxy ethanol).

In color coatings Nos. 1–5, 7 and 9–17, the emulsions contained a dispersion of a phenol coupler, e.g., couplers Nos. 1 to 6 of Fierke et al. U.S. Patent 2,801,171 (column 2), in a suitable solvent, such as tri-o-cresylphosphate or dibutylphthalate. In the color coatings Nos. 6 and 8, the emulsions contained a dispersion of 48 grams of a hydroxynaphthamide coupler, e.g., couplers Nos. 1 to 10 of Weissberger et al. U.S. Patent 2,474,293, issued June 28, 1949 (columns 1 to 3), 32 grams of a hydroxyphenylazonaphthanilide coupler, e.g., couplers Nos. 1 to 12 of Glass et al. U.S. Patent 2,521,908, issued September 12, 1950 (columns 3 to 5) in a mixture of 40 ccs. of N-n-butylacetanilide, 240 ccs. of ethyl acetate and 544 ccs. of a 10% aqueous gelatin solution containing 120 ccs. of a 5% aqueous solution of Alkanol-B (alkylnaphthalene sodium sulfonate). In the following table, there is shown the speed increase produced by our thiopolymer compounds, as well as the change in D_{max} in the reversal color process and the change in D_{min} in the color negative process.

TABLE F.—SINGLE LAYER—COLOR PROCESSED TO CYAN IMAGE

Color Coating No.	Addenda (g./mol. AgX)	Rev. Process		C. Neg. Process	
		Speed	Δ $D_{max.}$	Speed	Δ $D_{min.}$
1(a)	none	100	0	100	0
(b)	Product of Example 1 (.3)	218	−.75	153	+.08
2(c)	Product of Example 4 (.3)	206	−1.24	125	+.14
3(d)	Product of Example 3 (.3)	160	−1.18	160	+.12
4(e)	Product of Example 9 (.3)	120	+.18	126	+.01
5(f)	Product of Example 10 (.3)	300	−.96	225	+.05
6(g)	Product of Example 23* (.03)	132	+.19	126	0
(h)	Product of Example 23* (.3)	502	−.10	138	+.08
7(i)	Product of Example 22 (.1)	174	+.02	102	0
(j)	Product of Example 22 (.3)	251	−.09	138	+.08
8(k)	Product of Example 23 (.03)	140	+.19	133	0
(l)	Product of Example 23 (.1)	200	0	114	+.02
(m)	Product of Example 23 (.3)	334	−.10	146	+.08
(n)	Product of Example 23 (1.0)	400	−.40	82	+.05
9(o)	Product of Example 24 (.3)	------	------	140	+.05
(p)	Product of Example 24 (.05)	133	−.16	------	------
(q)	Product of Example 24 (.3)	197	−.42	------	------
10(r)	Product of Example 25 (.1)	229	+.06	115	0
(s)	Product of Example 25 (.3)	316	−.24	132	------
11(t)	Product of Example 26 (.3)	282	−.62	229	+.14
(u)	Product of Example 26 (3.0)	347	−1.12	302	+.26
12(v)	Product of Example 27 (.3)	263	−.18	251	+.10
(w)	Product of Example 27 (3.0)	316	−.86	363	+.26
13(x)	Product of Example 28 (.3)	166	0	174	+.02
(y)	Product of Example 28 (3.0)	182	−.10	200	+.02
14(z)	Product of Example 29 (.3)	166	+.18	145	0
(a′)	Product of Example 29 (3.0)	182	+.08	174	0
15(b′)	Product of Example 41 (.1)	263	−.06	126	+.02
(c′)	Product of Example 41 (.3)	331	−.28	138	+.04
16(d′)	Product of Example 42 (.1)	263	−.16	159	+.02
(e′)	Product of Example 42 (.3)	331	−.20	126	+.08
17(f′)	Product of Example 43 (.3)	363	−1.42	159	+.12

(*) =prepared like polymer of Example 23, except monomer was heated at 150° C. in a vacuum until polymer formed.
Rev.=reversal color.
C. Neg.=color negative.

In Table G below, there is shown the effect produced in negative speed silver bromiodide emulsions which had been sensitized to the green region of the spectrum, i.e., about 500–600 mμ. The emulsions all contained a coupler for the magenta image and had been digested to optimum sensitivity with a labile sulfur compound and a gold compound of the type used in arriving at the data for the emulsions of Table F. In the series of coatings shown in Table G, the emulsions were double coated, one of the emulsions being finished to a higher speed than the other, the faster emulsion being coated over the slower emulsion. Both of the emulsions contained the same ingredients. The emulsions of color coatings Nos. 18 and 20 contained a dispersion in tri-o-cresylphosphate of a pyrazolone coupler, e.g., couplers Nos. 7, etc. of Fierke et al. U.S. Patent 2,801,171 (column 2) and a phenylazopyrazolone coupler, e.g., coupler No. 8 of U.S. Patent 2,801,171. In color coating No. 19, the faster and slower emulsions each contained only the pyrazolone coupler containing no phenylazo color grouping, i.e., only the first-mentioned coupler. The speed and density for each of the coatings is shown in the following table after the coatings were exposed in an Eastman Type Ib Sensitometer to daylight quality radiation and after processing in the color negative process or the reversal color process.

TABLE G.—SINGLE COLOR FILM—COLOR PROCESSED TO MAGENTA IMAGE

Color Coating No.	Addenda (g./mol. AgX)	Rev. Process		C. Neg. Process	
		Speed	$\Delta D_{max.}$	Speed	$\Delta D_{min.}$
18(g')	Control	100	0	100	0
(h')	Product of Example 1 (.9)	233	−.06	212	+.10
19(i')	Product of Example 10 (.3)	150	−1.28	140	+.43
20(j')	Product of Example 23 (.3)	------	--------	170	+.08

In Table H below, there is shown the effect of the thiopolymers of our invention in photographic silver halide emulsions which have been sensitized to their optimum with a labile sulfur compound and a gold compound as described in connection with color coatings Nos. 1–17. Each of the emulsions was a high speed silver bromiodide emulsion containing a yellow image-forming coupler, e.g., couplers Nos. I to V of McCrossen et al. U.S. application Serial No. 575,099, filed March 30, 1956, dispersed in dibutyl phthalate. Each of the coatings was then processed exactly as described above in either the color negative process or the reversal color process. The speed and density measurements for each of the exposed coatings is shown in the following table.

TABLE H.—SINGLE COLOR FILM—COLOR PROCESSED TO YELLOW IMAGE

Color Coating No.	Addenda (g./mol. AgX)	Rev. Process		C. Neg. Process	
		Speed	$\Delta D_{max.}$	Speed	$\Delta D_{min.}$
21(k')	Control	100	0	100	0
(l')	Product of Example 1 (3.0)	------	--------	160	+.08
22(m')	Product of Example 1 (1.0)	260	−.60	------	------
23(n')	Product of Example 10 (.3)	333	not available	206	+.08

In Table J below, there is illustrated the effect obtained using one of the thiopolymers of our invention in a photographic element containing a plurality of selectively sensitized photographic silver halide emulsion layers. The photographic element used comprised a transparent support having coated thereon a high-speed, red-sensitized negative silver bromiodide emulsion containing a mixture of couplers for the cyan image dispersed in a conventional coupler solvent, such as a tri-o-cresyl phosphate. The couplers for the cyan image were the same ones used in color coatings Nos. 6 and 8 above. Over the red-sensitive emulsion was coated a high-speed, green-sensitized negative silver bromiodide emulsion containing the mixture of couplers illustrated in color coating No. 20(j') of Table G above. These couplers were added in the form of a coupler dispersion in a suitable vehicle, such as tri-o-cresyl phosphate.

Over the green-sensitive layer was coated a conventional yellow filter layer, such as Carey-Lea, colloidal silver dispersed in gelatin. Over the yellow filter layer was coated an ordinary photographic silver bromiodide emulsion (blue-sensitive) containing a coupler dispersion of the type shown in color coatings Nos. 21–23 of Table H above.

Each of the differentially-sensitized layers, i.e., the red-, green- and blue-sensitive layers, contained approximately 1 gram per mole of silver halide of the thiopolymer of Example 23 above as a sensitizer. Prior to the addition of the thiopolymer, the emulsions were sensitized to their optimum, or near-optimum, in the manner described for emulsions of color coatings Nos. 1–17 above with a gold and labile sulfur compound. A second color element was prepared in exactly the same manner except that no thiopolymer was added. Each of the color elements was then processed through the color negative process or the reversal color process. The relative speed and density measurements (D_{min} for the color negative and D_{max} for the reversal color process) for each of the layers are shown in the following table.

TABLE J.—MULTI-LAYER—COLOR PROCESSED

Color Coating No.	Processing	Relative Speed			ΔD from Control		
		Red	Green	Blue	Red	Green	Blue
24(o')	Control (no thiopolymer).	100	100	100	0	0	0
(p')	Color negative.	183	233	147	+.01	+.08	+.03
(q')	Reversal color.	221	290	136	+.14	+.12	+.13

The above examples and coatings illustrate the photographic effect obtained with various classes of polymeric materials containing thioether sulfur atoms in a linear polymeric chain. While the invention has been illustrated with respect to particular groups of thiopolymers, it is to be understood that other polymeric materials belonging to the generic class embraced by Formula I above, can be employed in our invention. Among other thiopolymeric materials which can be employed in our invention, which are embraced by Formula I above, are the linear polyamides illustrated in Beavers U.S. application Serial No. 779,875, filed on even date herewith.

It has also been found that the linear thiopolymers of our invention can be added to photographic developers, which may or may not contain color-forming compounds or coupler, in order to increase the effective speed of photographic silver halide emulsions which have not been previously sensitized by incorporation of the thiopolymers of our invention in the emulsions themselves. This discovery has been found to apply to a number of photographic silver halide emulsions, including emulsions containing color-forming compounds or couplers, as well as photographic silver halide emulsions containing no such color-forming compounds. The latter emulsions can be used in black-and-white photography, or alternatively, they can be used in a photographic color process wherein the color-forming components are incorporated in the color developers.

Of course, in the event that the thiopolymers of our invention are incorporated in photographic developers in lieu of incorporation in the emulsions as hereinbefore described, it is apparent that a speed increase can be obtained even in cases wherein the emulsions contain some thiopolymer, provided that sufficient thiopolymer has not been incorporated in the emulsion in order to produce optimum sensitivity. In order to incorporate the thio-

polymers of our invention in photographic developers, it is convenient to dissolve the thiopolymers in organic solvents, such as acetone, methylethyl ketone, etc., and add the desired amount of these solutions to the photographic developers. While some precipitation of the thiopolymer occurs in the developing solution, it has been found that such precipitation has no apparent harmful effect upon the sensitizing action, provided that the developer is agitated sufficiently during use to prevent sedimentation of the thiopolymer.

The following two examples will serve to illustrate the effect of our thiopolymers in photographic developers, both in emulsions intended for color photography, as well as emulsions intended for conventional black-and-white negative processes. The thiopolymers of our invention can be used in conjunction with conventional photographic developers, including polyhydroxybenzenes (e.g., hydroquinone, etc.), aminophenols (e.g., N-methyl-p-aminophenol, etc.), phenylenediamines (e.g., N,N-diethyl-p-phenylenediamine, etc.), Phenidone developers, etc. The effect of our thiopolymers has been found to be particularly outstanding in MQ developers, i.e., developers containing both hydroquinone and N-methyl-p-aminophenol sulfate.

EXAMPLE (*a*)

A three-colored silver bromiodide film containing cyan, magenta and yellow color formers in separate layers as described above for the coatings of Table J (but containing no thiopolymer) was exposed for 1/50 second to a 500-watt tungsten lamp, adjusted to a color temperature of 6100° K., in an intensity scale sensitometer. The control strip described below was processed to a color positive in the reversal color process, described below, at a temperature of 75° F. The experimental strips were processed in a similar process differing only in that the black-and-white developer (MQ) contained varying amounts of the polymer of Example 26.

COLOR PROCESS

	Min.
(1) Negative development	7–10
(2) Reversal flash exposure.	
(3) Color development	7
(4) Clearing	5
(5) Silver bleaching	8
(6) Fixing	3
Wash and dry.	

The negative developer (MQ) had the following composition:

Water, 90° F. (32° C.)	liters	1.0
Sodium hexametaphosphate	gm	2.0
N-methyl-p-aminophenol sulfate	gm	6.0
Sodium sulfite, desiccated	gm	50.0
Hydroquinone	gm	6.0
Sodium carbonate, monohydrate	gm	35.0
Potassium bromide	gm	2.0
Sodium thiocyanate	gm	1.5
6.5% solution of 6-nitrobenzimidazole nitrate	cc	12.0
0.1% solution of potassium iodide	cc	10.0

The color developer had the following composition:

Water, 70° to 80° F. (21° to 27° C.)	liters	1.0
Benzyl alcohol	cc	6.0
Sodium hexametaphosphate	gm	2.0
Sodium sulfite, desiccated	gm	5.0
Trisodium phosphate	gm	40.0
Potassium bromide	gm	0.25
0.1% solution of potassium iodide	cc	10.0
Sodium hydroxide	gm	6.5
4-amino-N-(β-methanesulfonamidoethyl)-m-toluidinesesquisulfate monohydrate	gm	11.33
Ethylenediamine sulfate	gm	7.8
Citrazinic acid (2,6-dihydroxyisonicotinic acid)	gm	1.5

The clearing bath had the following composition:

Water	liters	1.0
Sodium bisulfite	gm	10.0
Hydroquinone	gm	.5

The silver bleaching solution had the following composition:

	Gm.
Sodium ferricyanide	60.0
Sodium hypophosphate·H_2O	17.6
Sodium bromide	15.0
Sodium hydroxide	3.5
Sodium thiocyanate	5.0

Water to 1 liter.

The fixing bath had the following composition:

Water 80° F. (27° C.)	liters	1.0
Sodium thiosulfate	gm	95.6
Sodium bisulfite	gm	20.0

	Red		Green		Blue	
	D_{max}	Relative Speed	D_{min}	Relative Speed	D_{max}	Relative Speed
Film processed in normal color process	2.90	100	3.00	100	3.70	100
Film processed in modified process (MQ developer contained .25 gm. polymer/liter	2.85	151	3.80	151	3.06	263
Film processed in modified process (MQ developer contained 1.0 gm. polymer/liter	2.69	209	2.63	200	2.93	316

EXAMPLE (*b*)

A single layer film was made by coating a red-sensitized, coarse-grained silver bromiodide emulsion onto conventional cellulose acetate film. The emulsion contained no color-forming component. A sample of this coating was exposed to a light source similar to the one described in Example (*a*), but exposure being made through a Wratten No. 15 Filter (a filter transmitting only light having a wavelength greater than 510 mμ). The strips of film were then put through either the modified or unmodified black-and-white developer (MQ) having the composition described in Example (*a*) above. The strips were then fixed and washed in the conventional manner.

	D_{min}	Relative Speed
Unmodified—control developed 5 minutes in MQ developer	.25	100
Modified—experiment developed 5 minutes in MQ developer containing .25 gm. polymer/liter	.32	138

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 wherein the vehicle for the silver halide is a water-permeable, hydrophilic colloid and wherein said emulsion contains (1) a color-forming compound capable of coupling with the oxidation products of a color developer containing a color developing agent containing at least one primary aminoaryl group to produce a colored compound and (2) a sensitizing amount of a linear polymer consisting essentially of polymer units represented by the following general formula:

$$\text{—(R—S)}_x\text{—}$$

wherein R represents an aliphatic radical and x represents a positive integer of at least 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.

2. A photographic silver halide emulsion wherein the vehicle for the silver halide consists of gelatin and wherein said emulsion contains (1) a color-forming compound capable of coupling with the oxidation products of a color developer containing a color developing agent containing at least one primary aminoaryl group to produce a colored compound and (2) a sensitizing amount of a linear polymer consisting essentially of polymer units represented by the following general formula:

$$\text{-}(R\text{—}S)_x\text{-}$$

wherein R represents an aliphatic radical and x represents a positive integer of at least 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 wherein the vehicle for the silver halide consists of a water-permeable, hydrophilic colloid and wherein said emulsion contains a color-forming compound capable of coupling with the oxidation products of a color developer containing a p-phenylenediamine color developing agent to produce a colored compound, said emulsion being sensitized with (1) a labile sulfur compound, (2) a gold salt and (3) a sensitizing amount of a linear polymer consisting essentially of polymer units represented by the following general formula:

$$\text{-}(R\text{—}S)_x\text{-}$$

wherein R represents an aliphatic radical and x represents a positive integer of at least 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.

4. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of a linear polymer consisting essentially of groups represented by the following general formula:

$$\text{-}R_1\text{—}(X\text{—}R_2)_{p-1}\text{—}S\text{—}R_3\text{—}(X_1\text{—}R_4)_{m-1}\text{—}S\text{-}_n$$

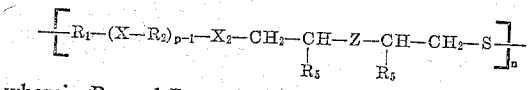
wherein R_1, R_2, R_3 and R_4 each represents alkylene containing from about 2 to 20 carbon atoms, X and X_1 each represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, carbonylamido, carbonyl, oxycarbonyloxy, oxycarbonyl and carbonyloxy, p and m each represents a positive integer of from 1 to 5 and n represents a positive integer of at least 2.

5. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of (1) a labile sulfur compound, (2) a sensitizing gold compound and (3) a linear polymer consisting essentially of groups represented by the following general formula:

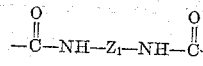
$$\text{-}R_1\text{—}(X\text{—}R_2)_{p-1}\text{—}S\text{—}R_3\text{—}(X_1\text{—}R_4)_{m-1}\text{—}S\text{-}_n$$

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, carbonylamido, carbonyl, oxycarbonyloxy, oxycarbonyl and carbonyloxy, p and m each represents a positive integer of from 1 to 5 and n represents a positive integer of at least 2.

6. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of a linear polymer consisting essentially of groups represented by the following general formula:



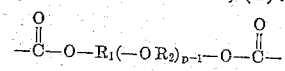
wherein R_1 and R_2 each represents a hydrocarbon alkylene group containing from 2 to 20 carbon atoms, R_5 represents a member selected from the class consisting of hydrogen and low alkyl, X represents a member selected from the class consisting of oxygen, sulfur, amino, carbamyl, carbonylamido, carbonyl, oxycarbonyloxy, oxycarbonyl and carbonyloxy, a carbonyl group, an oxycarbonyloxy group, an oxycarbonyl group and a carbonyloxy group, X_2 represents a member selected from the class consisting of oxygen and sulfur, n represents a positive integer of at least 2 and p represents a positive integer of from 1 to 5, and Z represents a member selected from the class consisting of (1):



wherein Z_1 represents alkylene containing from 2 to 20 carbon atoms or



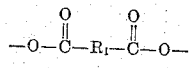
wherein R_7 and R_8 each represents a member selected from the class consisting of hydrogen, lower alkyl and monocyclic aryl of the benzene series, (2):



wherein R_1 and R_2 each represents alkylene containing from about 2 to 20 carbon atoms and p represents a positive integer of from 1 to 5, (3):

$$\text{—}R_6\text{—}$$

wherein R_6 represents alkylene containing from about 1 to 6 carbon atoms, and (4):



wherein R_1 represents a hydrocarbon alkylene group containing from about 2 to 20 carbon atoms.

7. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of a linear polymer consisting essentially of groups represented by the following general formula:

$$\text{-}R_1\text{—}COO\text{—}R_2\text{—}S\text{-}_n$$

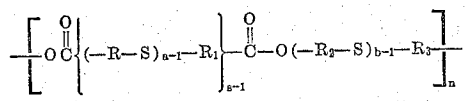
wherein R_1 and R_2 each represents alkylene containing from 2 to 20 carbon atoms and n represents a positive integer of at least 2.

8. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of (1) a labile sulfur compound, (2) a sensitizing gold compound and (3) a linear polymer consisting essentially of groups represented by the following general formula:

$$\text{-}R_1\text{—}COO\text{—}R_2\text{—}S\text{-}_n$$

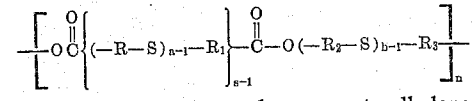
wherein R_1 and R_2 each represents alkylene containing from 2 to 20 carbon atoms and n represents a positive integer of at least 2.

9. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of a linear polymer consisting essentially of groups represented by the following general formula:



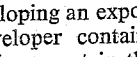
wherein R, R_1, R_2 and R_3 each represents alkylene containing from about 1 to 10 carbon atoms, a and b each represents a positive integer of from 1 to 4, provided that a and b do not simultaneously represent 1, n represents a positive integer of at least 2, and s represents a positive integer of from 1 to 2.

10. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of (1) a labile sulfur compound, (2) a sensitizing gold compound and (3) a linear polymer consisting essentially of groups represented by the following general formula:



wherein R, R_1, R_2 and R_3 each represents alkylene containing from about 1 to 10 carbon atoms, s represents a positive integer of from 1 to 2, and a and b each represents a positive integer of from 1 to 4, provided that a and b do not simultaneously represent 1, and n represents a positive integer of at least 2.

11. A process for increasing the speed of a photographic silver halide emulsion wherein the vehicle for the silver halide consisting of a water-permeable, hydrophilic colloid, comprising developing an exposed silver halide emulsion in a color developer containing a p-phenylenediamine color developing agent in the presence of a color coupler capable of coupling with the oxidation products of said p-phenylenediamine color developing agent, and a linear polymer consisting essentially of polymer units represented by the following general formula:



wherein R represents an aliphatic radical and x represents a positive integer of at least 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.

12. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of poly(β-hydroxyethylmercaptoacetic acid), said polymer being a linear condensate and having a molecular weight of at least about 250.

13. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of poly(3-thiapentylene glutarate), said polymer having a molecular weight of at least about 500.

14. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer, said photographic emulsion containing a sensitizing amount of a polymer obtained by the condensation of 1,2-bis(2-chloroethoxy)ethane and sodium sulfide, said polymer having a molecular weight of at least about 500.

15. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of poly(3-thiapentyleneadipate), said polymer having a molecular weight of at least about 500.

16. A photographic silver halide emulsion containing a color-forming compound capable of coupling with the oxidation products of a phenylenediamine color developer to produce a colored compound, said emulsion containing a sensitizing amount of poly(3-thiapentylenesuccinate), said polymer having a molecular weight of at least about 500.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,046,129 July 24, 1962

James L. Graham 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 4, line 50, formula (IIb) should appear as shown below instead of as in the patent:

$$HS-R_3-(X_1-R_4)_{m-1}-SH$$

column 6, line 15, formula (XI) should appear as shown below instead of as in the patent:

$$CH_2=CH(-CH_2)_{q-1}-Z(-CH_2)_{q-1}-CH=CH_2$$

column 12, TABLE B, Example 44, second column, for "ethanol-1,2-diol (1.50)" read -- ethane-1,2-diol (1.50) --; column 20, lines 18 and 19, for "2,339,083" read -- 2,399,083 --; column 21, line 23, for "2,904,854" read -- 2,940,854 --; column 28, first table, under the heading "Green" for "D_{min}" read -- D_{max} --; column 30, lines 15 and 16, for "a hydrocarbon alkylene group" read -- alkylene --; lines 21 to 23, strike out "a carbonyl group, and oxycarbonyloxy group, an oxycarbonyl group and a carbonyloxy group,"; line 53, for "a hydrocarbon alkylene group" read -- alkylene --.

Signed and sealed this 27th day of November 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
~~ERNEST W. SWIDER~~
Attesting Officer

DAVID L. LADD
Commissioner of Patents