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

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

A number of methods have been previously described for increasing the sensitivity of photographic silver halide emulsions, other than methods of optical or spectral sensitization which involve the incorporation of certain colored compounds or dyes in the emulsions. The incorporation of such dyes in the emulsions increases the optical range of sensitivity, and for this reason such dyes are commonly referred to as optical or spectral sensitizing dyes.

It is also well known to increase the sensitivity of photographic emulsions by addition of sulfur compounds capable of reacting with silver salts to form silver sulfide, or with reducing agents (compounds of these types are also naturally present in gelatin), or with salts of gold or other noble metals, or with combinations of two or more of the aforementioned compounds generally known as chemical sensitizers. Such chemical sensitizers are believed to react with the silver halide to form, on the surface of the siver 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.

I 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. My 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. My 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 my 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 my 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 my invention, however, can be used to sensitize photographic silver halide emulsions containing no other sensitizers, if desired. The novel sensitizers of my invention are not strictly chemical sensitizers, since chemical sensitizers do not generally provide the additive effects of the type mentioned.

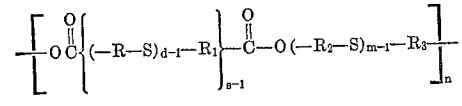
It is, therefore, an object of my invention to provide photographic silver halide emulsions which have been sensitized with various polymeric compounds containing a plurality of sulfur atoms. Another object of my invention is to provide photographic silver halide emulsions which have increased sensitivity without concomitant increases in fog or poor keeping qualities to a degree which might seriously affect the usefulness of the emulsions. Another object is to provide a new class of photographic sensitizers which can provide additional sensitivity to photographic silver emulsions already sensitized with certain chemical sensitizers, such as sulfur sensitizers. Other objects of my invention will become apparent from a consideration of the following description and examples.

According to my invention, I have found that the sensitivity of ordinary photographic silver halide emulsions can be materially increased by incorporating therein linear polyesters containing a plurality of sulfur atoms. The polyester compounds useful in practicing my invention contain their sulfur atoms in the form of thioether linkages. By thioether linkages, I mean a linkage wherein the sulfur atom is a divalent atom which is joined to two non-carbonylic carbon atoms. My invention does not contemplate polyester compounds contaning disulfide linkages, such as linkages of the type commonly found in vulcanizable, rubbery materials. Moreover, the polyester compounds of my invention are linear polymeric materials wherein the ether-sulfur atoms are present in the linear polymeric chain, as contrasted with polymeric materials containing their sulfur atoms as substituents on the chain or as part of a cross-linked arrangement. The linear polyester compounds of my invention should have sufficient dispersibility in water (or a dilute alkaline solution), or an organic solvent, such as acetone, the lower alcohols, 1,4-dioxane, ethyl acetate, etc., (directly, or in a colloid mill, or by other means, such as by a dispersing agent, e.g., sodium laurylsulfate, etc.), so that a sensitizing amount of the linear polyester can be adsorbed by or associated with the silver halide grains. Frequently, when a small amount of a solution of my thioethers in an organic solvent such as acetone, is added to water, a colloidal "solution" results.

The linear polyester compounds of my invention can be regarded as condensation polymers obtained from a dicarboxylic acid and a glycol, at least one of these reactants containing a thioether linkage of the type defined above. It is to be understood, of course, that my invention is not limited in its application only to polyesters obtained from dicarboxylic acids and glycols, but that functional equivalents of either of these reactants can be employed to advantage. For instance, instead of employing the free acid in the condensations, acid anhydrides can be employed where they are available. (Of course, certain dicarboxylic acids do not form monomeric

carboxylic anhydrides with ease.) Other functional derivatives, such as lower monohydric alcohol or phenyl esters of dicarboxylic acids or carboxylic acid halides (e.g., chloride, etc.), can be employed to advantage. The obvious methods for preparing these linear polyesters of my invention are described in detail below.

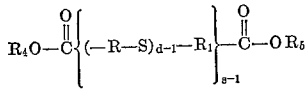
The linear polyesters of my invention include those represented by the following general formula:

(I) 

wherein R, R_1, R_2 and R_3 each represents a hydrocarbon alkylene group containing from about 1 to about 10 carbon atoms (e.g., methylene, ethylene, 1,2-propylene, trimethylene, tetramethylene, pentamethylene, octamethylene, decamethylene, etc.), *d* and *m* each represents a positive integer of from about 1 to 4 (provided that *d* and *m* do not simultaneously represent 1), *n* represents a positive integer, such as a positive integer of at least about 2, and *s* represents a positive integer of from 1 to 2. The molecular weight of the polyesters represented by Formula I above can vary over rather wide ranges, although I have found that polymeric materials having a molecular weight of about 350 to 10,000 are particularly useful, while polyester compounds having a molecular weight of from about 500 to 3,500 have been found to be outstanding.

The terminal groups of the polymers of my invention, such as those represented by Formula I above, are generally hydrogen atoms, hydroxyl groups, thiol groups, carboxylic groups (including carboxylic acid, carboxylic ester, and carboxylic halide groups), vinyl groups, etc., or combinations of these groups. It is quite apparent that the nature of the terminal groups will depend upon what reactants are employed in the preparation of the linear polyesters of my invention.

The linear polyesters of my invention can be prepared according to methods which have been previously 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:

(II) 

wherein R, R_1, *d* and *s* each have the values given above, and R_4 and R_5 each represents a hydrogen atom, a lower alkyl group (e.g., methyl, ethyl, propyl, butyl, etc.) or a phenyl group, with a glycol compound, such as those represented by the following general formula:

(III) $HO(—R_2—S)_{m-1}—R_3—OH$

wherein R_2, R_3 and *m* each have the values given above. As indicated above, at least one of the reactants, II and/or III, should contain thioether linkages. While the carboxylic component represented by Formula II above has been depicted as either an acid or an ester of a low-boiling alcohol or a phenol, 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 II, 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, my invention comprises mixed polyester compounds.

It has also been found that linear polyesters of the type useful in practicing my invention (the term polyester as used herein has the conventiontal definition, such as given in "The Condensed Chemical Dictionary" by A. and E. Rose, Reinhold, 1956), can be prepared by interacting a dithiol, such as one embraced by the following general formula:

(III*a*) $HS(—R_2—S)_{m-1}—R_3—SH$

wherein R_2, R_3 and *m* each have the values given above, together with a compound selected from those represented by the following general formula:

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

wherein Z represents an acyloxy group of an aliphatic dicarboxylic acid, such as oxalic, malonic, succinic, glutaric, adipic, pimelic, sebacic, and the corresponding thia analogues thereof, and *q* represents a positive integer of from 1 to 2. Typical esters embraced by Formula IV above include divinyl succinate, diallyl succinate, diallyl sebacate, etc.

Condensations of the type involving the reactants of Formula IV have previously been described in the prior art, such as Coffman U.S. Patent 2,347,182, issued April 26, 1944.

In Examples 1 to 16 of Table I 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 1 to 16, 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-dispersing it in a suitable organic solvent or water. 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 1 which follows.

EXAMPLE 1

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 temperautre 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[1] 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 Buchner 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.

[1] It has been found beneficial to give the solution a treatment with decolorizing carbon before filtering.

The polyesters of Examples 2 to 16 were obtained in exactly the manner described in Example 1 above, and the results obtained, together with those of Example 1, are summarized in Table I.

otherwise indicated, boiling with decolorizing carbon (Norite), filtered, and used. The solids content of the solution was calculated from weight of polymer and weight of solution.

Table I

Example	Dialcohol (g.)	Dibasic Acid Anhydride (g.) or Acid *	Yield (g.)	m.p., ° C.	Analysis		
					C	H	S
1	3-thiapentane-1,5-diol (18.33)	succinic (14.85)	24.7	55–6	47.3	6.2	15.5
2	3-thiapentane-1,5-diol (6.1)	glutaric (5.6)	9.0		49.2	6.3	14.7
3	3-thiapentane-1,5-diol (6.11)	adipic * (7.13)		59–60	57.4	6.9	13.6
4	do	azelaic * (9.32)		54–5	57.2	8.05	10.7
5	do	sebacic * (10.0)		73–5	57.7	8.3	9.7
6	3-thiapentane-1,5-diol (12.2)	pimelic * (15.86)	11.5	46–8	53.4	7.3	12.3
7	3-thiapentane-1,5-diol (6.11)	suberic * (8.6)	8.0	62–4	55.1	7.5	12.4
8	3,6-dithiaoctane-1,8-diol (9.1)	succinic (4.9)	6.5	72			24.2
9	4,10-dithiatridecane-1,13-diol (3.78)	succinic (1.49)	(left in acetone)				
10	4,15-dithiaoctadecane-1,18-diol (3.22)	succinic (1.00)	3.4		57.0	8.4	15.6
11	7,13-dithianonadecane-1,19-diol (6.72)	succinic (2.00)	5.6	40.5–41.5	60.1	9.1	15.3
12	7,18-dithiatetracosane-1,24-diol (6.09)	succinic (1.50)	6.4	54–5	63.1	9.5	13.1
13	4,8-dithiaundecane-2,10-diol (6.72)	succinic (6.72)	(left in acetone)	The following polymers were left in solution			
14	3-thiahexane-1,6-diol (6.8)	succinic (4.95)	A				
15	4-thiaheptane-1,7-diol (7.5)	do	B				
16	3-thianonane-1,9-diol (8.91)	do	C				
17	ethane-1,2-diol (5.0)	4-thiapimelic* (7.5)	(left in acetone)				
18	do	3,6-dithiasuberic* (10.5)	do				
19	do	3,7-dithiaazelaic* (11.2)	do				
20	ethane-1,2-diol (1.50)	3,8-dithiasebacic* (4.76)	do				
21	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 17 to 21 of Table I 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 17 to 21, and this method can be illustrated by the following example.

EXAMPLE 18

[Summarized in Table I 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 17, 19, 20 and 21, 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 were continued. The melt was cooled, dissolved in a solvent, acetone unless

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
17	2	1½	[1] 3	4½	48	16.7
19	17½	¾	13		62.7	12.7
20	17⅛	⅛	2⅛	5⅛	13	[2] 13.8
21	17¼	¼	2⅓	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 my 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 22

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-thiapentane-1,5-diol 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 22 above, and the physical data for certain of the polyesters thus obtained are given in the following table.

Table II

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

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

EXAMPLE 26

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 product was 2.6 g., M.P. 66–67.5° C.

In exactly the manner illustrated in Example 26 above, other polyesters were obtained and the data for such preparations are given in the following table.

Table III

Example	Dithiol (g.)	Ester (g.)	Yield (g.)
26	ethane-1,2-dithiol(1.88)	divinyl succinate(3.50)	2.6
27	ethane-1,2-dithiol(5.64)	diallyl adipate(13.44)	5.0
28	ethane-1,2-dithiol(2.82)	diallyl sebacate(8.46)	4.5
29	do	diallyl succinate(6.0)	3.4

Other linear polyesters can be obtained according to the above-described methods and these polymers used to effectively sensitize photographic silver halide emulsions. For instance, methylene bis-mercaptoacetic acid can be condensed with ethylene glycol to provide a linear polyester having useful sensitizing properties. In like manner, a useful thiopolymer has been prepared by condensing 2,2-dimethylglutaric acid with 3-thiapentane-1,5-diol to provide a linear polyester having useful sensitizing properties.

The linear polyesters of my invention can also be treated with various organic sulfonic acid esters, such as methyl sulfate, ethyl sulfate, methyl benzenesulfonate, methyl-p-toluenesulfonate, etc., to provide ternarized sulfonium polyesters having improved solubility in water or various water-miscible solvents. In general, it is sufficient to merely heat the polyester together with the organic sulfonic acid ester to the fusion point to obtain the desired sulfonium compounds. The quantity of organic sulfonic acid ester can be varied, although it is generally preferred to use a sufficient quantity to provide for salt formation of from about 10 to substantially 100 percent of the linear thioether atoms. This method of treatment of linear thiopolymers is described in the copending application of J. R. Dann and J. J. Chechak, Serial No. 779,874, filed on even date herewith.

The dibasic acids (or their anhydrides, where available), and glycols useful in practicing my invention have been previously described in the prior art, and their methods of preparation are well known. The preparation of dibasic acids and glycols containing a thioether atom can generally be effected using the well-known Williamson synthesis. This synthesis involves the reaction of an aliphatic halogen compound with another aliphatic compound containing at least one mercapto group. The reaction is generally effected in alkaline medium so that the alkali metal salt of the mercapto compound is formed, this latter compound then reacting with the halogenated compound. See, for example, "Chemical Abstracts," vol. 33, page 5825, and vol. 34, pages 2683 and 2791, for the preparation of typical dibasic acids. See "Chemical Abstracts," vol. 16, page 409 and page 1559, and vol. 38, page 954, for the preparation of typical glycols. It is immediately apparent that other glycols and acids can be prepared in similar manner.

Flory U.S. application, Serial No. 738,221, published March 24, 1953, describes certain linear polyesters containing thioether atoms which are useful in practicing my invention.

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

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

The particular quantity of polyester used in a given emulsion can vary, depending upon the effects desired, degree of ripening, silver content of the emulsion, etc. The amount used is also dependent upon the particular stage at which the sensitizer is added during the preparation of the emulsion. I have found that generally from about 50 mg. to about 3 g. of polyester per mole of silver halide are quite adequate to accomplish the desired sensitization.

The linear thiopolymers of my invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the thiopolymers can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. As indi-

cated 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 alone is a dispersing medium for a few of the polyesters of my invention. In other cases, the polyester 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 polyesters can be prepared in finely-divided form by dispersion in water alone, or in the presence of a suitable dispersing agent and added to the emulsion in this form. It is quite apparent that the polyesters of my invention should have sufficient water-dispersibility so that they can be adsorbed to the grains of the silver halide present in the emulsion in sufficient amount to sensitize the emulsion. It is apparent that the optimum amount for each of the polyesters will vary somewhat from emulsion to emulsion and from polyester to polyester. The optimum amount for any given polyester can be determined for any particular emulsion by running a series of tests in which the quantity of polyester 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 polyester in that particular emulsion. Such matters are well understood by those skilled in the art.

The emulsions of my invention 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, and Sheppard et al. 1,623,499, issued April 5, 1927, and Sheppard and Brigham U.S. Patent 2,410,689, issued November 5, 1946.

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

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

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene 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 as indicated above, 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 2,444,508, 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, 1949; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patent 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956; and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene-bis-benzothiazolium perchlorate); and the zinc and cadmium salts of Jones U.S. patent application Serial No. 493,047, filed March 8, 1955 (now U.S. Patent 2,839,405, issued June 17, 1958).

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956 (now U.S. Patent, 2,960,404, issued November 5, 1960); an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. application Serial No. 662,564, filed May 31, 1957 (now U.S. Patent 2,904,434, issued September 15, 1959); bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956 (now U.S. Patent 2,940,854, issued June 14, 1960), or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. patent application Serial No. 311,319, filed September 24, 1952 (now U.S. Patent 2,852,386, issued September 16, 1958). The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion 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-(methanesulfonoxy)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness U.S. patent application Serial No. 556,031, filed December 29, 1955 (now abandoned); a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. patent application Serial No. 599,891, filed July 25, 1956 (now U.S. Patent 2,950,197, issued August 23, 1960); or 2,3-dihydroxy dioxane as described in Jeffreys U.S. patent application Serial No. 624,968, filed November 29, 1956 (now U.S. Patent 2,870,013, issued January 20, 1959).

The emulsions may contain a coating aid such as saponin; a lauryl or oleoyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent No. 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. patent application Serial No. 485,812, filed February 2, 1955 (now U.S. Patent 2,843,487, issued July 15, 1958); a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Sternberg U.S. patent application Serial No. 691,125, filed October 21, 1957.

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 aceate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 or an imidized polyacrylamide of like acrylimide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. application Serial No. 527,872 of Illingsworth, Dann and Gates, filed August 11, 1954 (now U.S. Patent 2,852,382, issued September 16, 1958).

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

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

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

The following examples will serve to illustrate more fully the manner of sensitizing photographic silver halide emulsions according to my invention.

An ordinary photographic silver bromiodide emulsion containing a sensitizing dye, a sulfur sensitizer of the type mentioned in Sheppard U.S. Patent 1,623,499, mentioned above, and gold sensitized in the manner indicated in U.S. Patent 2,399,083, mentioned above, was divided into several portions. Linear polyester compounds of the type obtained in the above examples were then added in solutions in an organic solvent, such as acetone or N,N-dimethylformamide, in the amounts indicated in the table. The various portions of emulsions were then coated on a transparent support, such as cellulose acetate and dried. The dried coatings were exposed for about 1/25 sec. to daylight quality radiation in an Eastman type Ib sensitometer. The exposed coatings were then developed for

about 5 minutes in a photographic developer having the following composition:

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

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

Table IV

Coating No.	Polymer of Example (g./mol. AgX)	Relative Speed	Gamma	Fog
1(a)	none (control)	100	1.42	.13
(b)	1 (1.5)	186	1.24	.20
2(c)	none	100	1.17	.14
(d)	2 (3.0)	214	1.00	.21
3(e)	none	100		.11
(f)	3 (3.0)	204		.15
4(g)	none	100		.11
(h)	4 (3.0)	123		.11
5(i)	none	100	1.26	.13
(j)	8 (0.3)	115	1.14	.20
6(k)	none	100	1.43	.12
(l)	9 (3.0)	138	1.22	.31
7(m)	none	100	1.43	.12
(n)	10 (3.0)	138	1.41	.13
8(o)	none	100	1.33	.11
(p)	11 (3.0)	144	1.17	.12
9(q)	none	100	1.33	.11
(r)	12 (3.0)	115	1.20	.19
10(s)	none	100	1.33	.11
(t)	13 (3.0)	135	1.02	.15
11(u)	none	100	1.30	.12
(v)	17 (0.6)	141	1.41	.14
12(w)	none	100	1.34	.12
(x)	18 (3.0)	159	1.16	.23
13(y)	none	100	1.26	.13
(z)	19 (3.0)	155	.97	.24
14(a')	none	100	1.18	.13
(b')	20 (3.0)	195	1.05	.19
15(c')	none	100	1.40	.13
(d')	29 (3.0)	123	1.24	.20
16(e')	none	100	1.14	.14
(f')	27 (3.0)	148	.89	.21
17(g')	none	100	1.14	.14
(h')	28 (.03)	132	1.35	.15
18(i')	none	100	1.32	.12
(j')	26 (0.3)	148	1.94	.18

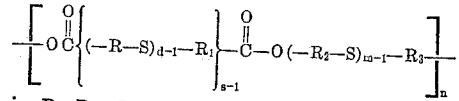
The effect of my new polyesters has been illustrated above with particular reference to ordinary photographic silver-bromiodide emulsions, although it is to be understood that other silver halide emulsions can be employed to like advantage. The polyesters of my invention can be used in emulsions which are acidic in character or in emulsions which are alkaline. Of course, when adding polyesters to such emulsions, it is generally desirable to adjust the pH of the sensitizing solution so that it will not seriously alter the pH of the emulsion to be treated. It is apparent that certain of the polyesters may be present in salt form when present in acidic (e.g., where polyester contains amino groups) or alkaline (e.g., where polyester contains free acid groups) emulsions, and it is to be understood that my invention contemplates these polyesters either in their salt or non-salt forms.

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 I claim as my invention and desire secured by Letters Patent of the United States is:

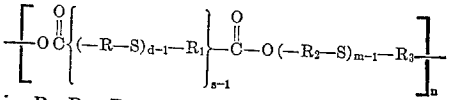
1. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of a dicarboxylic acid, said linear polyester containing intralinear thioether atoms and where the ester linkages are within the linear polymer chain, said linear polyester having a molecular weight of at least 350.

2. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester, the polymeric chain of which consists essentially of groups represented by the following general formula:



wherein R, R_1, R_2 and R_3 each represents an alkylene group containing from about 1 to 10 carbon atoms, *d* and *m* each represents a positive integer of from about 1 to 4, provided that *d* and *m* do not simultaneously represent 1, *n* represents a positive integer of at least about 2, and *s* represents a positive integer of from 1 to 2, provided *s* and *m* do not simultaneously represent 1, said linear polyester having a molecular weight of at least about 350.

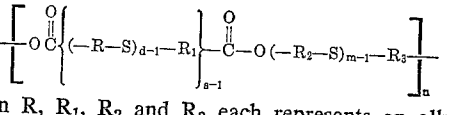
3. A photographic gelatino-silver-bromiodide emulsion containing a sensitizing amount of a linear polyester, the polymeric chain of which consists essentially of groups represented by the following general formula:



wherein R, R_1, R_2 and R_3 each represents an alkylene group containing from about 1 to 10 carbon atoms, *d* and *m* each represents a positive integer of from about 1 to 4, provided that *d* and *m* do not simultaneously represent 1, *n* represents a positive integer of at least about 2, and *s* represents a positive integer of from 1 to 2 provided *s* and *m* do not simultaneously represent 1, said linear polyester having a molecular weight of at least about 350.

4. A photographic silver halide emulsion sensitized with (1) a gold compound and (2) a compound containing a labile sulfur atom and containing a sensitizing amount of (3) a linear polyester containing intralinear thioether atoms and where the ester linkages are within the linear polymer chain, said linear polymer having a molecular weight of at least 350.

5. A photographic silver halide emulsion sensitized with (1) a gold compound and (2) a compound containing a labile sulfur atom and containing a sensitizing amount of (3) a linear polyester, the polymeric chain of which consists essentially of groups represented by the following general formula:



wherein R, R_1, R_2 and R_3 each represents an alkylene group containing from about 1 to 10 carbon atoms, *d* and *m* each represents a positive integer of from about 1 to 4, provided that *d* and *m* do not simultaneously represent 1, *n* represents a positive integer of at least about 2, and *s* represents a positive integer of from 1 to 2 provided *s* and *m* do not simultaneously represent 1, said linear polyester having a molecular weight of at least about 350.

6. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of 3-thiapentane-1,5-diol and succinic acid, said linear polyester having a molecular weight of at least 350.

7. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of 3-thiapentane-1,5-diol and glutaric acid, said linear polyester having a molecular weight of at least 350.

8. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of 3-thiapentane-1,5-diol and adipic acid, said linear polyester having a molecular weight of at least 350.

9. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of ethane-1,2-diol and 4-thiapimelic acid, said linear polyester having a molecular weight of at least 350.

10. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of ethane-1,2-

diol and 3,7-dithia-azelaic acid, said linear polyester having a molecular weight of at least 350.

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