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3,046,133

SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS WITH POLYESTER COMPOUNDS CONTAINING THIOETHER-SULFUR ATOMS IN THE SIDE CHAIN

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12 Claims. (Cl. 96-108)

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

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

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 frequently 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 are thus 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. Still another object of my invention is to provide photographic silver halide emulsions which have increased sensitivity without concomitant in-

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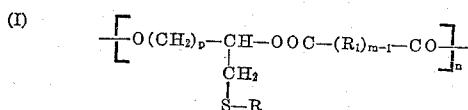
creases in fog or poor keeping qualities to a degree which might seriously affect the usefulness of the emulsions. Another object is to provide a new class of photographic sensitizers which can provide additional sensitivity to photographic silver emulsions already sensitized with certain chemical sensitizers, 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 substantially increased by incorporating therein linear polyesters containing thioether atoms as substituents on the linear chain. The polyester compounds of my invention contain sulfur atoms in the form of thioether linkages, by which 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 containing disulfide linkages, such as linkages of the type commonly found in vulcanized, rubbery, or elastomeric materials. Moreover, the polyester compounds of my invention contain thioether atoms as substituents on the linear chain, as contrasted with polymeric materials containing their ether-sulfur atoms in the linear polymeric chain. Linear polyesters of the latter type are described in my copending application, Serial No. 779,840, filed on even date herewith.

The linear polyesters used in 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 to the surface of the silver halide grains. Linear polyester compounds containing polar groupings are particularly useful in my invention, since they generally have a rather high degree of water-dispersibility, so that they can be conveniently incorporated in photographic silver halide emulsions in sensitizing amounts.

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 polyesters represented by the following general formula:

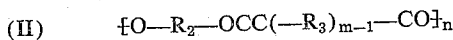


wherein R represents an alkyl group, such as methyl, ethyl, propyl, butyl, hexyl, etc. (e.g., an alkyl group containing from 1 to 6 carbon atoms), R₁ represents an alkylene group e.g., methylene, ethylene, trimethylene, 1,2-propylene, tetramethylene, 2,3-butylene, oxapropylene, thiapropylene, hexamethylene, etc. (e.g., an alkylene group containing from 1 to 6 carbon atoms, and, if desired, one

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or more sulfur or oxygen ether atoms), m represents an integer of from 1 to 2, p represents a small positive integer, e.g., 1 to 3 (provided p and m do not simultaneously represent 1), and n represents a small, positive, whole number, such as 2 or more. 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 350 to 10,000 are particularly useful, while polyester compounds having a molecular weight of from about 500 to 3,500, have particularly outstanding properties.

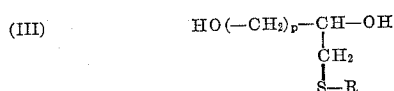
Another group of useful polyesters included within my invention are those represented by the following general formula:



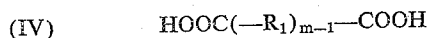
wherein m has the values given above and R_2 and R_3 each represents an alkylene group, such as an alkylene group defined by R_1 above, at least one of these alkylene groups containing at least one (e.g., 1 or 2) alkylmercapto group as a substituent, and n has the values given above. Typical alkylmercapto groups include, for example, methylmercapto, ethylmercapto, propylmercapto, etc. As in the case of the polyesters of Formula I, the polyesters of Formula II have a molecular weight of at least about 350, while the polyester compounds having a molecular weight of from about 500 to 3,500 have outstanding properties.

The terminal groups of the linear polymers of my invention, such as those represented by Formula I or Formula II above, are generally hydrogen atoms, carboxylic groups (including carboxylic acid, carboxylic ester, and carboxylic halide groups), hydroxyl groups, or combinations of these groups. It is apparent that the nature of the terminal groups will depend upon the method of synthesizing the polyesters.

The linear polyesters of my invention can be prepared according to methods which have been previously described in the prior art. For example, the linear polyesters of Formula I above can be prepared by condensing at least one glycol compound selected from those represented by the following general formula:



wherein p and R have the values given above, with at least one dicarboxylic acid (or dicarboxylic anhydride or ester thereof) represented by the following general formula:

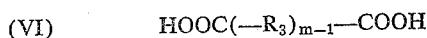


wherein m and R_1 have the values given above. The condensations can be carried out merely by heating two or more of these ingredients together, alone, or in the presence of an inert solvent. Temperatures of from about 100 to 200° C. are generally sufficient to effect condensation. The products obtained are generally in the form of syrupy liquids or crystalline or semi-crystalline solids. The condensates need not be separated from the reaction mixture prior to use, but they can be added directly to photographic silver halide emulsions, with or without another dispersing medium.

The linear polyesters of Formula II above can advantageously be prepared by condensing together a glycol selected from those represented by the following general formula:



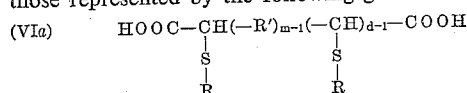
wherein R_2 has the values given above, with a dibasic acid (or anhydride, or ester, or carboxylic halide), represented by the following general formula:



wherein m and R_3 have the values given above. A partic-

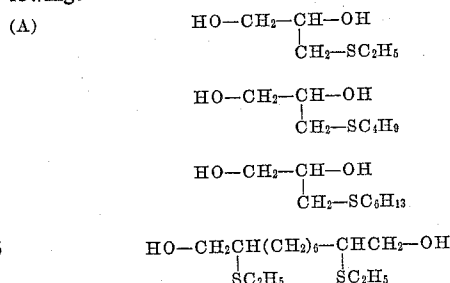
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ularly useful group of acids embraced by Formula VI are those represented by the following general formula:

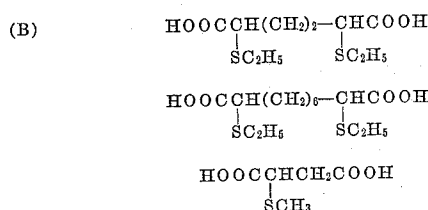


wherein R has the values given above, R' represents an alkylene group, such as methylene, ethylene, trimethylene, 1,2-propylene, etc., and m and d each represents a positive integer of from 1 to 2. The method of preparing the linear polyester of Formula II above is similar to that used for preparing the polyesters of Formula I.

Typical glycols, including those of Formula III, which are useful in practicing my invention include the following:



Typical dicarboxylic acids containing alkylmercapto groups for instance, include the following:



Other glycols which can be used in my invention for condensation with a dicarboxylic acid containing an alkylmercapto group include ethylene glycol, propylene glycol, 1,2-propylene glycol, butylene glycol, hexamethylene glycol, etc.

Typical dicarboxylic acids which can be condensed with glycols containing an alkylmercapto substituent include oxalic acid (reaction with a vicinal glycol might tend to produce cyclic products in some instances), succinic acid, glutaric acid, 2,2-dimethyl glutaric acid, adipic acid, pimelic acid, sebacic acid, etc. As indicated above, functional equivalents of these acids can be used where they are available.

The following examples will serve to illustrate the method of preparing various polyesters useful in practicing my invention.

EXAMPLE 1

In an all-glass outfit equipped with an air condenser and a means for admitting dry nitrogen below the level of the melt were placed 5.60 g. of 1,2-dihydroxy-3-ethylmercaptopropane and 4.00 g. of succinic anhydride. The flask was immersed in an oil bath thermostatically controlled at 150° C. The reaction mixture went to a clear melt. After 4 hours of heating, a gentle stream of nitrogen was passed through the melt, and heating at 150° C. was continued for an additional 16½ hours. With the flask still maintained at 150° C., a water pump vacuum was attached for 20 minutes, followed by high vacuum mechanical pump. After 1½ hours at 150° C., the temperature was raised to 170° C. and maintained there for 6 hours. The melt was cooled under vacuum and then dissolved in 40 ml. of acetone, boiled with decoloring carbon (Norite) and filtered. Thirty-seven and two-tenths grams of solution were obtained with a solids content of 18.5%.

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EXAMPLE 2

In a manner similar to that illustrated in Example 1 above, a molecularly equivalent amount of 1,2-dihydroxy-3-butylmercaptopropane was used in place of the ethylmercapto compound of Example 1. The condensation was with succinic anhydride. The resulting polymer was used without separation from the reaction mixture.

EXAMPLE 3

In a manner similar to that illustrated in Example 1 above, the ethylmercapto compound of Example 1 was replaced by a molecularly equivalent amount of 1,2-dihydroxy-3-hexylmercaptopropane and condensed with succinic anhydride. The resulting polymer was used to sensitize photographic silver halide emulsions without separation from the reaction mixture.

EXAMPLE 4

In a 50 ml. round-bottomed flask equipped with a short air condenser were placed 1.50 grams of ethylene glycol and 3.28 grams of methylmercaptosuccinic acid. The reaction mixture was heated at 150° C. for 20 hours, during the last 18 of which a slow stream of nitrogen was passed through the melt. A vacuum of 0.1 mm. was then applied for 3 hours with the bath temperature maintained at 150° C. after which the bath temperature was raised to 170° C. for 4½ hours while vacuum was continued. A colorless, very viscous syrup was obtained. This was dissolved in 25 ml. of acetone, boiled with Norite decolorizing carbon and filtered. The product was used in this acetone solution without isolation. Twenty grams of solution, with a solids content of 14.2%, were obtained.

EXAMPLE 5

2.66 g. of α,α' -bis(ethylmercapto)adipic acid were condensed with 1.50 g. of ethylene glycol. The heating cycle consisting of about 3 to 4 hours at 150° C., followed by overnight heating at 150° C., with a gentle stream of nitrogen gas passing through the melt, followed by 3 hours heating at 150° C./0.03–0.05 mm. and concluded by 4½ hours heating at 170° C./0.03–0.05 mm. The resulting product was dissolved in acetone, boiled together with Norite decolorizing carbon and then filtered. The weight of solution was 31 g., of which the solids content was 8.55%. The solids content of solution was determined by drying a weighed portion at 110° C.

EXAMPLE 6

In a manner similar to that illustrated in Example 5 above, 2.94 g. of 1,10-dihydroxy-2,9-bis(ethylmercapto)decane were condensed with 1.00 g. of succinic anhydride. There were thus obtained 29 g. of solution having a solids content of 10.65%.

EXAMPLE 7

In a manner similar to that illustrated in Example 5 above, 3.22 g. of α,α' -bis(ethylmercapto)sebacic acid were condensed with 0.70 g. of ethylene glycol. There were thus obtained 34.5 g. of solution having a solids content of 8.22%.

The polymers of the above examples had the following molecular weights (by end-group titration):

Example No.:	Molecular weight
1	1480
2	3000
3	3280
4	2140
5	3080
6	2680

The above examples are merely illustrative, and it is to be understood that other polymers can be prepared and used as described above.

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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 non-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 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 emulsion 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. My new photographic sensitizers are unique in that no special final digestion or after-ripening are required in order to obtain optimum sensitization.

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 5 g. of polyester per mole of silver halide are quite adequate to accomplish the desired sensitization.

The linear polyesters of my invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the polyesters can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. As indicated above, the solvent should be selected so that it has no harmful effect upon the emulsion, and generally solvents or diluents which are miscible with water are to be preferred. Water 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 absorbed to the grains of the silver halide present in the emulsion in sufficient amount to sensitize the emulsion. It is apparent that the optimum amount for each of the 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 chloropalladate, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurate, 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; VanLare 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; and 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; the bis-quaternary salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene bisbenzothiazolium perchlorate, etc.), and the zinc and cadmium salts of Jones U.S. patent application Serial No. 493,047, filed March 8, 1955 (now U.S. Patent 2,839,405, issued June 17, 1958).

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

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

The emulsions may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic acid or 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-(methanesulfonoxo)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxy-methylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2-3 carbon atoms, such as β -methylglutaraldehyde bis-sodium bisulfite as described in Allen and Burness U.S. patent application Serial No. 556,031, filed December 29, 1955 (now

abandoned); a bisaziridine 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 No. 2,719,087, issued September 27, 1955; and 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. octylphenoxy)pentaoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg U.S. patent application Serial No. 691,125, filed October 21, 1957.

The addenda which 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 bromiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955, or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

They may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No. 586,705, filed May 23, 1956. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while

the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, issued July 24, 1956, and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19-26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanalamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30-60% and a specific viscosity of 0.25-1.5 or an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. 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 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 illustrated in U.S. Patent 2,399,083, for example, was divided into several portions. Linear polyester compounds of the type obtained above were then added directly, or preferably in a solution of an organic solvent, such as acetone, ethanol, etc., 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 $\frac{1}{25}$ second 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:

	Grams
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 obtained were as follows:

Table I

Coating No.	Polymer (g./mol. AgX) of Example	Rel. Speed	Gamma	Fog
1(a)-----	None-----	100	1.33	.11
(b)-----	1 (0.3)-----	120	1.30	.12
(c)-----	1 (3.0)-----	166	1.06	.18
2(d)-----	None-----	100	.89	.09
(e)-----	2 (3.0)-----	148	.87	.10
3(f)-----	None-----	100	.89	.09
(g)-----	3 (3.0)-----	117	.95	.10
4(h)-----	None-----	100	-----	.11
(i)-----	4 (3.0)-----	120	-----	.13
5(j)-----	None-----	100	1.28	.15
(k)-----	5 (0.9)-----	135	1.75	.17
6(l)-----	None-----	100	1.28	.15
(m)-----	6 (3.0)-----	155	1.50	.19

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.

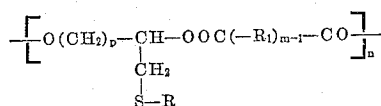
The above examples illustrate linear polyesters and their effects in emulsions, where the polyesters have been obtained from a single acid or anhydride and a glycol. It is, of course, to be understood that mixed esters can be obtained and used in like manner in employing a mixture of one or more acids (or anhydrides, etc.), together with one or more glycols of the type illustrated above.

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 carboxylic acid, said linear polyester containing a plurality of alkylmercapto radicals as substituents to the intralinear chain and the ester linkages of said linear polyester being within the linear polymer chain, said linear polyester having a molecular weight of at least 350.

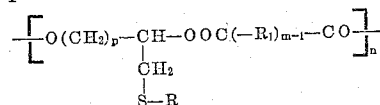
2. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester, the polymeric chain of which consists essentially of groups represented by the following general formula:



wherein R represents an alkyl group, R₁ represents an alkylene group, m represents a positive integer of from 1 to 2 while p represents a small positive integer, provided that m and p do not simultaneously represent 1, and n represents a positive integer of at least about 2, said linear polyester having a molecular weight of at least about 350.

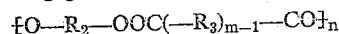
3. A photographic silver halide emulsion sensitized with (1) a gold compound, (2) a compound containing a labile sulfur atom, and (3) a sensitizing amount of a linear poly-

ester, the polymeric chain of which consists essentially of groups represented by the following general formula:



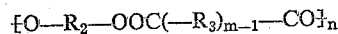
wherein R represents an alkyl group, R₁ represents an alkylene group, m represents a positive integer of from 1 to 2 while p represents a small positive integer, provided that m and p do not simultaneously represent 1, and n represents a positive integer of at least about 2, said linear polyester having a molecular weight of at least about 350.

4. 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:



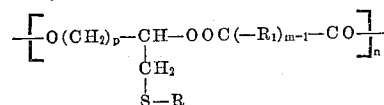
wherein R₂ and R₃ each represents a member selected from the class consisting of an alkylene group and an alkylmercapto-substituted alkylene group, at least one of the radicals selected from the class consisting of R₂ and R₃ being an alkylmercapto-substituted alkylene group, m represents a positive integer of from 1 to 2, and n represents a positive integer of at least about 2, said linear polyester having a molecular weight of at least about 350.

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



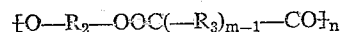
wherein R₂ and R₃ each represents a member selected from the class consisting of an alkylene group and an alkylmercapto-substituted alkylene group, at least one of the radicals selected from the class consisting of R₂ and R₃ being an alkylmercapto-substituted alkylene group, m represents a positive integer of from 1 to 2, and n represents a positive integer of at least about 2, said linear polyester having a molecular weight of at least about 350.

6. 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 represents an alkyl group, R₁ represents an alkylene group, m represents a positive integer of from 1 to 2 while p represents a small positive integer, provided that m and p do not simultaneously represent 1, and n represents a positive integer of at least about 2, said linear polyester having a molecular weight of at least about 350.

7. 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 R₂ and R₃ each represents a member selected from the class consisting of an alkylene group and an alkylmercapto-substituted alkylene group, at least one of the radicals selected from the class consisting of R₂ and R₃ being an alkylmercapto-substituted alkylene group, m represents a positive integer of from 1 to 2, and n represents a positive integer of at least about 2, said linear polyester having a molecular weight of at least about 350.

8. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of 1,2-dihydroxy-3-ethyl-mercaptopropane and succinic anhydride, said

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linear polyester having a molecular weight of at least about 350.

9. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of 1,2-dihydroxy-3-butylmercaptopropane and succinic anhydride, said linear polyester having a molecular weight of at least 350. 5

10. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of 1,2-dihydroxy-3-hexylmercaptopropane and succinic anhydride, said linear polyester having a molecular weight of at least about 350. 10

11. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of methylmercaptosuccinic acid and ethylene glycol, said linear polyester having a molecular weight of at least 350. 15

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12. A photographic silver halide emulsion containing a sensitizing amount of a linear polyester of α, α' -bis(ethylmercapto)-adipic acid and ethylene glycol, said linear polyester having a molecular weight of at least 350.

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