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3,426,029

POLYFUNCTIONAL POLYALKYLENEGLYCOLS AND THEIR POLYQUATERNARY AMMONIUM SALTS

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No Drawing. Original application June 12, 1962, Ser. No. 201,788, now Patent No. 3,253,919, dated May 31, 1966. Divided and this application Sept. 28, 1965, Ser. No. 512,586

U.S. Cl. 260—294.8

Int. Cl. C07c 103/54, 31/48

7 Claims

ABSTRACT OF THE DISCLOSURE

Polyfunctional polyalkyleneglycols and their polyquaternary ammonium salts which are derived from ethylenediamine tetraacetic acid, alkylaminopropylamine-N,N',N'-trisacetic acid, polyamino alcohols, N-methylgluconamine (or N-methylglucamine) and contain at least 6 alkylene-glycol units per molecule are used to advantage to increase the sensitivity of photographic emulsions which have already been sensitized to their optimum or near optimum with chemical sensitizers.

This is a divisional application of U.S. patent application Ser. No. 201,788, Sensitizers for Photographic Silver Halide Emulsions, filed June 12, 1962, now Patent 3,253,919, issued May 31, 1966.

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 or extends 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 the 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 a very large factor. However, there is a definite limit beyond which further additions of chemical sensitizers or of further digestion with the sensitizer present, merely increases fog of the photographic emulsion with constant or decreasing emulsion speed.

We have now found a means of further increasing the sensitivity of photographic emulsions which may be applied even through the ordinary processes of chemical sensitization have been carried to the effective limit of the photographic emulsion in question. Our process is to be distinguished from hypersensitization which is produced by bathing a finished coating with water or with solutions of ammonia, amines or silver salts. Such processes act primarily on optically sensitized photographic emulsions and tend to increase the free silver ion concentration of the emulsion and greatly diminish its stability. Our process is also to be distinguished from hypersensitization by mer-

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cury vapor which gives a transitory effect that is lost on storage of the film. The compounds used in our invention do not appear to be chemical sensitizers in the usual sense, since they increase speed by their presence during exposure and processing, and require no digestion with the photographic emulsions to produce an increase in speed nor does their chemistry indicate that they are likely to react with silver halide under normal emulsion conditions.

The novel sensitizers of our invention, the polyfunctional polyalkyleneglycol compounds and their polyquaternary ammonium salts which are derived from ethylenediamine tetraacetic acid, alkylaminopropylamine-N,N',N'-trisacetic acid, polyamino alcohols, N-methylgluconamine (or N-methyl-glucamine) and contain at least six alkylene-glycol units per molecule, are unique in that the effects produced are additive in photographic emulsions which have already been sensitized to their optimum or near optimum with conventional chemical sensitizers, such as labile sulfur compounds. The novel sensitizers of our invention, however, can be used to sensitize photographic silver halide emulsions containing no other sensitizers if desired. The novel sensitizers of our invention are not strictly chemical sensitizers since chemical sensitizers do not generally provide the additive effects of the type mentioned. It is therefore an object of our invention to provide photographic emulsions that have been sensitized with our polyfunctional polyalkyleneglycol sensitizer compounds or polyquaternary ammonium salts derived from them.

It is a further object of our invention to increase the light sensitivity of ordinary photographic silver halide emulsions which have been sensitized with chemical sensitizers, such as compounds containing labile sulfur atoms or gold containing compounds without increases in fog which might seriously effect the usefulness of the emulsions.

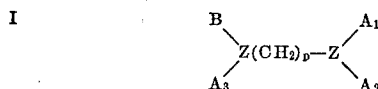
A further object is to provide a novel class of sensitizers which are readily dissolved in water and added to gelatin-silver halide emulsions.

A still further object is to provide a novel class of sensitizers which when added to photographic silver halide emulsions, produce their sensitizing effects without further digestion of the emulsion.

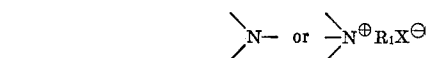
Other objects will become apparent from the following specification and claims.

According to our invention the sensitivity of ordinary high speed silver halide emulsions chemically sensitized in the conventional way is substantially increased by the incorporation of our polyfunctional polyalkyleneglycol sensitizers or polyquaternary ammonium salts derived from them. Our novel sensitizers are particularly useful since they have a high degree of water solubility and are readily incorporated in the silver halide emulsions in sensitizing amounts.

Included in the compounds of our invention are those having the formula:



in which p represents an integer of from 2 to 10; Z represents



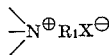
in which R_1 is an alkyl group having from 1 to 20 carbon atoms such as methyl, ethyl, butyl, octyl, decyl, dodecyl, pentadecyl, heptadecyl, octadecyl, phytol, etc., and X^- is an acid anion, such as chloride, bromide, perchlorate, a lower alkylsulfonate, e.g., methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, etc., an arylsulfonate, e.g., p-toluenesulfonate, benzenesulfonate,

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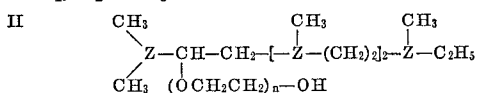
etc.; A₁, A₂ and A₃ each represents a polyalkylene oxide chain derivative of a short alkyl chain having from 2 to 3 carbon atoms and containing an —OH or a



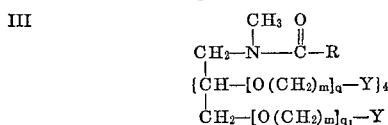
group in which the number of alkylene oxide units may be the same or different and in which the alkylene oxide units may have from 2 to 3 carbon atoms per unit, such as ethylene or propylene and such that when the alkylene oxide units have 3 carbon atoms, Z represents a



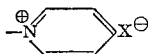
group; and B represents an alkyl group having from 1 to 20 carbon atoms, such as methyl, ethyl, propyl, butyl, heptyl, octyl, decyl, dodecyl, pentadecyl, heptadecyl, octadecyl, nonadecyl, phytlyl, etc., or may be the same as A₁, A₂ or A₃.



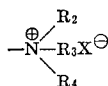
in which Z is as defined previously, and *n* is an integer such that the average value of *n* is from 8 to 100;



in which R represents an alkyl group having from 1 to 20 carbon atoms, such as methyl, ethyl, propyl, butyl, hexyl, octyl, dodecyl, pentadecyl, hexadecyl, phytlyl, etc.; *m* is an integer from 2 to 3; *q* and *q*₁ each represent an integer such that the total of the 4 *q*'s and *q*₁ has an average value of from 6 to 100; Y represents a hydroxyl group, a



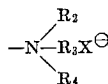
group or a



group in which R₂, R₃ and R₄ each represents an alkyl group having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, butyl, etc., and X[⊖] represents an acid anion as described previously, such that when *m* is the integer 3, Y represents a

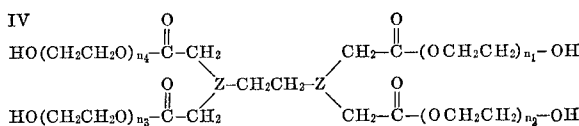


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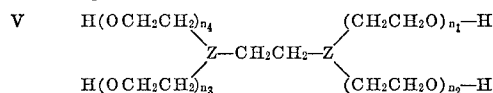
Included among our sensitizers of Formula I are those of Formulas IV, V, VI, and VII which follow.



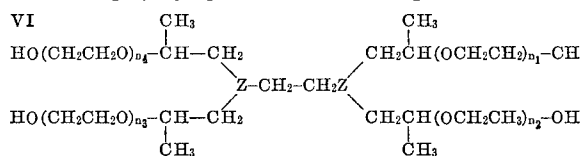
in which *n*₁, *n*₂, *n*₃, and *n*₄ are each integers which may be the same or different, such that the total of *n*₁, *n*₂, *n*₃, and *n*₄ has an average value of from 6 to 100, and Z is as defined previously.

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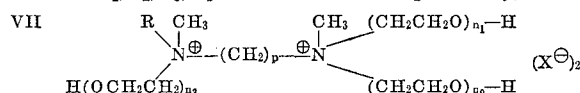
*n*₃, *n*₄ has an average value of from 6 to 100, and Z is as defined previously.



in which *n*₁, *n*₂, *n*₃, *n*₄ and Z are as defined previously.

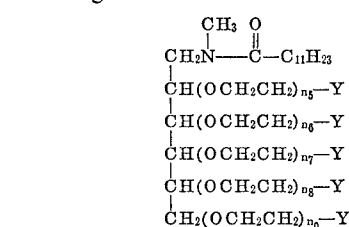


in which *n*₁, *n*₂, *n*₃, *n*₄ and Z are as defined previously, and



in which R represents an alkyl group having from 1 to 20 carbon atoms such as methyl, ethyl, propyl, butyl, heptyl, octyl, decyl, dodecyl, pentadecyl, heptadecyl, octadecyl, nonadecyl, phytlyl, etc.; *n*₁, *n*₂ and *n*₃ each represent an integer such that the sum of *n*₁+*n*₂+*n*₃ has an average value of from 8 to 100; and *p* and X[⊖] are as described previously.

Our sensitizers of Formula III include those of the following formula:



in which Y is as defined previously and *n*₉ is an integer that can be the same or different from *n*₅, *n*₆, *n*₇ and *n*₈ such that the total of *n*₅+*n*₆+*n*₇+*n*₈+*n*₉ has an average value in the range from 6 to 100.

Included among the polyfunctional polyethyleneglycol (i.e., polyfunctional PEG) sensitizing compounds and their polyquaternary salts are the following representative examples used to illustrate but not limit our invention.

Sensitizer number	Sensitizer name
1	Ethylenediamine tetraacetic acid-tetrakis (nonaethylene glycol ester) or polymeric product therefrom.
2	Tetrahydroxyethylethylenediamine polyethylene glycol 704 (Average of 16 ethylene oxide units per molecule).
3	Tetrahydroxyethylethylenediamine polyethylene glycol 550 (Average of 12.5 ethylene oxide units per molecule).
4	Tetrahydroxyethylethylenediamine polyethylene glycol 396 (Average of 9 ethylene oxide units per molecule).
5	Tetrahydroxyethylethylenediamine polyethylene glycol-176-bis(methyl p-toluene-sulfonate).
6	Heptadecylaminopropylamino-N,N',N'-trispolyethylene-glycol-1320-bis(methyl p-toluene-sulfonate).
7	1-dimethylamino-3,6,9-trimethyl-3,6,9-triazaundecanol-1-polyethyleneglycol 525 (Average of 12.1 ethylene oxide groups per molecule).
8	1-dimethylamino-3,6,9-trimethyl-3,6,9-triazaundecanol-1-polyethyleneglycol 977 (Average of 22.2 ethylene oxide units per molecule).
9	1-trimethylammonium-3,6,9-triaza-3,3,6,6,9,9-hexamethyl-undecyl ether of polyethylene-glycol-977-tetrakis (p-toluenesulfonate).
10	N-lauroyl-N-methylgluconamine polyethylene-glycol-264 (Average of 6 ethylene oxide units per molecule).
11	N-lauroyl-N-methylgluconamine polyethylene-glycol-264-tetrakis(methanesulfonate).
12	N-lauroyl-N-methylgluconamine polyethylene-glycol-792-tetrakis methanesulfonate (Average of 18 ethylene oxide units per molecule).
13	N-lauroyl-N-methylgluconamine polyethylene-glycol-792-tetrakis (pyridinium methanesulfonate).
14	N-lauroyl-N-methylgluconamine polyethylene-glycol-264-tetrakis(pyridinium methanesulfonate).

Also included among the sensitizers of our invention

are the polyfunctional polypropyleneglycol sensitizers and the polyquaternary ammonium salts derived from them as defined by the Formulas I and III.

In general the polyalkyleneglycol derivatives are prepared by reacting the amino alcohols and acids with ethylene oxide (or propylene oxide) in the presence of catalysts, such as Lewis-type acids, tertiary amines, acids or inorganic bases.

However, the addition of polyethylene glycol (or polypropylene glycol) chains to a polycarboxylic acid or amide can most conveniently be accomplished by reacting the polycarboxylic acid or amide with the desired polyethyleneglycol, such as nonaethyleneglycol, using an acid catalyst. *p*-Xylene is used to azeotrope off the water formed in the reaction and is collected in a Dean-Stark trap. The preparation of ethylenediamine tetraacetic acid-tetrakis (nonaethyleneglycol ester) was accomplished in this manner. It is understood that this product may contain a monomeric type unit, or may polymerize to give very large molecules containing many ester or amide functions. Epoxides, such as propylene oxide, may be added to acids and also amides under high temperatures and pressures in an autoclave with the usual catalyst, if desired. Monomers and polymers may form in this reaction.

The polyethyleneglycol or polyalkylene oxide derivatives of polycarboxylic acids, alcohols, or amides are further converted to the polymethanesulfonates, or hydroxyhalides, and the resulting poly intermediates are quaternized. The polysulfonate esters are formed by reaction of the polyhydroxy compounds with alkyl or aryl sulfonyl chlorides in pyridine; or a polyhydroxy halide may be readily prepared by reaction of the polyglycols with epihalohydrins. The esters and halides readily quaternize with tertiary bases, such as trialkylamines or tertiary nitrogen heterocyclics. Pyridine has been found a superior quaternizing agent for our sensitizing compounds. If desired, the sulfonate or halide anion may be converted to the perchlorate anion with sodium perchlorate.

The molecular weight of our sensitizing compounds can vary over rather wide ranges because of the different number of alkylene oxide units, such as ethylene oxide or propylene oxide units that they may have per molecule. The alkylene oxide chains on a given molecule of the sensitizers may be of equal or varying lengths. The sensitizing compounds of our invention have molecules with a total of from 6 to 100 alkylene oxide units per molecule, and the total molecular weight of the alkylene oxide units in a molecule may vary from about 264 to about 7200.

Our invention is still further illustrated by a description of the preparations of the representative sensitizing compounds.

Sensitizer 1

Ethylenediamine tetraacetic acid, 14.6 g. (0.05 mole) was added to 150 ml. of *p*-xylene. Carbowax 400, a Carbide and Carbon Co. polyethylene glycol product, 80 g. (0.20 mole), was added along with half a milliliter of concentrated sulfuric acid. The resulting slurry was stirred vigorously while heating to reflux in a flask provided with a Dean-Stark trap and condenser. After 16 hours, the theoretical amount of water had been collected. The dark mixture was treated with decolorizing charcoal and filtered through a diatomaceous silica filter bed. The solvent was removed on the steam bath under vacuum leaving 70 g. of a dark, viscous oil which dissolved to a clear solution in water.

Sensitizer 2

Forty-one grams (0.10 mole) of tetrahydroxyethyl-ethylenediamine PEG-176 with 2 drops of boron trifluoride-ether complex (catalyst) was added to a flask

equipped with a stirrer, a Dry-Ice acetone condenser, and gas inlet. The flask was heated to 60° C. on a water bath, and 54 g. (1.2 moles) of ethylene oxide was bubbled into the reaction mixture under the surface of the liquid. After 6 hours, the mixture was heated on the steam bath to remove catalyst and unreacted ethylene oxide leaving a dark yellow oil weighing 95 g. The oil was dissolved in methanol, treated with decolorizing charcoal and diatomaceous filter aid and filtered. After removal of solvent under vacuum, 83 g. of a pale orange colored viscous oil remained which was soluble in water.

Sensitizer 3

The same process used for making Sensitizer 2 was used but 110.5 g. (2.5 moles) of ethylene oxide was reacted during 4 hours with 46.4 g. (0.20 mole) of tetrahydroxyethyl-ethylenediamine in the presence of the catalyst. After treatment with decolorizing charcoal and filter aid, 132.5 g. of a light-brown viscous syrup was obtained.

Sensitizer 4

This sensitizer was prepared as was Sensitizer 2 but by the reaction of 46.4 g. (0.20 mole) of tetrahydroxyethyl-ethylenediamine with 80 g. (1.8 mole) of ethylene oxide in the presence of three drops of the catalyst over a period of 5 hours. Following treatment with decolorizing charcoal and filter aid, filtration and removal of excess solvent under vacuum, 85.4 g. of Sensitizer 4, a dark viscous oil, was obtained.

Sensitizer 5

Ten grams of tetrahydroxyethyl-ethylenediamine PEG-176 and 9.1 g. of methyl *p*-toluenesulfonate were added together with stirring. A mild exothermic reaction raised the temperature to 58° C. The dark red, viscous liquid was heated on the steam bath for an additional two hours to insure complete reaction. The orange colored syrup was then slurried twice with hot benzene to remove unreacted starting material. The oil was dissolved in ethanol, heated with decolorizing charcoal and filtered through a filter bed formed with diatomaceous silica. The solvent was removed on the steam bath under vacuum, giving 11.5 g. of a viscous, water-soluble oil.

Sensitizer 6

Heptadecylaminopropylamino - *N,N',N'*-trispolyethyleneglycol-1320 (i.e., Armour and Co.'s Ethoduomeen T/40), was a dark, viscous syrup as obtained. It was dissolved in acetone, heated with decolorizing charcoal and filtered with diatomaceous silica filter aid through a filter bed, giving a clear, orange syrup. The excess solvent was removed on the steam bath under vacuum, leaving 19.8 g. of an orange syrup which partially solidified upon cooling.

To this product was added 4.5 g. of methyl *p*-toluenesulfonate and the mixture stirred while a mild exothermic reaction took place. After this had subsided, the mixture was heated on the steam bath for 4 hours. The product was slurried with ether several times, and the ether solution decanted each time. The remaining traces of ether were removed on a steam bath under vacuum, giving a viscous oil.

Sensitizer 7

1 - dimethylamino-3,6,9-trimethyl - 3,6,9 - triazundecanol-1, 26 g. (0.10 mole), was heated on the steam bath in a flask equipped with a Dry-Ice acetone condenser, stirrer, and submerged gas inlet tube. After two and one-half hours of ethylene oxide gas addition, and after removal of the unreacted gas on the steam bath under vacuum, the oil weighed 79.5 g. A weight increase of 53.5 g. indicated that 12.1 moles (PEG-525) ethylene oxide had reacted with the amino alcohol.

Sensitizer 8

Forty grams of the above ethylene oxide addition product containing 12.1 moles of ethylene oxide were heated and reacted under the same conditions as above. After approximately one and one-half hours of addition, 22.5 g. of ethylene oxide by weight were added, giving an oil which now contained 22.2 moles of ethylene oxide (PEG-977) per mole of amino alcohol. For a lighter-colored product, the oil was dissolved in methanol, decolorizing charcoal added, and the solution filtered through a diatomaceous silica filter bed. Concentration of the filtrate under vacuum on the steam bath gave 60 g. of a dark, water-soluble oil.

Sensitizer 9

The above polyethyleneglycol addition product, 12.4 g. (0.01 mole), and 8.6 g. (0.046 mole) of methyl p-toluenesulfonate were heated together on the steam bath for two hours. The resulting oil was slurried with ether several times to remove traces of unreacted sulfonate ester. The excess solvent was removed on the steam bath under vacuum. Twelve grams of a dark, viscous water-soluble oil was obtained.

Sensitizer 10

Ethylene oxide 26.5 g. (0.60 mole) was added to 37.7 g. (0.10 mole) of N-lauroyl-N-methylgluconamine in the presence of 3 drops of the catalyst as described in the preceding examples. The ethylene oxide was added over a period of about 4 hours. After purification, there remained 64.2 g. of a viscous orange colored oil soluble in water.

Sensitizer 11

N - methyl-N-lauroylgluconamine PEG 264, 25.0 g. (0.04 mole), was dissolved in pyridine and chilled to 0° C. Methane sulfonyl chloride, 17.2 g. (0.16 mole), was slowly added through a dropping funnel while the temperature of the reaction mixture was held at 0-10° C. After stirring for two hours, the mixture was allowed to warm up to room temperature. The slurry was acidified with cold hydrochloric acid (1:1) and saturated with sodium chloride. The acidic solution was extracted three times with 200 ml. of warm benzene, and the extract was dried over sodium sulfite. After treatment with decolorizing charcoal, the benzene was removed on a steam bath under vacuum leaving 24 g. of a dark viscous orange colored syrup.

Sensitizer 12

N-lauroyl-N-methylgluconamine PEG-792 was prepared in the usual manner by the addition of ethylene oxide in the presence of a boron trifluoride catalyst at 85°. Twenty-three grams of this addition product was dissolved in 100 ml. of dry pyridine, chilled to 0°, and methanesulfonyl chloride was added with rapid stirring, keeping the temperature below 5°. The slurry was stirred at 0° for two hours, then at room temperature for two hours. The slurry was acidified, saturated with sodium chloride and extracted with three 200-ml. portions of warm benzene. Concentration of the extracts under vacuum on the steam bath gave 16.5 g. of an orange oil.

Sensitizer 13

The above tetrakis methanesulfonate ester, 16.5 g., 50 ml. of pyridine and 20 ml. of ethanol were refluxed for 1½ hours. The excess pyridine was removed under vacuum on the steam bath. The residual oil was dissolved in methanol and precipitated with ether. The ether was decanted and the procedure repeated twice. The oil was then dissolved in methanol, treated with decolorizing charcoal, the solution was filtered through a diatomaceous silica filter bed, and the solution concentrated. The tetraquater-

nary salt was isolated as 15.4 g. of a yellow, viscous, water-soluble oil.

Sensitizer 14

N - methyl - N - lauroylgluconamine PEG 264-tetrakis (methanesulfonate), 10 g. and 25 ml. of pyridine were refluxed together for 1½ hours. The excess pyridine was relieved on the steam bath under vacuum. The oil was dissolved in 10 ml. ethanol and precipitated out with ether. The ether was decanted and the process repeated two more times removing all traces of solvent and excess pyridine under vacuum on the steam bath. Nine grams of an extremely viscous orange colored oil was obtained which was readily soluble in water.

The compounds of our invention are added to ordinary photographic silver halide emulsions for the purpose of increasing the sensitivity thereof as has been indicated above.

The preparation of photographic silver halide emulsions involves three separate operations:

- (1) Emulsification and digestion of silver halide,
- (2) The freeing of the emulsion of excess water soluble salts usually by washing with water, and
- (3) The second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity.

Mees, "The Theory of the Photographic Process," 1954. The sensitizers of our invention can be added to the emulsion before the final digestion or "after-ripening" or they can be added immediately prior to coating. Our new photographic sensitizers are characterized by not requiring any final digestion or "after-ripening" in order to obtain optimum sensitivity.

The particular quantity of our sensitizer compound used in a given emulsion will 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. Generally, from about 50 mg. to about 5 g. of our compounds per mole of silver halide are quite adequate to accomplish the desired sensitization.

Our sensitizers can be added to photographic emulsions using any of the well known techniques in emulsion making. Generally these compounds are soluble enough in water so that the required concentrations are readily obtained. If an auxiliary solvent is needed, solvents such as ethanol, acetone, pyridine, etc., can be used.

It is apparent that the optimum amount of sensitizer compound needed will vary somewhat from emulsion to emulsion and from sensitizer to sensitizer. The optimum amount for a given sensitizer can be determined for any particular emulsion by making a series of tests in which the quantity of our sensitizer is varied over a given range. Exposure of the treated emulsion in a conventional photographic testing apparatus such as an intensity scale sensitometer, followed by development, and image density measurement, will reveal the most advantageous concentration for that sensitizer in that particular emulsion. Such matters are well understood by those skilled in the art.

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

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued Mar. 2, 1926; Sheppard et al. U.S. Patent 1,623,499, issued Apr. 5, 1927; and Sheppard et al. U.S. Patent 2,410,689, issued Nov. 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 Aug. 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued Aug. 28, 1951 and 2,566,263, issued Aug. 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 Apr. 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 chloraurate, 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 Nov. 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698, issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued Sept. 12, 1950), or bis(β -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued Sept. 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued Feb. 23, 1932; 1,846,302, issued Feb. 23, 1932; and 1,942,854, issued Jan. 9, 1934; White U.S. Patent 1,990,507, issued Feb. 12, 1935; Brooker and White U.S. Patents 2,112,140, issued Mar. 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued Jan. 10, 1950; and 2,739,964, issued Mar. 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued Jan. 10, 1950; Sprague U.S. Patents 2,503,776, issued Apr. 11, 1950 and 2,519,001, issued Aug. 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued Jan. 19, 1954; Heseltine U.S. Patent 2,734,900, issued Feb. 14, 1956; Van Lare U.S. Patent 2,739,149, issued Mar. 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 Dec. 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued Dec. 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued Dec. 27, 1955; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605, and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948 and 2,450,397, issued Sept. 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 Apr. 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued Aug. 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued Feb. 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 Nov. 27, 1956; and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, p. 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 Sept. 27, 1938 or the polymethylene bis-benzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued Nov. 16, 1954 (e.g., decamethylene-bis-benzothiazolium perchlorate); or the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958; and the carboxymethylmercapto compounds of Murray, Reynolds and Van Allan U.S. Patent 2,819,965, issued Jan. 14, 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 Aug. 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30-60% and a specific viscosity of 0.25-1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued Feb. 13, 1961; zein as described in Lowe U.S. Patent 2,563,791, issued Aug. 7, 1961; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued Oct. 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 Oct. 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued Sept. 16, 1958.

Our emulsions may contain hydrophilic colloid plasticizers, hardeners, coating aids and other addenda as described in Beavers U.S. Ser. No. 853,009, filed Nov. 16, 1959.

The sensitizing effects produced by our polyfunctional polyethylene glycols and their polyquaternary salts when they were added to high speed gelatino-silver halide emulsions is illustrated by the following example.

EXAMPLE 1

A high-speed gelatino-silver iodobromide emulsion panchromatically sensitized with a cyanine dye was coated on a clear cellulose acetate support to yield a silver coverage of 430 mg. per square foot and a gelatin coverage of 1080 mg. per square foot. This material served as a control. Identical coatings of this same emulsion were made which were sensitized by adding our sensitizers in the amounts indicated in Table 1. A sample of the control coating and the coatings sensitized with sensitizer No. 1 were given identical sensitometric exposures in an Eastman 1-B Sensitometer, given identical 5 minutes development in a developer having the formula:

Water about 125° F. (50° C.)	cc	500
p-Methylaminophenol sulfate	g	2.5
Sodium sulfite (desiccated)	g	30.0
Hydroquinone	g	2.5
Sodium metaborate · 8H ₂ O	g	10.0
Potassium bromide	g	0.5
Water to make 1 liter.		

then fixed by treating in a fixing bath having the formula:

Sodium thiosulfate	g	240.0
Sodium sulfite (desiccated)	g	15.0
Acetic acid 28%	cc	48.0
Boric acid crystals	g	7.8
Potassium alum	g	15.0
Water to make 1 liter.		

washed and dried. The optical densities of the developed images were measured with a densitometer and from these data relative speeds (photographic) were determined for each sample based on a speed of 100 for the control sample. The gammas and fog values were also determined for each sample. This procedure was repeated with a separate control for coatings sensitized with each of the sensitizers 2, 5, 6, 7, 9, 13 and 14. The data obtained are listed in Table I.

TABLE I

Silver halide emulsion sensitized with sensitizer number	Concentration of sensitizer in grams/mole of silver	Relative speed	Gamma	Fog in density units
Control.....	0	100	1.18	.16
1.....	0.15	102	1.12	.16
1.....	0.75	138	1.10	.22
1.....	3.00	182	1.04	.23
Control.....	0	100	1.38	.16
2.....	3.00	126	1.38	.18
Control.....	0	100	1.43	.13
5.....	0.15	102	1.57	.13
5.....	3.00	115	1.52	.15
Control.....	0	100	1.43	.13
6.....	0.15	151	1.35	.18
6.....	0.75	240	1.43	.21
6.....	3.00	251	1.27	.27
Control.....	0	100	1.18	.16
7.....	0.15	105	1.36	.19
Control.....	0	100	1.09	.18
9.....	0.15	100	1.07	.18
9.....	0.75	126	1.14	.20
9.....	3.00	126	1.08	.24
Control.....	0	100	1.20	.13
13.....	0.15	166	1.17	.16
13.....	0.75	269	1.00	.24
13.....	2.25	316	1.14	.30
Control.....	0	100	1.28	.13
14.....	0.75	182	0.91	.32

These data show that high speed photographic emulsions are sensitized by the addition of representative members of our polyfunctional polyethyleneglycol sensitizers and their polyquaternary salts up to relative speeds as high as 316 compared to the control speed of 100. The amount of sensitization produced by a given sensitizer depended upon the concentration of the sensitizer used. The optimum concentration of sensitizer can be determined similarly for other of our sensitizers in other silver halide emulsions.

Incorporation of our sensitizers 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 has indicated their utility therein.

Incorporation of our sensitizers in silver halide emulsions and coated layers designed for use in silver halide diffusion transfer processes of the type described in Rott U.S. Patent 2,532,014; Land U.S. Patents 2,584,029 and 2,543,181; and in Yackel et al. U.S. Patent 3,020,155 gave useful black-and-white transfer systems.

Our sensitizers, when added to silver halide emulsions and coated layers designed for dye transfer color processes of the type described in Yutzky U.S. Patent 2,756,142, or in Whitmore and Mader U.S. patent application Ser. No. 734,191, filed May 9, 1958; or in dye developer transfer color processes of the type described in Land U.S. Patents 2,559,643 and 2,698,798; Land and Rogers Belgian Patents 554,933 and 554,934; and in International Polaroid Belgian Patents 554,212 and 554,935, produced color images of improved quality.

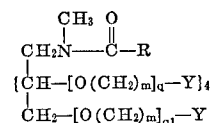
The effect of our new sensitizing compounds has been illustrated above with particular reference to ordinary high speed photographic silver bromide emulsions, although it is to be understood that other silver halide emulsions can also be employed to advantage. Our sensitizers can be used in emulsions which are acidic in character or in emulsions which are alkaline. When adding our sensitizers 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.

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.

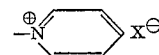
We claim:

1. A polyfunctional polyalkylene compound and the corresponding polyquaternary salt of said compound

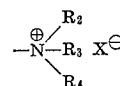
selected from the group consisting of those having the formula:



wherein R represents an alkyl group having from 1 to 20 carbon atoms; m is an integer of from 2 to 3; q and q_1 each represent an integer such that the total of the 4 q 's and q_1 has an average value of from 6 to 100; Y represents a member selected from the class consisting of a hydroxyl group, a

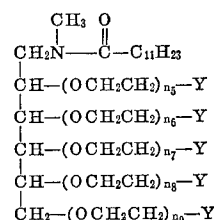


group and a

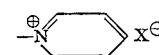


group; R_2 , R_3 and R_4 each represents an alkyl group having from 1 to 4 carbon atoms; and X^- represents an anion selected from the group consisting of a halide, perchlorate, a lower alkylsulfonate, toluenesulfonate and benzenesulfonate.

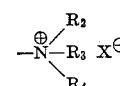
2. A polyfunctional polyalkyleneglycol compound selected from those having the formula:



wherein n_5 , n_6 , n_7 , n_8 , n_9 each represents an integer such that the total of $n_5+n_6+n_7+n_8+n_9$ has an average value of from 6 to 100; Y is a member selected from the class consisting of a hydroxyl group, a



and a



R_2 , R_3 and R_4 each represents a member selected from the class consisting of an alkyl group having from 1 to 4 carbon atoms; and X^- represents an anion selected from the class consisting of a halide, perchlorate, a lower alkylsulfonate, toluenesulfonate and benzenesulfonate.

3. The polyfunctional polyalkyleneglycol compound N-lauroyl-N-methylgluconamine polyethyleneglycol-792-tetrakis (pyridinium methanesulfonate).

4. The polyfunctional polyalkyleneglycol compound N-lauroyl-N-methylgluconamine polyethyleneglycol-264-tetrakis (pyridinium methanesulfonate).

5. The polyfunctional polyalkylene compound N-lauroyl-N-methylgluconamine polyethyleneglycol-264.

6. The polyfunctional polyalkylene compound N-lauroyl-N-methylgluconamine polyethyleneglycol-264-tetrakis (methanesulfonate).

7. The polyfunctional polyalkylene compound N-lauroyl-N-methylgluconamine polyethyleneglycol-792-tetrakis (methanesulfonate).

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U.S. Cl. X.R.

260—295, 404, 404.5, 482, 501.15, 561, 567.6, 584, 401;
96—107, 108, 50