

United States Patent [19]
Ponticello et al.

[11] 3,860,428
[45] Jan. 14, 1975

[54] SILVER HALIDE PEPTIZERS CONTAINING
BIS(THIOETHER) LINKAGES

3,615,624 10/1971 Smith et al..... 96/114
3,692,753 9/1972 Smith et al..... 96/114

[75] Inventors: Ignazio S. Ponticello; Ernest J.
Perry; Richard C. Tuites, all of
Rochester, N.Y.

Primary Examiner—Ronald H. Smith
Attorney, Agent, or Firm—A. H. Rosenstein

[73] Assignee: Eastman Kodak Company,
Rochester, N.Y.

[22] Filed: Dec. 20, 1973

[21] Appl. No.: 426,839

[57] ABSTRACT

[52] U.S. Cl. 96/114
[51] Int. Cl. G03c 1/04
[58] Field of Search 96/114

An ethylenically unsaturated monomer containing bis-
(thioether) linkages is polymerized with at least one
additional monomer to yield polymers which are use-
ful as silver halide peptizers and which are resistant to
hydrolysis.

[56] References Cited

UNITED STATES PATENTS

3,536,677 10/1970 Hollister et al. 96/114 X

20 Claims, No Drawings

SILVER HALIDE PEPTIZERS CONTAINING BIS(THIOETHER) LINKAGES

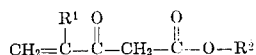
BACKGROUND OF THE INVENTION

This invention relates to photography and more particularly to photographic emulsions containing certain polymeric materials compatible therewith and elements containing such emulsions.

The initial steps in the preparation of a photographic silver halide emulsion are usually precipitation and ripening. A peptizing agent, to be effective, plays a significant role in each of these steps. Gelatin is generally used as a peptizer in commercial emulsions, but certain disadvantages are associated with its use. Gelatin is susceptible to attack by molds and bacteria. Also, as a further consequence of the natural origin of gelatin, a supply from a given source often varies in properties from time to time. Finally, the use of gelatin restricts the type of crystal irregularities obtainable by a given emulsion precipitation procedure to those types which are related to the inherent colloid-chemical nature of gelatin.

Many attempts have been made to prepare satisfactory synthetic polymeric peptizers for silver halide emulsions. However, these materials are frequently unsatisfactory or only partially satisfactory. In certain instances, for example, when one attempts to obtain emulsions known to those skilled in the art as "neutral emulsions" in the presence of polyacrylamide, the peptizing action of this polymer proves to be inadequate and extensive clumping of the emulsion grains occurs. Other polymers, for example poly(vinyl alcohol) or poly(vinylpyrrolidone) provide adequate peptization but exert such potent restraint on grain growth that the emulsion grains obtained are too small for most applications. Various modifications of poly(vinyl alcohol) have previously been made to provide silver halide peptizers, but these derivatives have been met by only limited success.

Belgian Pat. No. 762,833 discloses certain peptizers, among them the terpolymers 1/7/2 3-thiapentyl acrylate/methacrylic acid/dimethylaminoethyl methacrylate, 1/7/2 3-thiapentyl methacrylate/methacrylic acid/diethylaminoethyl methacrylate and 1/7/2 3-thiapentyl acrylate/methacrylic acid/diethylaminoethyl methacrylate which confer the capability of coagulation, washing and redispersion of the silver halide grains by manipulation of the acidity of the medium. Belgian Pat. No. 561,161 describes copolymers of diethylaminoethyl methacrylate and methacrylic acid which are said to be useful as silver halide peptizers. Photographic elements and emulsions containing binders based upon polymerized



are described in U.S. application Ser. No. 394,002 filed Sept. 4, 1973, wherein R^1 is hydrogen, methyl or an ester group and R^2 is alkyl, cycloalkyl or aryl. Copolymers of N,N-dialkylaminoalkyl acrylates and alkyl acrylates are disclosed in *Product Licensing Index*, Vol. 85, May, 1971, item 8525, pages 30-32. U.S. Pat. No. 3,749,577 relates to polymeric peptizers which can contain acrylic and methacrylic acids polymerized with certain quaternary ammonium salts and Belgian Pat. No. 798,894 issued Oct. 29, 1973 relates to peptizers

of acrylic and methacrylic acids polymerized with certain tertiary amines.

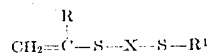
U.S. Pat. No. 3,615,624 and U.S. Pat. No. 3,536,677 disclose sulfur-containing polymers useful as silver halide peptizers. In these polymers, the sulfur groups serve as silver halide interaction sites. However, all the sulfide-bearing peptizers described thus far fall into the general category of acrylic polymers; i.e., the sulfide group is located in a side chain that is attached to the polymer through an acrylic ester or amide linkage. These linkages are susceptible to hydrolysis at high or low pH. Under such conditions, the polymer loses its sulfide-bearing groups and is no longer an effective peptizer. It is evident, therefore, that a peptizing substitute for gelatin which would be resistant to hydrolysis would be highly desirable.

SUMMARY OF THE INVENTION

In accordance with this invention, it has been found that an ethylenically unsaturated monomer containing bis(thioether) linkages can be polymerized with at least one additional monomer to yield polymers which are useful as silver halide peptizers and which are resistant to hydrolysis.

More particularly, the present invention comprises a photographic silver halide emulsion containing a peptizer comprising an addition interpolymer comprising

A. from about 1 to about 20 mole percent of a polymerized monomer having the formula

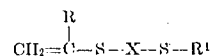


wherein

R is hydrogen or methyl, R^1 is alkyl, cycloalkyl, aryl or substituted aryl and X is alkylene or an alkylene having a cycloalkylene or an arylene group interposed in the backbone of the alkylene chain; and B. from about 80 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

In another aspect, the present invention comprises a photographic element comprising a support having coated thereon at least one photographic silver halide emulsion containing a peptizer comprising an addition interpolymer comprising

A. from about 1 to about 20 mole percent of a polymerized monomer having the formula

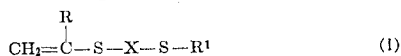


wherein

R is hydrogen or methyl, R^1 is alkyl, cycloalkyl, aryl or substituted aryl and X is alkylene or an alkylene having a cycloalkylene or an arylene group interposed in the backbone of the alkylene chain; and B. from about 80 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The vinyl sulfide monomers employed to form the polymers used in the practice of this invention have the general formula:



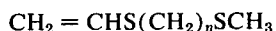
wherein R is hydrogen or methyl.

R¹ can be either an alkyl group, a cycloalkyl group, an aryl group of a substituted aryl group. Where R¹ is an alkyl group, it is preferably one having from one to 10 carbon atoms, especially from one to five carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl or isomers thereof. Where R¹ is cycloalkyl, it preferably contains from five to seven carbon atoms, e.g., cyclopentyl, cyclohexyl, or cycloheptyl; where aryl, it is preferably phenyl or naphthyl. If R¹ is a substituted aryl group, it can be substituted with alkyl groups, again preferably of from one to 10 carbon atoms and most preferably from one to five carbon atoms, as described above; carboxyl groups; alkoxycarbonyl groups, e.g., methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, etc.; and other similar substituents well-known to those of ordinary skill in the art.

In the above formula, X is an alkylene group, preferably having from one to 10 carbon atoms, e.g., methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene and isomers thereof, and, most preferably, having from one to five carbon atoms. X can also be an alkylene group having a cycloalkylene or an arylene group interposed in the backbone of the alkylene chain. Particularly useful cycloalkylene groups contain from five to seven carbon atoms, such as cyclopentylene, cyclohexylene and cycloheptylene. Arylene groups that can be employed include phenylene and phenylene substituted as described above for aryl.

The polymers employed in the practice of this invention contain from about one to about 20 mole percent of at least one of the above described bis(thioether) linkage-containing polymerized monomers. Clearly, in a given polymer, more than one of these monomers can be included provided, of course, that the combined mole percentage does not exceed 20. A more preferred range for the mole percentage of polymerized bis(thioether) linkage-containing monomer is from about 1 to about 15 and the most preferred range for this percentage is from about 3 to about 10.

A particularly useful class of vinyl sulfide monomers which can be polymerized to form the polymers employed in the practice of this invention have the formula:



wherein *n* is an integer of from 1 to 10 and, preferably, from 1 to 4, inclusive.

Any ethylenically unsaturated monomer or monomers which can polymerize with the above described vinyl sulfide monomers without adversely affecting the desired peptizing properties of the final polymer can be used to comprise the remaining 80 to 99 mole percent of the polymer. As exemplary of such monomers, which are known in the art, may be listed: vinyl esters, amides, nitriles, ketones, halides, ethers, alpha-beta unsaturated acids or esters thereof, olefins, diolefins and the like, as exemplified by acrylonitrile, methacrylonitrile; styrene, alpha-methyl styrene, acrylamide, vinyl chloride, methyl vinyl ketone, methyl methacrylate, ethyl acrylate, fumaric, maleic and itaconic esters,

2-chloroethylvinyl ether, 2-acetoacetoxyethyl methacrylate, acrylic acid, sodium methacryloyloxyethyl sulfate, methacrylic acid, 2-(methacryloyloxy) ethyltrimethylammonium methosulfate, dimethylaminoethyl methacrylate, 4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate, N-vinylsuccinamide, N-vinylphthalimide, N-vinylpyrazolidone, butadiene, isoprene, vinylidene chloride, ethylene and the like. Sulfocrylate salts are particularly useful as comonomers in the practice of this invention. For example, sodium 3-methacryloyloxypropane-1-sulfonate, sodium 3-acryloyloxypropane-1-sulfonate, sodium 4-acryloyloxybutane-2-sulfonate and others as described in Dykstra, U.S. Pat. NO. 3,411,911 issued Nov. 19, 1968.

In addition to the foregoing, N-(alkylthioalkyl)-acrylamides and methacrylamides, e.g., N-(1,1-dimethyl-2-methylthioethyl)acrylamide, N-(1,1-dimethyl-3-methylthiopropyl) acrylamide, N-(1,1-dimethyl-3-ethylthiopropyl)acrylamide, N-(1,1-dimethyl-3-ethylthiopropyl)acrylamide and the like, are especially useful comonomers in the preparation of the polymers employed in the practice of this invention.

Where compounds of Formula II are polymerized with 3-acryloyloxypropane-1-sulfonic acid, sodium salt, and other compounds disclosed in Dykstra, U.S. Pat. No. 3,411,911; sodium methacryloyloxyethyl sulfate; or 2-(methacryloyloxy)ethyltrimethylammonium methosulfate, the molar ratio of Formula II monomer to the second monomer is advantageously in the range 1:90 to 1:6, and preferably 1:12 to 1:18.

Other particularly advantageous polymer compositions for use in the present invention include:

35 Terpolymers comprising: (a) a compound of Formula II, (b) acrylic acid, and (c) methacrylic acid provided in molar ratios such as, for example, 1:1:7.

Amphoteric terpolymers comprising: (a) a compound of Formula II, (b) methacrylic acid, and (c) a weakly basic acrylic amine, e.g., 2-(N,N-dimethylamino)ethyl methacrylate, provided in molar ratios of from 1:7:2 to 1:15:5, preferably 1:13.5:4.5 to 1:15:3.

45 Terpolymers comprising: (a) a compound of Formula II, (b) sodium methacryloyloxyethyl sulfate, and (c) an acrylic monomer containing an active methylene group, e.g., 2-aceto-acetoxyethyl methacrylate and like compounds disclosed in Smith U.S. Pats. 3,459,790 and 3,488,708, provided in molar ratios of 0.2:12.2 to 1:10.2.

50 Terpolymers comprising: (a) a compound of Formula II, (b) an alkyl acrylate, e.g., methyl methacrylate, and (c) acrylic acid provided in molar ratios of from 1:4.5:4.5 to 1:10:10, preferably 1:8:10.

55 The copolymers of the invention are generally soluble in water and have inherent viscosities (0.25 g. polymer in 100 ml. 1N sodium chloride at 25°C) ranging from 0.10 to 0.90, desirably 0.19 to 0.50.

60 The preparation of vinylthio(methylthio)methane and 1-vinylthio-2-methylthioethane follow procedures described by K. D. Gollmer, F. H. Muller and H. Ringsdorf, *Makromolekulare Chem.*, 92, 122 (1966) and R. Brown and R. C. G. Moggridge, *J. Chem. Soc.*, 816 (1946), respectively.

65 The temperature at which the polymers described herein are prepared is subject to wide variation since this temperature depends upon such variable features

as the specific monomer used, duration of heating, pressure employed and like considerations. However, the polymerization temperature generally does not exceed about 110°C., and most often it is in the range of about 50° to about 100°C. The polymerization can be carried out in a suitable vehicle, for example, water or mixtures of water with water miscible solvents, as exemplified by methanol, ethanol, propanol, isopropyl alcohol, butyl alcohol, and the like. The pressure employed in the polymerization, if any, is usually only sufficient to maintain the reaction mixture in liquid form, although either superatmospheric or subatmospheric pressures can be used where such use is advantageous. The concentration of polymerizable monomer in the polymerization mixture can be varied widely with concentrations up to about 40 percent, by weight, and preferably, about 20 to about 40 percent, by weight, based on the weight of the vehicle, being satisfactory. Suitable catalysts for the polymerization reaction include, for example, the free radical catalysts, such as hydrogen peroxide, cumene hydroperoxide, water soluble azo type initiators and the like. In redox polymerization systems the usual ingredients can be employed. If desired, the polymer can be isolated from the reaction vehicle by freezing, salting out, precipitation or any other procedure suitable for this purpose.

As indicated in U.S. Pat. No. 3,142,568, issued July 28, 1964, it is sometimes advantageous to include a surface active agent or compatible mixtures of such agents in the preparation of vinyl or addition polymers and in coating photographic materials containing such polymers. Suitable wetting agents include the non-ionic, ionic and amphoteric types as exemplified by the polyoxyalkylene derivatives, amphoteric amino acid dispersing agents, including sulfobetaines and the like. Such wetting agents are disclosed in U.S. Pat. No. 2,600,831 issued June 17, 1952; U.S. Pat. No. 2,271,623 issued Feb. 3, 1942; U.S. Pat. No. 2,275,727 issued Mar. 10, 1942 and U.S. Pat. 2,787,604 issued Apr. 2, 1957; U.S. Pat. No. 2,816,920 issued Dec. 17, 1957 and U.S. Pat. No. 2,739,891 issued Mar. 27, 1956.

The silver halide employed in the preparation of light sensitive coatings described herein includes any of the photographic silver halides as exemplified by silver bromide, silver chloride and silver iodide, or mixed silver halides such as silver chlorobromide, silver bromoiodide, and the like. Very good results are obtained with high contrast silver halide emulsions in which the halide comprises at least 50 mole percent chloride. Preferred emulsions of this type contain at least 60 mole percent chloride; less than 40 mole percent bromide and less than 5 mole percent iodide.

The photographic compositions described herein can be coated on a wide variety of supports. Typical supports include polymeric films such as cellulose acetate film, polyvinyl acetal film, polystyrene film, polypropylene film and other polyolefin film, polycarbonate film, polyethylene terephthalate film and other polyester film as well as glass, paper, wood and the like. Supports such as paper which are coated with alpha-olefin polymers, particularly of alpha-olefins containing 2-10 carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like, give good results.

The emulsions containing the interpolymers can be chemically sensitized with compounds of the sulfur

group as described in Sheppard et al. U.S. Pat. No. 1,623,499 issued Apr. 5, 1927, noble metal salts such as gold salts, reduction sensitized with reducing agents, and combinations of these. The emulsion layers and other layers present in photographic elements made according to this invention can be hardened with any suitable hardener such as aldehyde, mucochloric acid and the like, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxystarch, oxy plant gums and the like. Such hardened layers will have a melting point in water greater than about 150°F and preferably greater than 200°F.

The emulsion can also contain additional additives, particularly those known to be beneficial in photographic emulsions, including for example, stabilizers or antifoggants, particularly the water-soluble inorganic acid salts of cadmium cobalt, manganese and zinc as disclosed in U.S. Pat. No. 2,829,404, the substituted triazindolizines as disclosed in U.S. Pat. Nos. 2,444,605 and 2,444,607, speed increasing materials, absorbing dyes, plasticizers and the like. Sensitizers which give particularly good results in the photographic compositions disclosed herein are the alkylene oxide polymers which can be employed alone or in combination with other materials, such as quaternary ammonium salts, as disclosed in U.S. Pat. No. 2,886,437 or with mercury compounds and nitrogen containing compounds, as disclosed in U.S. Pat. No. 2,751,299.

The interpolymers of this invention can be used in various kinds of photographic emulsions. For example, they can be used in direct positive silver halide emulsions, X-ray and other non-spectrally sensitized emulsions as well as in orthochromatic, panchromatic and infrared sensitive emulsions, particularly those sensitized with merocyanine dyes, cyanine dyes, carbocyanine dyes and the like. Furthermore, these polymers can 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. In addition, these polymers can be used in photographic emulsions containing developers, e.g., polyhydroxybenzenes, as well as in emulsions intended for use in diffusion transfer processes which utilize the non-developed silver halide in the non-image areas of the negative to form a positive by dissolving the underdeveloped 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. Pat. No. 2,352,014; Land U.S. Pat. No. 2,543,181 and Yackel et al. U.S. Pat. No. 3,020,155. The polymers described herein can 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 transfer processes of this type are described in Yutzy U.S. Pat. No. 2,856,142; Land et al. U.S. Pat. No. 2,983,606; Whitmore et al. British Pat. Nos. 904,364 and 840,731 and Whitmore et al. U.S. Pat. No. 3,227,552. These polymers can also be used in unhardened colloid layers, particularly those designed for processing in hardening developers, as disclosed in British Pat. No. 825,544, published Dec. 16, 1959. Silver halide emulsions containing these polymers can be processed in monobath processes such as described in

Haist et al. U.S. Pat. No. 2,875,048 or in stabilization type processes.

The following examples are included for a further understanding of the invention:

EXAMPLE 1

1-Vinylthio-3-methylthiopropene

To 2-mercaptoethanol (212 g., 2.7 M) dissolved in a sodium ethoxide solution [from sodium (61.0 g., 2.65 M) and absolute ethanol (1200 ml)], 3-chloropropyl methyl sulfide (292 g., 2.35 M) was added, and the mixture was stirred at room temperature overnight. The sodium chloride thus formed and ethanol were removed. The residue was fractionated giving the hydroxy compound. b.p. 125°C/0.5 mm, Yield 85 percent.

Analysis Calculated for $C_6H_{14}OS_2$: C, 43.3; H, 8.4; S, 38.6
Found: C, 42.9; H, 8.1; S, 40.1

To 1-methylthio-3-(2-hydroxyethylthio)propane (166 g., 1.0 M) in chloroform (600 ml) was added thionyl chloride (90 ml) over a period of 30 minutes. The mixture was heated at reflux for 30 minutes and the solution was then filtered. The chloroform was removed and the residue fractionated giving 1-methylthio-3-(2-chloroethylthio)propane, b.p. 115°C/2.5 mm, yield 80 percent.

Analysis Calculated for $C_6H_{13}S_2Cl$: C, 39.1; H, 7.0; Cl, 19.2; S, 34.7
Found: C, 39.1; H, 7.3; Cl, 20.1; S, 36.0

To a solution of sodium (17.7 g., 0.77 M) in absolute ethanol (500 ml) at reflux was added 1-methylthio-3-(2-chloroethylthio)propane (142 g., 0.77 M) over a period of 30 minutes. The mixture was refluxed an additional 2 hours and then the sodium chloride and ethanol were removed. Distillation of the residue gave 1-vinylthio-3-methylthiopropene, b.p. 75°C/0.15 mm, yield 60 percent.

Analysis Calculated for $C_6H_{12}S_2$: C, 48.6; H, 8.1; S, 43.3
Found: C, 48.6; H, 8.2; S, 42.7

EXAMPLE 2

1-Vinylthio-4-methylthiobutane

To a solution of methyltetramethylenesulfonium iodide (230 g., 1 M) in absolute ethanol (800 ml) at reflux was added sodium mercaptide solution [from sodium (23.0 g., 1 M), 2-mercaptoethanol (78.0 g., 1M) and absolute ethanol (400 ml)] over a period of 30 minutes. After addition, the solution was heated at reflux for 2 days and then the ethanol was removed on a rotary evaporator. To the residue was added saturated sodium chloride solution (200 ml) and the aqueous solution was extracted three times with chloroform. The chloroform was dried over anhydrous magnesium sulfate, filtered and removed on a rotary evaporator. Distillation of the residue gave 1-methylthio-4-(2-

hydroxyethylthio)butane, b.p. 150°C/2 mm Hg, yield 30 percent.

Analysis Calculated for $C_7H_{16}OS_2$: C, 46.7; H, 8.9; S, 35.6
Found: C, 46.7; H, 8.9; S, 33.8

To 1-methylthio-4-(2-hydroxyethylthio)butane (64.0 g., 0.36 M) in chloroform (250 ml) was added thionyl chloride (45.0 g., 0.4 M) over a period of 30 minutes. After addition, the mixture was heated at reflux for two hours. On cooling to room temperature, Norit, decolorizing carbon (3 g.), was added and stirred for 1 hour. The suspension was filtered, volatiles removed on a rotary evaporator and the residue distilled giving 1-methylthio-4-(2-chloroethylthio)butane b.p. 135°C/2 mm, yield 89 percent.

Analysis Calculated for $C_7H_{15}ClS_2$: C, 42.4; H, 7.6; Cl, 17.9
Found: C, 42.1; H, 7.7; Cl, 20.6; S, 28.4

To a solution of sodium (9.1 g., 0.4 M) in absolute ethanol (250 ml) at reflux was added 1-methylthio-4-(2-chloroethylthio)butane (78.0 g., 0.4 M) over a period of 30 minutes. The mixture was refluxed an additional 2 hours and then the sodium chloride and ethanol were removed. Distillation of the residue gave 1-vinylthio-4-methylthiobutane, b.p. 80°C/0.6 mm, yield 58 percent.

Analysis Calculated for $C_7H_{14}S_2$: C, 51.9; H, 8.6; S, 39.5
Found: C, 51.7; H, 8.6; S, 33.9

EXAMPLE 3

Poly[vinylthio(methylthio)methane-co-sodium 3-acryloyloxypropene-1-sulfonate] (Molar ratio 1:12)

A solution of vinylthio(methylthio)methane (10.0 g., 0.083 mole), sodium 3-acryloyloxypropene-1-sulfonate (216.0 g., 1.0 mole) and 2,2'-azobis(2-methylpropionitrile) (2.5 g.) in absolute ethanol (100 ml) and water (600 ml) was heated at 65°-70°C under nitrogen overnight. The polymer was precipitated from the aqueous solution with acetone (38 liters), filtered, washed, and dried. Yield of white powder was 195 g. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.22.

EXAMPLE 4

Poly[vinylthio(methylthio)methane-co-2-(methacryloyloxy)ethyltrimethylammonium methosulfate] (Molar Ratio 1:12)

A solution of vinylthio(methylthio)methane (4.0 g., 0.0334 M), 2-(methacryloyloxy)ethyltrimethylammonium methosulfate (113 g., 0.4 M) and 2,2'-azobis(2-methylpropionitrile) (1.0 g.) in absolute ethanol (50 ml) and water (300 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was precipitated from the aqueous solution with isopropanol (19 liters), filtered, washed, and dried. Yield 77 g. The

polymer had an inherent viscosity in 1 N sodium chloride solution of 0.23.

EXAMPLE 5

Poly[1-vinylthio-2-methylthioethane-co-sodium 3-acryloyloxypropene-1-sulfonate] (Molar Ratio 1:12)

A solution of 1-vinylthio-2-methylthioethane (12.0 g., 0.083 M), sodium 3-acryloyloxypropene-1-sulfonate (162 g., 0.75 m) and 2,2'-azobis(2-methylpropionitrile) (2.2 g.) in absolute ethanol (100 ml) and water (600ml) was heated at 60°-65°C under nitrogen overnight. The polymer was isolated by precipitation in acetone (19 liters), filtered, washed and dried. Yield - quantitative. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.33.

EXAMPLE 6

Poly[1-vinylthio-2-methylthioethane-co-2-(methacryloyloxy)-ethyltrimethylammonium methosulfate] (Molar Ratio 1:6)

A solution of 1-vinylthio-2-methylthioethane (13.4 g., 0.1 M), 2-(methacryloyloxy)ethyltrimethylammonium methosulfate (170 g., 0.6 M) and 2,2'-azobis(2-methylpropionitrile) (3.0 g) in absolute ethanol (150 ml) and water (600 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was precipitated from the aqueous solution with isopropanol, filtered, washed, and dried. Yield 132 g. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.19.

EXAMPLE 7

Poly[1-vinylthio-3-methylthiopropene-co-sodium 3-acryloyloxypropene-1-sulfonate] (Molar Ratio 1:12)

A solution of 1-vinylthio-3-methylthiopropene (7.4 g., 0.05 M), sodium 3-acryloyloxypropene-1-sulfonate (130 g., 0.60 M) and 2,2'-azobis(2-methylpropionitrile) (1.5 g.) in absolute ethanol (60 ml) and water (360 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was isolated by precipitation in acetone (19 liters), filtered, washed, and dried. Yield 125 g. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.46.

EXAMPLE 8

Poly[1-vinylthio-3-methylthiopropene-co-2-(methacryloyloxy)ethyltrimethylammonium methosulfate] (Molar Ratio 1:6)

A solution of 1-vinylthio-3-methylthiopropene (14.8 g., 0.1 M), 2-(methacryloyloxy)ethyltrimethylammonium methosulfate (170 g., 0.6 M) and 2,2'-azobis(2-methylpropionitrile) (3.0 g.) in absolute ethanol (150 ml) and water (600 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was precipitated from the aqueous solution with isopropanol, filtered, washed, and dried. Yield 140 g. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.24.

EXAMPLE 9

Poly[1-vinylthio-4-methylthiobutane-co-sodium 3-acryloyloxypropene-1-sulfonate] (Molar Ratio 1:12)

A solution of 1-vinylthio-4-methylthiobutane (8.1 g., 0.05 M), sodium 3-acryloyloxypropene-1-sulfonate (130 g., 0.6 M) and 2,2'-azobis(2-methylpropionitrile)

(1.5 g.) in absolute ethanol (60 ml) and water (350 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was isolated by precipitation in isopropanol (19 liters), filtered, washed, and dried. Yield quantitative. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.35.

EXAMPLE 10

Poly[1-vinylthio-4-methylthiobutane-co-2-(methacryloyloxy)ethyltrimethylammonium methosulfate] (Molar Ratio 1:6)

A solution of 1-vinylthio-4-methylthiobutane (16.2 g., 0.1 M) 2-(methacryloyloxy)ethyltrimethylammonium methosulfate (170 g., 0.6 M), and 2,2'-azobis(2-methylpropionitrile) (3.0 g.) in absolute ethanol (200 ml) and water (600 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was precipitated from the aqueous solution with isopropanol, washed, filtered, and dried. Yield 120 g. The polymer had an inherent viscosity in 1 N sodium chloride solution of 0.34.

EXAMPLE 11

Poly[vinylthio(methylthio)methane-co-acrylic acidco-methacrylic Acid] (Molar Ratio 1:1:7)

A solution of vinylthio(methylthio)methane (18.0 g., 0.15 M), acrylic acid (10.8 g., 0.15 M), methacrylic acid (90.3 g., 1.05 M), and 2,2'-azobis(2-methylpropionitrile) (1.0 g.) in absolute ethanol (100 ml) and water (300 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was precipitated from the aqueous solution in water, filtered, washed, and dried. Yield 98.0 g.

EXAMPLE 12

Poly[vinylthio(methylthio)methane-co-methacrylic acid-co-2-(N,N-dimethylamino)ethyl methacrylate] (Molar Ratio 1:13.5:4.5)

A solution of vinylthio(methylthio)methane (2.4 g., 0.02 M), methacrylic acid (23.2 g., 0.27 M), 2-(N,N-dimethylamino)ethyl methacrylate (14.1 g., 0.09 M), and 2,2'-azobis(2-methylpropionitrile) (0.2 g) in dimethyl sulfoxide (170 ml) was heated at 65°-70°C under nitrogen overnight. The polymer was isolated by precipitation in acetone, filtered, washed, and dried. Yield 42.0 g. The polymer had an inherent viscosity in dimethyl sulfoxide of 0.36.

EXAMPLE 13

Poly[vinylthio(methylthio)methane-co-methyl methacrylate-co-acrylic acid] (Molar Ratio 1:9:9)

A solution of vinylthio(methylthio)methane (3.0 g., 0.025 M), methyl methacrylate (22.5 g., 0.225 M), acrylic acid (16.2 g., 0.225 M), and 2,2'-azobis(2-methylpropionitrile) (0.23 g.) in formula 3A alcohol (190 ml) was heated at 60°-65°C under nitrogen overnight. The polymer was isolated by precipitation in 0.1 percent sulfuric acid solution, filtered, washed, and dried. Yield 30 g. The polymer had an inherent viscosity in acetone of 0.26.

The next two examples demonstrate the utility of poly[vinylthio(methylthio)methane-co-sodium 3-acryloyloxypropene-1-sulfonate], prepared as described in Example 3, as a peptizer for photographic silver halide emulsions by showing that when said pep-

tizer is used to prepare a photographic silver halide emulsion, the results obtained are at least as good as, or superior to, those obtained where gelatin is employed as the peptizer in the same type emulsion.

EXAMPLE 14

A high-speed silver bromiodide (94:6) negative emulsion, similar to the type of emulsion described by Trivelli and Smith [PSA J., 79, 330 (1939)] was prepared using poly[vinylthio(methylthio)methane-co-sodium 3-acryloyloxypropene-1-sulfonate] as the peptizer (24 g. polymer per silver mole). Removal of soluble salts was accomplished in a manner similar to that described in U.S. Pat. No. 2,614,928, i.e., by addition of phthalated gelatin (32 g. per silver mole) to the polymer-peptized silver halide emulsion, followed by a lowering of the pH of the emulsion to 3.7. After decantation of the supernatant liquid from the coagulated emulsion, redispersion of the coagulum and repetition of this coagulation-decantation-redispersion cycle, the emulsion was digested to optimum speed, mixed with customarily employed adjuvants and coated on a transparent support so as to yield a coverage of 540 mg/ft² silver and 1,000 mg/ft² gelatin. Exposure (500 W, 5400°K) and development (5 minutes in Kodak Developer DK-50) (20°C) yielded the following sensitometric data as compared to a similarly prepared gelatin-peptized emulsion.

Emulsion	Relative Speed	Gamma	Net Fog (Total Fog Minus Base Density)
Polymer-peptized	298	1.32	0.06
Gelatin-peptized	100	0.87	0.07

EXAMPLE 15

A second silver bromiodide (94:6) ammoniacal emulsion was prepared using poly[vinylthio(methylthio)methane-co-sodium 3-acryloyloxypropene-1-sulfonate] as the peptizer (24 g/mole silver). The emulsion was washed as described in Example 14 and chemically sensitized to optimum speed. Coating, exposure, and processing, as described above, gave sensitometric data compared to a similarly prepared gelatin-peptized control emulsion as follows:

Emulsion	Green Spectral Sensitization	Relative Speed		Gamma		Net Fog	
		to blue light	to green light	to blue light	to green light	to blue light	to green light
Polymer-peptized	yes	158	177	1.60	1.85	0.10	0.10
Polymer-peptized	no	173	0	1.70	0	0.09	0.09
Gelatin-peptized	yes	156	175	1.85	2.30	0.10	0.10
Gelatin-peptized	no	156	0	1.55	0	0.05	0.06

Emulsion	Relative Speed	Gamma	Net Fog
Polymer-peptized	253	1.70	0.07
Gelatin-peptized	233	2.40	0.06

The same emulsions were coated, exposed through a granularity step tablet and processed in Kodak Developer, DK-50, at 20°C, to give similar density vs. log exposure curve shapes. Comparison of the coatings in RMS granularity and relative speed measurements showed that the polymer-peptized emulsion exhibited

a speed/grain advantage over the gelatin-peptized emulsion; i.e., the polymer-peptized emulsion showed a speed gain over the gelatin-peptized emulsion of 0.05 to 0.1 log exposure units for equal grain size.

EXAMPLE 16

This example demonstrates the utility of poly[vinylthio(methylthio)ethane-co-sodium 3-acryloyloxypropene-1-sulfonate] prepared as described in Example 5 as a peptizer for photographic silver halide emulsions.

A polymer peptized emulsion similar to that of Example 15 but using poly[vinylthio(methylthio)ethane-co-sodium-3-acryloyloxypropene-1-sulfonate] as the peptizer was prepared coated as above and compared to a similarly prepared gelatin-peptized control emulsion to give the following sensitometric results:

Emulsion	Relative Speed	Gamma	Net Fog
Polymer-peptized	231	2.25	0.03
Gelatin-peptized	236	2.46	0.04

Results similar to the polymer-peptized emulsion are obtained when the following peptizers are employed:

1. poly[1-vinylthio-3-methylthiopropene-co-sodium 3-acryloyloxypropene-1-sulfonate] (Example 7).
2. poly[1-vinylthio-4-methylthiobutane-co-sodium 3-acryloyloxypropene-1-sulfonate] (Example 9).

EXAMPLE 17

This example demonstrates the utility of a photographic emulsion peptized with a polymer peptizer as described in Example 3 in films requiring spectral sensitization.

A polymer-peptized emulsion similar to that of Example 15 except that the ratio of the monomers was changed to lower by a factor of about 1.5 the percentage of the sulfide-containing component in the final polymer composition was treated with typical green sensitizing cyanine dyes and coated as described in Example 15. Exposure through a color chart, processing in Kodak Developer, DK-50, at 20°C, and comparison with a similarly prepared and processed gelatin-peptized control emulsion gave the following sensitometric results:

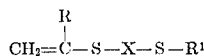
Emulsion	Green Spectral Sensitization	Relative Speed		Gamma		Net Fog	
		to blue light	to green light	to blue light	to green light	to blue light	to green light
Polymer-peptized	yes	158	177	1.60	1.85	0.10	0.10
Polymer-peptized	no	173	0	1.70	0	0.09	0.09
Gelatin-peptized	yes	156	175	1.85	2.30	0.10	0.10
Gelatin-peptized	no	156	0	1.55	0	0.05	0.06

This invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A photographic silver halide emulsion containing a peptizer comprising an addition interpolymer comprising
 - A. from about 1 to about 20 mole percent of a polymerized monomer having the formula

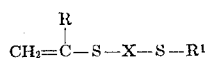
13



wherein

R is hydrogen or methyl,
R¹ is alkyl, cycloalkyl, aryl or substituted aryl and
X is alkylene or an alkylene having a cycloalkylene
or an arylene group interposed in the backbone
of the alkylene chain; and

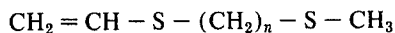
- B. from about 80 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.
2. An emulsion as in claim 1 wherein R¹ is alkyl.
3. An emulsion as in claim 1 wherein X is alkylene.
4. An emulsion as in claim 3 wherein R¹ is alkyl.
5. An emulsion as in claim 1 wherein the polymerized monomer having the formula



comprises from about 1 to about 15 mole percent of the addition interpolpolymer.

6. An emulsion as in claim 5 wherein R¹ is alkyl.
7. An emulsion as in claim 5 wherein X is alkylene.
8. An emulsion as in claim 7 wherein R¹ is alkyl.
9. A photographic silver halide emulsion containing a peptizer comprising an addition interpolpolymer comprising

- A. from about 1 to about 20 mole percent of a polymerized monomer having the formula



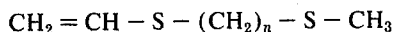
wherein

n is an integer of from 1 to 10 inclusive; and

- B. from about 80 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

10. A photographic silver halide emulsion containing a peptizer comprising an addition interpolpolymer comprising

- A. from about 1 to about 15 mole percent of a polymerized monomer having the formula



wherein

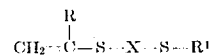
n is an integer of from 1 to 4 inclusive; and

- B. from about 85 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

11. A photographic element comprising a support having coated thereon at least one photographic silver halide emulsion containing a peptizer comprising an addition interpolpolymer comprising

14

- A. from about 1 to about 20 mole percent of a polymerized monomer having the formula

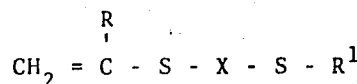


wherein

R is hydrogen or methyl,
R¹ is alkyl, cycloalkyl, aryl or substituted aryl and
X is alkylene or an alkylene having a cycloalkylene
or an arylene group interposed in the backbone
of the alkylene chain; and

- B. from about 80 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

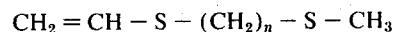
12. An element as in claim 11 wherein R¹ is alkyl.
13. An element as in claim 11 wherein X is alkylene.
14. An element as in claim 13 wherein R¹ is alkyl.
15. An element as in claim 11 wherein the polymerized monomer having the formula



comprises from about 1 to about 15 mole percent of the addition interpolpolymer.

16. An element as in claim 15 wherein R¹ is alkyl.
17. An element as in claim 15 wherein X is alkylene.
18. An element as in claim 17 wherein R¹ is alkyl.
19. A photographic element comprising a support having coated thereon at least one photographic silver halide emulsion containing a peptizer comprising an addition interpolpolymer comprising

- A. from about 1 to about 20 mole percent of a polymerized monomer having the formula



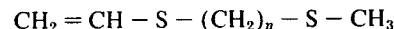
wherein

n is an integer of from 1 to 10, inclusive; and

- B. from about 80 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

20. A photographic element comprising a support having coated thereon at least one photographic silver halide emulsion containing a peptizer comprising an addition interpolpolymer comprising

- A. from about 1 to about 15 mole percent of a polymerized monomer having the formula



wherein

n is an integer of from 1 to 4, inclusive; and

- B. from about 85 to about 99 mole percent of at least one additional polymerized ethylenically unsaturated monomer.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,860,428

DATED : January 14, 1975

INVENTOR(S) : Ignazio S. Ponticello, Ernest J. Perry and
Richard C. Tuites

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 27, "interpolymerr" should read --interpolymer--.

Column 3, line 6, "of" should read --or--.

Column 4, lines 20-21, "N-(1,1-dimethyl-3-ethylthiopropyl) acrylamide" should be deleted; line 49, "0.2:12.2" should read --0.2:12:2--; line 50, "1:10.2" should read --1:10:2--.

Column 6, line 7, --as-- should be inserted after "such".

Column 8, line 22, "found" should be deleted; line 24, "found" should be inserted before "C".

Column 9, line 48, "vinlthio" should read --vinylthio--.

Column 10 line 26, "acidco-" should read --acid-co- --.

Signed and Sealed this

twenty-ninth Day of June 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks