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3,749,577

PHOTOGRAPHIC EMULSIONS CONTAINING POLYMERIC PEPTIZER WITH QUATERNARY AMMONIUM GROUPS

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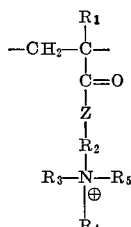
U.S. Cl. 96-114

19 Claims

ABSTRACT OF THE DISCLOSURE

A photographic silver halide emulsion contains a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) At least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound being selected from the group consisting of polymerized vinyl imidazolium compounds, polymerized vinyl pyridinium compounds and polymerized vinyl compounds which in the polymeric chain have the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or methyl,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms, R₃, R₄ and R₅ are either

- (1) independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or
- (2) R₃ and R₄ taken together represent the atoms necessary to complete a 5 or 6 membered heterocyclic ring and R₅ is selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or
- (3) R₃, R₄ and R₅ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring wherein the nitrogen atom which is attached to R₂ has one double bond attached thereto; and

(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photography and more particularly to photographic emulsions containing polymeric materials compatible therewith and methods of preparing

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photographic emulsions utilizing certain polymeric materials.

Description of the prior art

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(vinyl pyrrolidone) 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.

U.S. Pat. 3,615,624 discloses sulfide-bearing polymers useful as silver halide peptizers. Belgian Patent 762,833 discloses certain peptizers which confer the capability of coagulation, washing and redispersion of the silver halide grains by manipulation of the acidity of the medium. Belgian Patent 561,161 describes copolymers of diethylaminoethyl methacrylate and methacrylic acid which are said to be useful as silver halide peptizers. U.S. 3,385,839 describe polymers containing 1-99% by weight of a hydroxy ester of acrylic or methacrylic acid, 99-1% of a quaternary ammonium salt which may, for example, be 2-trimethylammoniummethyl methacrylate methosulphate and up to 80% by weight of other monomers which do not have a cross-linking reaction and which may, for example, be acrylic or methacrylic acid. The patent states that the copolymers can be used as sheet formers, e.g. for the production of coatings, impregnations or adhesive unions, for the surface sizing of paper, as sedimentation auxiliaries, retention agents, antistatic agents, as textile or especially as dyeing auxiliaries, for fixing predominantly acid dyestuffs, in pigment printing, as fungicides, bactericides and disinfectants.

U.S. 2,677,679 describes the preparation of quaternary ammonium polymers of the acrylic type, e.g., methacryloxyethyltrimethylammonium methyl sulfate. Copolymers containing, for example, acrylonitrile, methyl acrylate or methacrylamide are also described.

SUMMARY OF THE INVENTION

One object of this invention is to provide new photographic emulsions of excellent stability. Another object of this invention is to provide novel silver halide dispersions

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of excellent stability. Still another object of this invention is to provide silver halide grains which possess photographically desirable dimensional and crystallographic properties.

A further object of this invention is to provide a novel photographic element containing therein a polymeric gelatin substitute.

Another object of this invention is to provide a novel process for the preparation of photographic elements of high stability containing therein polymeric materials.

Still another object of this invention is to provide polymeric materials which effectively peptize the silver halide formed by the double decomposition reaction from aqueous solutions of alkali halide salts and solutions of soluble silver salts, either in the presence or the absence of ammonia.

Another object of this invention is to provide novel photographic emulsions which exhibit good physical development characteristics.

Still another object of this invention is to provide polymers which function effectively as silver halide peptizers and which, in addition confer the capability of coagulation, washing and redispersion of the silver halide grains.

It is another object of this invention to provide peptizers in which the coagulation, washing and redispersion steps can be accomplished effectively and easily without loss of silver halide grains by simply manipulating the acidity of the medium.

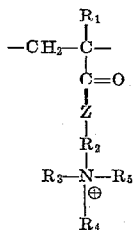
It is still another object of this invention to describe such peptizers which do not contain a sulfide-sulfur and which peptize effectively both in basic and neutral media.

Other objects and advantages of this invention will be apparent from the following description.

In accordance with the present invention, certain polymers of quaternary amine-containing monomers and carboxylic acid monomers are provided which are excellent silver halide peptizers which also confer the capability of a convenient method for the coagulation, washing, and redispersion of the silver halide grains. Coagulation, washing, and redispersion can be effected easily and effectively without loss of silver halide grains by manipulating the acidity of the medium. In addition, these materials peptize effectively under both basic and neutral conditions. More specifically, the polymers of the present invention are effective peptizers under the conditions generally employed for the preparation of emulsions well known in the art as ammoniacal emulsions.

More specifically, the peptizers of the present invention comprise polymers having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound being selected from the group consisting of polymerized vinyl imidazolium compounds, polymerized vinyl pyridinium compounds and polymerized vinyl compounds which in the polymer chain have the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms,

R₃, R₄ and R₅ are either

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(1) independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(2) R₃ and R₄ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring and R₅ is selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(3) R₃, R₄ and R₅ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring wherein the nitrogen atom which is attached to R₂ has one double bond attached thereto; and

(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the mole ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novel polymers of this invention are excellent substitutes for gelatin in photographic applications, since they exhibit not only excellent salt tolerance, but they also exhibit excellent photographic inertness, utility at temperatures below which gelatin can ordinarily be employed in the making of photographic emulsions and permit the production of silver halide grains having morphologies different from those which can be obtained with gelatin. In addition, these copolymers exhibit good compatibility with gelatin which makes it possible to replace only a small part of the gelatin in a photographic composition, depending upon the particular combination of properties desired.

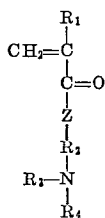
A significant feature of this invention is that the properties which make the novel polymers of this invention suitable gelatin substitutes are very closely related to the concentration and nature of the monomers from which the novel polymers are prepared. Thus, it is critical to the present invention that the molar ratio of quaternary ammonium functionality to carboxyl functionality be no greater than 1:1 and no less than 1:15. Outside of this range, the peptization characteristics of the polymer will be significantly diminished and the advantage which they provide of allowing the use of convenient and particularly effective means of coagulation, washing and redispersion of the silver halide grains will be essentially lost. It is preferred that the molar ratio of quaternary ammonium functionality to carboxyl functionality be in the range of 1:2 to 1:10 and a most preferred range for these ratios is 1:3 to 1:7.

As indicated above, the polymers to be employed in the practice of this invention are prepared by the polymerization of vinyl imidazolium compounds, vinyl pyridinium compounds or compounds which are the quaternary ammonium salts of alkyl amine-substituted amides or esters of acrylic acid or methacrylic acid, this polymerization being carried out in the presence of one or more polymerizable compounds having carboxyl functionality. It is not necessary to the practice of this invention that the monomers employed in the polymerization of the polymers contain the specified functional groups prior to polymerization. These groups can be added after polymerization, if desired.

Generally, the quaternary ammonium salts of this invention are prepared by reacting the corresponding tertiary amines with reagents such as alkyl p-toluenesulfonates, dialkyl sulfates, alkyl halides, propane sultone, butane sultone or the like. As exemplary of some of the tertiary amines with which these reagents may be reacted may be listed vinyl pyridines, such as 2-vinyl pyridine, 4-vinyl pyridine, 2-methyl-5-vinyl pyridine and the like and vinylimidazoles, such as 1-vinylimidazole, 1-vinyl-2-methylimidazole, 1-vinyl-2-ethylimidazole, 1-vinyl-2,5-dimethylimidazole, 1-vinyl-2-methyl-5-hydroxymethyl-

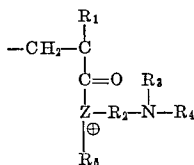
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imidazole, and the like. The quaternizing reagents may also be reacted with tertiary amine-substituted acrylamides, methacrylamides, acrylates and methacrylates having the structure:



Here Z is oxygen or =NH, R₁ is hydrogen or methyl and R₂ is a divalent alkylene radical of 1 to 6 carbon atoms such as, for example, methylene, ethylene, propylene, tetramethylene, pentamethylene, and hexamethylene. R₃ and R₄ may be alkyl radicals of from 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, and isomers thereof. R₃ and R₄ may alternatively be taken together to form a heterocyclic ring compound of 5 or 6 members wherein the other atoms of the ring may be carbon, oxygen or sulfur.

As pointed out above, the polymerized compound having at least one quaternary ammonium moiety can be of the structure:



wherein R₃, R₄ and R₅ are taken together and represent the atoms necessary to complete a heterocyclic ring comprised of 5 or 6 atoms whereby the nitrogen atom which is attached to R₂ has one double bond attached thereto. Exemplary of such species are methacryloyloxyethylpyridinium, methacryloyloxyethylpyridazinium, acryloyloxy-methylpyridinium, acryloyloxyethylpyrazinium and the like. Ring-substituted species of compounds such as the foregoing are also within the scope of this invention.

The carboxylic functionality of the polymers employed in the practice of this invention can be supplied by one or more ethylenically unsaturated mono- or polycarboxylic acids. As exemplary of such acids may be listed acrylic acid, methacrylic acid, itaconic acid, citraconic acid, α-methylene glutaric acid, maleic acid, fumaric acid and the like. Mixtures of these acids may be employed in the polymers of this invention and polymers which contain a mixture of polymerized acrylic and methacrylic acids are particularly preferred.

The silver halide emulsions of this invention can comprise, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide crystals or mixtures thereof. The emulsions may be coarse or fine grain emulsions prepared by any of the well-known techniques, e.g., single jet emulsions such as those described in Trivelli and Smith *The Photographic Journal*, vol. LXXIX, May 1939 (pp. 330-338), double jet emulsions such as Lippman emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. 2,222,264, issued Nov. 19, 1940; Illingsworth U.S. Pat. 3,320,069, issued May 16, 1967; and McBride U.S. Pat. 3,271,157, issued Sept. 6, 1966. Surface image emulsions may be used or internal image emulsions may be used such as those described in Davey et al. U.S. Pat. 2,592,250, issued May 8, 1952; Porter et al. U.S. Pat. 3,206,313, issued Sept. 14, 1965; Berriman U.S. Patent 3,367,778, issued Feb. 6, 1968; and Bacon et al. U.S. Pat. 3,447,927, issued June 3, 1969. If desired, mix-

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tures of surface and internal image emulsions may be used as described in Luckey et al. U.S. Pat. 2,996,382, issued Aug. 15, 1961. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, vol. 12, No. 5, Sept./Oct., 1964, pp. 242-251. Negative type emulsions may be used or direct positive emulsions may be used such as those described in Leermakers U.S. Pat. 2,184,013, issued Dec. 19, 1939; Kendall et al. U.S. Pat. 2,541,472, issued Feb. 13, 1951; Berriman U.S. Pat. 3,367,778, issued Feb. 6, 1968; Schouwenaars British Pat. 723,019, issued Feb. 2, 1955; Illingsworth et al. French Pat. 1,520,821, issued Mar. 4, 1968; Illingsworth U.S. Pat. 3,501,307, issued Mar. 17, 1970; Ives U.S. Pat. 2,563,785, issued Aug. 7, 1951; Knott et al. U.S. Pat. 2,456,953, issued Dec. 21, 1948; and, Land U.S. Pat. 2,861,885, issued Nov. 25, 1958.

The emulsions of this invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. 1,623,499, issued Apr. 5, 1927; Waller et al. U.S. Pat. 2,399,083, issued Apr. 23, 1946; McVeigh U.S. Pat. 3,297,447, issued Jan. 10, 1967; and, Dunn U.S. Pat. 3,297,446, issued Jan. 10, 1967.

The silver halide emulsions of this invention may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. 2,886,437, issued May 12, 1959; Dann et al. U.S. Pat. 3,046,134, issued July 24, 1962; Carroll et al. U.S. Pat. 2,944,900, issued July 12, 1960; and, Goffe U.S. Pat. 3,294,540, issued Dec. 27, 1966.

The silver halide emulsions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. 2,131,038, issued Sept. 27, 1938; and Allen et al. U.S. Pat. 2,694,716, issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. 2,886,437, issued May 12, 1959; and Heimbach et al. U.S. Pat. 2,444,605, issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. 2,728,663, issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. 3,287,135, issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. 3,236,652, issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. 623,448, issued May 18, 1949; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. 2,403,927, issued July 16, 1946; Kennard et al. U.S. Pat. 3,266,897, issued Aug. 16, 1966; and Luckey et al. U.S. Pat. 3,397,987, issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. 2,839,405, issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. 3,220,839, issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. 2,566,263, issued Aug. 28, 1951; and, Yutzy et al. U.S. Pat. 2,597,915, issued May 27, 1952.

The emulsions described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetate) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsions of this invention. For instance, additional spectral sensitization can be obtained by treating the emul-

sion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion as described in Owens et al. British Pat. 1,154,781 issued June 11, 1969. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. 2,526,632, issued Oct. 24, 1950; Sprague U.S. Pat. 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Pat. 2,493,748, issued Jan. 10, 1950; and Taber et al. U.S. Pat. 3,384,486, issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri- or tetranuclear) merocyanines, complex (tri- or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols.

Dyes of the cyanine classes may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei may contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and may be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes may be symmetrical or unsymmetrical and may contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes may contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei may be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups, or heterocyclic nuclei. Combinations of these dyes may be used, if desired. In addition, supersensitizing addenda which do not absorb visible light may be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. 2,933,390, issued Apr. 19, 1960; and Jones et al. U.S. Pat. 2,937,089, issued May 17, 1960.

The sensitizing dyes and other addenda used in the practice of this invention may be added from water solutions or suitable organic solvent solutions may be used. The compounds can be added using various procedures including those described in Collins et al. U.S. Pat. 2,912,343, issued Nov. 10, 1959; McCrossen et al. U.S. Pat. 3,342,605, issued Sept. 19, 1967; Audran U.S. Pat. 2,996,287, issued Aug. 15, 1961 and Johnson et al. U.S. Pat. 3,425,835, issued Feb. 4, 1969.

The emulsions of this invention can be used in elements designed for recording print out images as described in Fallesen U.S. Pat. 2,369,449, issued Feb. 13, 1945 or Bacon et al. U.S. Pat. 3,447,927, issued June 3, 1969; direct print images as described in Hunt U.S. Pat. 3,033,682, issued May 8, 1962 and McBride U.S. Pat. 3,287,137, issued Nov. 22, 1966; elements designed for processing by heat as described in Sorensen et al. U.S. Pat. 3,152,904, issued Oct. 13, 1964; Morgan et al. U.S. Pat. 3,457,075, issued July 22, 1969; Stewart et al. U.S. Pat. 3,312,550, issued Apr. 4, 1967; Colt U.S. Pat. 3,418,122, issued Dec. 24, 1968; Yutzy et al. U.S. Pat. 3,392,020, issued Feb. 8, 1965; Humphlett et al. U.S. Pat. 3,301,678, issued Jan. 31, 1967; and Haist et al. U.S. Pat. 3,531,285, issued Sept. 29, 1970.

The emulsions of this invention can be employed in elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frolich et al. U.S. Pat. 2,376,679, issued May 22, 1945; Jelley et al. U.S. Pat. 2,322,027, issued June 15, 1943; Fierke et al. U.S. Pat. 2,801,171, issued July 30, 1957; Godowsky U.S. Pat. 2,698,794, issued Jan. 4, 1955; Barr et al. U.S. Pat. 3,227,554, issued Jan. 4, 1966;

Graham et al. U.S. Pat. 3,046,129, issued July 24, 1962; Vittum et al. U.S. Pat. 2,360,290, issued Oct. 10, 1944; and Thirtle et al. U.S. Pat. 2,701,197, issued Feb. 1, 1955; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes et al. U.S. Pat. 2,252,718, issued Aug. 19, 1941; Carroll et al. U.S. Pat. 2,592,243, issued Apr. 18, 1952; and Schwan et al. U.S. Pat. 2,950,970, issued Aug. 30, 1966; and in false-sensitized color materials such as those described in Hanson U.S. Pat. 2,763,549 issued Sept. 18, 1956.

The silver halide emulsions of this invention can be used for making lithographic printing plates such as by the colloid transfer of undeveloped and unhardened areas of an exposed and developed emulsion to a suitable support as described in Clark et al. 2,763,553 issued Sept. 18, 1956; to provide a relief image as described in Woodward U.S. Pat. 3,402,045 issued Sept. 17, 1968 or Spencer U.S. Pat. 3,053,658 issued Sept. 11, 1962; to prepare a relief printing plate as described in Baxter et al. U.S. Pat. 3,271,150 issued Sept. 6, 1966; to prepare a silver salt diffusion transfer plate as described in Hephher et al. British Pat. 934,691 issued Aug. 21, 1963 and Agfa British Pat. 883,846 issued Dec. 6, 1961.

The silver halide emulsions of this invention can be used to prepare photographic elements designed for developing out processing, or print out exposure as described in Fallesen U.S. Pat. 2,369,449 issued Feb. 13, 1945; or for photodevelopment as described in Hunt U.S. Pat. 3,033,678 issued May 8, 1962, McBride U.S. Pat. 3,287,137 issued Nov. 22, 1966, and Colt U.S. Pat. 3,418,122 issued Dec. 24, 1968.

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

EXAMPLE 1

Poly[2 - (methacryloyloxy)ethyltrimethyl ammonium methosulfate-comethacrylic acid - coacrylic acid] (mole ratio 1:3.5:0.5) as a silver halide peptizer

Polymer preparation.—A flask is charged with 198.1 g. (0.70 mole) of 2-(methacryloyloxy)ethyltrimethylammonium methosulfate, 210.7 g. (2.45 moles) of methacrylic acid 25.2 g. (0.35 mole) of acrylic acid, 1736 ml. distilled water, 4.34 g. of potassium persulfate and 1.45 g. of sodium metabisulfite. After purging the solution with nitrogen for 20 minutes and heating to 60° C. overnight, a clear, viscous dope is formed which has a pH of 2.1. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a brittle white polymer results. The inherent viscosity of the polymer is determined using a 0.25 percent solution of the polymer in 0.1 M NaCl at 25° C. The inherent viscosity is found to be 0.83.

The remainder of the dope is treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4. At this point the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 10.2% solids.

Neutral silver halide emulsion.—A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as described by Merrill and Perry in Example 1 of British Pat. 1,057,976:

A breaker is charged with a solution of 5.0 g. (solids) of the above polymer, 30.37 g. of potassium bromide, 0.93 g. of potassium iodide, and a total of 278 ml. of distilled water. After adjusting the pH of the solution to 6.0, it is stirred continuously at 50° C. as a solution of 35.37 g. of silver nitrate in 185 ml. of water is added at constant rate over 18 minutes. The smooth dispersion thus formed is then cooled to room temperature.

A 50 ml. sample of the dispersion is then stirred at room temperature as the pH is lowered to 4.4 with dilute sulfuric acid. The dispersion coagulates and settles into a compact pad at the bottom of the vessel when the stirring is stopped. After a few minutes, the clear, supernatant liquid is decanted and replaced with distilled water. The decanting process is very convenient and effective and occurs without loss of precipitate. Upon stirring, the precipitate breaks up into small discrete particles. Raising the pH back to 6.0 with dilute aqueous sodium hydroxide causes rapid reformation of a smooth dispersion which does not settle out on standing. The process of coagulation, decantation, and redispersion are repeated twice more, occurring just as conveniently and effectively as the first time.

Ammoniacal silver halide emulsion.—An ammoniacal silver halide emulsion is also prepared in the presence of this polymer in essentially the same manner as described by Smith and Perry in Example 6 of U.S. 3,415,653.

A solution of 3.82 g. of silver nitrate in 16 ml. of water is treated with just enough ammonium hydroxide to redissolve the precipitate which forms at the beginning of the addition. The clear solution thus formed comprises 20 ml. and is added to 30 ml. of an aqueous solution containing 3.14 g. of potassium bromide, 0.1 g. of potassium iodide, and 1.0 g. (solids) of the above polymer. The addition is carried out with stirring at 45° C. over a period of about 85 seconds. Stirring is continued at 45° C. an additional 39 minutes and then the system is cooled to room temperature. A smooth homogeneous emulsion results which fails to settle out on standing. Its pH as made is 10.1.

The ammoniacal emulsion is then tested in the same manner as the neutral emulsion above for coagulation, washing, and redispersion. It behaves similarly.

EXAMPLE 2

Example 1 is repeated except that poly[2-(methacrylamido)ethyltrimethylammonium methosulfate - co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5) is substituted on an equal weight basis for the polymer employed therein. The behavior and properties of this system are substantially equivalent to those described in Example 1.

EXAMPLE 3

Poly[2-(methacryloyloxy)ethyltrimethylammonium tosylate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5) as a silver halide peptizer

Polymer preparation.—A flask is charged with 137.2 g. (0.40 mole) of 2-(methacryloyloxy)ethyltrimethylammonium tosylate, 120.4 g. (1.40 moles) of methacrylic acid, 14.4 g. (0.20 mole) of acrylic acid, 1088 ml. of distilled water, 4.96 g. of potassium persulfate, and 1.85 g. of sodium metabisulfite. After purging the system with nitrogen for 20 minutes and heating to 60° C. overnight, a clear, viscous dope is formed which has a pH of 2.2. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a white polymer results. The inherent viscosity as determined by the method of Example 1 is 1.06.

The remainder of the dope is treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4.5. At this point the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 9.4% solids.

Neutral silver halide emulsion.—A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described for the neutral emulsion in Example 1. The nature and behavior of the

resulting emulsion are essentially the same as described in Example 1.

EXAMPLE 4

Poly[2 - (methacryloyloxy)ethyltrimethylammonium methosulfate-co-acrylic acid] (mole ratio 1:4) as a silver halide peptizer

Polymer preparation.—A flask is charged with 14.15 g. (10.05 moles) of 2-(methacryloyloxy)ethyltrimethylammonium methosulfate, 14.40 g. (0.20 mole) of acrylic acid, 114 ml. distilled water, 0.29 g. of potassium persulfate, and 0.10 g. sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 60° C. overnight, a clear, very viscous dope is formed. It is diluted with 172 ml. of distilled water and found to have a pH of 2.2. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying, a white polymer results.

The inherent viscosity of a 0.25% solution of this polymer in 1 M NaCl is 1.11.

The remainder of the dope is treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4.2. At this point, the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 8.8% solids.

Neutral silver halide emulsion.—A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described for the neutral emulsion in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

Ammoniacal silver halide emulsion.—An ammoniacal silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

EXAMPLE 5

Poly[1,2 - dimethyl - 5-vinylpyridinium methosulfate-co-methacrylic acid-co-acrylic acid] (mole ratio 1.3.5:0.5) as a silver halide peptizer

Polymer preparation.—A flask is charged with 122.5 g. (0.50 mole) of 1,2-dimethyl-5-vinylpyridinium methosulfate, 150.5 g. (1.75 moles) of methacrylic acid, 18.0 g. (0.25 mole) of acrylic acid, 1100 ml. of distilled water, 2.91 g. of potassium persulfate, and 0.97 g. of sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 60° C. overnight, a clear, very viscous dope is formed which has a pH of 2.1. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a white polymer results. The inherent viscosity of the polymer is determined by the method of Example 1 and is found to be 1.17.

The remainder of the dope is diluted with 1700 ml. of water and treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4.8. At this point the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 7.5% solids.

Neutral silver halide emulsion.—A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described for the neutral emulsion in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

Ammoniacal silver halide emulsion. An ammoniacal silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described

in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

EXAMPLE 6

Poly[1,2-dimethyl-5-vinylpyridinium tosylate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5) as a silver halide peptizer

Polymer preparation.—A flask is charged with 61.0 g. (0.20 mole) of 1,2-dimethyl-5-vinylpyridinium tosylate, 60.2 g. (0.70 mole) of methacrylic acid, 7.2 g. (0.10 mole) of acrylic acid, 408 ml. distilled water, 25 ml. of ethanol, 1.27 g. of potassium persulfate, and 0.42 g. of sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 60° C. for 8 hours, a polymer is formed which precipitates from solution. A small sample of the sticky rubbery polymer lump is washed thoroughly in water and dried under vacuum at 40° C. The inherent viscosity by the method of Example 1 is 0.40.

After washing the remainder of the polymer thoroughly in water, it is dissolved in water by stirring and the addition of enough dilute aqueous sodium hydroxide to bring the pH to 6.0. The resulting clear, viscous dope contains 10.6% solids.

Neutral silver halide emulsion.—A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described for the neutral emulsion in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

Ammoniacal silver halide emulsion.—An ammoniacal silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

EXAMPLE 7

Poly[3-methyl-1-vinylimidazolium methosulfate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:2:2) as a silver halide peptizer

Polymer preparation.—A flask is charged with 8.8 g. (0.04 mole) of 3-methyl-1-vinylimidazolium methosulfate, 6.88 g. (0.08 mole) of methacrylic acid, 5.76 g. (0.08 mole) of acrylic acid, 82 ml. of distilled water, 0.20 g. of potassium persulfate, and 0.07 g. of sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 80° C. for 4 hours, a hazy, viscous dope forms. It is diluted with 100 ml. of distilled water and is found to have a pH of 2.2. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a sticky, rubbery polymer results. The inherent viscosity as measured by the method of Example 4 is 0.49.

Neutral silver halide emulsion.—A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described for the neutral emulsion in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

Ammoniacal silver halide emulsion.—An ammoniacal silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as that described in Example 1. The nature and behavior of the resulting emulsion are essentially the same as described in Example 1.

EXAMPLE 8

This example shows that the speed/fog ratio, obtainable in a high-speed negative emulsion containing gelatin-peptized grains dispersed in gelatin, can be satisfactorily matched by replacing the peptizing gelatin, used during the preparation of the emulsion, with poly[2-(methacrylo-

xyloxy)ethyltrimethylammonium methosulfate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5).

A high speed silver bromide (94:6) negative emulsion, similar to the type of emulsion described by Trivelli and Smith (The Photographic Journal, vol. LXXIX, May 1939, pp. 330-338) is prepared using poly[2-(methacryloxy)ethyltrimethylammonium methosulfate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5) as the peptizer. Removal of soluble salts is accomplished by lowering the pH of the emulsion to 4.1 with dilute sulfuric acid, allowing the silver halide coagulum to settle, removing the supernatant liquid by siphoning, replacing the supernatant liquid with distilled water containing 101 g. potassium nitrate per silver mole, redispersing the emulsion by raising the pH to 6.4, and repeating the above coagulation-redispersion cycle two more times. The emulsion is then digested to optimum speed, dispersed in gelatin (130 g. gelatin per silver mole), mixed with customarily employed in adjuvants and coated on a transparent support so as to yield a silver coverage of 540 mg./ft.² silver and 650 mg./ft.² gelatin. Exposure (500 w., 5400° K.) and development in an Elon-hydroquinone developer (Kodak DK-50 Developer) for five minutes at 20° C. yielded the following sensitometric data as compared to a similarly prepared gelatin-peptized emulsion. See Table 1.

TABLE 1

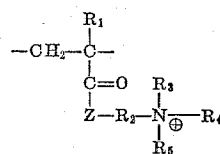
Emulsion	Relative speed	Gamma	Net fog (Total fog minus base density)
Polymer-peptized	100	1.15	0.06
Gelatin-peptized	100	0.87	0.06

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.

What is claimed is:

1. A photographic silver halide emulsion containing a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound being selected from the group consisting of polymerized vinyl imidazolium compounds, polymerized vinyl pyridinium compounds and polymerized vinyl compounds which in the polymeric chain have the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms;

R₃, R₄ and R₅ are either:

(1) independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(2) R₃ and R₄ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring and R₅ is selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

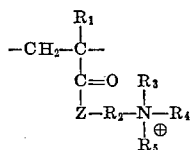
(3) R₃, R₄ and R₅ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring wherein the nitrogen atom which is attached to R₂ has one double bond attached thereto; and

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(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

2. A photographic silver halide emulsion containing a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety having in the polymer chain the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms,

R₃, R₄ and R₅ are selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms; and

(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical such that, the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

3. The photographic silver halide emulsion of claim 2 wherein R₁ is a methyl radical.

4. The photographic silver halide emulsion of claim 2 wherein R₃, R₄ and R₅ are methyl radicals.

5. The photographic silver halide emulsion of claim 3 wherein R₃, R₄ and R₅ are methyl radicals.

6. The photographic silver halide emulsion of claim 2 wherein Z is oxygen.

7. The photographic silver halide emulsion of claim 5 wherein Z is oxygen.

8. The photographic silver halide emulsion of claim 2 wherein R₂ is an ethylene radical.

9. The photographic silver halide emulsion of claim 7 wherein R₂ is an ethylene radical.

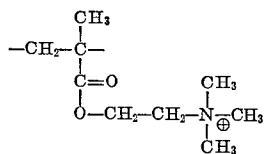
10. The photographic silver halide emulsion of claim 2 wherein the ethylenically unsaturated compound having at least one carboxyl radical is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

11. The photographic silver halide emulsion of claim 9 wherein the ethylenically unsaturated compound having at least one carboxyl radical is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

12. The photographic silver halide emulsion of claim 2 wherein the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:2-10.

13. A photographic silver halide emulsion containing a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound having in the polymer chain the structure:



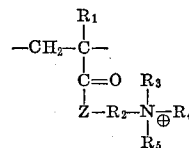
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and

(B) at least one polymerized ethylenically unsaturated compound selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

14. A method of preparing a photographic silver halide emulsion comprising precipitating a photographic silver halide in the presence of a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety said polymerized compound being selected from the group consisting of polymerized vinyl imidazolium compounds, polymerized vinyl pyridinium compounds and polymerized vinyl compounds which in the polymer chain have the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms,

R₃, R₄ and R₅ are either:

(1) independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

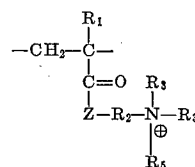
(2) R₃ and R₄ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring and R₅ is selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(3) R₃, R₄ and R₅ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring wherein the nitrogen atom which is attached to R₂ has one double bond attached thereto; and

(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

15. A method of preparing a photographic silver halide emulsion comprising precipitating a photographic silver halide in the presence of a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound having in the polymer chain the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms,

R₃, R₄ and R₅ are independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, and

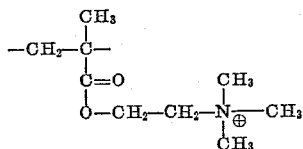
(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such

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that, the molar ratio in the polymer compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

16. A method of preparing a photographic silver halide emulsion comprising precipitating a photographic silver halide in the presence of a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound having in the polymer chain the structure:

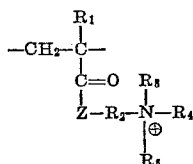


and

(B) at least one polymerized ethylenically unsaturated compound selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

17. A photographic element comprising a support having coated thereon a photographic silver halide emulsion containing a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound being selected from the group consisting of polymerized vinyl imidazolium compounds, polymerized vinyl pyridinium compounds and polymerized vinyl compounds which in the polymer chain have the structure:



wherein

Z is oxygen or =NH,

R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms,

R₃, R₄ and R₅ are either:

(1) independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(2) R₃ and R₄ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring and R₅ is selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms or,

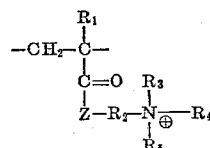
(3) R₃, R₄ and R₅ taken together represent the atoms necessary to complete a 5- or 6-membered heterocyclic ring wherein the nitrogen atom which is attached to R₂ has one double bond attached thereto; and

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(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

18. A photographic element comprising a support having coated thereon a photographic silver halide emulsion containing a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

(A) at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound having in the polymer chain the structure:



wherein

Z is oxygen or =NH,

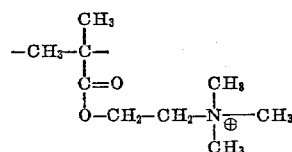
R₁ is hydrogen or a methyl radical,

R₂ is a divalent alkylene radical of 1 to 6 carbon atoms,

R₃, R₄ and R₅ are independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms and

(B) at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the molar ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

19. A photographic element comprising a support having coated thereon a photographic silver halide emulsion containing a peptizer comprising a polymer having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:



and

(B) at least one polymerized ethylenically unsaturated compound selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

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RONALD H. SMITH, Primary Examiner

U.S. Cl. X.R.

96-33, 35, 87