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2,863,769

PROCESS OF PREPARING SILVER HALIDE DISPERSIONS

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8 Claims. (Cl. 96—114)

This invention relates to photography and more particularly to the preparation of dispersions of light sensitive silver halide in a water-permeable synthetic amphoteric copolymer having protective colloid properties. Still more particularly, it relates to a process of removing soluble salts and water from aqueous dispersions of silver halide precipitated in such a copolymer.

Various synthetic amphoteric copolymers have been investigated for use as binding agents for silver halide grains. These copolymers, in general, differ from gelatin in that they generally are not thermally gellable and hence the soluble salts resulting from the precipitation of silver halide in the copolymer cannot be removed by the usual setting, noodling and washing steps used with silver halide which has been precipitated in gelatin.

Several methods have been proposed for removing soluble salts from silver halide which has been precipitated in synthetic amphoteric copolymers. They include:

- (1) Mixing with a thermally gellable material (e. g., gelatin) and washing in the conventional manner,
- (2) Insolubilizing the dispersion by the addition of an organic solvent, e. g., acetone and ethanol,
- (3) Coagulation with acid-insoluble organic resins containing COOH groups, and
- (4) Coagulation with acid-insoluble gelatin derivatives.

Method (1) is time consuming and uneconomical and method (2) requires solvent recovery apparatus in large-scale operations, for purposes of economy. Methods (3) and (4) require the use of large amounts of the materials, e. g., 33 to 200% by weight of the amphoteric copolymer.

An object of this invention is to provide a new process of preparing dispersions of silver halide in synthetic amphoteric colloids which dispersions are relatively free from water-soluble salts. A related object is to provide a process of precipitating silver halide in aqueous synthetic amphoteric colloid solutions and removing water-soluble salts and water therefrom. Another object is to provide such a process which is simple and effective. Yet another object is to provide such a process of precipitating silver halides in synthetic amphoteric colloids and removing water-soluble salts which do not require chilling, noodling and washing steps. A further object is to provide such a process which can be carried out economically on a large scale. Still other objects will be apparent from the following description of the invention.

The process of this invention, in its broad aspect, comprises precipitating a synthetic amphoteric colloid containing dispersed silver halide from an aqueous solution with a water-soluble, acid-soluble polymer containing periodically occurring anion groups, which is soluble in water at 25° C. and in 1% nitric acid to the extent of at least 1% by weight, and removing the soluble salts and water from the precipitate by elutriation. The precipitate or coagulum is finely divided and contains the silver halide grains which were enveloped by the synthetic amphoteric copolymer which now exists in the form of a chemical complex with the polymer containing anion

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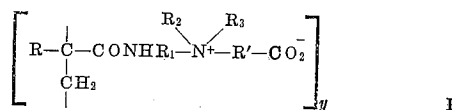
groups. It can be redispersed readily in a synthetic amphoteric copolymer or other water-permeable colloid by raising the pH of an aqueous medium containing it and stirring the mixture. Redispersion can be accomplished without the substantial addition of water or solvent, thus yielding a washed high solids photographic emulsion, in a simple manner.

In a preferred aspect of the invention, the process comprises admixing a water-soluble silver salt and a water-soluble halide in an aqueous solution containing a synthetic amphoteric polymer having protective colloid properties, adding an aqueous solution containing the water-soluble, acid-soluble polymer having periodically occurring anion groups, adding an aqueous solution of an acid to reduce the pH to a value below the isoelectric point of the amphoteric polymer, usually between 2 and 3 at a temperature between 65° and 100° C., allowing the precipitate or coagulum, which consists of a chemical complex formed between the acid soluble polymer and the amphoteric polymer having dispersed therethrough light-sensitive silver halide, to settle and removing the soluble salts and water by elutriation.

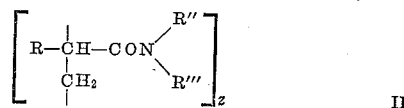
Any of the usual water-soluble silver salts can be used in the precipitation, e. g., silver nitrate, silver sulfamate, silver citrate and silver acetate or mixtures of two or more of such salts. Similarly any of the usual water-soluble halides can be used in the precipitation. Among such halides are sodium, potassium, and ammonium and chlorides, bromides and iodides. When two or more different halides are used, mixed silver salts are precipitated, e. g., silver chlorobromide and silver iodobromide. If desired, two or more soluble chlorides or bromides or iodides can be used.

In a further aspect of the invention, the coagulated complex (coagulum), after removal of the soluble salts and water, is redispersed by adding an aqueous solution containing an alkaline material, such as sodium or potassium hydroxide, to raise the pH above the isoelectric point. The particular pH used is dependent upon factors which include the specific nature of the amphoteric polymer and the salt and polyanion concentration. After redispersion is accomplished, the mixture is admixed with additional synthetic amphoteric polymer or other water-permeable colloid binding agent for silver halide grains.

A class of synthetic amphoteric polymers useful in practicing the invention is the addition copolymers described in assignee's Shacklett U. S. application Ser. No. 415,163 filed March 9, 1954. These copolymers contain periodically occurring intralinear units of the formulae:



wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent, aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and

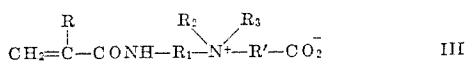


wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl. In the above formulae, y and z represent the number of units in the copolymer molecules. These copolymers may contain one, two or more different

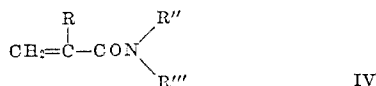
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units of Formula I and one, two or more different units of Formula II.

The copolymers described in the previous paragraph can be made by the addition polymerization processes described in the aforesaid application (Ser. No. 415,163). This process comprises copolymerizing in a suitable solvent, at a temperature above the freezing point of the solvent and below its boiling point, and preferably from 40° C. to 70° C., for a period of 1 to 50 hours or more, (1) one, two or more ethylenically unsaturated amides of the general formulae:



wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent, aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated aliphatic hydrocarbon radical of 1 to 4 carbon atoms, and (2) one, two or more ethylenically unsaturated amides of the general formula:

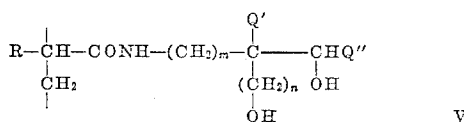


where R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl. In these two formulae, as well as I and II, the alkyl radicals include methyl, ethyl, propyl and isopropyl.

The reactants (1) and (2) are copolymerized in the proportions of 5 to 80 and preferably 5 to 50 mole percent of the former to 95 to 20 and preferably 95 to 50 mole percent, respectively, of the latter. The polymerization can be carried out in the presence of a suitable solvent or diluent, e. g., water or mixtures of water with water-miscible solvents, e. g., methanol, ethanol, propanol, isopropyl alcohol, and tertiary-butyl alcohol, and may be accelerated by heat, actinic light of wave-lengths between 1800 and 7000 Å. U., and/or an addition polymerization initiator, e. g., an organic or inorganic peroxide, an alkali metal or ammonium persulfate, an azonitrile, or an azoamidine hydrochloride. The polymerization preferably is carried out at 40° C. to 70° C., since polymers of especially useful molecular weight can be obtained within these ranges. At higher temperatures lower molecular weight polymers are formed, and at lower temperatures polymers of higher molecular weight are formed.

Various concentrations of monomers may be present in the solvent medium and concentrations from 1/2 to 2 molar are preferred. It has been found that an increase in monomer concentration results in copolymers of higher molecular weight, while a decrease in polymer concentration results in copolymers of lower molecular weight.

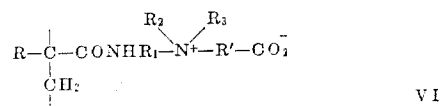
Another class of useful polymers is the copolymers described in assignee's Shacklett U. S. application Ser. No. 415,161 filed March 9, 1954. These copolymers, which can be made by the processes described in said application including any application referred to therein, contain periodically occurring intralinear units of the formulae:



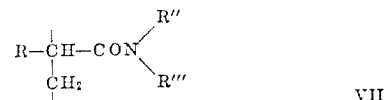
wherein R is a member taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, Q' and Q'' are members taken from the group consisting of hydrogen and alkyl of 1 to 3 carbon atoms,

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m is 0, 1, 2, 3, or 4, and n is 0 or 1 and the sum of m and n is at least 1;

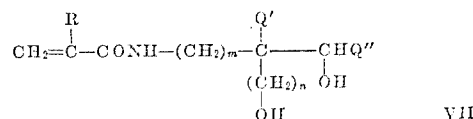


wherein R is a member taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated divalent aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ is an alkyl radical of 1 to 3 carbon atoms, R₃ is an alkyl radical of 1 to 3 carbon atoms, and R' is a saturated divalent aliphatic hydrocarbon radical of 1 to 4 carbon atoms; and

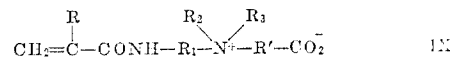


wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl. These copolymers may contain one, two or more different units of each of Formulae V, VI, and VII. Suitable alkyl radicals comprehended by the above formulae include methyl, ethyl, propyl, and isopropyl. In the case of (CH₂)_m, the useful radicals are methylene, bimethylene, trimethylene, and tetramethylene.

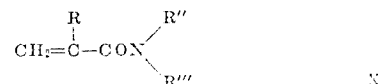
The addition copolymers described in the previous paragraph can be prepared by copolymerizing in solution in a suitable solvent, at a temperature above the freezing point of the solvent and below its boiling point and preferably from 40° to 70° C., for a period of 1 to 50 hours or more, (1) one, two, or more ethylenically unsaturated amides taken from the group consisting of (a) those which have the general formula:



wherein the various radicals have the above significance; and (b) the hydrolyzable acetal derivatives of the dihydroxy compounds of Formula VIII which yield the latter compounds on hydrolysis, (2) one, two, or more ethylenically unsaturated amides taken from the group consisting of (a) those which have the general formula:



wherein the various radicals have the above significance; and (b) the hydrolyzable ester halide derivatives of the betaines of formula IX which yield the latter compounds on hydrolysis, and (3) one, two, or more ethylenically unsaturated amides of the general formula:



wherein the various radicals have the above significance.

The acetals contemplated in 1 (b) above are those which can be purified by distillation. Such acetals are those obtainable from carbonyl compounds of 1 to 7 carbon atoms and are described in assignee's Shacklett U. S. application Serial No. 389,872, filed November 2, 1953.

The ester halide derivatives contemplated in 2 (b) above are those which are obtainable from α-halogenated esters and are described in U. S. application Ser. No. 389,873, filed November 2, 1953 (U. S. Patent 2,777,872, Jan. 15, 1957).

The reactants (1), (2), and (3) are copolymerized in the proportions of 5 to 60, 5 to 60 and 30 to 90 mol percent, respectively. The proportions are adjusted within

these ranges to obtain the desired properties in particular copolymers designed for specific applications. The polymerization, as stated above, is carried out in a suitable solvent, e. g., water or mixtures of water with a water-miscible solvent, including methanol, ethanol, propanol, isopropyl alcohol, and tertiary butyl alcohol, and may be accelerated by heat, actinic light of wavelengths between 1800 and 7000 A. U. and an addition polymerization initiator, or a combination of these conditions. Suitable initiators include organic and inorganic peroxides, alkali metal and ammonium persulfates, azonitriles and azoamidine hydrochlorides. The polymerization preferably is carried out between 40° C. and 70° C. since polymers of suitable molecular weight are obtained within this range. At higher temperatures there is a tendency for lower molecular weight polymers to be formed, and at lower temperatures higher molecular weight polymers are formed.

A large number of other synthetic amphoteric polymers which are useful in accordance with the present invention are the addition copolymers described in U. S. patents Jones 2,508,718, Azorlosa 2,592,107 and Jones 2,611,763. They contain free amine groups and free acid groups, and have good protective colloid properties.

Various water-soluble, acid-soluble organic polymers, containing a multiplicity of anion groups which are soluble in water at 25° C. to the extent of at least 1% by weight and in 1% nitric acid to the extent of at least 1% by weight, are available for use in accordance with the present invention as coagulants. The acid groups in these polymers have at least one replaceable hydrogen atom and include carboxylic, sulfonic, sulfuric, phosphoric, phosphonic, and phosphinic acid groups. The polymers may be added in the form of the free acids or in the form of a water-soluble salt, e. g., the sodium, potassium, or ammonium salts.

The preferred coagulants are the polyvinyl acetals containing sulfonic acid groups, e. g., those made from o-sulfobenzaldehyde, alpha- and beta-sulfonaphthaldehydes, beta-sulfopropionaldehyde, and polyvinyl alcohol or a partially hydrolyzed polyvinyl acetate, etc. Polyvinyl acetals of these types and their preparation are described in U. S. Patents 2,462,527, 2,609,290, and German Patent 643,650. They should contain sufficient anion groups to be acid-soluble.

Redispersion of the silver halide can usually be carried by raising the pH to about 6 to 7 by the addition of an alkaline compound, e. g., aqueous sodium or potassium hydroxide, sodium or potassium carbonate or other alkaline compound which does not have an adverse photographic effect. By accomplishing redispersion with a small amount of water a washed, high silver halide content emulsion can be obtained in a simple operation.

Still other useful water-soluble, acid-soluble polymers containing periodically occurring anion groups are the polyvinyl phosphates described in U. S. Patent 2,609,360 and the polystyrene sulfonic acids of U. S. Patent 2,533,210, which have the requisite solubility characteristics. These compounds are generally used in the form of the sodium, potassium and ammonium salts.

In general, the coagulant polymers have molecular weights from 5,000 to 50,000. The synthetic amphoteric polymers likewise are macromolecular and have molecular weights from 5,000 to 70,000 or more. The former can be used in an amount of 5 to over 30% and preferably 10 to 30% by weight of the weight of the amphoteric polymer.

The isoelectric points of the amphoteric polymers disclosed in the examples were determined by stirring 50 ml. of a 1% aqueous solution of the polymer with 10 ml. of a 50:50 mixture of the hydroxyl form of an exchange resin, e. g., "Amberlite" IRA400, made by Rohm & Haas Company, Philadelphia, Pennsylvania, and the acid form of exchange resin, "Amberlite" IR120, made by Rohm and Haas Company, Philadelphia, Pennsylvania. The

value at which the pH became constant was recorded as the isoelectric point of the material.

The invention will be further illustrated but is not intended to be limited by the following examples.

EXAMPLE I

To 84 grams of an unwashed emulsion containing 60 millimoles of silver halides composed of 1.5 mol percent iodide and 98.5 mol percent bromide, 2 grams of a copolymer prepared as described in Example III of Shacklett application Serial No. 415,163 filed March 9, 1954 from a mixture of methacrylamide and N,2-methacrylamidoethyl-N,N-dimethyl-β-aminopropionate betaine, in the mol ratio of 9:1 respectively (isoelectric pt.=9.2) and 88 millimoles of the water-soluble inorganic salts resulting from the precipitation of the silver halides from water-soluble silver and halide salts was added 12 ml. of a 2½% aqueous liquor of a water and acid-soluble partial acetal of polyvinyl alcohol and o-sulfobenzaldehyde containing 5% sulfur. To the resulting emulsion at a temperature of 80° F. and a pH of 6.3, there was added 200 ml. of a dilute aqueous nitric acid solution at 80° F. to lower the pH to 2.1. A rapidly settling coagulate of the silver halide and the copolymer-polyanion complex formed and the soluble inorganic salts were removed by elutriation. The coagulated emulsion was then redispersed by raising the pH above 6 with dilute aqueous NaOH and stirring at room temperature. The resulting emulsion when mixed with additional copolymer and/or gelatin is useful in the preparation of a photographic silver halide emulsion layer.

EXAMPLE II

To 63 grams of unwashed emulsion containing 33 millimoles of silver halides composed of 3.4 mol percent iodide and 96.6 mol percent bromide, 0.5 gram of the amphoteric copolymer described in Example I, and 47 millimoles of water-soluble inorganic salts resulting from the precipitation of the silver halides from water-soluble silver and halide salts there was added 20 ml. of a 0.5% by weight aqueous solution of carrageenin, a natural polysulfate of polygalactan containing 25% sulfur ("Seakem" Type 8). To the resulting mixture at a room temperature of 80° F. and a pH of 6.3, there was added 65 ml. of water and enough 3N H₂SO₄ to lower the pH to 3.6. A coagulate of the silver halide and the copolymer-polysulfate complex settled out and the soluble salts were removed by elutriation. The coagulate was then redispersed by raising the pH to 8.5 with dilute aqueous NaOH and stirring at room temperature. The resulting emulsion when mixed with additional copolymer and/or gelatin and sensitized is useful in the preparation of a photographic emulsion layer.

EXAMPLE III

To 63 grams of a silver iodobromide emulsion of the type made by precipitation of silver halides as described in Example II, there was added 5 ml. of a 2½% by weight aqueous solution of a water and acid-soluble addition polymer of methyl vinyl ether and maleic anhydride having a specific viscosity of 0.5. (Viscosity in centipoise of 1 gram in 100 ml. of 2-butanone at 25° C.) The resulting mixture was at room temperature and had a pH of 6.3. Sixty-five ml. of water and enough 3 N H₂SO₄ was added to lower the pH to 2.5. The coagulate of the silver halides and the amphoteric polymer-polycarboxylate complex settled out and the soluble salts resulting from the silver halide precipitation were removed by elutriation. The coagulate was then redispersed by raising the pH to 8.5 with dilute aqueous sodium hydroxide and stirring at room temperature. The resulting silver halide emulsion had properties and utility similar to that prepared in Example II.

EXAMPLE IV

To 63 grams of a silver iodobromide emulsion of the type made after the manner described in Example II, there was added 25 ml. of a 0.5% by weight aqueous solution of a water and acid-soluble sulfonated styrene polysulfone containing 18% sulfur. The resulting mixture was at room temperature and had a pH of 6.3. Sixty-five ml. of water and enough 3 N H₂SO₄ was added to lower the pH to 3.0. A coagulate of the silver halides and the amphoteric copolymer-polyanion complex settled out and the soluble salts were removed by elutriation. It was then redispersed by raising the pH to 5.7 with dilute aqueous NaOH and stirring at room temperature. The resulting emulsion had properties and utility similar to that of Example II.

EXAMPLE V

To 63 grams of an unwashed emulsion containing 33 millimoles of silver halides composed of 3.4 mol percent iodide and 96.6 mol percent bromide 0.5 gram of an addition copolymer prepared by polymerizing a mixture of methacrylamide, methacrylic acid and N,2-methacrylamidoethyl dimethylamine in the mole ratio of 18:1:1 respectively (isoelectric pt. = 8.2) prepared according to the general method described in Jones U. S. 2,611,763, and 47 millimoles of the water-soluble inorganic salts resulting from the precipitation of the silver halides from water soluble silver and halide salts was added 20 ml. of a 0.5% aqueous liquor of a water and acid-soluble partial acetal of polyvinyl alcohol and o-sulfonbenzaldehyde containing 5% sulfur. The resulting mixture was at room temperature and had a pH of 6.3. Sixty-five ml. of water and enough 3 N H₂SO₄ was added to reduce the pH to 4.0. A coagulate of the silver halides and the amphoteric copolymer-polyacetal complex settled out and the soluble salts were removed by elutriation. It was then redispersed by raising the pH to 6.8 with NaOH and stirring at room temperature. The resulting emulsion when admixed with additional copolymer and/or gelatin and sensitized is useful in the preparation of a silver halide emulsion layer.

EXAMPLE VI

Sixty-three grams of a silver iodobromide emulsion prepared after the manner described in Example V was adjusted to pH 8. Five ml. of a 2 percent by weight aqueous solution of sulfonated polystyrene (visc.=200 cps.) and 65 ml. of water were then added to the emulsion. The pH was then lowered to pH 6.0 with 3 N H₂SO₄. A coagulate of silver halides and the amphoteric copolymer-polystyrene sulfonic acid complex settled out and the soluble salts were removed by elutriation. Redispersion was accomplished by adjusting the pH to 8.0 with NaOH and stirring at room temperature. The resulting emulsion had properties and utility similar to that prepared in Example V.

EXAMPLE VII

To 63 grams of an emulsion equivalent to the one described in Example V, there was added 20 cc. of a 0.5% by weight aqueous solution of a water and acid-soluble addition copolymer of methyl vinyl ether and maleic anhydride (sp. visc. = 0.5). The resulting mixture was at room temperature and had a pH of 6.3. Sixty-five ml. of water and enough 3 N H₂SO₄ was added to reduce the pH to 2.0. A coagulate of silver halides and the amphoteric copolymer-polyanion complex settled out and the soluble salts were removed by elutriation. Redispersion was accomplished by adjusting the pH to 6.0 with the NaOH and stirring at room temperature. The resulting emulsion had properties and utility similar to that prepared in Example V.

EXAMPLE VIII

To 63 grams of a silver iodobromide emulsion pre-

pared after the manner in Example V there was added 15 ml. of a 0.5% by weight aqueous solution of a water and acid-soluble sulfonated styrene polysulfone containing 18% sulfur. The resulting mixture was at room temperature and had a pH of 6.3. Sixty-five ml. of water and enough 3 N H₂SO₄ was added to reduce the pH to 4.0. A coagulate of the silver halide and the amphoteric copolymer-polystyrene sulfonic acid complex settled out and the soluble salts were removed by elutriation. Redispersion was accomplished by adjusting the pH to 6.4 with NaOH and stirring at room temperature. The resulting emulsion had properties and utility similar to that prepared in Example V.

EXAMPLE IX

Sixty-three grams of a silver iodobromide emulsion prepared after the manner described in Example V was adjusted to pH 7.7. Ten ml. of a 0.5% aqueous solution of carrageenin and 65 ml. of water was added to the emulsion. The pH was lowered to 6.0 where coagulation was noted and then to 2.0 where good settling occurred. The soluble salts were removed by elutriation and the coagulate of silver halide and the amphoteric copolymer-polysulfate complex was redispersed by adjusting the pH to 7.0 with NaOH and stirring at room temperature. The resulting emulsion had properties and utility similar to that prepared in Example V.

EXAMPLE X

To 100 grams of an unwashed emulsion containing 72 millimoles of silver halides composed of 1.5 mol percent iodide and 98.5 mol percent bromide, 1.2 grams of an addition copolymer prepared by polymerizing a mixture of methacrylamide and N,3-acrylamidopropyl β-dimethylaminopropionate betaine in the mole ratio of 9:1 respectively in the presence of α,α' azobis (isobutyramidine hydrochloride) as described in Example VII of Shacklett application ser. No. 415,163 filed March 9, 1954 (isoelectric pH = 9.9) and 106 millimoles of water-soluble inorganic salts was added 8 ml. of a 2½% by weight aqueous solution of a water- and acid-soluble partial acetal of polyvinyl alcohol and o-sulfobenzaldehyde containing 5% sulfur. The resulting mixture was at room temperature and had a pH of 6.3. Two hundred ml. of a nitric acid solution was then added to the mixture to lower the pH to 2.2. A coagulate of the silver halides and the amphoteric copolymer-polyanion complex settled out and the soluble salts were removed by elutriation. Redispersion was accomplished by adjusting the pH above 4.5 with NaOH and stirring. The resulting emulsion when mixed with additional copolymer and/or gelatin is useful in the preparation of a photographic silver halide emulsion layer.

EXAMPLE XI

To 80 ml. of an unwashed photographic emulsion containing 36 millimoles of silver halides composed of 1.0 mol percent iodide and 99 mol percent bromide, 0.5 gram of the same amphoteric copolymer used in Example X, and 45 millimols of water-soluble inorganic salts, there was added 24 ml. of a 0.5% by weight aqueous liquor of a water and acid-soluble polyglycidyl methacrylate phosphate containing 11.2% phosphorus and having neutral equivalents of 269 (methyl orange) and 134.5 (phenolphthalein) prepared as described in assignee's Jackson U. S. appl. Ser. No. 337,672. The resulting mixture was at room temperature and had a pH of 6.3. 3 M HNO₃ was then added to lower the pH to 2.1. A coagulate of silver halides and the amphoteric copolymer-polyanion complex settled out and the soluble salts were removed by elutriation. Redispersion was accomplished by adjusting the pH to 6.8 with NaOH and stirring. The resulting emulsion when mixed with additional copolymer and/or gelatin is useful in the preparation of a photographic silver halide emulsion layer.

EXAMPLE XII

To 125 ml. of an unwashed emulsion containing 75 millimols of silver halides composed of 1.5 mol percent iodide and 98.5 mol percent bromide, 1.2 grams of an addition copolymer prepared by polymerizing a mixture of methacrylamide, N,2-methacrylamidoethyl-N,N-dimethyl- β -aminopropionate betaine, and N-(2,3-dihydroxypropyl)methacrylamide in the mol ratio of 5:2:3 respectively in the presence of α,α' -azobis(isobutyramidine hydrochloride) as described in Example V of Shacklett application Ser. No. 415,161, filed March 9, 1954 (isoelectric pt.=9.3), and 110 millimols of water-soluble inorganic salts, there was added 25 ml. of a 1% by weight aqueous solution of a water and acid-soluble addition copolymer of methyl vinyl ether and maleic anhydride (sp. visc.=0.5). To the resulting emulsion at 80° F. and pH 6.3, there was added 200 ml. of water and 3 M HNO₃ to lower the pH. Coagulation started at pH 3.4 and good settling occurred at 1.5–3.0. Soluble salts were removed by elutriation and the coagulate of silver halide and the amphoteric copolymer-polyanion complex was redispersed by adjusting the pH to 6.0 with NaOH and stirring. The resulting emulsion when mixed with additional copolymer and/or gelatin is useful in the preparation of a photographic silver halide emulsion layer.

EXAMPLE XIII

To 200 ml. of an unwashed emulsion containing 90 millimols of silver halides composed of 1.0 mol percent iodide and 99 mol percent bromide, 1.2 grams of an addition copolymer of acrylic acid and β -diethylaminoethyl methacrylate in a 2:1 mol ratio and having an isoelectric point of 4.9 (made by admixing under an atmosphere of nitrogen) 36 grams of acrylic acid and 92.6 grams of β -diethylaminoethyl methacrylate dissolved in 600 ml. of dry benzene, heating the admixture to 55°–60° C. for 2½ hours in the presence of 40 milligrams of α,α' -azobis(α,γ -dimethylvaleronitrile) and separating, filtering and washing the copolymer with benzene and ether and 114 millimols of water-soluble inorganic salts, there was added 48 cc. of a 0.5% by weight of an aqueous solution of a water and acid-soluble polyglycidyl methacrylate phosphate containing 11.2% phosphorus and neutral equivalents of 269 (methyl orange) and 134.5 (phenolphthalein). The resulting mixture was at room temperature and had a pH of 6.3. 3 M H₂SO₄ was then added to lower the pH. At pH 4.0 coagulation was started and good settling occurred at 2.0–3.0. Soluble salts were removed by elutriation and the coagulate of silver halides and the amphoteric copolymer-polyanion complex was redispersed by adjusting the pH to 6.0 with ammonium hydroxide and stirring. The resulting emulsion could then be mixed with a suitable binder to prepare a useful photographic product.

EXAMPLE XIV

To 80 ml. of an unwashed photographic emulsion containing 36 millimoles of silver halides composed of 1.0 mol percent iodide and 99.0 mol percent bromide, 0.5 gram of an addition copolymer prepared from a mixture including methacrylamide, methacrylic acid and 2-methyl-5-vinyl-pyridine prepared according to the general procedure disclosed in Jones, U. S. Patent 2,611,763 in the mole ratio of 8:1:1 respectively (isoelectric point 5.8), and 45 millimoles of water-soluble inorganic salts was added 8 ml. of a 0.5% by weight aqueous solution of a water and acid-soluble partial acetal of o-sulfobenzaldehyde of polyvinyl alcohol containing 5% sulfur. The resulting mixture was at room temperature and pH 6.3. Nitric acid was added to lower the pH to 4.0. A coagulate of the silver halides and the amphoteric copolymer-polyanion complex settled out and the soluble salts were removed by elutriation. Redispersion was accomplished

by adjusting the pH to 7.5 with NaOH and stirring at room temperature.

EXAMPLE XV

One hundred ml. of a photographic emulsion containing 38 millimoles of silver halide composed of 30 mol percent bromide and 70 mol percent chloride, 0.5 gram of an addition copolymer prepared from a mixture methacrylamide and N,3-methacrylamidopropyl-N,N-dimethylaminoacetate betaine in the mole ratio of 8:2 respectively, made according to the procedure in Example X of Shacklett application Ser. No. 415,163, filed March 9, 1954 (isoelectric pt.=3.0) and 43 millimoles of water-soluble inorganic salts was prepared with a resultant pH of 5.6. A mixture of 20 ml. of a 0.5% aqueous solution of a water and acid-soluble copolymer of methyl vinyl ether and maleic anhydride (sp. visc.=0.5) and nitric acid was then added to the mixture to give a pH of 2.5. A coagulate of the silver halides and the amphoteric copolymer-polyanion complex settled out and the soluble salts removed by elutriation. The coagulate was redispersed by adjusting the pH to 6.5 with NaOH and stirring. The resulting emulsion when mixed with additional copolymer and/or gelatin is useful in the preparation of a photographic silver halide emulsion layer. The water-soluble, acid-soluble sulfonated styrene polysulfone described in Examples IV and VIII was made by the following procedure:

Procedure A

To a solution of 18 g. of styrene polysulfone in 150 ml. of chloroform at –20° C. there was added a sulfonating agent consisting of 189 g. of β,β' -dichloroethyl ether, 95 g. of distilled sulfur trioxide and 200 ml. of ethylene chloride. The solutions were maintained at –10 to –20° C. during mixing. The mixture was allowed to warm to room temperature gradually. A precipitate formed. The reaction mixture was poured into 1000 ml. of methylene chloride and the polymeric precipitate was separated and triturated in ethyl ether. After drying, 26 g. of sulfonated styrene polysulfone polymer was obtained.

The sulfonated polystyrene of Example VI was made by the following procedure:

Procedure B

A solution of 106 g. of a mixture of potassium bromide and potassium styrenesulfonate (80% of the latter) in 325 ml. of oxygen-free water was heated to 73 C. and 0.5 g. of α,α' -azodiisobutyramidine hydrochloride was added. The solution was maintained at 70–73° C. with stirring for 3 hours and an additional 0.2 g. of the azo polymerization catalyst added. After 4 hours' heating and stirring, the mixture was poured into 1 liter of ethanol. The polymeric styrenesulfonate precipitated and the polymer was dissolved in water, reprecipitated in alcohol and dried. There was obtained 88 g. of dried polymer.

Various photographically inert acids can be used in the processes of this invention to lower the pH. The strong mineral acids, e. g., nitric, sulfuric, hydrochloric are preferred. Other useful acids include phosphoric acid, acetic acid and chloracetic acid. Any acid is suitable which will be photographically inert and lower the pH of the emulsion below the isoelectric point of the synthetic amphoteric colloid being used. The hydrogen form of cation exchange resins may also be used.

As will be apparent from the above, the invention is not limited to the order in which the acid and water-soluble, acid-soluble polymer are added in the processes. Thus the polymer may be added to the aqueous dispersion of silver halide in the amphoteric polymer before or after the acid used to lower the pH, or, if desired, the two reactants can be added simultaneously.

The processes of the invention are not limited to the removal of soluble salts from unwashed silver halide dispersions in the amphoteric polymers. The precipitation or coagulation with the water-soluble, acid-soluble polymer can also be used to remove solvents from silver halide dispersions in the amphoteric polymers, at any stage during their manufacture prior to coating.

An advantage of the invention is that it provides practical and economical processes for preparing silver halide dispersions in synthetic amphoteric polymer which are of markedly reduced soluble salt content or are essentially free from such salts. Another advantage is that the invention provides such practical and economical processes wherein the water is substantially removed. The invention has the further advantage that it eliminates the necessity of setting and noodling the emulsion prior to the removal of soluble salts by washing.

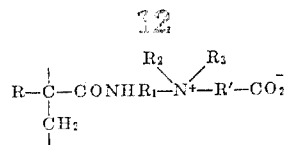
The invention admits of the manufacture of silver halide dispersions in synthetic amphoteric polymers which are not sufficiently fluid to coat, since substantially all of the water is removed during the precipitation or coagulation step. The concentration of the amount of binding agent in the final coated emulsion can be easily controlled during redispersion. The invention simplifies the preparation of silver halide dispersions suitable for coating. During the conventional washing operation the water content of the emulsion is generally increased while substantially all of the water can be removed by coagulation. This offers the simple means of increasing the solids content of the emulsion after "make" and obtaining emulsions that have a higher silver halide/binder ratio than can be obtained with emulsion washed by the conventional method. Still other advantages of the invention will be apparent from the above.

In assignee's copending Moede application Ser. No. 354,410 filed May 10, 1953 (U. S. Patent 2,772,165, Nov. 27, 1956), there is described a process of precipitating silver halide dispersions in water-permeable protein colloids of natural origin, which have protective colloid properties, with water-soluble, acid-soluble organic polymers of high molecular weight containing recurring oxy groups and free acid and acid salt groups. The present invention is based on the discovery that the processes can be extended to the synthetic amphoteric polymers which differ from the protein colloids in that they are generally not thermally gellable.

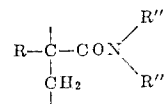
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process which comprises admixing (1) an aqueous dispersion of light-sensitive silver halide in a synthetic water-permeable amphoteric addition polymer of high molecular weight having protective colloid properties and containing acid groups and groups taken from the class consisting of amine and quaternary ammonium groups, and (2) an aqueous solution having dissolved therein from 3% to 20% by weight based on said amphoteric polymer of a water-soluble, acid-soluble anionic organic polymer of high molecular weight having periodically occurring groups taken from the class consisting of free acid groups and salts thereof, said anionic polymer being taken from the group consisting of polyvinyl acetals, carrageenin, alkyl vinyl ether/maleic anhydride copolymers, polystyrene sulfonates, polyvinyl phosphates and phosphates of polyglycidyl methacrylates, which anionic polymers are soluble both in water and 1% nitric acid to the extent of at least 1% by weight, and (3) then adding an acid in an amount sufficient to lower the pH below the isoelectric point of such amphoteric polymer, and recovering the resulting precipitated chemical complex of said acid-soluble anionic polymer and said amphoteric polymer containing dispersed silver halide.

2. A process as set forth in claim 1 wherein said amphoteric polymer contains periodically occurring intralinear units of the formulae:

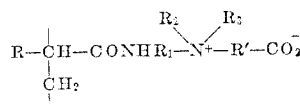
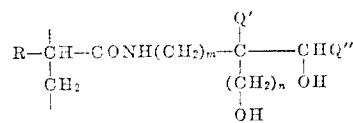


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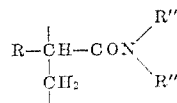


wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated bivalent aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₁ and R₂ are hydrocarbon radicals of 1 to 3 carbon atoms and R' is a saturated hydrocarbon radical of 1 to 4 carbon atoms.

3. A process as set forth in claim 1 wherein said amphoteric polymer contains periodically occurring intralinear units of the formulae:



and



wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated bivalent aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ and R₃ are alkyl radicals of 1 to 3 carbon atoms, R' is a saturated bivalent aliphatic hydrocarbon radical containing 1 to 4 carbon atoms, Q' and Q'' are members taken from the group consisting of hydrogen and alkyl radicals of 1 through 3 carbon atoms, m is a number taken from the group consisting of 0, 1, 2, 3, and 4, and n is a number taken from the group consisting of 0 and 1 and the sum of m and n is at least 1.

4. A process as set forth in claim 1 wherein said acid-soluble polymer is a polyvinyl acetal of an aldehyde containing sulfonic acid groups, said acetal containing a plurality of intralinear $-\text{CH}_2-\text{CHOH}-$ groups.

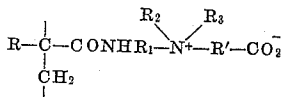
5. A process as set forth in claim 4 wherein said aldehyde is o-sulfobenzaldehyde.

6. A process which comprises admixing (1) an aqueous dispersion of light-sensitive silver halide in a synthetic water-permeable amphoteric addition polymer of high molecular weight having protective colloid properties and containing acid groups and groups taken from the class consisting of amine and quaternary ammonium salt groups, and (2) an aqueous solution having dissolved therein from 3% to 20% by weight based on said amphoteric polymer of a water-soluble, acid-soluble anionic organic polymer of high molecular weight having periodically occurring groups taken from the class consisting of free acid groups and salts thereof, said anionic polymer being taken from the group consisting of polyvinyl acetals, carrageenin, alkyl vinyl ether/maleic anhydride copolymers, polystyrene sulfonates, polyvinyl phosphates and phosphates of polyglycidylmethacrylates, which anionic polymers are soluble both in water and 1% nitric acid to the extent of at least 1% by weight, and (3) then adding an acid in an amount sufficient to lower the pH below the isoelectric point of such amphoteric

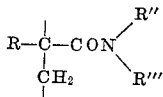
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polymer, and recovering the resulting precipitated chemical complex of said acid-soluble anionic polymer and said amphoteric polymer containing dispersed silver halide, and removing by elutriation the water-soluble salts and water from the precipitated complex of the amphoteric polymer and the anionic polymer.

7. A process as set forth in claim 6 wherein said amphoteric polymer contains periodically occurring intralinear units of the formulae:

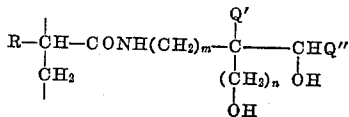


and

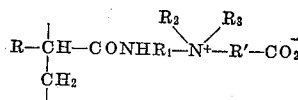


wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl radicals of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated bivalent aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ and R₃ are hydrocarbon radicals of 1 to 3 carbon atoms and R' is a saturated hydrocarbon radical of 1 to 4 carbon atoms.

8. A process as set forth in claim 6 wherein said amphoteric polymer contains periodically occurring intralinear units of the formulae:

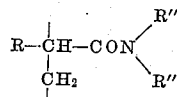


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wherein R, R'' and R''' are members taken from the group consisting of hydrogen, alkyl of 1 to 3 carbon atoms, phenyl and cyclohexyl, R₁ is a saturated bivalent aliphatic hydrocarbon radical of 2 to 6 carbon atoms, R₂ and R₃ are alkyl radicals of 1 to 3 carbon atoms, R' is a saturated bivalent aliphatic hydrocarbon radical containing 1 to 4 carbon atoms, Q' and Q'' are members taken from the group consisting of hydrogen and alkyl radicals of 1 through 3 carbon atoms, m is a number taken from the group consisting of 0, 1, 2, 3, and 4, and n is a number taken from the group consisting of 0 and 1 and the sum of m and n is at least 1.

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