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**PHOTOGRAPHIC COMPOSITIONS CONTAINING
AN ADMIXTURE OF ORGANIC AND INOR-
GANIC SILVER SALTS**

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8 Claims

ABSTRACT OF THE DISCLOSURE

Photographic compositions are disclosed which comprise an admixture of an organic silver salt and an inorganic silver salt wherein the crystals of said inorganic silver salt have been formed in the presence of an amphiphilic copolymeric silver halide peptizer. In certain embodiments, the amphiphilic copolymer comprises units of a (N,N-dialkylamino)alkyl acrylate. In another aspect, a process is disclosed for forming a photographic composition which comprises (1) forming inorganic silver salt crystals in a liquid medium in the presence of an amphiphilic copolymer which is a silver halide peptizer and (2) mixing said inorganic silver salt crystals with an organic silver salt in an organic liquid medium.

This invention relates to photographic compositions and to processes for making photographic compositions. In one aspect, this invention relates to an improved photographic composition comprising in admixture an organic silver salt and an inorganic silver salt wherein said inorganic silver salt has been prepared in the presence of an amphiphilic copolymer which is a silver halide peptizer. In another aspect, this invention relates to a process of preparing an improved silver salt composition comprising (1) precipitating a silver halide in an aqueous medium in the presence of an amphiphilic copolymeric peptizer and then (2) mixing said silver halide with an organic silver salt in an organic solvent.

Photographic elements which comprise mixtures of inorganic silver salts with organic silver salts are known in the art, for example, as described in U.S. Pats. 3,152,903 by Sheppard issued Oct. 13, 1964, 3,152,904 by Sorenson et al. issued Oct. 13, 1964, 3,457,075 by Morgan et al. issued July 22, 1969, and 3,392,020 by Yutzy et al. issued July 9, 1968, and British Pat. 1,161,777. In most instances where photographic elements are required with high-exposure speed, inorganic silver salts have been used in combination with the organic silver salts. However, there are indications in the art that it is necessary to prepare the inorganic silver salt *in situ* with the other components of the photographic composition, such as *in situ* with an organic silver salt such as silver behenate, to obtain the catalytic proximity required. Methods of this type are disclosed, for instance, in U.S. Pats. 3,152,904 by Sorensen et al. issued Oct. 13, 1964, 3,437,075 by Morgan et al. issued July 22, 1969, and the like. As indicated in these references, so-called preformed photosensitive inorganic silver salt, i.e., silver halide formed *ex situ*, upon addition to a similar element, has not provided as desired photosensitivity or as desired an image upon development as the element in which photosensitive silver halide is formed *in situ*.

It is desirable to provide a photographic system and a means for obtaining a system based on inorganic silver salts and organic silver salts wherein the inorganic silver salt could be prepared by means, such as conventional silver halide precipitation techniques, to obtain better photosensitive properties; better control of purity, grain size, composition; and the like.

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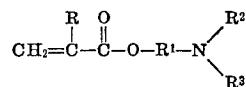
I have now found that when inorganic silver salts are prepared in the presence of certain amphiphilic copolymers in an aqueous medium, they can later be combined with the organic silver salts and other essential ingredients in an aqueous or preferably organic solvent medium and then coated on a support to make a photographic element with good photographic and thermographic response characteristics.

In one preferred embodiment, the amphiphilic copolymer is a copolymer comprising from 0 to 20 mole percent of units of an ethylenically unsaturated monomer containing groups therein comprising at least one thioether moiety, from about 35 to 75 mole percent of units of an alkyl acrylate and from 25 to 65 mole percent of a (N,N-dialkylamino)alkyl acrylate.

In another preferred embodiment, the amphiphilic polymeric peptizer is a copolymer consisting essentially of units of (N,N-dialkylamino)alkylene acrylates and units of alkyl acrylates.

20 In accordance with this invention, the inorganic silver salt can be formed by precipitating a salt such as silver halide in an aqueous medium containing an amphiphilic copolymer which is a silver halide peptizer. The precipitation is normally commenced by reacting silver nitrate with
25 an alkali metal halide in accordance with techniques known in the art. The precipitant can be coagulated, decanted and then, if desired, redispersed in an organic solvent, especially when the preferred amphiphilic copolymers of this invention are utilized in the precipitation
30 medium. The redispersed silver halide is then mixed with the remaining ingredients, such as the organic silver salts, to make the photographic composition. This technique allows one to use the conventional aqueous precipitation means for precipitating silver halide to make a pre-
35 formed inorganic silver salt ex situ of the other ingredients, and then combine them later to produce a alkyl acrylates. It is understood, of course, that when the term "acrylates" is used herein, it is used generally to composition similar to or better than those formed in
40 situ.

The amphiphilic copolymers which have been found to be very useful in systems in accordance with this invention generally contain units of (N,N-dialkylamino) include methacrylates and the like. Typical preferred 45 compounds of this type are represented by the formula:



50 wherein R is a hydrogen atom or a methyl group; R¹ is an alkylene group preferably containing from 1 to 8 carbon atoms, including branched-chain alkylene groups such as methylene, ethylene, propylene, trimethylene, butylene, isobutylene and the like; and R² and R³ are alkyl groups of from 1 to 6 carbon atoms, including branched-chain alkyl groups, aryl groups of from 6 to 15 carbon atoms such as phenyl, substituted phenyl, naphthyl and the

60 In a highly preferred embodiment wherein the silver salts are prepared in an aqueous medium and then subsequently redispersed in a non-aqueous medium, the polymeric peptizer comprises units of 2-(N,N-dimethylamino)ethyl methacrylate.

65 The alkyl acrylates used in making the copolymers of this invention are generally referred to as unsubstituted acrylic esters (which form hydrophobic units when polymerized) and, of course, include the alkyl methacrylates, as well as the alkyl acrylates. Typical useful acrylic esters 70 include methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isopropyl acrylate, isobutyl acrylate, t-butyl acrylate, the respective methacrylates, and the

like. Preferably, the alkyl acrylate is a simple compound such as methyl acrylate or methyl methacrylate.

The polymeric peptizers of this invention can also comprise units of an ethylenically unsaturated compound comprising groups having thioether moieties or sulfide-sulfur atoms therein. In a preferred embodiment, these compounds include those derived from monomers of amides and esters of ethylenically unsaturated acids, including maleic acids, acrylic acids, methacrylic acids and the like, in which the respective amine and alcohol condensation residues in said amides and esters contain at least one organic group having at least one sulfide-sulfur atom linking two methylene groups ($-\text{CH}_2-$). Typical units of this type useful in certain embodiments according to this invention are disclosed in U.S. Ser. No. 701,084 filed Jan. 29, 1968 now Pat. No. 3,615,624, which is incorporated herein by reference. These units can be obtained from monomers such as

N-(3-thiabutyl)acrylamide;
 N-(thiopentyl)acrylamide;
 N-(4-methyl-2-thiapentyl)acrylamide;
 N-(2,5-dimethyl-4-thiahexyl)acrylamide;
 N-(5-thiaheptyl)acrylamide;
 N-(4-thiaheptyl)acrylamide;
 N-(6-methyl-4-thiaheptyl)acrylamide;
 N-(3-thiaoctyl)acrylamide;
 N-(7-thianonyl)acrylamide;
 N-(6-ethyl-2-methyl-4-thiaoctyl)acrylamide;
 N-(6-thia-2,4,9-trimethyldecyl)acrylamide;
 N-(4-thiadodecyl)acrylamide;
 3-thiapentyl acrylate;
 bis(2-thiabutyl) methyl acrylate;
 methylthioethyl acrylate; and
 methacryloylpropylmethionine methyl ester.

The interpolymers of this invention can be generally polymerized by solution polymerization, emulsion polymerization or bulk polymerization procedures, but they are preferably polymerized by solution polymerization procedures. The polymerization is carried out to obtain a molecular weight of the interpolymer of at least about 10,000 to about 500,000 and preferably from about 30,000 to about 100,000. The inherent viscosities of the interpolymers generally range from about 0.1 to about 2.

The term "amphiphilic" is used herein to characterize copolymers comprising both polar water-soluble groups and hydrophobic water-insoluble groups wherein the compound can be put into a stable water solution and also a stable organic solvent solution. The amphiphilic copolymers of this invention can be characterized as being at least 3% soluble, by weight, in water at room temperature at a pH of less than 5 and at least 3%, by weight, soluble in an organic solvent. Preferably, the amphiphilic copolymers are at least 3% soluble in an organic solvent such as acetone. Moreover, the preferred copolymers of this invention comprise separate repeating units which respectively contain the hydrophobic and polar water-soluble groups.

The term "copolymer which is a silver halide peptizer" is understood to mean a copolymer which will aid in prevention of clumping of crystal grains and help maintain the separate crystal entity during the growth of the crystal when present in a precipitation medium for forming silver halide crystals.

In accordance with the invention, an organic or non-aqueous solvent can be used in the preparation of the silver halide salt and preferably it is used for redispersing the silver salt-polymeric peptizer dispersion followed by coating from an organic liquid carrier. The term "organic solvent" generally refers to those compounds comprising carbon and hydrogen atoms which generally have boiling points below 165° C. and preferably lower than about 90° C. In certain preferred embodiments of this invention, the amphiphilic polymers are soluble in organic solvents such as alcohols, ketones, amides, nitriles, ethers including the cyclic ethers, and the like. Other solvents such as

organic acids, organic sulfoxides and organic sulfones can also be used, including mixtures of any of the above organic solvents. Typical useful organic solvents include acetone, dimethylformamide, methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, dioxane, dimethylsulfoxide, sulfolane, acetonitrile, tetrahydrofuran, dimethylacetamide, 1,2-dimethoxyethane, acetic acid, triethylamine, and the like. Preferably, the organic solvents used in dispersing the amphiphilic polymers are water-miscible, especially if an aqueous medium is used for either the silver halide grain formation or the redispersion.

The photographic elements of this invention comprise the inorganic silver salt in admixture with the organic silver salt. A typical concentration range of the described 15 photosensitive silver halide prepared in the process of the invention is from about 0.005 to about 0.50 mole of silver salt per mole of silver salt of organic acid, e.g., per mole of silver behenate. Preferred inorganic silver salts are photosensitive silver halide, e.g., silver chloride, silver bromide, silver chlorobromide, silver iodide, silver bromoiodide, silver chloroiodide, silver chlorobromooiodide, or mixtures thereof. The photosensitive silver halide can be coarse- or fine-grain; in one embodiment, the very fine-grain silver halide is especially useful. 20 A supplemental photosensitive silver halide emulsion can be employed in combination with the photosensitive inorganic silver salt prepared according to the invention and the organic silver salt, if desired. The silver halide emulsion can be prepared by any of the well-known procedures in the photographic art, such as single-jet emulsions or double-jet emulsions such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions, such as those described in U.S. Pats. 2,222,264 of Nietz et al. issued Nov. 14, 1940, 3,320,069 of Illingsworth issued May 15, 1967, and 3,271,157 of McBride issued Sept. 6, 1966. Surface-image silver halide emulsions can be used, as well as mixtures of surface- and internal-image silver halide emulsions, as described in U.S. Pat. 2,996,332 of Luckey et al. issued Apr. 15, 1961. Negative-type emulsions can be used. The silver halide emulsion can be a regular-grain emulsion such as described in Klein and Moisar, Journal of Photographic Science, vol. 12, No. 5, September-October 1964, pp. 242-251.

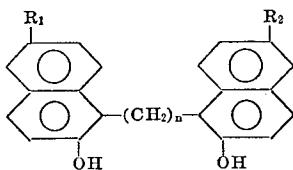
The inorganic silver salts employed in the practice of the invention can be sensitized with chemical sensitizers, 45 such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described, for example, in U.S. Pats. 1,623,499 of Sheppard issued Apr. 5, 1927, 2,399,083 of Waller et al. issued Apr. 23, 50 1946, 3,297,447 of McVeigh issued Jan. 10, 1967, and 3,297,446 of Dunn issued Jan. 10, 1967.

Photosensitive, inorganic, silver salt compositions employed in the practice of the invention can be protected against the production of fog and can be stabilized against 55 loss of sensitivity during keeping. Suitable antifoggants and stabilizers, e.g., used alone or in combination, include, for example, thiazolium salts; azaindenes; mercury salts as described for example, in U.S. Pat. No. 2,728,663 of Allen et al. issued Dec. 27, 1955; urazoles; sulfocatechols; 60 oximes described, for example, in British Pat. No. 623,448; nitron; nitroindazoles; polyvalent metal salts described, for example, in U.S. Pat. No. 2,839,405 of Jones issued June 17, 1958; platinum, palladium and gold salts described, for example, in U.S. Pats. Nos. 2,566,263 of Trivelli et al. issued Aug. 28, 1951, and 2,597,915 of Yutzy et al. issued May 27, 1952.

The photographic elements of this invention comprise an oxidizing agent, especially a silver salt of an organic acid. The silver salt of the organic acid should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable class of silver salts of organic acids is represented by the water-insoluble silver salts of long-chain fatty acids which are stable to light. Compounds which are suitable

silver salts include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caproate, silver myristate and silver palmitate. Other suitable oxidizing agents are silver benzoate, silver phthalazinone, silver benzotriazole, silver saccharin, silver 4'-n-octadecyl-oxydiphenyl - 4 - carboxylic acid, silver O-aminobenzoate, silver acetamidobenzoate, silver furoate, silver camphorate, silver P-phenylbenzoate, silver phenylacetate, silver salicylate, silver butyrate, silver terephthalate, silver phthalate, silver acetate and silver acid phthalate. Oxidizing agents which are not silver salts can be employed, if desired, in place of the silver salts, such as zinc oxide, gold stearate, mercuric behenate, auric behenate and the like, but silver salts are preferred.

Organic reducing agents can be employed in certain embodiments of the described composition and/or element which include, for example, substituted phenols and naphthols. The bis-naphthol which is preferred is a bis- β -naphthol of the formula:



wherein R₁ and/or R₂ are hydrogen, alkyl containing 1 to 3 carbon atoms, alkoxy, e.g., alkoxy containing 1 to 2 carbon atoms such as methoxy or ethoxy, halogen, nitro, amino or a diazonium halide salt, and n is 0 to 1. Suitable bis- β -naphthols which can be employed in the practice of the invention include:

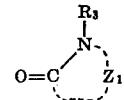
2,2'-dihydroxy-1,1'-binaphthyl,
6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthyl,
6,6'-dinitro-2,2'-dihydroxy-1,1'-binaphthyl and/or
bis-(2-hydroxy-1-naphthyl)methane.

The described reducing agents are suitable in a range of concentration; however, they are especially suitable at a concentration from about 0.10 to about 0.75 mole of reducing agent per mole of oxidizing agent.

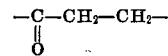
Other reducing agents, which are typically silver halide developing agents, can be used alone or in conjunction with the above bis-naphthol reducing agents. Suitable silver halide developing agents include, for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g., hydroquinone, alkyl-substituted hydroquinones as exemplified by tertiary butylhydroquinone, methylhydroquinone, 2,5-dimethylhydroquinone and 2,6-dimethylhydroquinone; catechols and pyrogallol; halo-substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy-substituted hydroquinones such as methoxyhydroquinone or ethoxyhydroquinone; methylhydroxynaphthalene; phenylenediamine developing agents; methylgallate; aminophenol developing agents such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals and ascorbic acid derivatives such as those described in U.S. Pat. No. 3,337,342 of Green issued Aug. 22, 1967; hydroxylamine developing agents such as N,N'-di-(2-ethoxyethyl)hydroxylamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone including those described in British Pat. No. 930,572 published July 3, 1963; hydroxytetronic acid, and hydroxytetronamide developing agents; reductone developing agents such as anhydrosodihydropyrrrolidone hexose reductone; and the like.

It is desirable to employ an activator-toning agent in the certain embodiments of the elements and compositions of the invention to obtain a desired image, particularly when phenolic reducing agents are used. A suitable acti-

vator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom and of the formula:



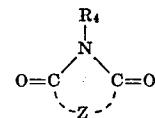
wherein R₃ is hydrogen, hydroxyl or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z₁ represents atoms completing a heterocyclic nucleus, especially a 5- or 6-member heterocyclic nucleus. The atoms completing the heterocyclic nucleus can be, for example,



or an alkylene group containing 3 or 4 carbon atoms. The atoms completing the heterocyclic nucleus can contain

20 various substituent groups such as amino, alkyl amino, e.g., methylamino or ethylamino, hydroxyl, carbamyl and the like. An especially suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom which is preferably a cyclic imide of the

25 formula:

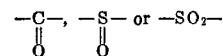


wherein R₄ is hydrogen, hydroxyl or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z₂ represents carbon atoms of a series completing a cyclic

35 imide nucleus, typically consisting of from 5 to 6 carbon atoms, e.g., a phthalimide or succinimide nucleus. The atoms of the cyclic imide nucleus can contain various substituent groups, especially amino, alkyl, such as alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl, propyl, butyl or pentyl or aryl, such as aryl containing 6 to 20 carbon atoms, such as phenyl, tolyl and xylyl. Suitable activator-toning agents which can be employed in the practice of the invention include, for instance, phthalimide, N-hydroxyphthalimide, N-potassium phthalimide, N-silver phthalimide, N-mercury phthalimide, succinimide and/or N-hydroxysuccinimide. The described activator-toning agents are suitable in a range of concentration; however, they are especially suitable at a concentration from about 0.10 mole to about 1.05 moles of activator-toning agent per mole of oxidizing agent.

Other so-called activator-toning agents can be employed in combination with other components of the described photosensitive and thermosensitive element in the practice of the invention. Various so-called toners can be employed for this purpose. Typically, a heterocyclic organic toning agent containing at least two hetero atoms in the heterocyclic ring of which at least one is a nitrogen atom is employed. These are described, for example, in U.S. Pat. 3,080,254 of Grant issued Mar. 5, 1963. Suitable toners include, for example, phthalazinone, 2-acetylphthalazinone and 2-phthalylphthalazinone. Other suitable toners are described, for example, in U.S. Pat. 3,446,648 of Workman issued May 27, 1969.

Nonaqueous, polar, organic solvents, such as com-
65 pounds containing a



70 moiety, are also useful in certain embodiments of photosensitive and thermosensitive elements prepared in accordance with this invention for dry processing with heat; improved maximum image densities are provided with solvents such as tetrahydrothiophene-1,1-dioxide, 4-hydroxybutanoic acid lactone, methylsulfinylmethane, and the like.

A photosensitive and thermosensitive element and compositions described and used in the practice of the invention can contain various colloids alone or in combination as vehicles, binding agents and in various layers. Suitable materials are typically hydrophobic, but hydrophilic materials can also be employed. They are transparent or translucent and include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinyl pyrrolidone), acrylamide polymers and the like. Other synthetic polymeric compounds which can be employed include dispersed vinyl compounds such as in latex form, and particularly those which increase dimensional stability of photographic materials. Suitable synthetic polymers include those described in U.S. Pats. 3,142,586 of Nottorf issued July 28, 1964, 3,193,386 of White issued July 6, 1955, 3,062,674 of Houck et al. issued Nov. 6, 1962, 3,220,844 of Houck et al. issued Nov. 30, 1965, 3,287,289 of Ream et al. issued Nov. 22, 1966, and 3,411,911 of Dykstra issued Nov. 19, 1968. Effective polymers include latex polymers and water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, and those which have cross-linking sites which facilitate hardening or curing, as well as those having recurring sulfobetaine units as described in Canadian Pat. 774,054. Preferred high-molecular-weight materials and resins include polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, poly(vinyl pyrrolidone), ethyl cellulose, polystyrene, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid and polyvinyl alcohol.

The photosensitive and thermosensitive layers and other layers of an element employed in the practice of the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) 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, ethylene-butene copolymers and the like.

In one preferred embodiment of this invention, a support is provided with coatings thereon of a light-stable organic silver-salt oxidizing agent, an organic reducing agent and a photosensitive, inorganic silver salt, preferably silver halide, which provides a photosensitive and thermosensitive element. A visible image in the photographic element can be produced within a few seconds after imagewise exposure by heating the element to moderately elevated temperatures, e.g., about 80° to about 250° C.

The invention can be further illustrated by the following examples of preferred embodiments thereof.

EXAMPLE 1

A light-sensitive fine-grain silver halide photographic emulsion is prepared. Several solutions are prepared as follows:

SOLUTION A¹

Copolymer I² (7.9% in water) _____ ml. 90
Water _____ ml. 1000
Temp. _____ °C. 23

SOLUTION B

Sodium bromide _____ g. 14.6
Water to total vol. _____ ml. 104
Temp. _____ °C. 23

SOLUTION C

Silver nitrate _____ g. 24.0
Water to total vol. _____ ml. 91.0
Temp. _____ °C. 23

5 ¹ pAg adjusted to 8.5 with 0.368 N solution of potassium bromide.
2 Copoly[3-thiapentyl acrylate-methyl methacrylate-2-(N,N-dimethylamino)ethyl methacrylate] [1:5:4 molar].

Solutions B and C are added at a controlled rate of 10 addition (about 25 ml. per minute) to Solution A. When all of the solutions have been combined, the resulting silver bromide dispersion is washed by the procedure which follows. The pH of the aqueous dispersion is adjusted with a 2.5 N solution of sodium hydroxide to the iso-15 electric point (about pH 7.8). At the iso-electric point, the silver halide dispersed in the copolymer coagulates and settles out of the aqueous phase. The aqueous phase containing unwanted salts is decanted leaving only the silver halide polymeric coagulum. The remaining coagulum is 20 redispersed in acetone.

EXAMPLE 2

A light-sensitive fine-grain silver halide photographic 25 emulsion is prepared. Several solutions are prepared as follows:

SOLUTION A¹

Copolymer I² (10.5% in water) _____ ml. 675
30 Water _____ ml. 1525
Temp. _____ °C. 23

SOLUTION B

Sodium bromide _____ g. 146.0
35 Water to total volume _____ ml. 1010.0
Temp. _____ °C. 23

SOLUTION C

Silver nitrate _____ g. 240
40 Water to total volume _____ ml. 950
Temp. _____ °C. 23

¹ See footnote 1 to table in Example 1, Solution A.

² See footnote 2 to table in Example 1, Solution A.

A portion of Solutions B and C are added at a controlled rate of addition (about 250 ml. per minute) to 45 Solution A for 30 seconds. At the end of this time, the pAg of Solution A is readjusted to 8.5 by stopping the flow of Solution C. The remainder of Solutions B and C are added at a controlled rate of addition (about 250 ml. 50 per minute) to Solution A and the pAg is held constant at 8.5±0.2. When all of the solutions are combined, the pAg is lowered to 4.8 with silver nitrate (1% solution) and held for 5 minutes. At the end of this time period, the pAg is readjusted to 8.5 with the potassium bromide 55 solution described above. The resulting silver bromide dispersion is washed, employing the iso-electric coagulation technique described in Example 1. The resulting silver bromide coagulum is redispersed in acetone.

EXAMPLE 3

A light-sensitive fine-grain silver halide photographic emulsion is prepared. Several solutions are prepared as follows:

SOLUTION A¹

Copolymer II² (12.0% in water) _____ ml. 590
Water _____ ml. 1610
Temp. _____ °C. 23

SOLUTION B

Sodium bromide _____ g. 146
70 Water to total volume _____ ml. 1010
Temp. _____ °C. 23

¹ See footnote 1 to table in Example 1, Solution A.

² Copoly[methyl methacrylate-2-(N,N-dimethylamino)ethyl methacrylate] [1:1 molar].

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SOLUTION C

| | | |
|-----------------------|----|-----|
| Silver nitrate | g | 240 |
| Water to total volume | ml | 950 |
| Temp. | °C | 23 |

Solutions B and C are added to Solution A following the procedure described in Example 2. After all of the solutions have been combined, the resulting silver halide dispersion is washed using the iso-electric coagulation technique described in Example 1. The resulting silver bromide coagulum is redispersed in acetone.

EXAMPLE 4

A silver behenate dispersion is prepared by ball-milling the following composition for 20-64 hours:

| | | |
|-----------------------|----|-------|
| Silver behenate | g | 42.0 |
| Behenic acid | g | 32.0 |
| Polyvinyl butyral | g | 15.0 |
| Phthalimide | g | 8.5 |
| Acetone-toluene (1:1) | ml | 400.0 |

A photographic coating is prepared by coating the following composition on a suitable photographic paper support at a wet thickness of 0.004 inch:

| | | |
|--|-----|-----|
| Silver bromide emulsion (prep. of Example 1) | ml. | 0.4 |
| Silver behenate dispersion (described above) | ml. | 2.0 |
| 1,1'-bi-2-naphthol (3% acetone) | ml. | 2.0 |
| 3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinylidene)isopropylidene]rhodanine (0.01% methanol) | ml. | 1.0 |
| Acetone | ml. | 2.6 |

A sample of the coating of this example is exposed to a tungsten light source for 1/2 second and heat-processed for 19 seconds on a curved hot block at a temperature of 135° C. A visible line image of high density results comprising eight visible steps.

EXAMPLE 5

A photographic coating is prepared by coating the following composition on a suitable photographic paper support at a wet thickness of 0.004 inch.

| | | |
|--|-----|------|
| Silver bromide emulsion (prep. of Example 2) | ml. | 0.08 |
| Silver behenate dispersion (described in Example 4) | ml. | 2.00 |
| 1,1'-bi-2-naphthol (3% acetone) | ml. | 2.00 |
| 3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinylidene)isopropylidene]rhodanine (0.01% methanol) | ml. | 0.19 |
| Acetone | ml. | 3.25 |

A sample of the coating of this example is exposed to a tungsten light source for 1/2 second and heat-processed for 25 seconds on a curved hot block at a temperature of 135° C. A visible line image results comprising ten visible steps.

EXAMPLE 6

A photographic coating is prepared by coating the following composition on a suitable photographic paper support at a wet thickness of 0.004 inch.

| | | |
|--|-----|------|
| Silver bromide emulsion (prep. of Example 3) | ml. | 0.30 |
| Silver behenate dispersion (described in Example 4) | ml. | 2.00 |
| 1,1'-bi-2-naphthol (3% acetone) | ml. | 2.00 |
| 3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinylidene)isopropylidene]rhodanine (0.01% methanol) | ml. | 0.19 |
| Acetone | ml. | 3.50 |

A sample of the coating of this example is exposed to a tungsten light source for 1/2 second and heat-processed on a curved hot block for 26 seconds at a temperature of

75° C. A visible line image of high density results comprising ten visible steps.

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135° C. A visible line image of high density results comprising ten visible steps.

EXAMPLE 7

5 This example is included to demonstrate that the copolymers of this invention are useful not only as peptizers, but also as vehicles.

A silver behenate dispersion is prepared by ball-milling the following composition for 5-6 hours:

| | | |
|--|-----|--------|
| Silver behenate | g | 6.53 |
| Copoly[3-thiapatetyl acrylate-methyl methacrylate-2-(N,N-dimethylamino)ethyl methacrylate] [1:5:4 molar] | g | 1.46 |
| Phthalimide | g | 1.27 |
| 1,1'-bi-2-naphthol | g | 1.98 |
| Acetone | ml. | 100.00 |

A photographic coating is prepared by coating the following composition on a suitable photographic paper support at a wet thickness of 0.004 inch.

| | | |
|--|-----|------|
| Silver bromide emulsion (prep. of Example 1) | ml. | 0.75 |
| Silver behenate dispersion (described above) | ml. | 3.00 |
| 3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinylidene)isopropylidene]rhodanine (0.01% methanol) | ml. | 1.00 |
| Acetone | ml. | 3.25 |

30 A sample of the coating of this example is exposed to a tungsten light source for 1/2 second and heat-processed on a curved hot block for about 25 seconds at a temperature of about 135° C. A visible line image of high density results comprising eight visible steps.

EXAMPLE 8 (COMPARISON)

A coating composition is prepared by mixing the following components:

| | | |
|--|-----|------|
| Silver behenate | g | 42.0 |
| Behenic acid | g | 32.0 |
| Polyvinyl butyral | g | 15.0 |
| Silver bromide (prepared ex situ in the absence of a peptizer) | g | 0.45 |
| Phthalimide | g | 8.5 |
| Acetone-toluene (1:1 parts by volume) | ml. | 500 |

After ball-milling for 18 hours, 141 ml. of the resulting dispersion is combined with the following solutions:

| | | |
|---|-----|------|
| Acetone containing 0.08% by weight 3-ethyl-5-[(3-ethyl-2(3H)-benzothiazolylidene)isopropylidene]-2-thio-2,4(3,5)-oxazolidenedione | ml. | 4.4 |
| Acetone containing 6.25% by weight 2,2'-dihydroxy-1,1'-binaphthyl | ml. | 52.5 |

55 The composition is mixed and then coated on a suitable resin-coated paper support at a wet thickness of 0.004 inch and dried.

60 The photosensitive element is placed into contact with an original transparent film containing a developed image and exposed for 5 seconds by a 100-watt lamp at a distance of 1 foot. The photosensitive element is separated from the original and the resulting latent image is developed by holding the element in contact with a curved metal block for 10 seconds at 120° C. A very faint but distinguishable image results.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

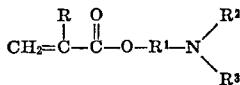
I claim:

1. A photographic element comprising (A) a support and (B) at least one layer comprising an admixture of (1) an organic silver salt and (2) an inorganic silver halide salt wherein the crystals of said inorganic salt

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have been formed in the presence of an amphiphilic copolymer which is a silver halide peptizer consisting of:

(a) from 25 to 65 mole percent of units of an (N,N-dialkylamino) alkyl acrylate represented by the formula



wherein R is a hydrogen atom or a methyl group, R¹ is an alkylene group containing from 1 to 8 carbon atoms, and R² and R³ are alkyl groups of from 1 to 6 carbon atoms or aryl groups of from 6 to 15 carbon atoms;

(b) from about 35 to 75 mole percent of units of an alkyl acrylate; and

(c) from 0 to 20 mole percent of units of an ethylenically unsaturated monomer containing groups therein comprising at least one thioether moiety; said amphiphilic copolymer being characterized as being at least 3% soluble, by weight, in water at room temperature at a pH of less than 5 and at least 3%, by weight, soluble in an organic solvent.

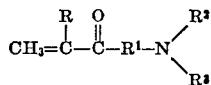
2. A photographic element according to claim 1 wherein said crystals of inorganic salt are formed in an aqueous medium, coagulated and then redispersed in an organic liquid before mixing with said organic silver salt.

3. A photographic element according to claim 1 comprising at least one layer containing a reducing agent.

4. A photographic element according to claim 1 comprising at least one layer containing an activator-toner agent.

5. A process for forming a photographic composition comprising (A) forming inorganic silver halide salt crystals in a liquid medium in the presence of an amphiphilic copolymer which is a silver halide peptizer consisting of:

(a) from 25 to 65 mole percent of units of an (N,N-dialkylamino) alkyl acrylate represented by the formula



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wherein R is a hydrogen atom or a methyl group, R¹ is an alkylene group containing from 1 to 8 carbon atoms, and R² and R³ are alkyl groups of from 1 to 6 carbon atoms or aryl groups of from 6 to 15 carbon atoms;

(b) from about 35 to 75 mole percent of units of an alkyl acrylate; and

(c) from 0 to 20 mole percent of units of an ethylenically unsaturated monomer containing groups therein comprising at least one thioether moiety; said amphiphilic copolymer being characterized as being at least 3% soluble, by weight, in water at room temperature at a pH of less than 5 and at least 3%, by weight, soluble in an organic solvent; and (B) mixing said inorganic silver halide salt crystals with an organic silver salt in an organic liquid medium.

6. A process according to claim 5 wherein said inorganic silver salt crystals are formed in an aqueous medium, coagulated and then redispersed in an organic liquid before mixing with said organic silver salt.

7. A process according to claim 5 wherein said amphiphilic copolymer is characterized as being at least 3%, by weight, soluble in water at room temperature and at least 3%, by weight, soluble in an organic solvent having a boiling point of less than 90° C.

8. A photographic element comprising at least one layer of said composition of claim 5 which has been coated from an organic liquid.

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