

[54] **PREPARATION OF SILVER SALTS IN AN ORGANIC LIQUID MEDIUM**

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[58] Field of Search.....**96/114.1, 114.6, 114**

[56] **References Cited**

UNITED STATES PATENTS

3,615,624	10/1971	Smith et al.	96/114
3,457,075	7/1969	Morgan et al.	96/114.6

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[57] **ABSTRACT**

Photographic silver halide salt compositions are formed in the presence of certain synthetic polymers in an organic solvent medium. In one aspect, silver halide grains having metal ions occluded therein can be made by this technique. In another aspect, inorganic silver halide slats made by this technique can be admixed with organic silver salts in an organic solvent and coated on a support to provide improved heat-developable photographic elements.

9 Claims, No Drawings

PREPARATION OF SILVER SALTS IN AN ORGANIC LIQUID MEDIUM

This invention relates to the preparation of silver salts and especially photographic silver salts. In one aspect, this invention relates to the precipitation or formation of silver salts in an organic liquid medium in the presence of certain synthetic polymers which are soluble in acetone. In another aspect, this invention relates to the precipitation of silver salts in an organic liquid medium in the presence of vinyl copolymers comprising groups appended thereto which contain thioether atoms and wherein said copolymer can be dissolved in acetone in concentrations of at least 3 percent, by weight, based on acetone. In another aspect, this invention relates to improved processes for making silver halide grains tailored for specific photographic applications such as heat-developable compositions comprising inorganic silver salts and organic silver salts and also compositions containing silver halide grains having metal ions occluded therein.

It is known in the art to prepare silver salts in the presence of gelatin in an aqueous medium wherein the gelatin acts to peptize the silver salt, preventing clumping of grains and providing somewhat uniform photographic properties throughout the silver halide composition. It is also known in the art to precipitate or form silver salt crystals in the presence of synthetic polymeric compounds which act as peptizers such as, for example, by procedures as disclosed in U.S. Ser. No. 701,084 by Smith et al. filed Jan. 29, 1968, now Pat. No. 3,615,624, and U.S. Pat. Nos. 3,419,397 by Merrill and Perry issued Dec. 31, 1968, 3,003,879 by Priest and Perry issued Oct. 10, 1961, 3,392,025 by Whiteley and Perry issued July 9, 1968, and 2,752,246 by Weaver issued June 26, 1956. However, improved methods of forming silver salts are desired which provide greater versatility in tailoring the particular silver salts to specific photographic systems.

We have now found an improved process for preparing photographic silver salts in an organic liquid medium in the presence of certain synthetic polymers which are more soluble in said organic liquid medium than in water at the same temperature. Generally, the silver salts can be prepared in a medium which is substantially free of proteinaceous compounds such as gelatin which has been commonly used in the preparation of silver halide grains.

In one preferred embodiment, the synthetic polymer used in the precipitation medium is a vinyl polymer comprising recurring units having thioether groups appended thereto.

In another preferred embodiment, the silver salts of this invention are precipitated in a medium wherein the liquid consists essentially of organic liquids.

In another embodiment, said organic liquid is one which is miscible with water and the silver salts are prepared in a mixture of water and the water-miscible organic liquid.

In another embodiment, silver salt crystals are formed in an organic solvent in the presence of a vinyl polymer comprising from 5 to 50 mole percent, and preferably from 10 to 30 mole percent, of recurring units having thioether groups thereon.

In still another highly preferred embodiment, the synthetic copolymers used in the organic liquid medi-

um for forming silver salts comprise recurring units having groups containing thioether groups and said copolymers can be further characterized as being 3% and preferably 5%, by weight, soluble in acetone at 25° C. and preferably are less than 3%, by weight, soluble in a water medium at a pH number less than 5 at 25° C.

The present process can be utilized for forming most silver salts including, for example, the silver halides and the silver salts of organic acids. In one preferred embodiment, the process is used to precipitate grains or crystals of inorganic silver salts such as silver bromide grains, silver chloride grains, silver iodide grains, silver chlorobromide grains, silver chlorobromiodide grains and the like.

The organic solvents referred to herein are those compounds which are solvents for the polymeric compounds used in the precipitation medium. The term "organic solvent" generally refers to those compounds comprising carbon atoms and generally 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 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. Of course, in those embodiments wherein water is also present during the precipitation step, the organic liquid is preferably water-miscible.

In one preferred embodiment of this invention, the synthetic polymers present during the precipitation comprise recurring units therein having groups appended thereto which have thioether or sulfide-sulfur atoms therein. In a preferred embodiment, the units of this type are 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, which is incorporated herein by reference. These units can be obtained from monomers such as:

N-(3-thiabutyl)acrylamide
 N-(3-thiapentyl)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
methacryloylprolylmethionine methyl ester

The useful synthetic polymers also generally include recurring units of alkyl acrylates. 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 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 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 copolymers used in the process of this invention generally are those which comprise from about 5 to about 50, and preferably from about 10 to about 30, mole percent of recurring units having groups appended thereto which have thioether or sulfide-sulfur atoms therein. Typical useful copolymers can be further characterized as being at least 3 percent preferably at least about 5 percent, by weight, soluble in acetone at 25° C. Moreover, the useful polymers are generally less than 3 percent soluble in water at 25° C. which has been adjusted to a pH number of less than 5. As a result, units which contain highly ionizable groups such as, for example, units containing sulfonic acid groups as 3-acryloxypropane-1-sulfonic acid sodium salt can be tolerated in only minor amounts such as mole percents of less than 10 percent, and preferably the useful copolymer is substantially free of units comprising sulfoxy groups (i.e., sulfur-oxygen groups). On the other hand, units such as those derived from acrylic acid which has a low ionization constant can be tolerated in much larger amounts. The copolymers of this invention can, of course, and generally do contain units which are regarded as being hydrophobic or neutral as long as the solubility of the copolymer can be characterized as defined above.

The silver salts prepared according to this invention can 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, for example, in U.S. Pat. Nos. 1,623,499 of Sheppard issued Apr. 5, 1927, 2,399,083 of Waller et al. issued Apr. 23, 1946, 3,297,447 of McVeigh issued Jan. 10, 1967, and 3,297,446 of Dunn issued Jan. 10, 1967.

Photosensitive, silver salt compositions prepared according to this invention can be protected against the production of fog and can be stabilized against 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; 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. Pat. Nos. 2,566,263 of Trivelli et al. issued Aug. 28, 1951, and 2,597,915 of Yutzky et al. issued May 27, 1952.

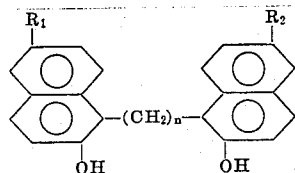
In one preferred embodiment of this invention, a support is provided with coatings thereon of a light-stable organic silver-salt oxidizing agent, an organic reducing agent and a photosensitive, inorganic, silver salt, preferably silver halide, which provides a photographic and thermographic element. 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 photographic and thermographic elements comprise the inorganic silver salt in admixture with the organic silver salt. A typical concentration range of the described 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 halides, e.g., silver chloride, silver bromide, silver chlorobromide, silver iodide, silver bromiodide, silver chloriodide, silver chlorobromiodide, or mixtures thereof. The photosensitive silver halide can be coarse- or fine-grain; in one embodiment, the very fine-grain silver halides are especially useful.

The photographic and thermographic elements 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-octadecyloxydiphenyl-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 thermographic 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:

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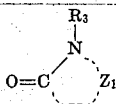
wherein R_1 and/or R_2 are hydrogen, alkyl containing one to three carbon atoms, alkoxy, e.g., alkoxy containing one to two carbon atoms such as methoxy or ethoxy, halogen, nitro, amino or a diazonium halide salt, and n is 0 or 1. Suitable bis- β -naphthols which can be employed in the practice of the 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.

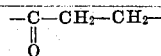
Other reducing agents, which are typically silver halide developing agents, can be used alone or in conjunction with the above bis-naphthol reducing agents. Suitable silver halide developing agents include, for example, polyhydroxybenzenes such as hydroquinone developing agents, e.g., hydroquinone, alkyl-substituted 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 anhydrodihydropyridino hexose reductone; and the like.

It is desirable to employ an activator-toning agent in the certain embodiments of the thermographic elements to obtain a desired image, particularly when phenolic reducing agents are used. A suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom and of the formula:

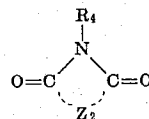


6

wherein R_3 is hydrogen, hydroxyl or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z_1 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 three or four carbon atoms. The atoms completing the heterocyclic nucleus can contain 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 formula:



wherein R_4 is hydrogen, hydroxyl or a metal ion such as potassium, sodium, lithium, silver, gold or mercury; Z_2 represents carbon atoms of a series completing a cyclic imide nucleus, typically consisting of from five to six 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 one to five carbon atoms, such as methyl, ethyl, propyl, butyl or pentyl or aryl, such as aryl containing six 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 photographic and thermographic 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. No. 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. No. 3,446,648 of Workman issued May 27, 1969.

In another preferred embodiment, the procedures of this invention are used to prepare silver halide grains having polyvalent metal ions occluded therein. Generally, the organic medium permits greater versatility in incorporating metal ions in the silver halide

grain, especially with polyvalent metal salts which complex or react with water. Typical silver halide emulsions of this type which can be advantageously prepared by the procedures of this invention include those described in U.S. Pat. Nos. 3,447,927 by Bacon et al. issued June 3, 1969, 3,271,152 by McBride issued Sept. 6, 1966, 3,367,778 by Berriman issued Feb. 6, 1968, and 3,531,291 by Bacon issued Sept. 29, 1970, British Pat. No. 1,151,782 by Berriman, and the like. When emulsions are prepared in accordance with U.S. Pat. No. 3,447,927 in one preferred embodiment of this invention, improved heat-stabilization properties and image characteristics are observed when elements containing these emulsions are processed by the procedure of Colt, U.S. Pat. No. 3,418,122 issued Dec. 24, 1968. Of course, additional polyvalent metal ions may be added to emulsions containing grains having occluded polyvalent metal ions therein prepared in accordance with this invention in the same manner as for emulsions prepared in the presence of gelatin; polyvalent metal ion salts, such as lead salts, rhodium salts and the like, generally promote heat stabilization of silver halide emulsions and improve image characteristics upon chemical development and heat development.

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

Example 1: Preparation of copoly(3-thiapentyl acrylate — ethyl acrylate) mole ratio 1:9)

A flask is charged with a solution of 8.0 g. (0.05 mole) of 3-thiapentyl acrylate, 45.0 g. (0.45 mole) of ethyl acrylate and 0.27 g. of 2,2'-azobis(2-methylpropionitrile) in 250 ml. of acetone. After purging the solution with nitrogen for 10 minutes, it is heated to 60° C. under a reflux condenser overnight. A clear, colorless, viscous dope results which is found to contain 21.7% solids. The dope is used directly without further purification.

A portion of another sample prepared in the same manner is poured slowly into a large excess of a 1:1 (vol.) mixture of methanol and water with stirring. The slightly sticky, rubbery, white polymer which precipitates is thoroughly washed in the same nonsolvent mixture and dried under vacuum. A sticky, colorless product is obtained which has an inherent viscosity in acetone of 0.66.

Analysis calculated for $C_{52}H_{84}O_{20}S$: 58.8% C, 8.0% H, 3.0% S.

Found: 58.4% C, 7.5% H, 2.9% S.

Example 2: Preparation of copoly(3-thiapentyl acrylate — ethyl acrylate — acrylic acid) (mole ratio 1:4:5)

A flask is charged with a solution of 16.0 g. (0.10 mole) of 3-thiapentyl acrylate, 40.0 g. (0.40 mole) of ethyl acrylate, 36.0 g. (0.50 mole) of acrylic acid and 0.46 g. of 2,2'-azobis(2-methylpropionitrile) in 360 ml. of acetone. After purging the solution with nitrogen for 10 minutes, it is heated to 60° C. under a reflux condenser overnight. A clear, colorless, viscous dope results which is found to contain 25.6% solids.

A small portion of the dope is poured slowly into a large excess of a 1:1 (vol.) mixture of methanol and water with stirring. The sticky, rubbery product which precipitates is thoroughly washed in the same nonsolvent mixture and dried under vacuum. It is found to have an inherent viscosity in acetone of 0.90.

Analysis calculated for $C_{42}H_{64}O_{20}S$: 54.8% C, 7.0% H, 3.5% S.

Found: 54.6% C, 7.1% H, 3.3% S.

Example 3: Preparation of copoly(3-thiapentyl acrylate—ethyl acrylate—acrylic acid) (mole ratio 1:6:3)

A flask is charged with a solution of 16.0 g. (0.10 mole) of 3-thiapentyl acrylate, 60.0 g. (0.60 mole) of ethyl acrylate, 21.6 g. (0.30 mole) of acrylic acid and 0.48 g. of 2,2'-azobis(2-methylpropionitrile) in 390 ml. of acetone. After purging the solution with nitrogen for 10 minutes, it is heated to 60° C. under a reflux condenser overnight. A clear, colorless, viscous dope results which is found to contain 25.4% solids.

A small portion of the dope is poured slowly into a large excess of a 1:1 (vol.) mixture of methanol and water with stirring. The sticky, rubbery product which precipitates is thoroughly washed in the same nonsolvent mixture and dried under vacuum. It is found to have an inherent viscosity in acetone of 0.97.

Analysis calculated for $C_{46}H_{72}O_{20}S$: 56.5% C, 7.4% H, 3.3% S.

Found: 55.6% C, 8.0% H, 3.1% S.

Example 4: Preparation of copoly(3-thiapentyl acrylate — butyl acrylate) (mole ratio 1:6)

A flask is charged with a solution of 72.0 g. (0.45 mole) of 3-thiapentyl acrylate, 345.6 g. (2.70 moles) of butyl acrylate and 1.25 g. of 2,2'-azobis(2-methylpropionitrile) in 1600 ml. of p-dioxane. The solution is purged with nitrogen for 20 minutes and then heated to 60° C. under a blanket of nitrogen overnight. The clear, colorless, viscous dope which results is poured slowly into a large excess of a 3:2 (vol.) mixture of methanol and water with stirring. The sticky white polymer which precipitates is thoroughly washed in 3:1 (vol.) mixture of methanol and water. It is dried under vacuum yielding 406.7 g. (98% yield) of a sticky, colorless polymer. The product has an inherent viscosity in acetone of 0.31.

Analysis calculated for $C_{43}H_{84}O_{14}S$: 63.3% C, 9.1% H, 3.4% S.

Found: 62.8% C, 8.8% H, 3.3% S.

Example 5: Preparation of AgBr grains in the presence of copoly[3-thiapentylacrylate — ethyl acrylate] (mole ratio 1:9)

To a mixture of 2 g. copoly[3-thiapentylacrylate — ethyl acrylate] in 20 ml. acetone are added simultaneously 20 ml. of a 0.25M solution of $AgClO_4$ in acetone and 20 ml. of a 0.25M solution of LiBr in acetone. The temperature is 23° C., and the constant rate of addition for each solution is 19.4 ml. per minute.

After the addition, hexane is added to precipitate copoly[3-thiapentylacrylate — ethyl acrylate], AgBr, and $LiClO_4$. The undesirable $LiClO_4$ is then removed by adding ethanol and decanting, leaving the gummy emulsion, which is redispersed in 30 ml. acetone.

Example 6: Preparation of AgBr grain incorporating Au^{-3}

To a solution of 19 ml. acetone, 2 g. of copoly[3-thiapentylacrylate — ethyl acrylate] (mole ratio 1:9), and 1 ml. of 0.0001M $KAuBr_4$ in acetone are added simultaneously 20 ml. of 0.25M $AgClO_4$ solution in acetone and 20 ml. of 0.25M LiBr solution in acetone. The reaction temperature is 23° C., and the constant rate of addition for each solution is 19.4 ml. per minute.

After the addition, hexane is added and the supernatant liquid is poured off. The precipitate is washed several times with ethanol to remove the LiClO_4 . The emulsion remaining is redispersed in 30 ml. acetone. The emulsion is then hand-coated on a film base with and without a halogen acceptor and tested for print-out by exposing 15 seconds to photoflood through a step wedge with 0.3 log E steps. The coating without the halogen acceptor shows about one step of print-out while the coating containing the halogen acceptor shows six steps of print-out.

Example 7:

A light-sensitive silver halide photographic emulsion is prepared. Silver perchlorate (AgClO_4) is added to an acetone solution in sufficient amount to result in a concentration of 10^{+1} molar. In a similar manner, lithium bromide (LiBr) is added to an acetone solution in quantities sufficient to result in a concentration of 10^{+1} molar. A third solution is prepared by dissolving copoly[3-thiapentylacrylate—ethyl acrylate] (mole ratio 1:9) in acetone.

Equal volumes of the silver salt and halide compound solution are added at a controlled flow rate to the third solution with rapid agitation. A fine-grain silver halide emulsion results. Table 1 describes several photographic emulsions which are prepared according to the method of this example. Table 1 further describes variations in preparation of each of the emulsions.

TABLE 1

Emulsion	Flow Rate (cc/min)		Concentration/Ag Mole of Copolymer* in Reaction Vessel	Reaction Temp.
	AgClO_3	LiBr		
A	0.25	0.25	50.0 g.	23°C.
B	0.25	0.25	200.0 g.	23°C.
C	1.00	1.00	50.0 g.	23°C.
D	1.00	1.00	200.0 g.	23°C.
E	8.00	8.00	50.0 g.	23°C.
F	8.00	8.00	200.0 g.	23°C.

*copoly[3-thiapentyl acrylate—ethyl acrylate] (mole ratio 1:9)

Example 8:

Several light-sensitive photographic materials are prepared containing the following components:

silver behenate (50 mg./ml. in acetone)	2.0 ml.
behenic acid (200 mg./ml. in acetone)	0.5 ml.
poly(vinyl butyral) (60 mg./ml. in acetone)	0.5 ml.

These components are dispersed with an ultrasonic probe and the following materials are then added:

silver halide emulsion (from Table 1; level described in Table 2)	
3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinyldene)isopropylidene]rhodanine (7 mg./ml. in acetone-methanol)	2.0 ml.
1,1'-bi-2-naphthol (3% in acetone)	2.0 ml.
phthalimide (1% in acetone)	2.0 ml.

The above photographic mixtures are coated on a resin-treated photographic paper support at a wet thickness of 0.004 inch. Table 2 will describe the light-sensitive silver halide photographic emulsion used in each coating.

TABLE 2

Coating	AgBr emulsion used	Level of AgBr Coated (mg./ft. ²)
5		
-1	-A	1.0
-2	-B	1.0
-3	-C	0.5
-4	-D	0.5
-5	-E	1.0
10	-6	1.0

Samples of the coatings of this example are exposed to a line copy for 5.0 seconds on a Kodak Verifax copier. The exposed samples are heat-processed on a curved hot block for 5—10 seconds at a temperature of 130°—140° C. In each case the samples produce a visible line image.

Example 9:

A light-sensitive silver halide photographic emulsion is prepared. Silver perchlorate (AgClO_4) is added to acetone in sufficient quantity to result in a concentration of 10^{-1} molar. Similarly, lithium bromide (LiBr) is added to acetone in amounts sufficient to result in a concentration of 10^{-1} molar. A third solution is prepared by dissolving 50.0 g. of copoly[3-thiapentyl acrylate — ethyl acrylate — acrylic acid] (mole ratio 1:4:5) per mole of silver bromide in 25.0 ml. of acetone.

When all solutions have been prepared, equal volumes of the silver salt and lithium bromide solutions are added at a controlled rate of flow (≈ 2.0 ml. per minute) to the third solution containing the copolymeric silver halide peptizer. A fine-grain silver bromide photographic emulsion results.

Example 10:

The procedure set out for the production of the fine-grain, light-sensitive, silver bromide, non-gelatin emulsion of Example 9 is repeated with the exception that copoly[3-thiapentyl acrylate — ethyl acrylate — acrylic acid] (mole ratio 1:6:3) is substituted for copoly[3-thiapentyl acrylate — ethyl acrylate — acrylic acid] (mole ratio 1:4:5).

Example 11:

The procedure set out for the production of the fine-grain, light-sensitive, silver bromide, non-gelatin, photographic emulsion of Example 9 is repeated with the exception that copoly[3-thiapentyl acrylate — n-butyl acrylate] (mole ratio 1:6) is substituted for copoly[3-thiapentyl acrylate — ethyl acrylate — acrylic acid] (mole ratio 1:4:5).

Example 12:

Several photosensitive and thermosensitive elements are prepared by coating the following composition on a suitable photographic paper support at a wet thickness of 0.004 inch.

60	silver emulsion (preparations described in Examples 9—11)	2.0 ml.
	silver behenate (50mg./ml. acetone)	2.0 ml.
	1,1'-bi-2-naphthol (3.0% acetone)	2.0 ml.
	phthalimide (1.0% acetone)	2.0 ml.
65	3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinyldene)isopropylidene]rhodanine (7mg./ml. acetone)	1.0 ml.
	poly(vinyl butyral) (3.5% acetone)	1.0 ml.

Table 3 describes the specific silver bromide photographic emulsion employed in each of the elements of this example. Table 3 further gives a visual analysis of the photographic images which result from exposing samples of the photographic and thermographic elements of this example to a tungsten light source for several seconds and heat-processing the exposed samples for about 5—15 seconds on a curved hot block whose temperature is about 120°—130° C.

TABLE 3

Example Number of Emulsion	Visual Evaluation
9	green image of 5 visible steps on pink background
10	green image of 7 visible steps on pink background
11	green mottled image on pink background

Example 13: (comparison)

A coating composition is prepared by mixing the following components:

silver behenate	42.0 g.	25
behenic acid	32.0 g.	
polyvinyl butyral	15.0 g.	
silver bromide (prepared ex situ in the absence of a peptizer)	0.45 g.	
phthalimide	8.5 g.	
acetone-toluene (1:1 parts by volume)	500 ml.	30

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	4.4 ml.	35
acetone containing 6.25% by weight 2,2'-dihydroxy-1,1'-binaphthyl	52.5 ml.	

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

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 compared with the elements made in accordance with Examples 9 and 10 wherein the inorganic silver halide

is prepared in the presence of a polymer which is a silver halide peptizer.

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.

We claim:

1. In a process of forming silver halide salt crystals in an organic solvent having a boiling point below 165° C, the improvement comprising forming said crystals in said organic solvent in the presence of a synthetic polymeric compound which is a vinyl copolymer comprising (1) recurring units having groups appended thereto which contain thioether moieties or sulfide-sulfur atoms therein and (2) recurring units of an alkyl acrylate.

2. A process according to claim 1 wherein said copolymer comprises from about 5 to about 50 mole percent of said recurring units having groups appended thereto which contain thioether or sulfide-sulfur atoms therein.

3. A process according to claim 1 wherein said copolymer is characterized as being at least 3 percent, by weight, soluble in acetone at 25° C.

4. A process according to claim 1 wherein said silver salt crystals are formed in the presence of polyvalent metal ions.

5. A process according to claim 1 wherein said silver salts are formed in the presence of trivalent or tetravalent metal ions.

6. A photographic element comprising (1) a support and (2) at least one layer thereon comprising an organic silver salt in admixture with an inorganic silver halide salt which has been formed in an organic solvent having a boiling point below 165° C in the presence of a synthetic vinyl copolymer comprising (a) recurring units having groups appended thereto which contain thioether moieties or sulfide-sulfur atoms therein and (b) recurring units of an alkyl acrylate.

7. A photographic element according to claim 6 wherein said synthetic vinyl copolymer is at least 3%, by weight, soluble in acetone and less than 3%, by weight, soluble in water at 25° C. at a pH number less than about 5.

8. A photographic element according to claim 6 wherein said synthetic vinyl copolymer is copoly(3-thiapentyl acrylate — ethyl acrylate).

9. A photographic element according to claim 6 wherein said synthetic vinyl copolymer is copoly(3-thiapentyl acrylate — ethyl acrylate — acrylic acid).

* * * * *

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60

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