

1

3,690,888

## PROCESS OF MAKING SILVER HALIDE EMULSIONS HAVING POLYVALENT METAL IONS OCCLUDED THEREIN

Robert Elwin Bacon, Ernest John Perry, and Evan Thomas Jones, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Filed June 4, 1970, Ser. No. 43,565

Int. Cl. G03c 1/02

U.S. Cl. 96-94

13 Claims

### ABSTRACT OF THE DISCLOSURE

An improved process is disclosed for preparing silver halide emulsions which contain grains having polyvalent metal ions occluded therein; the improvement comprises the step of forming the silver halide grains in the presence of (1) a peptizer consisting essentially of an acrylic polymer and (2) the polyvalent metal ions to be occluded inside the grains.

This invention relates to methods of precipitating silver salts and the products produced thereby. In one aspect, this invention relates to the preparation of silver halide crystals having polyvalent metal ions occluded therein wherein said silver halide crystals are formed in the presence of a polymeric acrylic peptizer. In another aspect, this invention relates to a process wherein very low concentrations of polyvalent metal ions can be used during the precipitation of silver salt crystals in the presence of a linear addition acrylic peptizer.

It is known in the art to form silver halide crystals having polyvalent metal ions occluded therein; emulsions of this type are generally disclosed in U.S. Pats. 3,367,771 by Berriman; 2,717,833 by Wark; 3,447,927 by Bacon; British Pat. 1,151,782 by Berriman; and French Pat. 1,574,038 by Bacon. Prior-art techniques have generally involved precipitation of the silver halide in the presence of a gelatinous medium, ripening the grains in a gelatinous medium or subsequent precipitation in a gelatinous medium to achieve occluded polyvalent metal ions within the silver salt crystal. Improved methods of forming grains of this type are desirable to provide improved photographic properties of the respective emulsions.

We have now found that improved silver salt compositions can be made by forming the silver halide grains in the presence of polyvalent metal ions and a peptizer wherein said peptizer consists essentially of a synthetic, linear addition, acrylic polymer. Silver halide crystals prepared by the present process are more regular in shape and more uniform in size than crystals prepared under similar conditions in the presence of gelatin. Moreover, foreign metal ion impurities are substantially reduced and apparently lower concentrations of the desired polyvalent metal ion can be used during the precipitation since it does not appear to be sequestered in the form of a complex with other ions or with gelatin. Many other quasi-peptizers such as, for example, polyvinyl alcohol, do not exhibit the same improvements, which is apparently due to relatively poor peptizing ability and the high contamination of catalysts, etc., during the polymerization reactions.

One preferred embodiment of this invention relates to precipitation of silver halide grains in the presence of

2

polyvalent metal ions and a peptizer which consists essentially of an acrylic polymer having groups appended thereto containing sulfide atoms and preferably thioether moieties wherein the sulfur atom in linking two alkyl groups.

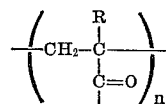
Another preferred embodiment relates to the precipitation of silver halide crystals in the presence of trivalent metal ions and an acrylic peptizer in an acidic medium.

Another highly preferred embodiment relates to the precipitation of silver halide crystals in the presence of bismuth, iridium, lead and/or osmium ions in an acrylic peptizer.

Still another preferred embodiment relates to improved silver halide emulsions wherein the silver halide grains are prepared in the presence of trivalent metal ions and in an acrylic, polymeric silver halide peptizer and wherein a direct-print-type halogen acceptor is contiguous to said silver halide grains.

Another embodiment relates to fogged, direct-positive silver halide emulsions wherein the fogged silver halide grains contain polyvalent metal ions occluded therein and the grains are formed in the presence of a peptizer which consists essentially of an acrylic polymer having groups appended thereto containing sulfide-sulfur atoms and preferably thioether moieties wherein the sulfur atom links two alkyl groups.

The synthetic linear addition polymers useful in this invention generally include any good silver halide peptizer which can be polymerized with a minimum of metal ion contaminant or wherein any contaminants can be effectively removed after polymerization. Polymers which have been found to be very effective for this purpose are those acrylic copolymers which are also good silver halide peptizers. It is understood that "acrylic" means that the polymer contains units of the formula:



where R is hydrogen or methyl, in the linear addition chain of the polymeric material. In one embodiment, the preferred copolymers of this invention which can be used as peptizers contain a peptizer unit which is derived from an amide or ester in which the respective amine or alcohol condensation residues comprise an organic radical having at least one sulfide-sulfur atom linking two alkyl carbon atoms. Typical polymers of this type are disclosed in U.S. Ser. No. 701,084, filed Jan. 29, 1968, now U.S. Pat. 3,615,624, such as, for example, peptizer units of acrylamides or acrylates containing an appended straight or branched chain alkyl group, preferably appended to the ester or amide group, of from about 2 to about 12 carbon atoms containing at least one sulfide-sulfur atom linking the respective alkyl carbon atoms in said chain. Typical preferred peptizing moieties are units such as, for example,

N-(3-thiabutyl)acrylamide

N-(3-thiapentyl)acrylamide

N-(4-methyl-2-thiapentyl)acrylamide

3

N-(2,5-dimethyl-4-thiabexyl)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  
 bis(2-thiabutyl)methyl acrylate  
 methylthioethyl acrylate  
 methacryloylpyrrolmethionine methyl ester

The copolymers used in this invention comprise at least 5% and preferably at least about 20% of units of the peptizing monomer, by weight, and preferably units of at least one other ethylenically unsaturated monomer. Typical useful ethylenically unsaturated monomers include acrylic acid; methacrylic acid; acrylic amines such as N,N-(dimethylacrylamide), 2-methyl-5-vinylpyridine, and the like; acrylic esters such as methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, 3-acryloxypropane-1-sulfonic acid, sodium salt, and the like. Preferably the ethylenically unsaturated monomers selected in making the peptizers used in this invention include moieties which will form water-solubilizing units and hydrophobic units.

In another embodiment, the units of the peptizing monomers are copolymerized with at least two other different monomers to provide a balanced polymer which can be coagulated and redispersed easily by mere change of pH. Typical polymers of this type are disclosed in Smith et al., U.S. Ser. No. 11,839, filed Feb. 16, 1970, entitled "Terpolymers and Their Use in Dispersions."

The copolymers 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 interpolmer 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 0.05 to about 4.

The procedure of this invention can generally be used to obtain improved photographic properties in any emulsion wherein the grains are prepared in such a manner to incorporate deliberately polyvalent metal ions therein. Typical useful emulsions where the grains are formed in the presence of a peptizing medium according to this invention and a polyvalent metal ion for occlusion therein include those described in U.S. Pats. 3,367,771 by Beriman; 2,717,833 by Wark; 3,447,927 by Bacon; and French Pat. 1,574,038 by Bacon.

In accordance with the invention, polyvalent metal ions are used in the precipitation or formation of the silver halide grains. Divalent ions such as lead ions, tetravalent ions such as osmium, platinum, iridium, etc., and preferably trivalent metal ions are used in the process. Typical suitable trivalent metal ions include those of antimony, bismuth, arsenic, gold, iridium, rhodium and the like. The polyvalent metal ion can be suitably added with the water-soluble silver salt (e.g., sodium or potassium iodide, bromide or chloride) that is conventionally reacted to prepare or precipitate photographic silver halide. Likewise, the polyvalent ions can be introduced into the silver halide precipitation vessel with the peptizer. The polyvalent metal ions can be added to the system as water-soluble inorganic salts, as organo-metallic materials, as complexes, or as any other form of material that results in the availability of the respective polyvalent metal ions during the formation of the silver halide. The amount of polyvalent metal utilized can be widely varied, although at least about  $1 \times 10^{-5}$ , and more generally  $1 \times 10^{-4}$  to 2, mole percent based on the silver halide is used. In one

4

highly preferred embodiment, the grains are formed in the presence of lead, osmium, bismuth or iridium ions.

In preparing the silver halide used in the invention, the water-soluble silver salt and the water-soluble halide are reacted to precipitate the silver halide, preferably under acidic conditions. The pH of the silver halide precipitation is typically less than 6 and preferably less than 5. Such acids or phosphoric, trifluoroacetic, hydrobromic, hydrochloric, sulfuric and nitric are typically utilized in the silver halide precipitating media to maintain acidic conditions. The silver halide grains useful in the invention generally have an average grain size of about .01 to 10 microns, and more generally about .05 to 2 microns, in diameter.

It is generally known in the art that changes in the halide ion concentration during precipitation of the silver halide grains having occluded trivalent metal ions therein result in a more stable maximum density, especially when bismuth ions are occluded therein and the photographic element containing said emulsion is exposed and processed by procedures as described in Colt, U.S. Pat. 3,418,122. Halide ion concentration changes during the precipitation after incorporation of polyvalent metal ions in the grains also result in improved maximum density and other photographic properties when the present procedure is used to prepare the emulsion, especially when reactant concentrations such as pH and pAg are closely monitored and controlled by an automatic control apparatus.

The invention can be further illustrated by the following examples.

#### EXAMPLE 1-A

A control radiation-sensitive gelatino-silver chlorobromide (5 mole percent chloride and 95 mole percent bromide) photographic emulsion is prepared by slowly adding simultaneously an aqueous solution of silver nitrate and an aqueous solution of alkali metal halides to an agitated aqueous acidic gelatin solution, which contains 75 mg. of bismuth trinitrate pentahydrate per silver mole.

#### EXAMPLE 1-B

A radiation-sensitive silver chlorobromide photographic emulsion is prepared according to the procedure of Example 1-A. This emulsion differs only in the replacement of the gelatin peptizer with 1/6 copoly[3-thiapentylacrylate-3-acryloxypropane-1-sulfonic acid, sodium salt]. Visual comparison of electron photomicrographs of this emulsion as compared with the emulsion of Example 1-A clearly shows that a more narrow grain size distribution is obtained in the emulsion of Example 1-B, i.e., a more monodispersed emulsion.

#### EXAMPLE 1-C

Several photographic emulsions of the type described in Example 1-A are prepared. These emulsions differ by the replacement of the gelatin peptizer with 1/2/5 (approximate by weight) copoly[3-thiapentylacrylate-acrylic acid-3-acryloxypropane-1-sulfonic acid, sodium salt] and varying the concentration of bismuth trinitrate pentahydrate (such levels are given in the table of Example 2, labeled Examples 1-C(a) through 1-C(e)).

#### EXAMPLE 2 (PHOTOGRAPHIC DATA)

The emulsions of Examples 1-A and 1-C are treated with a dithiourazole-methyl vinyl ketone adduct as described in Wise et al., U.S. Ser. No. 816,867 filed Apr. 4, 1969, now U.S. Pat. 3,615,618. The emulsion of Example 1-B is treated with dithiourazole hydrazine salt. A gelatin solution, acting as the vehicle, is added to each emulsion so as to have 5 percent by weight gelatin. Each sample is then coated on a photographic paper support at about 60 mg. of silver/ft.<sup>2</sup>.

Samples of each of these coatings are exposed 1 second on a Kodak Regent Printer through a 0.15-density increment step wedge, then placed in contact with a heated platen at 235° C. for 5 seconds, and then photodeveloped

for 5 minutes with two 8-watt BL fluorescent lamps. The results are recorded in the following table:

TABLE

Peptizer	Bi(NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O, mg./Ag mole	Number of visible steps #0.15 step	Reflection	
			D <sub>max</sub>	D <sub>min</sub>
Example:				
1-A-----Gelatin-----	75	12	1.05	0.02
1-B-----I <sup>1</sup> -----	75	13+	1.05	0.04
1-C(a)-----II <sup>2</sup> -----	0.75	14+	0.72	0.02
1-C(b)-----II <sup>2</sup> -----	2.5	15	0.92	0.02
1-C(c)-----II <sup>2</sup> -----	7.5	16+	1.00	0.02
1-C(d)-----II <sup>2</sup> -----	25	14	1.17	0.04
1-C(e)-----II <sup>2</sup> -----	75	13+	1.12	0.05

<sup>1</sup> 1:6 copoly[3-thiapentylacrylate-3-acryloxypropane-1-sulfonic acid, sodium salt].

<sup>2</sup> 1:2:5 (approximate) copoly[3-thiapentylacrylate-acrylic acid-3-acryloxypropane-1-sulfonic acid, sodium salt].

Similar improved results are obtained when the emulsions are prepared in the presence of a peptizer which consists essentially of the acrylic copolymers:

copoly(acryloylmethionine-acrylic acid) (3:1),  
copoly(methylthioethyl acrylate-acrylic acid) (3.33:1),  
copoly(acryloylmethionine methyl ester-acrylic acid-ethyl acrylate) (1.0:3.02:6.5) and  
copoly(N-(3,6 - dithioctyl)acrylamide - 3 - acryloxypropane-1-sulfonic acid, sodium salt) (1:15).

#### EXAMPLE 3

Fogged, direct-positive emulsions containing polyvalent metal ions occluded in the grains have improved photographic properties when the grains are formed in the presence of an acrylic peptizer and the polyvalent metal ion.

An internal sensitive emulsion is prepared by adding simultaneously aqueous solutions of silver nitrate and an alkali metal halide (97.5 mole percent potassium bromide and 2.5 mole percent potassium iodide) to a gelatin solution containing 100 mg. of potassium hexachloroiridate per silver mole.

A second internal-image emulsion is prepared similar to the procedure described above except the gelatin peptizer is replaced with copoly(3-thiapentylacrylate-3-acryloxypropane-1-sulfonic acid sodium salt) (1:6 by weight).

The above washed emulsions are then fogged by adding 0.5 mg. of thiourea dioxide per silver mole and 2.0 mg. of potassium chloraurate per silver mole and heated for 60 minutes at 65° C. The emulsions are coated on a film support at 100 mg. of silver/ft.<sup>2</sup>, exposed for 1 second on a Bausch and Lomb spectrograph and developed for 6 minutes in the following solvent developer:

G.	
1-phenyl-3-pyrazolidone -----	10
Sodium isoascorbate -----	40
Sodium sulfite -----	20
Phenylmercaptotetrazole -----	0.25
Potassium iodide -----	0.5
Water to 1 liter.	

The following reversal images are obtained:

Peptizer	D <sub>max</sub>	D <sub>min</sub>	ΔD
Gelatin-----	1.98	1.80	.18
Acrylic polymer-----	1.30	.58	.72

It is apparent from the above data that a reversal image having a substantially greater discrimination is obtained when the peptizer for a silver halide emulsion is an acrylic polymer.

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 for preparing silver halide emulsions

comprising preparing silver halide grains in the presence of a peptizer, said grains having polyvalent metal ions occluded therein, the improvement comprising the step of forming the silver halide grains in the presence of a peptizer which consists essentially of an acrylic polymer; said polymer being a copolymer comprising at least one recurring acrylic unit which has appended thereto by means of an amide or ester linkage an organic radical having at least one sulfide-sulfur atom linking two alkyl carbon atoms.

2. A process according to claim 1 wherein said polyvalent metal ions are present in a concentration of at least  $1 \times 10^{-5}$  mole percent based on the silver halide.

3. A process according to claim 1 wherein said polyvalent metal ions are trivalent metal ions.

4. A process according to claim 1 wherein said polyvalent metal ions are bismuth, osmium or iridium ions.

5. A process according to claim 1 wherein the polyvalent metal ions are occluded in the silver halide grains in an acidic medium.

6. A process according to claim 1 wherein said acrylic polymer comprises units of an acrylamide or an acrylate containing appended organic groups containing from about 2 to about 12 carbon atoms and containing at least one sulfide-sulfur atom linking 2 of said carbon atoms.

7. A process according to claim 1 wherein said peptizer is copoly(N-(3-thiabutyl)acrylamide-3-acryloxypropane-1-sulfonic acid, sodium salt).

8. A process according to claim 1 wherein said peptizer is copoly(3-thiapentylacrylate-acrylic acid -3-acryloxypropane-1-sulfonic acid, sodium salt).

9. A silver halide emulsion formed by the process of claim 1.

10. In a radiation-sensitive, silver halide emulsion comprising silver halide grains formed in the presence of trivalent metal ions in an acidic medium and a halogen acceptor contiguous to said silver halide grains, the improvement comprising the formation of said silver halide grains in the presence of a silver halide peptizer consisting essentially of an acrylic polymer in addition to the formation of said grains in the presence of said polyvalent metal ions; said polymer being a copolymer comprising at least one recurring acrylic unit which has appended thereto by means of an amide or ester linkage an organic radical having at least one sulfide-sulfur atom linking two alkyl carbon atoms.

11. An improved silver halide emulsion according to claim 10 wherein said polyvalent metal ions are water-soluble.

12. An improved silver halide emulsion according to claim 10 wherein said polyvalent metal ions are bismuth ions.

13. In a radiation-sensitive, direct-positive emulsion comprising fogged silver halide grains having iridium ions occluded therein, the improvement comprising the formation of said silver halide grains in the presence of a silver halide peptizer consisting essentially of an acrylic polymer; said polymer being a copolymer comprising at least

**7**

one recurring acrylic unit which has appended thereto by means of an amide or ester linkage an organic radical having at least one sulfide-sulfur atom linking two alkyl carbon atoms.

**References Cited****UNITED STATES PATENTS**

3,419,397	12/1968	Merrill	96—114
3,457,072	7/1969	Ditzer	96—94
3,511,662	5/1970	Jouy	96—114
3,520,857	7/1970	Merrill	96—114
3,531,289	9/1970	Wood	96—94

**8**

3,531,291	9/1970	Bacon	96—94
3,547,647	12/1970	Bacon	96—94

**FOREIGN PATENTS**

5	902,891	8/1962	Great Britain.
	1,173,532	12/1969	Great Britain 96—114.7

NORMAN G. TORCHIN, Primary Examiner

J. R. HIGHTOWER, Assistant Examiner

U.S. Cl. X.R.

96—114, 114.7