SILVER HALIDE EMULSION WITH GRAFT COPOLYMER BINDERS

Inventors: Maurice J. Fitzgerald, Canton; Lloyd D. Taylor, Lexington, both of Mass.


Filed: Oct. 8, 1971

Appl. No.: 187,827

U.S. Cl. ........................................... 96/113, 96/114
Int. Cl. ............................................. G03c 1/04
Field of Search ................................. 96/114, 113

References Cited
UNITED STATES PATENTS

3,186,973 6/1965 Maeder ................................. 96/114

ABSTRACT

A photosensitive silver halide emulsion wherein the emulsion binder comprises a graft copolymer of an amine acrylamide monomer on a polymer containing a plurality of hydroxyl groups.

23 Claims, No Drawings
1

SILVER HALIDE EMULSION WITH GRAFT COPOLYMER BINDERS

BACKGROUND OF THE INVENTION

This invention relates to photography and more particularly, to novel photosensitive photographic elements, particularly novel photosensitive emulsions.

As a result of the known disadvantages of gelatin, in particular, its variable photographic properties and its fixed physical properties, for example, its diffusion characteristics; much effort has been expended in the past in order to replace gelatin with a suitable synthetic colloid binder for photographic silver halide emulsions. Many synthetic polymeric materials have heretofore been suggested as peptizers for silver halide emulsions, however, these have generally not functioned satisfactorily and frequently have not fulfilled all of the basic requirements for a photosensitive silver halide emulsion binder listed following:

1. absent (or constant) photographic activity;
2. ability to form an adsorption layer on microcrystals of silver halide permitting stable suspensions to be obtained;
3. ability to form adsorption layers as described in 2 above which do not prevent growth of silver halide microcrystals during physical ripening; and
4. solubility in water solution.

In addition, heretofore, much emphasis has been placed on the ability of the synthetic polymeric material to mix with gelatin, as this property has been critical for employment in partial substitution reactions with gelatin. Consequently, many synthetic polymers of the prior art have been materials which allow for the growth of silver halide crystals only in the presence of gelatin.

A class of synthetic polymers has now been found which is not susceptible to the deficiencies of the prior art and which may replace Gelatin entirely in photosensitive silver halide emulsions.

Summary of the Invention

The present invention is directed to a photosensitive silver halide emulsion wherein the silver halide crystals are disposed in a synthetic polymeric binder comprising a graft copolymer of an amine acrylamide monomer, represented by the formula:

\[
\begin{array}{c}
R_1 \quad R_2 \\
\text{CH}_2 \quad \text{C}
\end{array}
\]

wherein \( R_1 \) is hydrogen, lower alkyl group, e.g., one to four carbon alkyl group, preferably methyl or ethyl, or halogen, e.g., chlorine, bromo or iodo; \( R_2 \) is hydrogen, lower alkyl, halogen or cyano; \( R_3 \) is hydrogen, lower alkyl or cycloalkyl, e.g., one to four carbon alkyl group, preferably methyl or ethyl; \( Y \) is a lower alkyne or cycloalkylene group, e.g., one to six carbon alkylene or cycloalkylene group; and \( R_4 \) and \( R_5 \) each is hydrogen, lower alkyl group or lower cycloalkyl group, e.g., one to four carbons on a polymer containing a plurality of hydroxyl groups. In an alternative embodiment, the graft copolymer also includes a second monomer grafted thereon, i.e., an ethylenically unsaturated monomer. In still another embodiment, the above-described polymer comprises only a portion of the binder, the remainder constituting gelatin or a second synthetic polymer.

Detailed Description of the Invention

The present invention is directed to photosensitive silver halide emulsions wherein photosensitive silver halide crystals are disposed in a synthetic polymeric binder comprising a polymer containing a plurality of hydroxyl groups having grafted thereon an amine acrylamide monomer represented by the formula:

\[
\begin{array}{c}
R_1 \quad R_2 \\
\text{CH} \quad \text{C}
\end{array}
\]

wherein \( R_1 \) is hydrogen, lower alkyl group, e.g., one to four carbon alkyl group, preferably methyl or ethyl, or halogen, e.g., chlorine, bromo or iodo; \( R_2 \) is hydrogen, lower alkyl, halogen or cyano; \( R_3 \) is hydrogen, lower alkyl or cycloalkyl, e.g., one to four carbon alkyl group, preferably methyl or ethyl; \( Y \) is a lower alkyne or cycloalkylene group, e.g., one to six carbon alkylene or cycloalkylene group; and \( R_4 \) and \( R_5 \) each is hydrogen, lower alkyl group or lower cycloalkyl group, e.g., one to four carbons.

Such polymers have been found to substantially provide all of the basic requirements for a gelatin substitute, as delineated above. The emulsions of the present invention are readily sensitized by conventional sensitizing agents and are characterized by excellent latent image stability and excellent film speed. In addition, the emulsions of the present invention are more stable against degradation, particularly hydrolysis and the growth of microorganisms than gelatin.

With regard to the backbone polymer of the graft copolymer, in general, any organic polymer comprising repeating units comprising structural units containing a plurality of groupings capable of being oxidized by, e.g., a transition metal ion catalyst is useful in the present invention. Preferred backbones are substituted or unsubstituted cellulosic or polyvinyl polymers, and most preferably, a backbone selected from the group consisting of polymeric polyls, polyvinyl alcohol, gelatin, polysaccharides, partial acetals or polyvinyl alcohol, etc.

It is believed that upon oxidation of the grouping, the free radical is formed, which attacks the double bond of the amine acrylamide monomer, thus initiating polymerization.
As examples of polymers containing a plurality of hydroxyl groups, mention may be made of the following:

(1) Cellulose

(2) Carboxymethyl cellulose

(3) Hydroxyethyl cellulose

(4) Alginic acid

(5) Propylene glycol alginate

(6) Cellulose sulfate

(7) Kappa carrageenan

(8) Lambda carrageenan

(9) Soluble starch

(10) Gelatin

(11) Poly-N-(3-hydroxypropyl)-L-glutamide

(12) Polyglycamic acid

(13) 1:1 copolymer of glutamic acid: serine

(14) 1:1 copolymer of glutamic acid: homoserine

(15) 1:1 copolymer of glutamic acid: threonine

(16) 1:1 copolymer of glutamic acid: L-proline
S (22) \[
\begin{align*}
\text{polyvinyl alcohol} & \\
\text{1:1 copolymer of vinyl alcohol-isopropenyl alcohol} & \\
\text{Poly-\(\beta\)-bromovinyl alcohol} & \\
\text{Poly-\(\beta\)-chlorovinyl alcohol} & \\
\text{Polypropene-1-ol} & \\
\text{Polyhydroxymethyl methacrylate} & \\
\text{Poly-\(\gamma\)-hydroxypropyl-\(\alpha\)-chlorocrotonate} & \\
\text{1:1 copolymer of acrylamide-2-hydroxy-\(\alpha\)-propyl \(\alpha,\beta\)-dibromocrolylate} & \\
\text{Poly-N-methyl acrylamide} & \\
\text{Poly-N-methyl-\(\gamma\)-hydroxyethyl methacrylamide} & \\
\text{Poly-N-\(\gamma\)-hydroxy-\(\alpha\)-propyl-N-\(\gamma\)-chloracrylamide} & \\
\text{1:1 copolymer of acrylamide-\(\alpha\)-hydroxy-\(\alpha\)-propyl-4-bromocrotonamide} & \\
\text{1:1 copolymer of acrylamide-\(\alpha\)-hydroxy-\(\alpha\)-propyl-4-bromocrotonamide} & \\
\text{Typical examples of monomers useful for employ-} & \\
\text{ment in the instant invention for grafting onto the polymer containing the plurality of hydroxyl groups include:} & \\
\text{N-\(\beta\)-(dimethylaminomethyl)acrylamide} & \\
\text{N-\(\beta\)-(dimethylaminomethyl)acrylamide} & \\
\text{N-\(\beta\)-(dimethylamino)ethylacrylamide} & \\
\text{N-\(\beta\)-(dimethylaminomethyl)acrylamide} & \\
\text{N-\(\beta\)-(dimethylaminomethyl)ethylacrylamide} & \\
\end{align*}
\]

3,746,548

5

(37)

Polyvinyl hydroxymethyl ether

10

(38)

Polyisopropenyl \(\beta\)-hydroxylethyl ether

15

(39)

Poly-\(\alpha\)-chlorovinyl \(\gamma\)-hydroxypropyl ether

20

(40)

Poly-\(\alpha\)-bromovinyl \(\beta\)-hydroxy-\(\alpha\)-propyl ether

25

(41)

Polyvinyl hydroxymethyl ketone

30

(42)

1:1 copolymer of acrylamide-isopropenyl \(\beta\)-hydroxethyl ketone

35

(43)

1:1 copolymer of acrylamide-\(\alpha\)-chlorovinyl \(\gamma\)-hydroxypropyl ketone

40

(44)

1:1 copolymer of acrylamide-\(\alpha\)-bromovinyl \(\beta\)-hydroxy-\(\alpha\)-propyl ketone

45

Poly-N-vinylpyrrolidone

55

(46)

N-\(\beta\)-(dimethylaminomethyl)acrylamide

60

(47)

N-\(\beta\)-(dimethylamino)ethylacrylamide

65

(48)

N-\(\beta\)-(dimethylaminomethyl)ethylacrylamide

N-\(\beta\)-(dimethylaminomethyl)ethyl-2-chlorocrotonamide
The instant graft copolymers may have, in addition to the structures defined above, any compatible repeating unit or various repeating units or additional grafted segments which are not detrimental to photographic silver halide emulsions and which permit the polymers to be soluble in water. Examples of typical comonomers which may be employed include the following ethylenically-unsaturated monomers:

59. CH₃=CH—COOH
acrylic acid

60. CH₃=CH—COO⁻
methacrylic acid
Polymerization of the indicated monomers is achieved by conventional transition metal ion catalyst techniques.

The following non-limiting examples illustrate the preparation of polymers within the scope of the present invention.

**EXAMPLE I**

A flask was charged with 10 ml of water, 1.0 g of acrylamide and 2.0 g of N-[β-(dimethylamino)ethyl] acrylamide. 20 ml of a 10 percent aqueous solution of polyvinyl alcohol (Elvanol 70-05, DuPont Co., Wilmington, Del.) was added to the flask. 1.4 g of concentrated nitric acid was added and nitrogen was bubbled through the solution for 2 hours. The solution was then heated to 55°C; 0.20 g of ceric ammonium nitrate in 2 ml of water was added and the solution was stirred for 3 hours. The solution was then cooled, adjusted to a pH of 9 with potassium hydroxide and dialyzed for 28 hours against distilled water. Analysis showed a 1:1:3 graft of acrylamide: N-[β-(dimethylamino)ethyl] acrylamide on polyvinyl alcohol.

**EXAMPLE II**

A 4:1:8 graft of acrylamide:N-[β-(dimethylamino)ethyl] acrylamide on polyvinyl alcohol was prepared according to the procedure of Example I.

**EXAMPLE III**

A 1:4 graft of N-[β-(dimethylamino)ethyl] acrylamide on polyvinyl alcohol was prepared according to the procedure of Example I.

The following general procedure may be used for preparing photographic emulsions using the graft copolymers of the instant invention as the colloid binders.

A water-soluble silver salt, such as silver nitrate, may be reacted with at least one water-soluble halide, such as potassium, sodium, or ammonium bromide, preferably together with potassium, sodium or ammonium iodide, in an aqueous solution of the above-described polymer. The emulsion of silver halide thus-formed contains water-soluble salts, as a by-product of the double decomposition reaction in addition to any unreacted excess of the initial salts. To remove these soluble materials, the emulsion may be centrifuged and washed with distilled water to a low conductance. The emulsion may then be redispersed in distilled water. To an aliquot of this emulsion may be added a known quantity of a solution of bodig or thickening polymer, such as polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. duPont deNemours & Co., Wilmington Del., designated Type 72-60). A Wilmington, such as dioctyl ester of sodium sulfate, designated Aerosol OT, (commercially available from American Cyanamid Co., New York, N.Y.), may be added and the emulsion slot coated onto a base of cellulose triacetate sheet 5 mils thick having a coating of 30 mg./sq. ft. of hardened gelatin.
Alternatively, the soluble salts may be removed by adding to the emulsion a solution of polyacid such as 1:1 ethylene-maleic acid copolymer and lowering the pH to below 5, thereby bringing about precipitation of the polyacid carrying the silver halide grains along with the precipitate, and then to wash and resuspend the resulting precipitate by redissolving the polyacid at pH 6-7.

The emulsions may be chemically sensitized with sulfur compounds such as sodium thiosulfate or thiourea, with reducing substances such as stannous chloride; with salts of noble metals such as gold, rhodium and platinum; with amines and polyamines; with quaternary ammonium compounds such as alkyl α-picolinium bromide; and with polyethylene glycols and derivatives thereof. The emulsions of the present invention require only 5 percent as much gold for chemical sensitization as do gelatin emulsions.

The graft copolymers employed as the binders in the emulsions of the present invention may be cross-linked according to conventional procedures. As an example, polymers containing amine groups may be cross-linked with zirconium salts under alkaline conditions wherein amine-containing polymer is coated with a zirconium salt, for example, zirconium sulfate, and the pH is raised cross-linking the polymer.

Cross-linking agents conventionally employed with hydroxyl-containing polymers, such as boric acid, may also be employed.

The emulsions of the present invention may also be optically sensitized with cyanine and merocyanine dyes more easily than are gelatin emulsions. Cyanine dyes tend to aggregate less on the polymers of the instant invention than with gelatin providing less light filtering and speed loss. Where desired, suitable antifoggants, toners, restrainers, developers, accelerators, preservatives, coating aids, plasticizers, hardeners and/or stabilizers may be included in the composition of the emulsion.

The emulsions of this invention may be coated and processed according to conventional procedures of the art. They may be coated, for example, onto various types of rigid or flexible supports, such as glass, paper, metal, and polymeric films of both the synthetic type and those derived from naturally occurring products. As examples of specific materials which may serve as supports, mention may be made of paper, aluminum, polyethylene, polyethylene, polyethylene, nylon, polyesters such as polymeric film derived from ethylene glycol-terephthalic acid, and cellulose derivatives such as cellulose acetate, triacetate, nitrate, propionate, butyrate, acetate propionate, and acetate butyrate. These novel emulsions of the instant invention have been found to adhere to supports in a most satisfactory manner.

The polymers employed in the practice of the instant invention may contain from 5-75 mole percent of the grafted monomer; preferably 20 mole percent. The specific amount employed may be selected by the operator depending upon the grain particle size and habit desired. For example, the grain size distribution of the emulsion may be varied by changing the mole ratio and type of monomer grafted on the hydroxyl-containing polymer backbone.

By selecting appropriate monomers to be grafted on the hydroxyl-containing polymers, the instant graft polymers may be made to be compatible with all water-soluble bodying polymers. Emulsions made from these novel polymers, may be bodied with any water-soluble polymers, overcoming the disadvantage encountered with gelatin which is only compatible with a very few polymers in a most limited pH range. As examples of specific materials which may serve as bodying polymers are polyvinyl alcohol, polyacrylamide, polyelectrolyte solutions, polyvinyl pyrrolidone, poly(β-hydroxyethyl acrylate), polyethylene imine and cellulose derivatives such as hydroxypropyl cellulose and methyl cellulose. It has been found that using only a small amount of one or more of the instant polymers, large amounts of photosensitive silver halide grains may be obtained.

An emulsion made from one of these polymers of the instant invention may therefore be bodied with a water-soluble polymer such that the polymeric constitution of the resulting emulsion comprises a relatively large percentage of the bodying polymer.

By selecting appropriate comonomers, copolymers with selected diffusion characteristics may be prepared.

The instant polymers containing acidic comonomers may be pH flocculated in order to remove the soluble salts formed as a byproduct of the double decomposition reaction between the water-soluble silver salt and the water-soluble halide, in addition to any unreacted excess of the initial salts. As an example, an acid copolymer may be precipitated by lowering the pH below 5 and then washed and resuspended by raising the pH to above 7.

The instant invention will be further illustrated by reference to the following nonlimiting examples in which the preparation of the emulsion was carried out in the following general manner.

**Procedure A**

A solution of 4.15 g. of the dry graft polymer in 266 ml. of distilled water was adjusted to pH 6.30 with dilute nitric acid and maintained at a temperature of 55° C. To this solution, 44.0 g. of dry potassium bromide and 0.50 g. of dry potassium iodide were added. A solution of 55 g. of silver nitrate in 500 ml. of distilled water was prepared. From this silver nitrate solution, 100 ml. was rapidly added with continuous agitation to the polymer-halide solution and an additional 396 ml. was added over a period of 22 minutes. Thereafter, the emulsion was ripened for 30 minutes at 55° C., and then rapidly cooled to below 20° C.

**Procedure B**

In an alternative procedure for preparing the emulsion, the pH of the polymer solution was adjusted to 3.0; the amount of dry potassium bromide used was 88.0 g. and the amount of dry potassium iodide used was 1.0 g. In addition, the emulsion was ripened for 60 minutes instead of for 30 minutes.

The emulsion mixture in both procedures was centrifuged and washed with water to a low conductance. The emulsion was then dispersed in distilled water. To an aliquot of this emulsion was added a known quantity of a solution of bodying or thickening polymer of polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. duPont de Nemours & Co., Wilmington, Del., designated Type 72-60). A surfactant, such as Aerosol OT, was added and the emulsion was slot coated onto a base of cellulose triacetate sheet 5 mils thick having a coat-
ing of 30 mg./sq. ft. of hardened gelatin, (Celfa, commercially available from Instar Supply Co., New York, N.Y.). This film so prepared was air dried, exposed on a sensitometer, and processed with a processing solution and an image-receiving sheet from a Type 107C film assembly (Polaroid Corp., Cambridge, Mass.). The negative and image-receiving element were maintained in superposed position for 15 seconds, after which they were stripped apart. The photographic characteristics of the resulting positive print were measured on an automatic recording densitometer.

The following table summarizes silver halide grain sizes obtained in emulsions prepared with polymers of the present invention.

| TABLE 2 |
|-----------------|-----------------|
| Grain Size (microns) | Range | Average |
| Graft copolymer of Example I | 0.2-1.5 | 0.4 |
| Graft copolymer of Example II | 0.3-2.0 | 1.0 |
| Graft copolymer of Example III | 0.5-3.0 | 1.5 |

In certain photographic applications, it may be desirable to replace part, but not all, of the gelatin in the photosensitive emulsion. In view of the characteristics of these polymers described above, and further, in view of their compatibility with gelatin in substantially all proportions, it will be obvious that these polymers are ideally suited for such work.

The term "photosensitive" and other terms of similar import are herein employed in the generic sense to describe materials possessing physical and chemical properties which enable them to form usable images when photo-exposed by radiation.

Since certain changes may be made in the above products and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative only and not in a limiting sense.

What is claimed is:

1. A photosensitive silver halide emulsion wherein the emulsion binder comprises a graft copolymer of an amine acrylamide monomer of the formula:

\[
\text{R}_1\text{CH}==\text{C}==\text{N}-\text{R}_2\text{CHN}_2\text{CH}_2\text{CH}_2\text{N}-\text{R}_3
\]

wherein \( \text{R}_1 \) is selected from the group consisting of hydrogen, lower alkyl and halogen; \( \text{R}_2 \) is selected from the group consisting of hydrogen, lower alkyl, halogen and cyano; \( \text{R}_3 \) is selected from the group consisting of hydrogen, lower alkyl and cycloalkyl; \( Y \) is selected from the group consisting of lower alkenes and cycloalkenes; and \( \text{R}_4 \) and \( \text{R}_5 \) each are selected from the group consisting of hydrogen, lower alkyl, lower cycloalkyl, onto a polymer containing a plurality of hydroxyl groups.

2. The product as defined in claim 1 wherein substantially all of said emulsion binder comprises said graft copolymer.

3. The product as defined in claim 1 wherein said graft copolymer comprises 5-75 mole percent of said amine acrylamide.

4. The product as defined in claim 1 wherein said silver halide emulsion is a silver iodobromide emulsion.

5. The product as defined in claim 1 wherein said emulsion includes at least one chemical sensitizing agent.

6. The product as defined in claim 1 wherein said graft copolymer includes a second ethylenically unsaturated monomer.

7. The product as defined in claim 1 wherein said graft copolymer includes a second ethylenically unsaturated monomer.

8. The product as defined in claim 7 wherein said amine acrylamide is \( \text{N}-(\beta-(\text{dimethylamino})\text{ethyl}) \text{acrylamide} \).

9. The product as defined in claim 7 wherein said second monomer is acrylamidoacetamide.

10. The product as defined in claim 7 wherein said second monomer is N-isopropylacrylamide.

11. The product as defined in claim 7 wherein said second monomer is acrylamidoacetamide.

12. The product as defined in claim 1 wherein said hydroxyl containing polymer is polyvinyl alcohol.

13. The product as defined in claim 1 wherein said hydroxyl containing polymer is gelatin.

14. The product as defined in claim 1 wherein said hydroxyl containing polymer is polyvinyl alcohol.

15. The product as defined in claim 14 wherein said hydroxyl containing polymer is hydroxyethyl cellulose.

16. The method of preparing a photosensitive silver halide emulsion which comprises reacting a water-soluble silver salt with a water-soluble halide salt in an aqueous solution containing a graft copolymer of an amine acrylamide of the formula: