United States Patent Office 3,832,185 Patented Aug. 27, 1974

3,832,185

SYNTHETIC SILVER HALIDE EMULSION BINDER

Maurice J. Fitzgerald, Canton, Mass., assignor to Polaroid Corporation, Cambridge, Mass.

No Drawing. Filed Jan. 2, 1973, Ser. No. 320,448
Int. Cl. G03c 1/72
U.S. Cl. 96—114 29 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive silver halide emulsion wherein the emulsion binder comprises a quaternary ammonium acrylate carboxybetaine polymer or copolymer.

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, hithertofore, 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. For example, Dykstra and Whitely, U.S. Pat. No. 3,411,912 discloses a photographic composition comprising a water-insoluble interpolymer having units of a sulfobetaine monomer. These interpolymers do not exhibit good peptizing action for silver halide and therefore emulsions in which they are employed must contain another binding agent which exhibits the required peptizing action, such as gelatin.

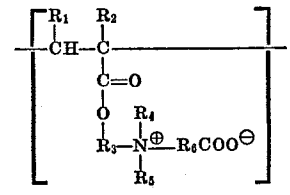
Great Britain Pats. 765,893 and 786,345 describe water-soluble copolymers comprising units of a carboxybetaine monomer, which copolymers are suitable for employment as synthetic silver halide emulsion binders; however, these copolymers are to be distinguished from the acrylate polymers of the instant invention in that the former are amides; and not esters, of acrylic acid.

Copending Application Ser. No. 320,452, filed Jan. 2, 1973 describes photographic silver halide emulsion binders of quaternary ammonium alkyl acrylate polymeric salts having "counter-ions" or anions bonded to the polymer by ionic forces and which may be relatively easily removed or interchanged, whereas the present invention is directed to silver halide emulsions employing polymers which are "inner salts," or "betaines" having a carboxyl group covalently bonded through a carbon chain to the quaternized nitrogen atom.

My copending application Ser. No. 294,979, filed Oct. 4, 1972 as a continuation-in-part of now-abandoned application Ser. No. 103,305, filed Dec. 31, 1970, discloses the employment of amine alkyl acrylate polymers as colloid binders in photographic silver halide emulsions; however, there is no mention or suggestion therein that the corresponding quaternary ammonium compounds, which would be expected by those skilled in the chemical arts to behave quite differently chemically than their amine analogs, would be suitable for such employment.

SUMMARY OF THE INVENTION

The present invention is directed to a photosensitive silver halid emulsion wherein the silver halide crystals are disposed in a synthetic polymeric binder comprising a water-soluble film-forming polymer having in its structure repeating units represented by the formula:



wherein R_1 is hydrogen, a lower alkyl group, i.e., 1–4 carbon alkyl group, preferably methyl or ethyl, or a halogen, i.e., chloro, bromo, or iodo; R_2 is hydrogen, a lower alkyl group, a halogen or cyano group; R_3 and R_6 each is a lower alkylene group, i.e., 1–4 carbon alkylene group or a lower cycloalkylene group, i.e., 3–6 carbon cycloalkylene group; and R_4 and R_5 each is a lower alkyl or a lower cycloalkyl group, i.e. a 3–6 cycloalkyl group; or a combination of R_3 and/or R_4 and/or R_2 and/or R_6 represents the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure. The above-described polymers are herein designated as quaternary ammonium acrylate carboxybetaine polymers, or for convenience, simply carboxybetaine polymers.

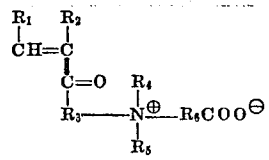
If desired, the above-mentioned carboxybetaine polymer may comprise only a portion of the binder, the remainder constituting gelatin or a second synthetic polymer.

DETAILED DESCRIPTION OF THE INVENTION

As indicated, the present invention is directed to photosensitive silver halide emulsions wherein photosensitive silver halide crystals are disposed in a synthetic polymeric binder comprising a water-soluble film-forming quaternary ammonium acrylate carboxybetaine polymer having in its structure repeating units represented by the formula set forth above. The term "film-forming" is intended to designate a molecular weight sufficiently high to form a film, for example, a molecular weight comparable to that of gelatin (i.e., around 15,000).

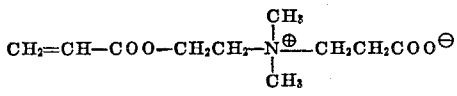
Such polymers have been found to substantially meet all the basic requirements for a gelatin substitute without possessing the deficiencies of gelatin as delineated above. The emulsions of the present invention are more stable against degradation than gelatin; particularly against hydrolysis of the polymeric backbone in acidic or basic media. This stability is due, in large part to the carbon-carbon linkages in the backbone of the instant polymers as opposed to the relatively easily hydrolyzable amide or ester linkages found in the polymeric backbone of gelatin. The polymers of this invention also show a resistance to the growth of microorganisms which is not exhibited by gelatin.

As examples of monomers represented by the formula:



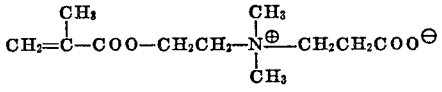
wherein R_1, R_2, R_3, R_4, R_5 and R_6 have the above-indicated definitions and which are contemplated as being suitable for providing the quaternary ammonium acrylate carboxybetaine polymers of the instant invention, mention may be made of the following:

(1)



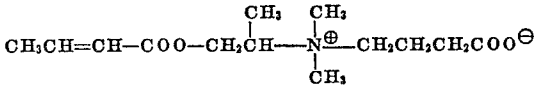
N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine

(2)



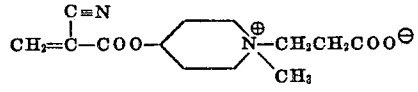
N-[β-(methylacryloyloxy)ethyl]-3-dimethylammonium propionate betaine

(3)



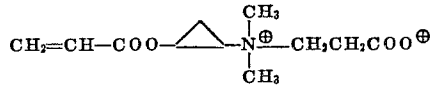
N-[1′-(2″-butenoyloxy)prop-2′-yl]-4-(methylpropylammonium) butanoate betaine

(4)



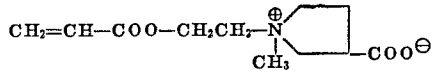
3-[4′-(α-cyanoacryloyloxy)-N-methylpiperdinium]-propionate betaine

(5)



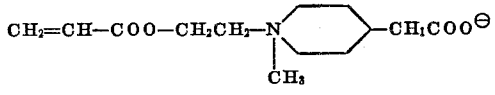
N-[2′-(acryloyloxy)cyclopropyl]-3-dimethylammonium propionate betaine

(6)



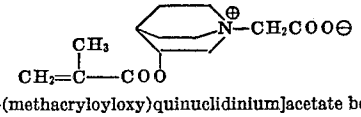
N-methyl-N-[β-(acryloyloxy)ethyl]-3-carboxypyrrolidine betaine

(7)



N-methyl-N-[β-(acryloyloxy)ethyl]-4-carboxymethyl piperidine betaine

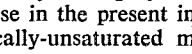
(8)



[3′-(methacryloyloxy)quinuclidinium]acetate betaine

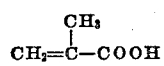
The instant polymers may be homopolymers or interpolymers having, in addition to the repeating units defined above, any compatible repeating unit or various repeating units which are not detrimental to photographic silver halide emulsions and which allow the resultant polymer to be soluble in water. Examples of typical comonomers which may be employed in forming the polymers suitable for use in the present invention include the following ethylenically-unsaturated monomers:

(9)



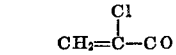
acrylic acid

(10)



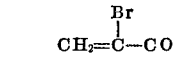
methacrylic acid

(11)



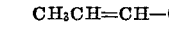
α-chloroacrylic acid

(12)



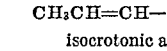
α-bromoacrylic acid

(13)



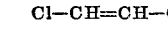
crotonic acid

(14)



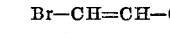
isocrotonic acid

(15)



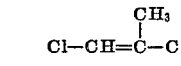
β-chloroacrylic acid

(16)



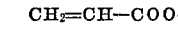
β-bromoacrylic acid

(17)



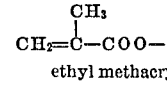
β-chloromethacrylic acid

(18)



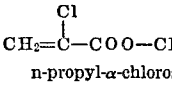
methyl acrylate

(19)



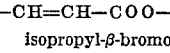
ethyl methacrylate

(20)



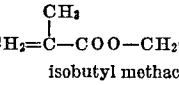
n-propyl-α-chloroacrylate

(21)



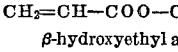
isopropyl-β-bromoacrylate

(22)



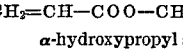
isobutyl methacrylate

(23)



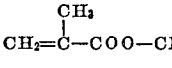
β-hydroxyethyl acrylate

(24)



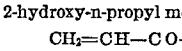
α-hydroxypropyl acrylate

(25)



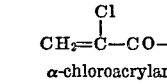
2-hydroxy-n-propyl methacrylate

(26)



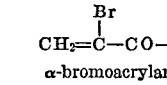
acrylamide

(27)



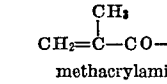
α-chloroacrylamide

(28)



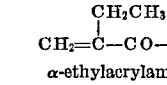
α-bromoacrylamide

(29)



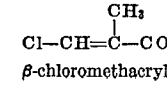
methacrylamide

(30)

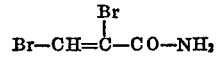


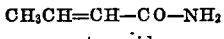
α-ethylacrylamide

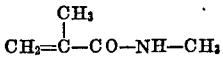
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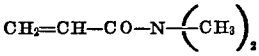


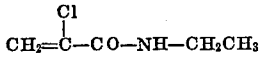
β-chloromethacrylamide

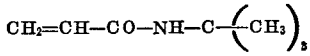
(32) 
2,3-dibromoacrylamide

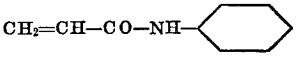
(33) 
crotonamide

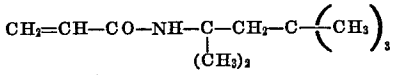
(34) 
N-methylmethacrylamide

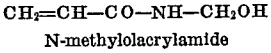
(35) 
N,N-dimethylacrylamide

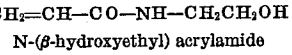
(36) 
N-ethyl-α-chloroacrylamide

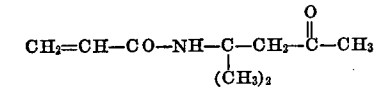
(37) 
N-tertiary butylacrylamide

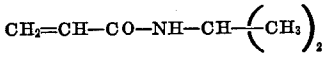
(38) 
N-cyclohexylacrylamide

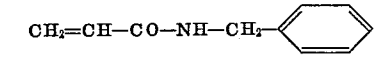
(39) 
N-tertiary octyl acrylamide

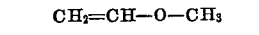
(40) 
N-methylolacrylamide

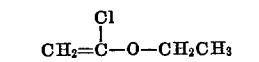
(41) 
N-(β-hydroxyethyl) acrylamide

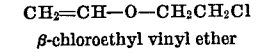
(42) 
diacetone acrylamide

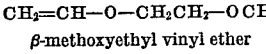
(43) 
N-isopropylacrylamide

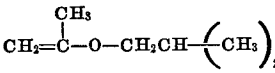
(44) 
N-benzylacrylamide

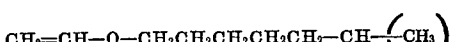
(45) 
methylvinyl ether

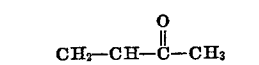
(46) 
ethyl α-chlorovinyl ether

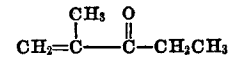
(47) 
β-chloroethyl vinyl ether

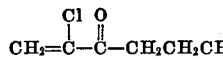
(48) 
β-methoxyethyl vinyl ether

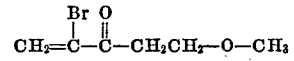
(49) 
isobutyl isopropenyl ether

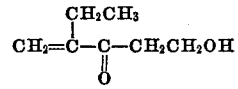
(50) 
isooctyl vinyl ether

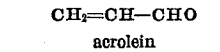
(51) 
methylvinyl ketone

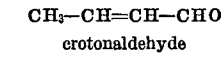
(52) 
ethyl isopropenyl ketone

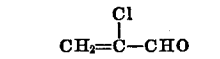
(53) 
n-propyl-α-chlorovinyl ketone

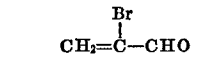
(54) 
β-methoxyethyl-α-bromovinyl ketone

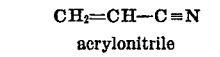
(55) 
β-hydroxyethyl-1-butene-2-yl ketone

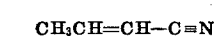
(56) 
acrolein

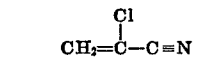
(57) 
crotonaldehyde

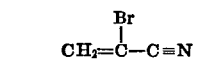
(58) 
α-chloroacrolein

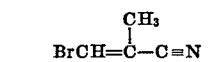
(59) 
α-bromoacrolein

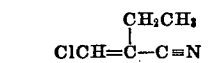
(60) 
acrylonitrile

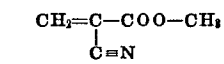
(61) 
crotononitrile

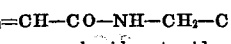
(62) 
α-chloroacrylonitrile

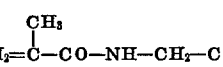
(63) 
α-bromoacrylonitrile

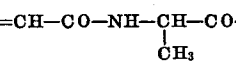
(64) 
β-bromomethacrylonitrile

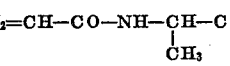
(65) 
β-chloroethacrylonitrile

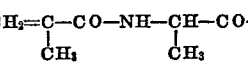
(66) 
methyl α-cyanoacrylate

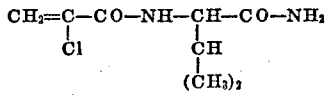
(67) 
acrylamidoacetamide

(68) 
methacrylamidoacetamide

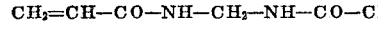
(69) 
2-crotonamido-N-methylpropionamide

(70) 
2-acrylamidopropionamide

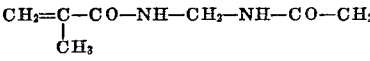
(71) 
2-methacrylamidopropionamide

(72) 

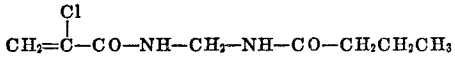
2-(α-chloroacrylamido)-3-methylbutyramide

(73) 

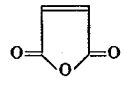
N-(acetamidomethyl)acrylamide

(74) 

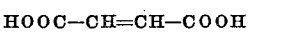
N-(propionamidomethyl)methacrylamide

(75) 

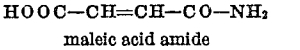
N-(n-butyramidomethyl)α-chloroacrylamide

(76) 

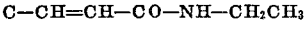
maleic anhydride

(77) 

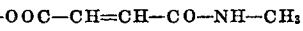
maleic acid

(78) 

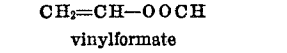
maleic acid amide

(79) 

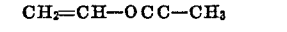
N-ethylmaleic acid amide

(80) 

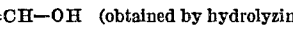
N-methyl methylmaleate amide

(81) 

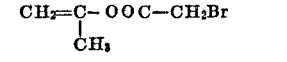
vinylformate

(82) 

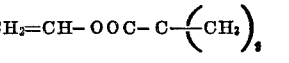
vinyl acetate

(83) 

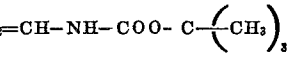
(copolymerized vinyl acetate vinyl acetate)

(84) 

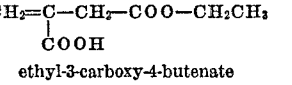
isopropenyl bromoacetate

(85) 

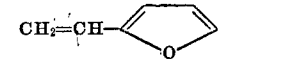
vinyl pivalate

(86) 

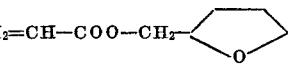
N-vinyl-tertiary butylcarbamate

(87) 

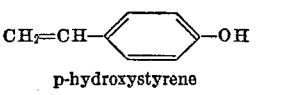
ethyl-3-carboxy-4-butenate

(88) 

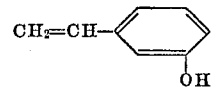
α-vinylfuran

(89) 

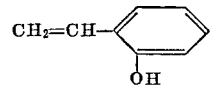
α-(acryloyloxymethyl)-tetrahydrofuran

(90) 

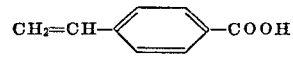
p-hydroxystyrene

(91) 

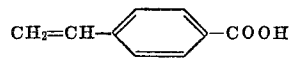
m-hydroxystyrene

(92) 

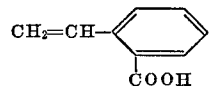
o-hydroxystyrene

(93) 

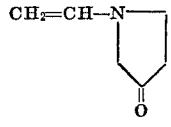
p-carboxystyrene

(94) 

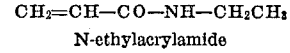
m-carboxystyrene

(95) 

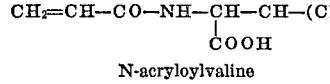
o-carboxystyrene

(96) 

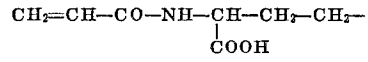
N-vinyl-2-pyrrolidone

(97) 

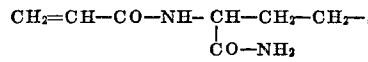
N-ethylacrylamide

(98) 

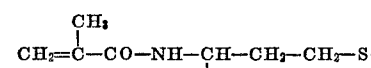
N-acryloylvaline

(99) 

N-acryloylmethionine

(100) 

N-acryloylmethionamide

(102) 

N-methacryloylmethionine

Polymerization of the indicated monomers is achieved by conventional free radical polymerization techniques. The following non-limiting examples illustrate the preparation of polymers within the scope of the present invention. The numerical ratio before the word copolymer in the following examples refers to the molar ratio of monomers in the reaction mixture forming the copolymer.

EXAMPLE 1

Poly N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine

A solution of 31.4 g. of dimethylaminoethyl methacrylate in 20.0 g. of methyl ethyl ketone was added to a solution of 14.4 g. of β-propicolactone in 20.0 g. of methyl ethyl ketone at −20° C. This mixture was allowed to stand overnight at −20° C. The product formed was filtered and then polymerized in a 25% (by weight) solution using 0.1 g. of 2,2′-azobis-[2-methylpropionitrile] in an evacuated sealed tube at 70° C. for 17 hours. After diluting with methanol, the polymer was precipitated from acetone, separated and dried to yield a white fluffy solid soluble in water and alcohol.

EXAMPLE 2

1:1 copolymer of acrylamide/N-[β-(methacryloyloxy) ethyl]-3-dimethylammonium propionate betaine

7.11 of acrylamide and 22.93 g. of N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine were added to 300 mls. of distilled water in a 3-neck 1-liter round-bottom flask with stirrer and under nitrogen. 10 mls. of isopropanol were added and the pH adjusted to 6.4 with HNO_3 or a 10% NaOH solution, and then 0.05 g. of $K_2S_2O_8$ was added. The solution was stirred until a clear viscous water-soluble liquid resulted. This liquid as analyzed to have about 9.69% solids and a free acrylamide content of about 20.5 g./l.

EXAMPLE 3

1:1 copolymer of N - isopropylacrylamide/N - [β-(methacryloyloxy)ethyl] - 3 - dimethylammonium propionate betaine

The procedure of Example 2 was followed replacing the acrylamide with 11.32 g. of N-isopropylacrylamide to yield a clear viscous water-soluble liquid which was analyzed to have 16.74% solids and a free N-isopropylacrylamide content of about 2.69 g./l., with the other monomer being present at less than 0.5 g./l.

EXAMPLE 4

9:1 copolymer of N - isopropylacrylamide/N-[β-(methacryloyloxy)ethyl] - 3-dimethylammonium propionate betaine

30.6 of N-isopropylacrylamide and 6.88 g. of N-[β-(methacryloyloxy)ethyl] - 3-dimethylammonium propionate betaine were reacted according to the procedure of Example 2 to yield a clear viscous water-soluble liquid (below 32° C.) which was analyzed to have 10.16% solids and an N-isopropylacrylamide content of about 1.70 g./l. with the other monomer being present at least than 0.5 g./l.

EXAMPLE 5

1:1:1 terpolymer of N - isopropylacrylamide/N-[β-methacryloyloxy)ethyl]-3 - dimethylammonium propionate betaine/acrylamide

The procedure of Example 2 was followed except that, in addition to the reagents already present, 11.32 g. of N-isopropylacrylamide was added to the polymerization solution, to yield a clear viscous water-soluble liquid which was analyzed to have about 12.85% solids and an N-isopropylacrylamide content of 6.71 g./l. with the content of the other monomers being present at less than 0.5 g./l.

EXAMPLE 6

Poly N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine

20 g. of N-[β-(acryloyloxy)ethyl]-3-dimethyl ammonium propionate betaine was polymerized in 60 g. of water using 0.1 g. of 2,2'-azobis-[2-methylpropionitrile] as catalyst in an evacuated sealed tube at 70° C. for 17 hours. The resultant viscous liquid was diluted with methanol and precipitated in acetone to yield a white fluffy solid.

EXAMPLE 7

7:3 copolymer of acrylamide/N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine

A solution was prepared comprising 9.95 of acrylamide and 11.6 g. of N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine in 194 mls. of distilled water and 2.2 mls. of isopropanol. The pH of this solution was adjusted to about 6.4 with a 10% NaOH solution or dilute HNO_3 and the solution was then polymerized with 0.01 g. of $K_2S_2O_8$ and 0.01 g. of $NaHSO_3$ under nitrogen at 26° C. for 18 hours. A clear liquid of medium viscosity was obtained which was analyzed to have 10.0% solids, a free acrylamide content of about 14.2 g./l. and about 0.8 g./l. of free betaine monomer.

EXAMPLE 8

1:1 copolymer of acrylamide/N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine

The procedure of Example 7 was followed employing 7.1 g. of acrylamide and 19.32 g. of N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine in 238 mls. of distilled water and 2.6 mls. of isopropanol, to yield a clear low-viscosity liquid which was analyzed to have 13.1% solids, a free acrylamide content of about 20.72 g./l. and about 8.9 g./l. free betaine.

EXAMPLE 9

3:7 copolymer of acrylamide/N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine

A solution of 3.2 g. of acrylamide and 20.3 g. of N-[β-(acryloyloxy)ethyl] - 3 - dimethylammonium propionate betaine in 21 mls. of distilled water and 2.3 mls. of isopropanol was adjusted to a pH of 6.4 with a 10% solution of NaOH or dilute HNO_3, and then polymerized under nitrogen for 90 minutes at 65–70° C. with 0.0075 g. of $K_2S_2O_8$ and 0.0075 g. of $NaHSO_3$ to yield a clear liquid of medium viscosity which was analyzed to have 8.3% solids, a free acrylamide content of about 4.93 g./l. and a free betaine monomer content of about 10.89 g./l.

EXAMPLE 10

9:1 copolymer of N-isopropylacrylamide/N-[β-(acryloyloxy) ethyl]-3-dimethylammonium propionate betaine

30.6 g. of N-isopropyl acrylamide and 6.4 g. of N-[β-(acryloyloxy)ethyl] - 3 - dimethylammonium propionate betaine were added to 300 mls. of distilled water under nitrogen in a 3-neck one-liter round-bottom flask with stirrer. 10 mls. of isopropanol were added and the pH adjusted to 6.4 with HNO_3 or a 10% NaOH solution. 0.05 g. of $K_2S_2O_8$ was added and the solution was stirred until viscous. The resultant liquid was analyzed to have 5.53% solids and a free N-isopropylacrylamide content of 0.542 g./l. with free betaine monomer content of less than 0.5 g./l.

The following general procedure may be used for preparing photographic emulsions using the above-described polymers 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 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 bodying or thickening polymer, such as polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. du Pont de Nemours & Company, Wilmington, Del., designated Type 72–60). A surfactant, such as dioctyl ester of sodium sulfosuccinic acid, designated Aerosol OT, (commercially available from American Cyanamid Company, New York, N.Y.), may be added and the emulsion coated onto a film base of cellulose triacetate sheet having a coating of hardened gelatin.

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 polymers employed as the binders in the emulsions of the present invention may be cross-linked according to conventional procedures. As an example, polymers may be ionically cross-linked with dibasic acids or cross-linked with succinaldehyde.

The emulsions of the present invention may also be optically sensitized with cyanine and merocyanine dyes. 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, polymethacrylic acid, methyl and ethyl esters, vinylchloride polymers, polyvinyl acetal, polyamides such as 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. Suitable subcoats may be provided on the supports, for example a layer of gelatin, if necessary or desirable for adherence, as is well known in the art.

The polymers employed in the practice of the instant invention may contain from 5–100 mole percent of the above-indicated repeating units. The specific amount employed may be selected by the operator depending upon the grain particle size and habit desired.

By selecting appropriate comonomers, the instant copolymers 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 gelatin, polyvinyl alcohol, polyacrylamide, polyalkylacrylamides, polyvinyl pyrrolidone, polymethacrylamidoacetamide, vinyl alcohol/N-vinylpyrrolidone copolymers, poly-N-ethylaziridine, poly-N-(2-hydroxyethyl) aziridine, poly-N-(2 - cyanoethyl) aziridine, poly(β-hydroxyethyl acrylate), polyethylene imine and cellulose derivatives such as hydroxyethyl cellulose, hydroxypropyl cellulose and methyl cellulose. It has been found that using only a small amount of on eor 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. For example, the rate of diffusion of alkali ion or a dye-developer through an emulsion comprising one of the polymers of this invention may be modified by varying the composition of the polymer.

The instant invention will be further illustrated by reference to the following nonlimiting examples in which silver halide emulsions were prepared employing the carboxybetaine polymers of Examples 1–3 and 5–9 as binders:

EXAMPLE 11

A solution of 4.15 g. of the dry polymer (based on percent solids if the polymer is a liquid) 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 the remainder 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.

Silver halide emulsions employing the polymers of Examples 4 and 10 as binders were also prepared by the following procedure:

EXAMPLE 12

The procedure of Example 11 was followed except that the emulsions were ripened for 90 minutes at 30° C. The addition of silver nitrate was also carried out at 30° C. for the emulsion employing the polymer of Example 10. All emulsions contained octahedral platelet crystals.

The following table summarizes the silver halide grain sizes obtained in the emulsions prepared in the above examples.

TABLE 1

Examples	Polymer	Grain size range	Microns, average
1 and 11	Poly N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine.	0.1–0.2	0.5
2 and 11	1:1 acrylamide/N-[β-(methacryloyloxy)]-3-dimethylammonium propionate betaine.	0.5–1.0	0.7
3 and 11	1:1 N-isopropylacrylamide/N-[β-(methacryloyloxy) ethyl]-3-dimethylammonium propionate betaine.	0.5–1.0	0.7
4 and 12	9:1 copolymer of the above monomers	0.3–1.2	0.6
4 and 11	1:1:1 N-isopropylacrylamide/N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine/acrylamide.	0.3–0.8	0.4
6 and 11	Poly N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.	0.1–0.5	0.3
7 and 11	7:5 acrylamide/N[β-(acryloyloxy) ethyl]-3-dimethylammonium propionate betaine.	0.2–2.0	0.6
8 and 11	1:1 copolymer of the above monomers	0.2–1.5	0.5
9 and 11	3:7 copolymer of the above monomers	0.1–1.0	0.2
10 and 12	9:1 N-isopropylacrylamide/N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.	0.3–1.5	0.7
13	Gelatin	0.2–1.8	1.0

EXAMPLE 14

The emulsion mixture of Example 11 employing the copolymer of Example 7 was centrifuged and washed with water to a low conductance and then redispersed in distilled water. To an aliquot of this emulsion was added a solution of bodying or thickening polymer of polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. du Pont de Nemours & Company; Wilmington, Del., designated Type 72–60) to give a silver to bodying polymer ratio of about 1:0.74. Another aliquot received no bodying polymer solution. A surfactant, Aerosol OT, was added and each emulsion aliquot was slot coated at various silver coverages onto a base of cellulose triacetate sheet 5 mils. thick subcoated with 30 mg./sq. ft. of hardened gelatin. This film so prepared was air dried, exposed on a sensitometer, and processed with a processing solution and an image-receiving sheet from a Polaroid Type 107 Land film assembly (Polaroid Corporation, Cambridge, Mass.). The negative and image-receiving element were maintained in superposed position for 10 seconds after which they were stripped apart. Alternatively, the processing was effected with a processing solution and an image-receiving element from a Polaroid Type 42 Land film or a Polaroid Type 20C Land film. The photographic characteristics of the resulting positive prints were then measured by an auto-

matic recording densitometer. The following table summarizes the densitometer readings obtained on samples of these positive prints:

TABLE 2

Grain-growing polymer	Bodying polymer	Ag./polymer ratio	Mg. Ag_2 t.	Film system	$D_{max.}$	$D_{min.}$	ΔD
7:3:acrylamide/N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.	None	∞	76.1	T-107	1.45	0.15	1.30
	Polyvinyl alcohol	1:0.74	16.1	T-42	1.03	0.53	0.50
				T-107	0.41	0.15	0.26
	do	1:0.74	105.2	T-20C	1.19	0.41	0.78
				T-42	0.77	0.14	0.63
				T-107	0.68	0.14	0.54

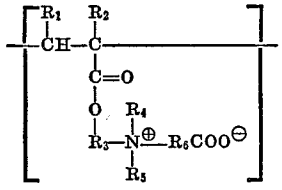
In certain photographic applications, it may be desirable to replace part, but not all, of the gelatin in the photosensitive emulsion. In view of the characteristics of these polymers described above, and further, in view of their compatibility with gelatin in substantially all proportions, it will be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

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 photoexposed by radiation actinic to silver halide.

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 water-soluble film-forming polymer having in its structure repeating units of the formula:



wherein R_1 is hydrogen, a lower alkyl group or a halogen; R_2 is hydrogen, a lower alkyl group, halogen or cyano group; R_3 and R_6 each is a lower alkylene or lower cycloalkylene group, and R_4 and R_5 each is a lower alkyl or lower cycloalkyl group; or a combination of R_3 and/or R_4 and/or R_5 and/or R_6 represents the atoms necessary to complete a 3 to 8-member heterocyclic ring structure.

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

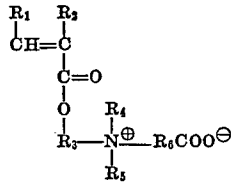
3. The product as defined in claim **1** wherein said polymer comprises 5–100 mole percent of said repeating units.

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 emulsion includes at least one optical sensitizing agent.

7. The product as defined in claim **1** wherein said polymer comprises a copolymer of a first monomer of the formula:



and a second ethylenically unsaturated monomer.

8. The product as defined in claim **7** wherein said first monomer is N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

9. The product as defined in claim **7** wherein said first monomer is N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

10. The product as defined in claim **7** wherein said second monomer is acrylamide.

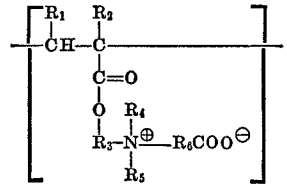
11. The product as defined in claim **7** wherein said second monomer is N-isopropylacrylamide.

12. The product as defined in claim **1** which includes a bodying polymer.

13. The product as defined in claim **12** wherein said bodying polymer is polyvinyl alcohol.

14. The product as defined in claim **12** wherein said bodying polymer is gelatin.

15. A photosensitive silver halide emulsion wherein the emulsion binder comprises a water-soluble film-forming homopolymer consisting essentially of repeating units of the formula:

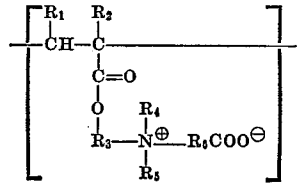


wherein R_1 is hydrogen, a lower alkyl group or a halogen; R_2 is hydrogen, a lower alkyl group, halogen or cyano group; R_3 and R_6 each is a lower alkylene or lower cycloalkylene group, and R_4 and R_5 each is a lower alkyl or lower cycloalkyl group; or a combination of R_3 and/or R_4 and/or R_5 and/or R_6 represents the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure.

16. The product as defined in claim **15** wherein said homopolymer is poly N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

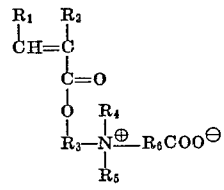
17. The product as defined in claim **15** wherein said homopolymer is poly N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

18. A 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 water-soluble film-forming polymer having in its structure repeating units of the formula:



wherein R_1 is hydrogen, a lower alkyl group or a halogen; R_2 is hydrogen, a lower alkyl group, a halogen or cyano group; R_3 and R_6 each is a lower alkylene or lower cycloalkylene group, and R_4 and R_5 each is a lower alkyl group or lower cycloalkyl group; or a combination of R_3 and/or R_4 and/or R_5 and /or R_6 represents the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure.

19. The method as defined in claim **18** wherein said polymer comprises a copolymer of a first monomer of the formula:



and a second ethylenically unsaturated monomer.

20. The method as defined in claim **19** wherein said first monomer is N-[β-(methacryloyloxy)ethyl] - 3 - dimethylammonium propionate betaine.

21. The method as defined in claim **19** wherein said first monomer is N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

22. The method as defined in claim **19** wherein said second monomer is acrylamide.

23. The method as defined in claim **19** wherein said second monomer is N-isopropylacrylamide.

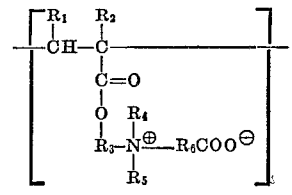
24. The method as defined in claim **18** wherein said aqueous solution includes a bodying polymer.

25. The method as defined in claim **24** wherein said bodying polymer is polyvinyl alcohol.

26. The method as defined in claim **24** wherein said bodying polymer is gelatin.

27. A 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 water-soluble film-forming homo-

polymer consisting essentially of repeating units of the formula:



wherein R_1 is hydrogen, a lower alkyl group or a halogen; R_2 is hydrogen, a lower alkyl group, a halogen or cyano group; R_3 and R_6 each is a lower alkylene or lower cycloalkylene group, and R_4 and R_5 each is a lower alkyl group or lower cycloalkyl group; or a combination of R_3 and/or R_4 and/or R_5 and/or R_6 represents the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure.

28. The method as defined in claim **27** wherein said polymer is poly N-[β-(methacryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

29. The method as defined in claim **27** wherein said polymer is poly N-[β-(acryloyloxy)ethyl]-3-dimethylammonium propionate betaine.

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DAVID KLEIN, Primary Examiner

R. L. SCHILLING, Assistant Examiner