

[54]	<b>SYNTHETIC SILVER HALIDE EMULSION BINDER</b>	3,411,912	11/1968	Dykstra et al. ....	96/114
		3,647,464	3/1972	Smith et al. ....	96/114
		3,681,079	8/1972	Fitzgerald .....	96/114
[75]	Inventor: <b>Maurice J. Fitzgerald</b> , Canton, Mass.	3,709,690	1/1973	Cohen et al. ....	96/114
		3,713,834	1/1973	Fitzgerald .....	96/114
[73]	Assignee: <b>Polaroid Corporation</b> , Cambridge, Mass.	3,746,548	7/1973	Fitzgerald .....	96/114
		3,749,577	7/1973	Hollister et al. ....	96/114

[22] Filed: **Jan. 2, 1973**

[21] Appl. No.: **320,452**

[44] Published under the Trial Voluntary Protest Program on January 28, 1975 as document no. B 320,452.

[52] U.S. Cl. .... **96/114; 96/94 R**  
 [51] Int. Cl.<sup>2</sup> ..... **G03C 1/02; G03C 1/72**  
 [58] Field of Search ..... **96/114, 94 R**

[56] **References Cited**

**UNITED STATES PATENTS**

2,839,401 6/1958 Gray et al. .... 96/114

*Primary Examiner*—Charles L. Bowers, Jr.  
*Assistant Examiner*—Richard L. Schilling  
*Attorney, Agent, or Firm*—Mart C. Matthews; Philip G. Kiely

[57] **ABSTRACT**

A photosensitive silver halide emulsion wherein the emulsion binder comprises a quaternary ammonium alkyl acrylate polymeric salt.

**29 Claims, No Drawings**

## SYNTHETIC SILVER HALIDE EMULSION BINDER

## 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.

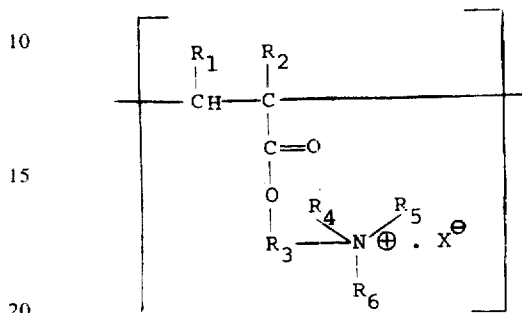
In addition, hithertofore, much emphasis has been placed on the ability of the synthetic polymeric material to mix with gelatin, as this property has been critical for employment in partial substitution reactions with gelatin. Consequently, many synthetic polymers of the prior art have been materials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

Dykstra and Whitely, U.S. Pat. No. 3,411,912 discloses a photographic composition comprising water-insoluble interpolymers to be used in the presence of a peptizing agent such as gelatin and comprising units of a sulfobetaine monomer and my copending application Ser. No. 320,448, filed Jan. 2, 1973 discloses water-soluble polymers and copolymers comprising units of a carboxybetaine monomer and which are suitable as peptizers, alone or with gelatin, in photographic silver halide emulsions. The above-mentioned polymers, however, are to be distinguished from the polymers of the instant invention in that the former polymers are "inner salts" or "betaines" having a carboxy or sulfo anion which is covalently bonded through a carbon chain to the quaternized nitrogen atom, whereas the instant invention is directed to silver halide emulsions employing polymeric salts whose anions are only bonded to the polymer by ionic forces and which may be relatively easily removed or interchanged in ways well known to those skilled in the art.

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 halide emulsion wherein the silver halide crystals are disposed in a synthetic polymeric binder comprising a water-soluble film-forming polymeric salt 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;  $R_3$  is a lower alkylene, i.e., 1-4 carbon alkylene group or a lower cycloalkylene group, i.e., 3-6 carbon cycloalkylene group; and  $R_4$ ,  $R_5$  and  $R_6$  each is a lower alkyl or a lower cycloalkyl group, i.e., a 3-6 carbon cycloalkyl group; or  $R_3$  and/or  $R_4$  and/or  $R_5$  and/or  $R_6$  taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure; and  $X$  is a salt-forming anion, e.g., halide, sulfate, alkyl sulfonate, arylsulfonate, nitrate, etc. The above-described polymers are herein designated as quaternary ammonium alkyl acrylate polymeric salts, or for convenience, simply polymeric salts.

If desired, the polymeric salts 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 alkyl acrylate polymeric salt 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).

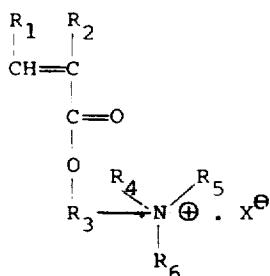
The polymers of the present invention have been found to substantially meet all of the basic requirements of a gelatin substitute without possessing the above-described deficiencies of gelatin. More specifically, the emulsions of the present invention are more stable against degradation than gelatin; 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 polymeric backbone of the instant polymers, as opposed to the relatively easily hydrolyzed ester and amide linkages found in the polymeric backbone of gelatin. The emulsions of this invention also show a resistance to the growth of microorganisms which is not exhibited by gelatin.

An important feature of the polymers of this invention is the presence of a mobile anion or "counter-ion"

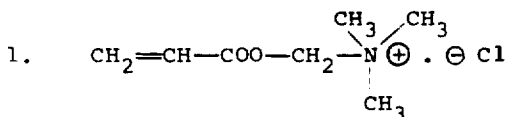
3

which is free to diffuse in the aqueous medium of the silver halide emulsion. This counter-ion may thus be used to introduce a photographically advantageous reagent into the emulsion, for example, by providing a counter-ion which is a photographic sensitizer, antifogant, stabilizer or the like. Of course, the counter-ion should be selected by one practicing this invention so as to be compatible with the silver halide emulsion and its intended usage; for example, if a silver bromide emulsion were contemplated, one would not use a polymeric binder with an iodide counterion since the greater insolubility of the silver iodide would result in the precipitation of silver iodide in preference to silver bromide.

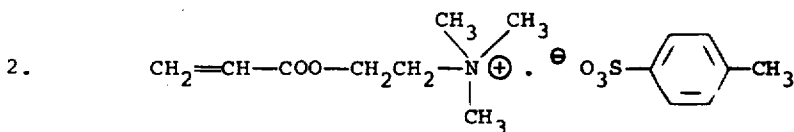
As examples of monomers represented by the formula:



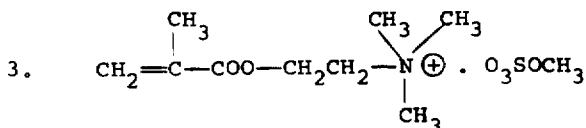
wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $X$  of the above-indicated definitions and which are contemplated as being suitable for providing the quaternary ammonium alkyl acrylate polymeric salts of this invention, mention may be may of the following:



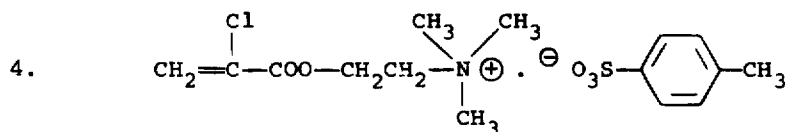
acryloyloxy methyl trimethyl ammonium chloride



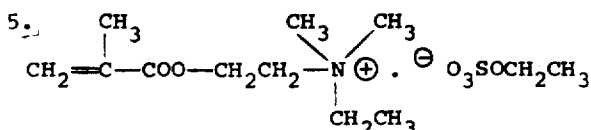
$\beta$ -(acryloyloxy)ethyl trimethyl ammonium p-toluenesulfonate



$\beta$ -(methacryloyloxy)ethyl trimethyl ammonium methyl sulfate

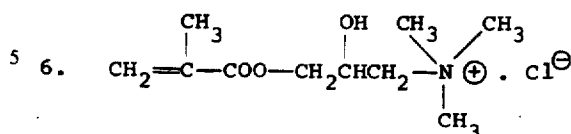


2-( $\alpha$ -chloroacryloyloxy)ethyl trimethyl ammonium p-toluenesulfonate

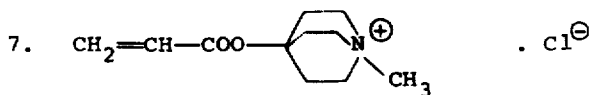


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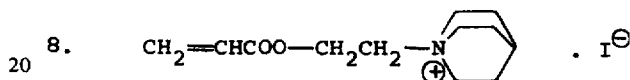
$\beta$ -(methacryloyloxy)ethyl(ethyl dimethyl ammonium) ethyl sulfate



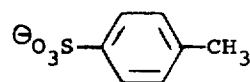
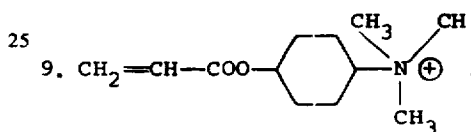
3-(methacryloyloxy)-2-hydroxyprop-1-yl trimethyl ammonium chloride



N-methyl-3-acryloyloxyquinuclidinium chloride

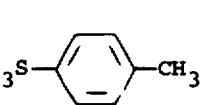


N-[ $\beta$ -acryloyloxy)ethyl]quinuclidinium iodide



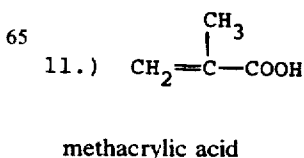
4-(acryloyloxy)cyclohexyl trimethyl ammonium p-toluenesulfonate

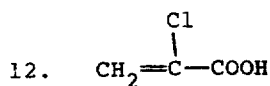
The instant polymers may be homopolymers or inter-polymers having, in addition to the repeating units defined above, any compatible repeating unit or various repeating units which are not detrimental to photographic silver halide emulsions and which allow the re-



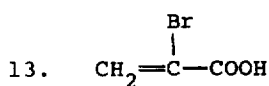
sultant polymer to be soluble in water. Examples of typical comonomers which may be employed in forming the polymers suitable for use in the present invention include the following ethylenically-unsaturated monomers.

10.  $CH_2=CH-COOH$   
acrylic acid

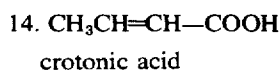




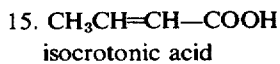
$\alpha$ -chloroacrylic acid



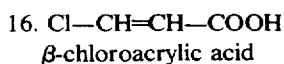
$\alpha$ -bromoacrylic acid



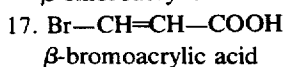
crotonic acid



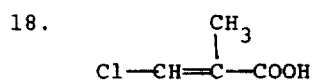
isocrotonic acid



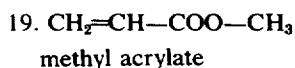
$\beta$ -chloroacrylic acid



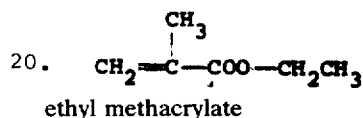
$\beta$ -bromoacrylic acid



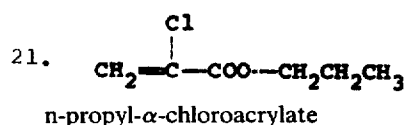
$\beta$ -chloromethacrylic acid



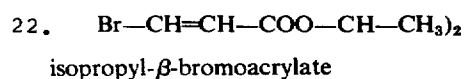
methyl acrylate



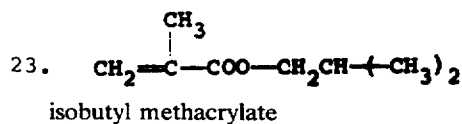
ethyl methacrylate



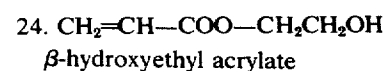
n-propyl- $\alpha$ -chloroacrylate



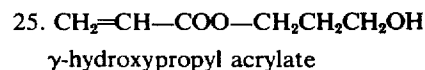
isopropyl- $\beta$ -bromoacrylate



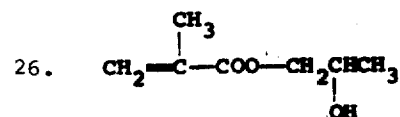
isobutyl methacrylate



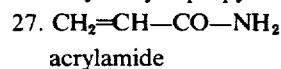
$\beta$ -hydroxyethyl acrylate



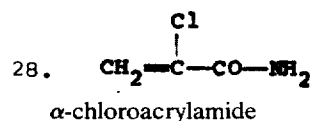
$\gamma$ -hydroxypropyl acrylate



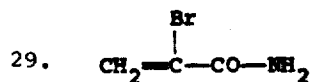
2-hydroxy-n-propyl methacrylate



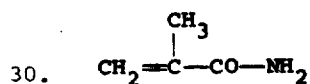
acrylamide



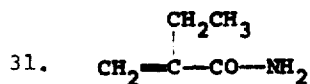
$\alpha$ -chloroacrylamide



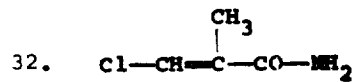
5  $\alpha$ -bromoacrylamide



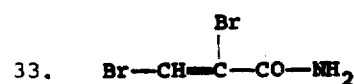
10 methacrylamide



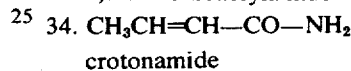
15  $\alpha$ -ethylacrylamide



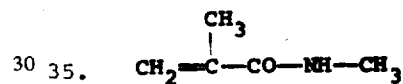
20  $\beta$ -chloromethacrylamide



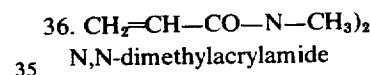
2,3-dibromoacrylamide



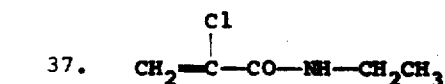
crotonamide



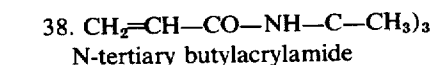
N-methylmethacrylamide



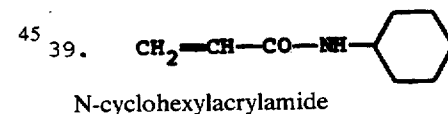
35 N,N-dimethylacrylamide



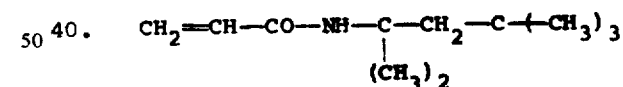
40 N-ethyl- $\alpha$ -chloroacrylamide



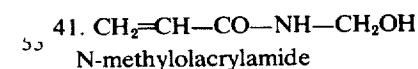
N-tertiary butylacrylamide



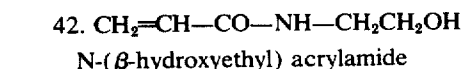
N-cyclohexylacrylamide



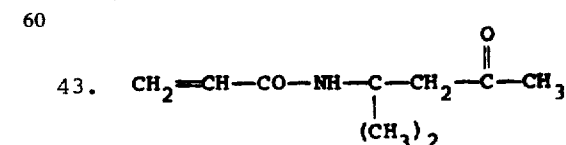
N-tertiary octyl acrylamide



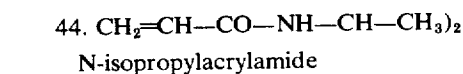
N-methylolacrylamide



N-( $\beta$ -hydroxyethyl) acrylamide




65 diacetone acrylamide



N-isopropylacrylamide

45.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{C}_6\text{H}_5$   
N-benzylacrylamide
46.  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$   
methylvinyl ether
47.  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{O}-\text{CH}_2\text{CH}_3$   
ethyl  $\alpha$ -chlorovinyl ether
48.  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{Cl}$   
 $\beta$ -chloroethyl vinyl ether
49.  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{OCH}_3$   
 $\beta$ -methoxyethyl vinyl ether
50.  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{O}-\text{CH}_2\text{CH}-(\text{CH}_3)_2$   
isobutyl isopropenyl ether
51.  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}-(\text{CH}_3)_2$   
isooctyl vinyl ether
52.  $\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$   
methylvinyl ketone
53.  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_3$   
ethyl isopropenyl ketone
54.  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_3$   
n-propyl- $\alpha$ -chlorovinyl ketone
55.  $\text{CH}_2=\overset{\text{Br}}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$   
 $\beta$ -methoxyethyl- $\alpha$ -bromovinyl ketone
56.  $\text{CH}_2=\overset{\text{CH}_2\text{CH}_3}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{OH}$   
 $\beta$ -hydroxyethyl-1-butene-2-yl ketone
57.  $\text{CH}_2=\text{CH}-\text{CHO}$   
acrolein
58.  $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$   
crotonaldehyde
59.  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CHO}$   
 $\alpha$ -chloroacrolein
60.  $\text{CH}_2=\overset{\text{Br}}{\text{C}}-\text{CHO}$   
 $\alpha$ -bromoacrolein
61.  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$   
acrylonitrile
62.  $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{N}$   
crotonitrile

63.  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{C}\equiv\text{N}$   
 $\alpha$ -chloroacrylonitrile
64.  $\text{CH}_2=\overset{\text{Br}}{\text{C}}-\text{C}\equiv\text{N}$   
 $\alpha$ -bromoacrylonitrile
65.  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{C}\equiv\text{N}$   
methyl acrylonitrile
66.  $\text{CH}_2=\overset{\text{BrCH}_2\text{CH}_3}{\text{C}}-\text{C}\equiv\text{N}$   
 $\beta$ -bromomethylacrylonitrile
67.  $\text{CH}_2=\overset{\text{CH}_2\text{CH}_3}{\text{C}}-\text{C}\equiv\text{N}$   
ethyl acrylonitrile
68.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}_2$   
acrylamidoacetamide
69.  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}_2$   
methacrylamidoacetamide
70.  $\text{CH}_3\text{CH}=\text{CH}-\text{CO}-\text{NH}-\overset{\text{CH}_3}{\text{CH}}-\text{CO}-\text{NH}-\text{CH}_3$   
2-crotonamido-N-methylpropionamide
71.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\overset{\text{CH}_3}{\text{CH}}-\text{CO}-\text{NH}_2$   
2-acrylamidopropionamide
72.  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}-\overset{\text{CH}_3}{\text{CH}}-\text{CO}-\text{NH}_2$   
2-methacrylamidopropionamide
73.  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CO}-\text{NH}-\overset{\text{CH}(\text{CH}_3)_2}{\text{CH}}-\text{CO}-\text{NH}_2$   
2-( $\alpha$ -chloroacrylamido)-3-methylbutyramide
74.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_3$   
N-(acetamidomethyl)acrylamide
75.  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2\text{CH}_3$   
N-(propionamidomethyl)methacrylamide
76.  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2\text{CH}_2\text{CH}_3$   
N-(n-butyramidomethyl)  $\alpha$ -chloroacrylamide
77.   
maleic anhydride
78.  $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$   
maleic acid
79.  $\text{HOOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}_2$   
maleic acid amide

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80.  $\text{HOOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_3$   
N-ethylmaleic acid amide
81.  $\text{CH}_3-\text{OOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}_3$   
N-methyl methylmaleate amide
82.  $\text{CH}_2=\text{CH}-\text{OOCH}$   
vinylformate
83.  $\text{CH}_2=\text{CH}-\text{OOC}-\text{CH}_3$   
vinyl acetate
84.  $\text{CH}_2=\text{CH}-\text{OH}$   
vinyl alcohol (obtained by hydrolyzing copolymerized vinyl acetate)
85.  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{OOC}-\text{CH}_2\text{Br}$   
isopropenyl bromoacetate
86.  $\text{CH}_2=\text{CH}-\text{OOC}-\text{C}(\text{CH}_3)_3$   
vinyl pivalate
87.  $\text{CH}_2=\text{CH}-\text{NH}-\text{COO}-\text{C}(\text{CH}_3)_3$   
N-vinyl-tertiary butylcarbamate
88.  $\text{CH}_2=\text{C}(\text{COOH})-\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_3$   
ethyl-3-carboxy-3-butenate
89.  $\text{CH}_2=\text{CH}-\text{C}_4\text{H}_3\text{O}$   
 $\alpha$ -vinylfuran
90.  $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2-\text{C}_4\text{H}_7\text{O}$   
 $\alpha$ -acryloyloxymethyl-tetrahydrofuran
91.  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$   
p-hydroxystyrene
92.  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$   
m-hydroxystyrene
93.  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$   
o-hydroxystyrene
94.  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{COOH}$   
p-carboxystyrene
95.  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{COOH}$   
m-carboxystyrene
96.  $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{COOH}$   
o-carboxystyrene
97.  $\text{CH}_2=\text{CH}-\text{N}-\text{C}_4\text{H}_7\text{O}$   
N-vinyl-2-pyrrolidone

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98.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_3$   
N-ethylacrylamide
99.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{COOH})-\text{CH}(\text{CH}_3)_2$   
N-acryloylvaline
100.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{COOH})-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$   
N-acryloylmethionine
101.  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{CO}-\text{NH}_2)-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$   
N-acryloylmethionamide
102.  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}(\text{COOH})-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$   
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 I

Poly  $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate

- 28.32 g of  $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate (commercially available under the trademark "Sipomer Q-5", from Alcolac Chemical Corporation, Baltimore, Maryland) and 0.01 g of 2,2'-azobis-[2-methylpropionitrile] catalyst were dissolved in 75 ml of  $\text{H}_2\text{O}$  and 5 ml of isopropanol. This solution was polymerized under nitrogen in a sealed tube at 65° C for 12 hours. The resultant clear viscous solution was then precipitated in acetone and the precipitate was dried under vacuum at 50° C for 12 hours to yield a water-soluble solid product.

## EXAMPLES II - VIII

Copolymers of acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate

- The procedure of Example I was followed except that, in addition to the reagents already present in the polymerization solution, various quantities of acrylamide were included. The amounts of acrylamide added in Example II, III, IV and V were 0.71 g, 1.42 g, 2.84 g and 5.69 g respectively. In example VI, 8.54 g of acrylamide, 10.62 g of the Sipomer Q-5 and 0.01 g of the catalyst were dissolved in the  $\text{H}_2\text{O}$ -isopropanol solution, polymerized and separated according to the procedure of Example I. In Example VII, 8.54 g of acrylamide, 7.08 g of the Sipomer Q-5 and 0.01 g of the catalyst were dissolved in the  $\text{H}_2\text{O}$ -isopropanol solution, polymerized and separated according to the procedure of Example I. In Example VIII a solution of 5.69 g of acrylamide, 14.17 g of Sipomer Q-5, and 0.01 g of the catalyst in 80 mls of  $\text{H}_2\text{O}$  and 5 mls of isopropanol was polymerized and separated according to the procedure of Example I.

## EXAMPLE IX

Poly 3-(methacryloyloxy)-2-hydroxyprop-1-yl trimethylammonium chloride.

40.0 g of 3-(methacryloyloxy)-2-hydroxyprop-1-yl trimethylammonium chloride in 160 g of 3A ethanol containing 0.1 g of 2,2'-azobis-[2-methylpropionitrile] catalyst was heated under nitrogen at 70° C for 20 hours. Upon cooling, the polymer precipitated and was washed in 2B ethanol and in ether and then dried under vacuum at 45° C to yield a white solid soluble in water and hot ethanol.

## EXAMPLE X

1:1 copolymer of acrylamide and 3-(methacryloyloxy)-2-hydroxyl-prop-1-yl trimethylammonium chloride

38.85 g of 3-(methacryloyloxy)-2-hydroxyl-prop-1-yl trimethylammonium chloride (commercially available under the trademark "Sipomer Q-1" from Alcolac Chemical Corporation, Baltimore, Maryland) and 10.66 g of acrylamide were added to 500 ml of distilled H<sub>2</sub>O in a 3-neck one-liter roundbottom flask with a stirrer and under nitrogen. Then, 100 mls of isopropanol were added and the pH adjusted to 6.4 with HNO<sub>3</sub>. 0.05 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.05 g of NaHSO<sub>3</sub> were then added and the solution stirred until a clear viscous solution was produced which was analyzed to have 9.19% solids.

## EXAMPLE XI

2:3 copolymer of diacetone acrylamide and 3-(methacryloyloxy)-2-hydroxy-prop-1-yl trimethylammonium chloride

46.62 g of the above-mentioned Sipomer Q-1 and 20.32 g of diacetone acrylamide were added to 500 ml of distilled H<sub>2</sub>O in a 3-neck one liter round-bottom flask with stirrer and under nitrogen. The pH was adjusted to 6.5 with HNO<sub>3</sub> and 0.05 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.05 g of NaHSO<sub>3</sub> were added to the solution. The solution was stirred until viscous and then dialyzed for 36 hours to yield a milky viscous liquid which was analyzed to have 7.3% solids.

## EXAMPLE XII

4:1 copolymer of acrylamide/ $\beta$ -(acryloyloxy) ethyl trimethylammonium p-toluenesulfonate

7.11 g of acrylamide, 8.24 g of  $\beta$ -(acryloyloxy) ethyl trimethylammonium p-toluenesulfonate and 0.01 g of 2,2'-azobis-[2-methylpropionitrile] catalyst were dissolved in 75 ml of H<sub>2</sub>O and 5 mls of isopropanol. This solution was polymerized under N<sub>2</sub> in a sealed tube at 65° C for 12 hours. A clear viscous solution resulted which produced a precipitate in acetone. The precipitate was collected and dried under vacuum at 50° C for 12 hours to yield a water-soluble white solid.

## EXAMPLE XIII

3:1 copolymer of acrylamide/ $\beta$ -(methacryloyloxy)ethyl (ethyl dimethylammonium) ethylsulfate

7.11 g of acrylamide, 10.38 g of  $\beta$ -(methacryloyloxy) ethyl (ethyldimethylammonium) ethylsulfate (commercially available from Alcolac Chemical Corporation under the designation DV-364) and 0.01 g of 2,2'-azobis-[2-methylpropionitrile] catalyst were dissolved

in 70 ml of dimethylformamide. This solution was polymerized in a sealed tube at 65° C for 12 hours under N<sub>2</sub>. The result was a white paste which was filtered and dried under vacuum at 45° C for 12 hours.

## EXAMPLE XIV

Poly 2-( $\alpha$ -chloroacryloyloxy) ethyl trimethylammonium p-toluenesulfonate

A mixture of 90 g of methyl- $\alpha$ -chloroacrylate and 45 g of dimethyl aminoethanol were heated and distilled on a steam bath in the presence of hydroquinone and potassium carbonate. 33 g of the thus-formed dimethyl-amino-ethyl- $\alpha$ -chloroacrylate was distilled (boiling point is about 80°C at 2 mm pressure). A solution of the above distilled acrylate was then prepared by dissolving 10 g in about 50 cc. of acetone. 11 g. of methyl p-toluenesulfonate was added to this solution and the resultant solution was allowed to stand overnight. The sulfonate salt crystallized from solution and about 16 g was collected and dried. Then, about 6 g of the salt was polymerized in methanol with 2,2'-azobis-[2-methylpropionitrile]. The polymerized product was precipitated in acetone and dried to yield a white powder soluble in water and methanol.

The following general procedure may be used for preparing photographic emulsions using the above-described polymeric salts 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. duPont deNemours & 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 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- $\alpha$ -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 the polymers may be ionically cross-linked with a dibasic acid 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, re-

strainers, 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 polymeric salts employed in the practice of the instant invention may contain from 5-100 mole % 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 copolymers of this invention 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 ( $\beta$ -hydroxy-ethyl 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 one or more of the polymeric salts, large amounts of photosensitive silver halide grains may be obtained. An emulsion made from one of the polymeric salts 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 copolymers of this invention may be modified by varying the composition of the copolymer.

The preparation and photographic utilization of the instant invention will be further illustrated by reference to the following nonlimiting examples:

#### EXAMPLE XV

Silver halide emulsions employing the polymeric salts of Examples I-VIII, XII and XIII as the colloid binders were prepared by the following procedure:

A solution of 4.15 g of the dry polymer (based on % solids if the polymer was a liquid) in 266 mls of distilled water was adjusted to pH 3.0 with dilute nitric acid and maintained at a temperature of 55° C. To this solution,

88.0 g of dry potassium bromide and 1.0 g of dry potassium iodide were added.

A solution of 55.0 g of silver nitrate in 500 mls of distilled water was prepared. From this silver nitrate solution, 100 mls were rapidly added to the polymerhalide solution and the remainder was added over a period of 22 minutes. Thereafter, the emulsion was ripened for 60 minutes at 55° C, with continuous agitation, at the end of which it was rapidly cooled to below 20° C.

#### EXAMPLE XVI

The procedure of Example XIV was followed to prepare a silver halide emulsion employing as the emulsion binder a 11:1 copolymer of acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methylsulfate (commercially available from Hercules Powder Co., Wilmington Del. under the designation Reten Lot. No. 2394-36), and also a silver halide emulsion employing as the emulsion binder a 7.7:1 copolymer of acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methylsulfate (commercially available from Hercules Powder Co., Wilmington, Del. under the designation Reten Lot No. 2394-36), and also a silver halide emulsion employing as the emulsion binder a 6.7:1 copolymer of acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate (commercially available from Hercules Powder Co., Wilmington, Del. under the designation Reten Lot No. 2394-38).

#### EXAMPLE XVII

Silver halide emulsions employing the polymeric salts of Examples IX, X and XI as the colloid binders were prepared by the following procedure:

A solution of 4.15 g of the dry 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 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., with continuous agitation, at the end of which it was rapidly cooled to below 20° C.

#### EXAMPLE XVIII

A silver halide emulsion employing the polymeric salt of Example XIV as the colloid binder was prepared by the following procedure:

A solution of 3.10 g of the dry polymer in 200 ml of distilled water was adjusted to pH 3.0 with dilute nitric acid and maintained at a temperature of 55° C. To this solution, 66.0 g of dry potassium bromide and 0.375 g of dry potassium iodide were added.

A solution of 41.25 g of silver nitrate in 375 ml of distilled water was prepared. From this silver nitrate solution, 75 ml was rapidly added to the polymer-halide solution and the remainder was added over a period of 13.5 minutes. Thereafter, the emulsion was ripened for 46.5 minutes at 55° C., with continuous agitation, at the end of which it was rapidly cooled to below 20°C.

#### EXAMPLE XIX (CONTROL)

A control silver halide emulsion employing gelatin as the colloid binder was prepared by following the procedures of Example XVII substituting gelatin for the synthetic polymeric salt.



The following table summarizes the silver halide grain sizes obtained in the emulsions prepared above: All emulsions contained octahedral platelet crystals.

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

TABLE I

Examples	Polymer	Grain Size (microns)	
		Range	Average
I and XV	poly- $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate	—	0.8
II and XV	1:10 acrylamide/ $\beta$ -methacryloyloxy(ethyl trimethylammonium methyl sulfate)	—	0.7
III and XV	1:5 acrylamide/ $\beta$ -(methacryloyloxy)ethyl trimethylammonium methyl sulfate	—	0.7
IV and XV	2:5 acrylamide/ $\beta$ -(methacryloyloxy)ethyl trimethylammonium methyl sulfate	—	0.7
V and XV	4:5 acrylamide/ $\beta$ -(methacryloyloxy)ethyl trimethylammonium methyl sulfate	0.2-1.8	0.7
VI and XV	3:2:1 acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate	0.3-1.7	0.8
VII and XV	4:8:1 acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate	0.3-2.5	1.1
VIII and XV	8:5 acrylamide/ $\beta$ -(methacryloyloxy)ethyl trimethylammonium methyl sulfate	0.4-2.1	0.9
XVI	6:7:1 acrylamide/ $\beta$ -(methacryloyloxy)ethyl trimethylammonium methyl sulfate	0.5-4.2	2.0
XVI	11:1 acrylamide/ $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate	0.2-2.8	1.3
IX and XVII	poly-(3-methacryloyloxy)-2-hydroxyprop-1-yl trimethylammonium chloride	0.4-3.5	1.5
X and XVII	1:1 acrylamide/3-hydroxyprop-1-yl(methacryloyloxy)-2-trimethylammonium chloride	—	0.5
XI and XVII	2:3 acrylamide/3-hydroxyprop-1-yl(methacryloyloxy)-2-trimethylammonium chloride	0.4-0.7	0.5
XII and XV	4:1 acrylamide/ $\beta$ -acryloyloxy) ethyl trimethylammonium p-toluenesulfonate	0.2-2.0	0.6
XIII and XV	3:1 acrylamide/ $\beta$ -(methacryloyloxy) ethyl (ethyl dimethylammonium) ethyl sulfate	0.4-3.0	2.0
XIV and XVIII	poly- $\beta$ -( $\alpha$ -chloroacryloyloxy) ethyl trimethylammonium p-toluenesulfonate	0.3-1.5	0.8
XIX	gelatin	—	0.4
		0.2-1.8	1.0

## EXAMPLE XX

The emulsion mixtures of Example XV were centrifuged and washed with water to a low conductance. The emulsions were then redispersed in distilled water. To 30 ml aliquots of each emulsion was added 20 mls of a 10% (by weight) solution of bodying or thickening polymer of polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. duPont deNemours & Company, Wilmington, Del., designated Type 72-60). A surfactant, Aerosol OT, was added and the emulsions were slot coated onto a base of cellulose triacetate sheet 5 mils thick

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 ten 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 assembly. The photographic characteristics of the resulting positive prints were measured on an automatic recording densitometer. The following table summarizes illustrative densitometer readings obtained on samples of these prints.

TABLE 2

Grain-growing Polymer	Mg. of Ag per ft. <sup>2</sup>	Film System	D <sub>max</sub>	D <sub>min</sub>	ΔD
6.7:1 acrylamide/ β-(methacryloyloxy) ethyl trimethyl- ammonium methyl sulfate	140.0	T-42	1.32	0.12	1.20
		T-107	1.31	0.21	1.10
11:1 acrylamide/ β-(methacryloyloxy) ethyl trimethyl- ammonium methyl sulfate	128.8	T-42	1.91	0.29	1.62
		T-107	1.91	0.17	1.74

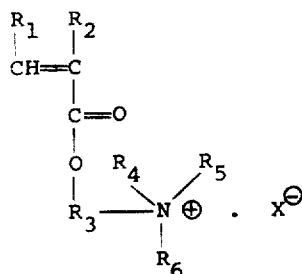
In certain photographic applications, it may be desirable to replace part, but not all, of the gelatin in the photosensitive emulsion. In view of the characteristics of these polymer salts described above, and further, in view of their compatibility with gelatin in substantially all proportions, it will 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 photo-exposed 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 described 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 consists essentially of a water-soluble film-forming copolymer of a first monomer of the formula:



wherein R<sub>1</sub> is hydrogen, a lower alkyl group or a halogen; R<sub>2</sub> is hydrogen, a lower alkyl group, halogen or cyano group; R<sub>3</sub> is a lower alkylene or lower cycloalkylene group and R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> each is a lower alkyl, or lower cycloalkyl group; or R<sub>3</sub> and/or R<sub>4</sub> and/or R<sub>5</sub> and/or R<sub>6</sub> taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure; and X is a salt-forming anion; and

a second monomer which is an acrylamide.

2. The product as defined in claim 1 wherein said copolymer comprises 5-100 mole percent of repeating units of said first monomer.

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

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

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

6. The product as defined in claim 1 wherein said first monomer is β-(methacryloyloxy) ethyl trimethylammonium ethyl sulfate.

7. The product as defined in claim 1 wherein said first monomer is 3-(methacryloyloxy-2-hydroxyprop-1-yl trimethylammonium.

8. The product as defined in claim 1 wherein said first monomer is β-(acryloyloxy) ethyl trimethylammonium p-toluenesulfonate.

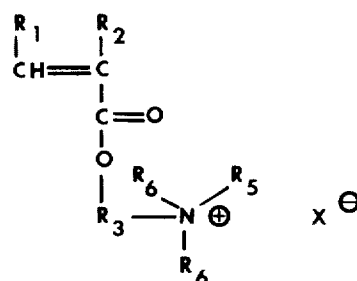
9. The product as defined in claim 1 wherein said first monomer is β-(methacryloyloxy) ethyl (ethyl dimethylammonium) ethyl sulfate.

10. The product as defined in claim 1 wherein said first monomer is 2-(α-chloroacryloyloxy) ethyl trimethylammonium p-toluenesulfonate.

11. The product as defined in claim 1 wherein said second monomer is acrylamide.

12. The product as defined in claim 1 wherein said second monomer is diacetone acrylamide.

13. 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 copolymer of a first monomer of the formula:



wherein R<sub>1</sub> is hydrogen, a lower alkyl group or a halogen; R<sub>2</sub> is hydrogen, a lower alkyl group, a halogen or cyano group; R<sub>3</sub> is a lower alkylene or lower cycloalkylene group and R<sub>4</sub>, R<sub>5</sub> and R<sub>6</sub> each is a lower alkyl group, or lower cycloalkyl group; or R<sub>3</sub> and/or R<sub>4</sub> and/or R<sub>5</sub> and/or R<sub>6</sub> taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure; and X is a salt-forming anion; and

a second monomer which is an acrylamide.

14. The method as defined in claim 13 wherein said first monomer is β-(methacryloyloxy) ethyl trimethylammonium ethyl sulfate.

15. The method as defined in claim 13 wherein said first monomer is 3-(methacryloyloxy)-2-hydroxyprop-1-yl trimethylammonium chloride.

16. The method as defined in claim 13 wherein said first monomer is β-(acryloyloxy) ethyl trimethylammonium p-toluenesulfonate.

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17. The method as defined in claim 13 wherein said first monomer is  $\beta$ -(methacryloyloxy) ethyl (ethyl dimethyl) ethyl sulfate.

18. The method as defined in claim 13 wherein said first monomer is 2-( $\alpha$ -chloroacryloyloxy) ethyl trimethylammonium p-toluenesulfonate.

19. The method as defined in claim 13 wherein said second monomer is acrylamide.

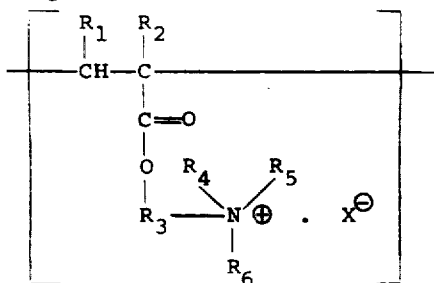
20. The method as defined in claim 13 wherein said second monomer is diacetone acrylamide.

21. The method as defined in claim 13 wherein said aqueous solution includes a bodying polymer.

22. The method as defined in claim 21 wherein said bodying polymer is polyvinyl alcohol.

23. The method as defined in claim 21 wherein said bodying polymer is gelatin.

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



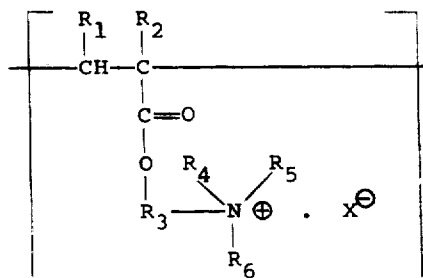
wherein  $R_1$  is hydrogen, a lower alkyl group or a halogen;  $R_2$  is hydrogen, a lower alkyl group, halogen or cyano group;  $R_3$  is a lower alkylene or lower cycloalkylene group and  $R_4$ ,  $R_5$  and  $R_6$  each is a lower alkyl, or lower cycloalkyl group; or  $R_3$  and/or  $R_4$  and/or  $R_5$  and/or  $R_6$  taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure; and X is a salt-forming anion.

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25. The product as defined in claim 24 wherein said homopolymer is poly  $\beta$ -(methacryloyloxy) ethyl trimethylammonium methyl sulfate.

26. The product as defined in claim 24 wherein said homopolymer is poly 3-(methacryloyloxy)-2-hydroxy-prop-1-yl trimethylammonium chloride).

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 homopolymer consisting essentially of repeating units of the formula:



25 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;  $R_3$  is a lower alkylene or lower cycloalkylene group and  $R_4$ ,  $R_5$  and  $R_6$  each is a lower alkyl group or lower cycloalkyl group; or  $R_3$  and/or  $R_4$  and/or  $R_5$  and/or  $R_6$  taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure; and X is a salt-forming anion.

28. The method as defined in claim 27 wherein said polymeric salt is poly 3-(methacryloyloxy)-2-hydroxy-prop-1-yl trimethylammonium chloride.

29. The method as defined in claim 27 wherein said polymeric salt is poly (1-methacryloyloxy-3-trimethylammonium-2-propanol chloride).

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