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3,799,781

SYNTHETIC SILVER HALIDE EMULSION BINDER
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Int. Cl. G03c 1/04

U.S. Cl. 96-113

28 Claims

ABSTRACT OF THE DISCLOSURE

A photosensitive silver halide emulsion wherein the emulsion binder comprises a vinyl aminoalkyl ether 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.

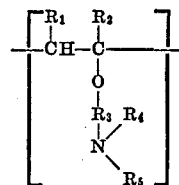
Although hydrophilic polymers having quaternary nitrogen atoms which are bonded to the polymer through ether linkages are described in the art as being suitable peptizers for silver halide dispersions in the preparation of photographic emulsions, for example as shown in Perry and Reynolds, U.S. Pat. No. 3,425,836, it has hithertofore been unknown to employ the corresponding vinyl aminoalkyl ether polymers for this purpose. Those skilled in the chemical arts are well aware of the substantial differences that exist in the chemical behavior of N-substituted amine derivatives when compared with their quaternized analogs and therefore it was quite unexpected to find that the vinyl aminoalkyl ether polymers of the present invention could also be employed to replace gelatin, either partly or entirely, in photographic silver halide emulsions.

SUMMARY OF THE INVENTION

The present invention is directed to a photosensitive silver halide emulsion wherein the silver halide crystals

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are disposed in a water soluble synthetic polymeric binder comprising a 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 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 and R_5 each is hydrogen, a lower alkyl or a lower cycloalkyl group; or R_3 and/or R_4 and/or R_5 taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure. The above-described polymers are herein designated for convenience as vinyl aminoalkyl ether polymers.

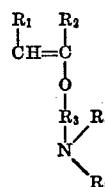
If desired, the vinyl aminoalkyl ether polymer may comprise only a portion of the binder, the remainder constituting gelatin or a second synthetic polymer.

DETAILED DESCRIPTION OF THE INVENTION

As indicated, the present invention is directed to photosensitive silver halide emulsions wherein photosensitive silver halide crystals and disposed in a water-soluble synthetic polymeric binder comprising a film-forming vinyl aminoalkyl ether 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, as delineated above. The emulsions of the present invention employing polymers having primary or secondary amino groups are characterized by excellent latent image stability. In addition, the emulsions of the present invention are more stable against degradation than gelatin; particularly against hydrolysis in acidic or basic media of the polymeric backbone and substituent groups by virtue of the carbon-carbon and ether linkages of the instant polymers. These polymers also show a resistance to the growth of microorganisms.

As examples of monomers represented by the formula:



wherein R_1 , R_2 , R_3 , R_4 and R_5 have the above-indicated definitions and which are contemplated as being suitable

for providing the vinyl aminoalkyl ether polymers, mention may be made of the following:

- (1) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{NH}_2$
aminomethyl vinyl ether
- (2) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{NH}_2$
 β -aminomethyl vinyl ether
- (3) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_3)_2$
 β -(dimethylamino)ethyl vinyl ether
- (4) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{NH}-\text{CH}_3$
 γ -(methylamino)propyl isopropenyl ether
- (5) $\text{CH}_2=\text{C}(\text{CH}_2\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)-\text{NH}-\text{CH}_2\text{CH}_3$
 β -(ethylamino)propyl 1-butene-2-yl ether
- (6) $\text{CH}_3\text{CH}=\text{C}(\text{Cl})-\text{O}-\text{C}(\text{CH}_3)_2-\text{N}(\text{CH}_3)_2$
2-(methylethylamino)prop-2-yl 1-chloro-1-propenyl ether
- (7) $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{Br})-\text{O}-\text{CH}(\text{CH}_3)\text{CH}_2-\text{NH}-\text{CH}_2\text{CH}_2\text{CH}_3$
1-(n-propylamino)prop-2-yl 1-bromo-1-butenyl ether
- (8) $\text{Cl}-\text{CH}=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{NH}-\text{C}(\text{CH}_3)_3$
4-(tert. butylamino)-n-butyl β -chlorovinyl ether
- (9) $\text{Br}-\text{CH}=\text{CH}-\text{O}-\text{Cyclopropyl}-\text{NH}-\text{CH}(\text{CH}_3)_2$
2-(isopropylamino)cyclopropyl β -bromovinyl ether
- (10) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}$ (piperidine ring)
N-(β -vinylloxyethyl) piperidine
- (11) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{N}$ (pyrrolidine ring)
N-(γ -vinylloxypropyl) pyrrolidine
- (12) $\text{CH}_2=\text{CH}-\text{O}-\text{Cyclohexyl}-\text{N}(\text{CH}_3)_2$
4-vinylloxy-1-methylpiperidine
- (13) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}(\text{CH}_3)_2$ (cyclopropyl)
N-[β -vinylloxyethyl]-N-cyclopropyl-N-methylamine
- (14) $\text{CH}_2=\text{CH}-\text{O}-\text{Cyclohexyl}-\text{N}(\text{CH}_3)_2$
1-dimethylamino-4-vinylloxycyclohexane
- (15) $\text{CH}_2=\text{C}(\text{C}\equiv\text{N})-\text{O}-\text{CH}_2\text{CH}_2-\text{N}$ (azetane ring)
N-[β -(1-cyanovinylloxy)ethyl] azetane
- (16) $\text{CH}_2=\text{CH}-\text{O}-\text{Quinoline ring}$
3-vinylloxyquinoline
- (17) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{N}$ (morpholine ring)
N-[β -(vinylloxy)ethyl] morpholine

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 resultant polymer to be soluble in water. Examples of typical comonomers which may be employed in forming the polymers suit-

able for use in the present invention include the following ethylenically-unsaturated monomers:

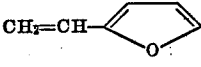
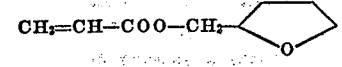
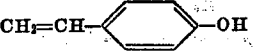
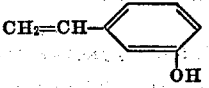
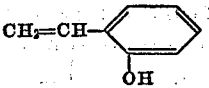
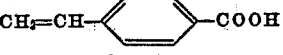
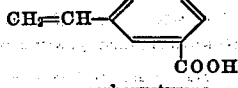
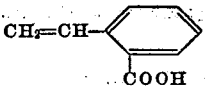
- (18) $\text{CH}_2=\text{CH}-\text{COOH}$
acrylic acid
- 5 (19) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOH}$
methacrylic acid
- 10 (20) $\text{CH}_2=\text{C}(\text{Cl})-\text{COOH}$
 α -chloroacrylic acid
- (21) $\text{CH}_2=\text{C}(\text{Br})-\text{COOH}$
 α -bromoacrylic acid
- 15 (22) $\text{CH}_3\text{CH}=\text{CH}-\text{COOH}$
crotonic acid
- (23) $\text{CH}_3\text{CH}=\text{CH}-\text{COOH}$
isocrotonic acid
- 20 (24) $\text{Cl}-\text{CH}=\text{CH}-\text{COOH}$
 β -chloroacrylic acid
- (25) $\text{Br}-\text{CH}=\text{CH}-\text{COOH}$
 β -bromoacrylic acid
- 25 (26) $\text{Cl}-\text{CH}=\text{C}(\text{CH}_3)-\text{COOH}$
 β -chloromethacrylic acid
- (27) $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_3$
methyl acrylate
- (28) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}_3$
ethyl methacrylate
- 35 (29) $\text{CH}_2=\text{C}(\text{Cl})-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_3$
n-propyl α -chloroacrylate
- (30) $\text{Br}-\text{CH}=\text{CH}-\text{COO}-\text{CH}(\text{CH}_3)_2$
isopropyl β -bromoacrylate
- 40 (31) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}(\text{CH}_3)_2$
isobutyl methacrylate
- 45 (32) $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{OH}$
 β -hydroxyethyl acrylate
- (33) $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 γ -hydroxypropyl acrylate
- 50 (34) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
2-hydroxy-n-propyl methacrylate
- 55 (35) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}_2$
acrylamide
- (36) $\text{CH}_2=\text{C}(\text{Cl})-\text{CO}-\text{NH}_2$
 γ -chloroacrylamide
- 60 (37) $\text{CH}_2=\text{C}(\text{Br})-\text{CO}-\text{NH}_2$
 γ -bromoacrylamide
- 65 (38) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}_2$
methacrylamide
- (39) $\text{CH}_2=\text{C}(\text{CH}_2\text{CH}_3)-\text{CO}-\text{NH}_2$
 α -ethylacrylamide
- 70 (40) $\text{Cl}-\text{CH}=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}_2$
 β -chloromethacrylamide

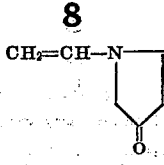
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- (41) $\text{Br}-\text{CH}=\text{C}(\text{Br})-\text{CO}-\text{NH}_2$
2,3-dibromoacrylamide
- (42) $\text{CH}_3\text{CH}=\text{CH}-\text{CO}-\text{NH}_2$
crotonamide
- (43) $\text{CH}_3-\text{CH}=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_3$
N-methylmethacrylamide
- (44) $\text{CH}_2=\text{CH}-\text{CO}-\text{N}(\text{CH}_3)_2$
N,N-dimethylacrylamide
- (45) $\text{CH}_2=\text{C}(\text{Cl})-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_3$
N-ethyl- α -chloroacrylamide
- (46) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_3$
N-tertiary butylacrylamide
- (47) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}_6\text{H}_{11}$
N-cyclohexylacrylamide
- (48) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_3$
N-tertiary octyl acrylamide
- (49) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{OH}$
N-methylolacrylamide
- (50) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2\text{OH}$
N-(β -hydroxyethyl) acrylamide
- (51) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$
diacetone acrylamide
- (52) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{CH}_3)_2$
N-isopropylacrylamide
- (53) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{C}_6\text{H}_5$
N-benzylacrylamide
- (54) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$
methylvinyl ether
- (55) $\text{CH}_2=\text{C}(\text{Cl})-\text{O}-\text{CH}_2\text{CH}_3$
ethyl α -chlorovinyl ether
- (56) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{Cl}$
 β -chloroethyl vinyl ether
- (57) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$
 β -methoxyethyl vinyl ether
- (58) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)_2$
isobutyl isopropenyl ether
- (59) $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)_2$
isooctyl vinyl ether
- (60) $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{CH}_3$
methylvinyl ketone
- (61) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3$
ethyl isopropenyl ketone
- (62) $\text{CH}_2=\text{C}(\text{Cl})-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{CH}_3$
n-propyl- α -chlorovinyl ketone

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- (63) $\text{CH}_2=\text{C}(\text{Br})-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$
 β -methoxyethyl- α -bromovinyl ketone
- (64) $\text{CH}_3\text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{OH}$
 β -hydroxyethyl-1-butene-2-yl ketone
- (65) $\text{CH}_2=\text{CH}-\text{CHO}$
acrolein
- (66) $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$
crotonaldehyde
- (67) $\text{CH}_2=\text{C}(\text{Cl})-\text{CHO}$
 α -chloroacrolein
- (68) $\text{CH}_2=\text{C}(\text{Br})-\text{CHO}$
 α -bromoacrolein
- (69) $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$
acrylonitrile
- (70) $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{N}$
crotononitrile
- (71) $\text{CH}_2=\text{C}(\text{Cl})-\text{C}\equiv\text{N}$
 α -chloroacrylonitrile
- (72) $\text{CH}_2=\text{C}(\text{Br})-\text{C}\equiv\text{N}$
 α -bromoacrylonitrile
- (73) $\text{BrCH}=\text{C}(\text{CH}_3)-\text{C}\equiv\text{N}$
 β -bromomethacrylonitrile
- (74) $\text{CH}_3\text{CH}=\text{C}(\text{Cl})-\text{C}\equiv\text{N}$
 β -chloroethacrylonitrile
- (75) $\text{CH}_2=\text{C}(\text{C}\equiv\text{N})-\text{COO}-\text{CH}_3$
methyl α -cyanoacrylate
- (76) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}_2$
acrylamidoacetamide
- (77) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}_2$
methacrylamidoacetamide
- (78) $\text{CH}_3\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_3$
2-crotonamido-N-methylpropionamide
- (79) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{CH}_3)-\text{CO}-\text{NH}_2$
2-acrylamidopropionamide
- (80) $\text{CH}_3-\text{C}(\text{CH}_3)=\text{C}-\text{CO}-\text{NH}-\text{CH}(\text{CH}_3)-\text{CO}-\text{NH}_2$
2-methacrylamidopropionamide
- (81) $\text{CH}_2=\text{C}(\text{Cl})-\text{CO}-\text{NH}-\text{CH}(\text{CH}_3)-\text{CO}-\text{NH}_2$
2-(α -chloroacrylamido)-3-methylbutyramide
- (82) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_3$
N-(acetamidomethyl)acrylamide
- (83) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2\text{CH}_3$
N-(propionamidomethyl)methacrylamide
- (84) $\text{CH}_2=\text{C}(\text{Cl})-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2\text{CH}_2\text{CH}_3$
N-(n-butyramidomethyl)- α -chloroacrylamide

- (85) 
maleic anhydride
- (86) $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$
maleic acid
- (87) $\text{HOOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}_2$
maleic acid amide
- (88) $\text{HOOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_3$
N-ethylmaleic acid amide
- (89) $\text{CH}_3-\text{OOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}_3$
N-methyl methylmaleate amide
- (90) $\text{CH}_2=\text{CH}-\text{OOC}-\text{H}$
vinylformate
- (91) $\text{CH}_2=\text{CH}-\text{OOC}-\text{CH}_3$
vinyl acetate
- (92) $\text{CH}_2=\text{CH}-\text{OH}$ (obtained by hydrolyzing
vinyl alcohol copolymerized vinyl
acetate)
- (93) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{OOC}-\text{CH}_2\text{Br}$
isopropenyl bromoacetate
- (94) $\text{CH}_2=\text{CH}-\text{OOC}-\text{C}(\text{CH}_3)_3$
vinyl pivalate
- (95) $\text{CH}_2=\text{CH}-\text{NH}-\text{COO}-\text{C}(\text{CH}_3)_3$
N-vinyl-tertiary butylcarbamate
- (96) $\text{CH}_2=\text{C}(\text{COOH})-\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_3$
ethyl-3-carboxy-3-butenate
- (97) 
 α -vinylfuran
- (98) 
 α -(acryloyloxymethyl)-tetrahydrofuran
- (99) 
p-hydroxystyrene
- (100) 
m-hydroxystyrene
- (101) 
o-hydroxystyrene
- (102) 
p-carboxystyrene
- (103) 
m-carboxystyrene
- (104) 
o-carboxystyrene

- (105) 
N-vinyl-2-pyrrolidone
- (106) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_3$
N-ethylacrylamide
- (107) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{COOH})-\text{CH}_2(\text{CH}_2)_2$
N-acryloylvaline
- (108) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{COOH})-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$
N-acryloylmethionine
- (109) $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{CO}-\text{NH}_2)-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$
N-acryloylmethionamide
- (110) $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{NH}-\text{CH}(\text{COOH})-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_3$
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 each of the following examples refers to the molar ratio of monomers in the copolymer.

EXAMPLE I

- 35 1:4 copolymer of acrylamide/ β -vinylxyethylpiperidine

1.0 g. of acrylamide was dissolved in 10.0 g. of β -vinylxyethylpiperidine. The resultant solution was polymerized with 0.1 g. of azoisobutyronitrile under vacuum in a sealed tube at 65° C. for 72 hours after initially flushing the tube with N_2 . The thus-formed polymer was precipitated into acetone and the precipitate was collected, washed with acetone and vacuum dried to yield a white powder soluble in H_2O and alcohol- H_2O mixtures.

EXAMPLE II

- 45 10:3 copolymer of acrylamide/ β -(dimethylamino)ethyl vinyl ether

7.11 g. of acrylamide and 11.51 g. of β -(dimethylamino)ethyl vinyl ether were dissolved in distilled water, and then 0.05 g. of azoisobutyronitrile was added. The solution was polymerized in a sealed tube at 65° C. overnight, precipitated into acetone and dried to yield a white powder soluble in H_2O .

EXAMPLE III

- 55 11:4 copolymer of acrylamide/ β -aminoethyl vinyl ether

14.3 g. of acrylamide and 60.0 g. of a 60% solution of β -aminoethyl vinyl ether in xylene were polymerized in a sealed tube under N_2 at 65° C. overnight with 0.15 g. of azoisobutyronitrile. The precipitated polymer was collected, washed with xylene and acetone and vacuum dried to yield a white powder which was soluble in H_2O and alcohol.

EXAMPLE IV

- 65 9:1 copolymer of ethyl acrylamide/amino ethyl vinyl ether

44.6 g. of ethyl acrylamide, 4.0 g. of amino ethyl vinyl ether, 0.097 g. of 0.2% $\text{K}_2\text{S}_2\text{O}_8$, 150 cc. of H_2O and 15 cc. of ethanol were heated at 70° C. under N_2 for 24 hours. The thus-formed polymer was isolated by precipitation into acetone and reprecipitated from methanol into ether, washed and dried under vacuum at 45° C. to yield a light tan solid soluble in H_2O and alcohol.

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 body 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.

Alternatively, the soluble salts may be removed by adding to the emulsion a solution of polyacid, such as 1:1 ethylene:maleic acid copolymer, and lowering the pH to below 5, thereby bringing about precipitation of the polyacid carrying the silver halide grains along with the precipitate. The resulting precipitate may then be washed and resuspended by redissolving the polyacid at pH 6-7.

The emulsions may be chemically sensitized with sulfur compounds such as sodium thiosulfate or 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 containing amine groups may be cross-linked with zirconium salts under alkaline conditions.

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 one or more of the instant polymers, large amounts of photosensitive silver halide grains may be obtained.

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

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

The instant invention will be further illustrated by reference to the following nonlimiting examples.

EXAMPLE V

A solution of 4.15 g. of a dry 10:3 copolymer of acrylamide/ β -(dimethylamino) ethyl vinyl ether as prepared in Example II above, 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.

EXAMPLE VI

An additional emulsion was also prepared according to the procedure of Example V, except that only 1.04 g. of the acrylamide/ β -(dimethylamino) ethyl vinyl ether copolymer was used.

EXAMPLE VII

Following essentially the same procedure as set forth in Example V with $\frac{1}{4}$ the amount of reagents (except potassium iodide, which was doubled), an emulsion was made employing a 1:4 acrylamide/N-(β -vinylxyethyl) piperidine copolymer, prepared generally according to the procedure of Example I. Also, the silver nitrate addition time was reduced to 5½ minutes and the ripening time increased to 46½ minutes for this emulsion.

EXAMPLE VIII

An emulsion employing a 11:4 acrylamide/ β -aminoethyl vinyl ether copolymer (generally as prepared in

Example III) was made following essentially the same procedure as set forth in Example IV with $\frac{1}{4}$ the amount of all reagents, except that the silver nitrate addition time was reduced to $8\frac{1}{2}$ minutes and the ripening time increased to $46\frac{1}{2}$ minutes.

EXAMPLE IX

An emulsion employing a 4:1 ethyl acrylamide/ β -aminoethyl vinyl ether copolymer (generally as prepared in Example IV) was made following essentially the same procedure as Example VIII, except that the silver nitrate addition time was 7 minutes and the ripening time was 45 minutes.

EXAMPLE X

An emulsion employing a 9:1 ethyl acrylamide/ β -aminoethyl vinyl ether copolymer (generally as prepared in

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 a predetermined processing time, 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 automatic recording densitometer. The following table summarizes the densitometer readings obtained on samples of these prints:

TABLE II

Bodding polymer	Silver/ polymer ratio	Silver (mg./ft. ²)	Film system	D _{max.}	D _{min.}	Δ D	Processing time (sec.)
None	∞	96.1	T-20C	0.90	0.44	0.46	5
Do.	∞	138.2	T-20C	1.26	0.51	0.75	5
Do.	∞	136.6	T-107	0.56	0.18	0.38	10
Polyvinyl alcohol	0.68	97.3	T-20C	1.32	0.50	0.82	10
Do.	0.68	97.3	T-42	1.20	0.24	0.96	10
Do.	0.68	97.3	T-107	0.99	0.14	0.85	10
Do.	0.68	105.9	T-20C	1.02	0.52	0.50	5
Do.	0.68	105.9	T-20C	1.44	0.57	0.87	15
Do.	0.68	105.9	T-42	1.17	0.25	0.92	10
Do.	0.68	105.9	T-107	0.70	0.17	0.53	5
Do.	0.68	105.9	T-107	0.90	0.18	0.72	10
Do.	0.68	135.7	T-42	1.26	0.36	0.90	10
Do.	0.68	135.7	T-107	0.76	0.20	0.56	10
Do.	0.34	78.8	T-20C	1.17	0.12	1.05	15
Do.	0.34	78.8	T-42	1.24	0.32	0.92	10
Do.	0.34	78.8	T-107	1.18	0.12	1.06	15

Example V) was made following essentially the same procedure as Example V with $\frac{1}{10}$ the amount of reagents and with a silver nitrate addition time of 7 minutes and a ripening time of 45 minutes.

EXAMPLE XI

An emulsion was prepared following the procedure of Example V, except that gelatin was employed as the binder rather than the synthetic polymer.

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

TABLE I

Example	Polymer	Grain size (microns)	
		Range	Average
V	10:3 acrylamide/ β -(dimethylamino) ethyl vinyl ether.	0.3-2.0	1.2
VI	do.	0.3-1.8	1.0
VII	1:4 acrylamide/N-(β -vinyl oxyethyl) piperidine.	0.6	0.6
VIII	11:4 acrylamide/ β -aminoethyl vinyl ether.	0.3-1.0	0.5
IX	4:1 ethylacrylamide/ β -aminoethyl vinyl ether.	0.1-1.0	0.3
X	9:1 ethylacrylamide/ β -aminoethyl vinyl ether.	0.2-1.2	0.5
XI	Gelatin	0.2-1.8	1.0

EXAMPLE XII

The emulsion mixture of Example V was centrifuged and washed with water to a low conductance and then redispersed in distilled water. To some aliquots of this emulsion were added solutions 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) at a silver to polymer ratio of about 1:3 or about 2:3. The remaining aliquots 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

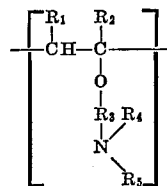
In certain photographic applications, it may be desirable to replace part, but not all, of the gelatin in the photosensitive emulsion. In view of the characteristics of these polymers described above, and further, in view of their compatibility with gelatin in substantially all proportions, it will be 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 is a lower alkylene or lower cycloalkylene group and R_4 and R_5 each is hydrogen, a lower alkyl, or lower cycloalkyl group; or R_3 and/or R_4 and/or R_5 taken together represent the atoms necessary to complete a 3 to 8-membered heterocyclic ring structure.

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

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

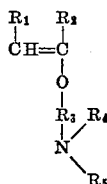
4. The product as defined in claim 1 wherein said silver halide emulsion is a silver iodobromide emulsion.

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 is a homopolymer.

8. 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.

9. The product as defined in claim 8 wherein said first monomer is β -aminoethyl vinyl ether.

10. The product as defined in claim 8 wherein said first monomer is N-(β -vinylxyethyl) piperidine.

11. The product as defined in claim 8 wherein said first monomer is β -(dimethylamino)ethyl vinyl ether.

12. The product as defined in claim 8 wherein said second monomer is acrylamide.

13. The product as defined in claim 8 wherein said second monomer is ethyl acrylamide.

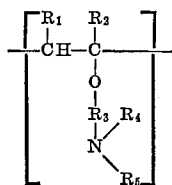
14. The product as defined in claim 1 which includes a bodying polymer.

15. The product as defined in claim 14 wherein said bodying polymer is polyvinyl alcohol.

16. The product as defined in claim 14 wherein said bodying polymer is hydroxymethyl cellulose.

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

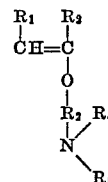
18. A method of preparing a photosensitive silver halide emulsion which comprises reacting a water-soluble silver salt with a water-soluble halide salt in an aqueous solution containing a water-soluble film-forming polymer having in its structure repeating units of the formula:



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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 and R_5 each is hydrogen, a lower alkyl group or lower cycloalkyl group; or R_3 and/or R_4 and/or R_5 taken together represent 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 18 wherein said first monomer is β -aminoethyl vinyl ether.

21. The method as defined in claim 18 wherein said first monomer is N-(β -vinylxyethyl) piperidine.

22. The method as defined in claim 18 wherein said first monomer is β -(dimethylamino) ethyl vinyl ether.

23. The method as defined in claim 18 wherein said second monomer is acrylamide.

24. The method as defined in claim 18 wherein said second monomer is ethyl acrylamide.

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

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

27. The method as defined in claim 25 wherein said bodying polymer is hydroxyethyl cellulose.

28. The method as defined in claim 25 wherein said bodying polymer is gelatin.

References Cited

UNITED STATES PATENTS

3,345,346	10/1967	Reynolds	96-114
3,425,836	2/1969	Perry et al.	96-114

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