

[54] SILVER HALIDE EMULSIONS  
COMPRISING POLYMERIC PEPTIZERS

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[73] Assignee: Polaroid Corporation, Cambridge, Mass.  
[22] Filed: Oct. 4, 1972  
[21] Appl. No.: 294,979

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 103,305, Dec. 31, 1970, abandoned.  
[52] U.S. Cl. .... 96/114  
[51] Int. Cl. .... G03c 1/04  
[58] Field of Search ..... 96/114

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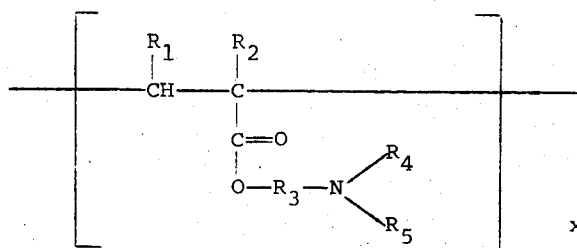
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Primary Examiner—Ronald H. Smith  
Attorney, Agent, or Firm—Philip G. Kiely; Mart C. Matthews

[57] ABSTRACT

A photosensitive silver halide emulsion wherein the emulsion binder comprises a water-soluble polymer having in its molecule repeating units of the structure which may be represented by the general formula:



wherein:

R<sub>1</sub> is hydrogen, lower alkyl such as methyl, ethyl or halogen; R<sub>2</sub> is hydrogen, lower alkyl, such as methyl or ethyl, cyano or halogen; R<sub>3</sub> is lower alkyl, or lower cycloalkyl; R<sub>4</sub> and R<sub>5</sub> are each hydrogen, lower alkyl, or lower cycloalkyl; R<sub>3</sub> and/or R<sub>4</sub> and/or R<sub>5</sub> may be chemically joined to form a ring structure; and x is a positive integer greater than 1.

23 Claims, No Drawings

# SILVER HALIDE EMULSIONS COMPRISING POLYMERIC PEPTIZERS

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 103,305 filed Dec. 31, 1970 now abandoned.

## BACKGROUND OF THE INVENTION

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:

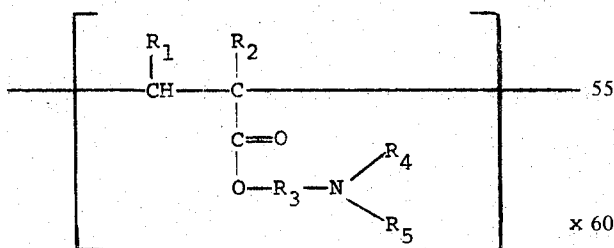
1. absent (or constant) photographic activity;
2. ability to form an adsorption layer on microcrystals of silver halide permitting stable suspensions to be obtained;
3. ability to form adsorption layers as described in (2) above which do not prevent growth of silver halide microcrystals during physical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

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.

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

## SUMMARY OF THE INVENTION

The present invention is directed to a photosensitive silver halide emulsion wherein the silver halide crystals are disposed in a water-soluble synthetic polymeric binder, namely, a polymer having in its molecule repeating units of the structure which may be represented by the general formula:



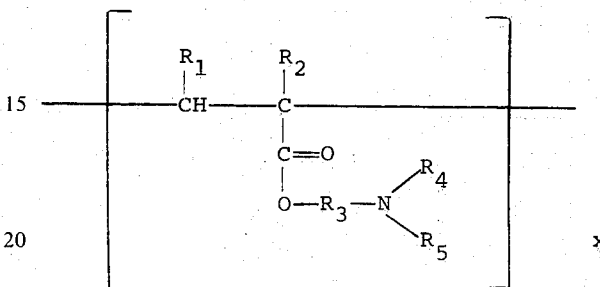
wherein:

$R_1$  is hydrogen, lower alkyl such as methyl or ethyl or halogen;  $R_2$  is hydrogen, lower alkyl such as methyl or ethyl, cyano or halogen;  $R_3$  is lower alkyl, or lower cycloalkyl;  $R_4$  and  $R_5$  are each hydrogen, lower alkyl, or

lower cycloalkyl;  $R_3$  and/or  $R_4$  and/or  $R_5$  may be chemically joined to form a ring structure; and  $x$  is a positive integer greater than 1.

## DETAILED DESCRIPTION OF THE INVENTION

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



wherein:

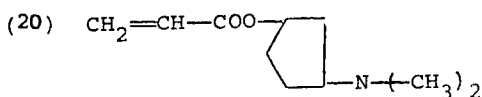
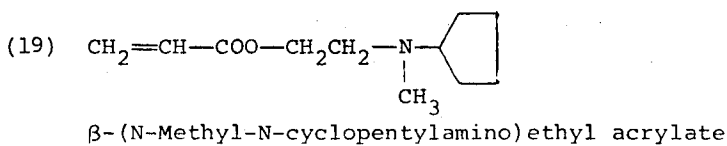
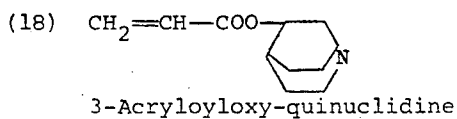
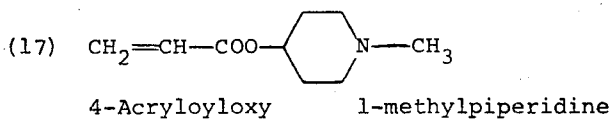
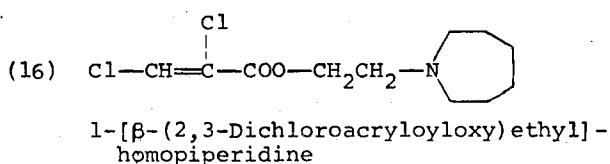
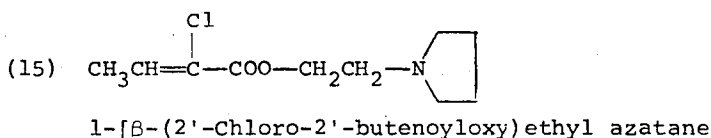
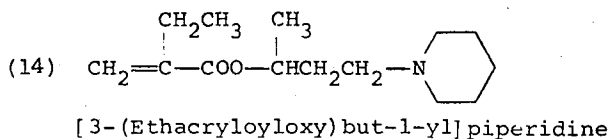
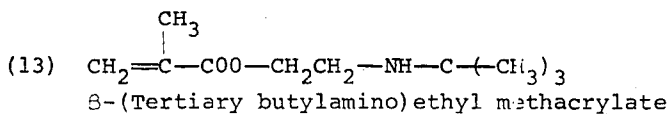
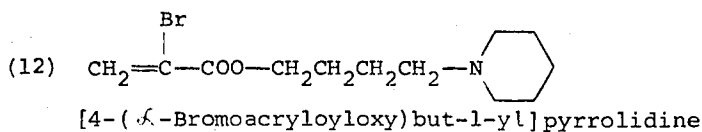
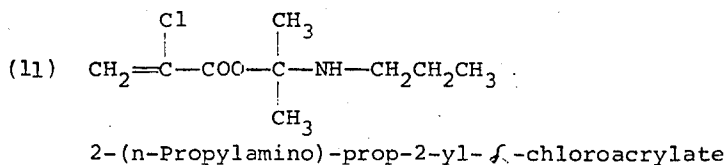
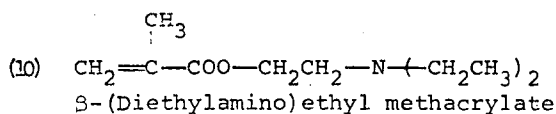
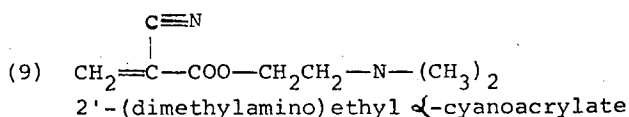
$R_1$  is hydrogen, lower alkyl such as methyl or ethyl or halogen;  $R_2$  is hydrogen, lower alkyl, such as methyl or ethyl, cyano or hydrogen;  $R_3$  is lower alkyl, or lower cycloalkyl;  $R_4$  and  $R_5$  are each hydrogen, lower alkyl, or lower cycloalkyl;  $R_3$  and/or  $R_4$  and/or  $R_5$  may be chemically joined to form a ring structure; and  $x$  is a positive integer greater than 1. In a preferred embodiment  $x$  is at least 50.

Such polymers have unexpectedly been found to substantially meet the basic requirements for a gelatin substitute, as delineated above. In particular, the resulting emulsions effectively peptize silver halide crystals providing novel silver halide dispersions which are readily sensitized and are characterized by excellent latent image stability and excellent film speed.

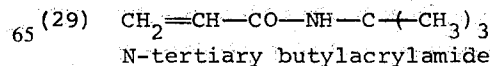
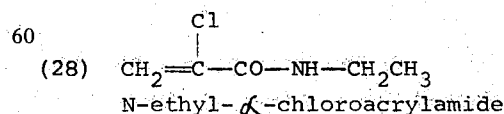
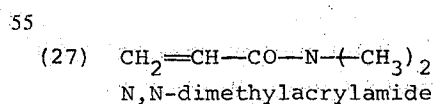
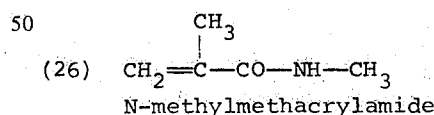
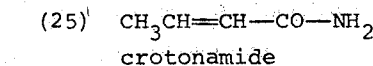
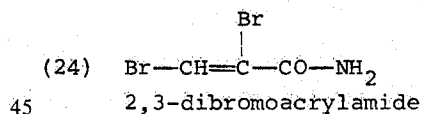
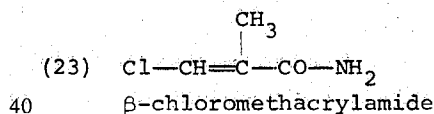
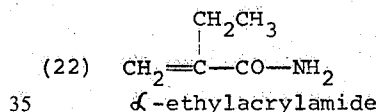
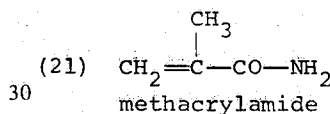
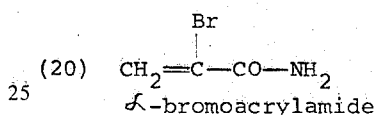
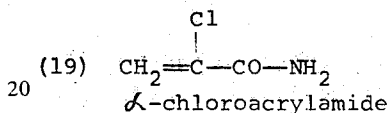
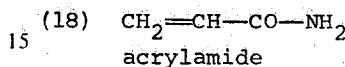
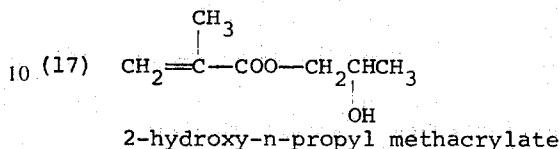
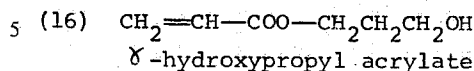
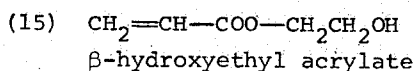
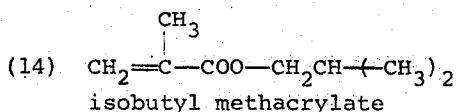
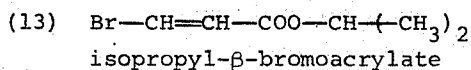
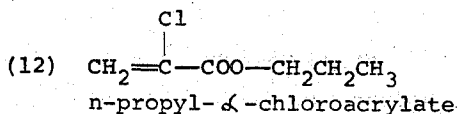
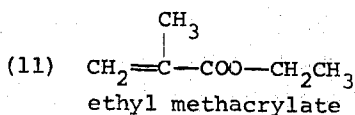
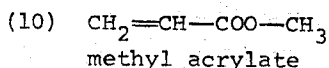
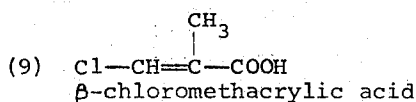
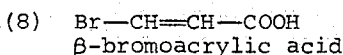
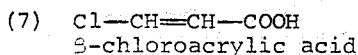
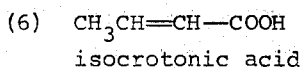
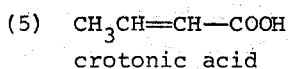
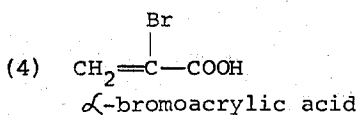
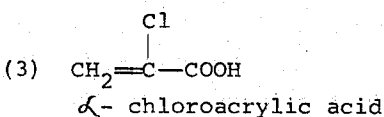
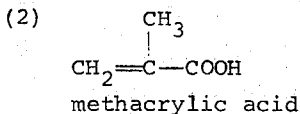
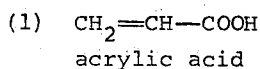
Typical examples of monomers useful for preparing polymers for employment in the instant invention include:

1.  $CH_2=CH-COO-CH_2-NH_2$   
Aminomethyl acrylate
2.  $CH_3CH=CH-COO-CH_2CH_2NHCH_3$   
 $\beta$ -(Methylamino)ethyl 2-butenate
- (3)  $CH_3CH_2CH=CH-COO-CHCH_3$   
 $N-(CH_3)_2$   
 $\alpha$ -(Dimethylamino)ethyl 2-pentenoate
4.  $CH_2=CH-COO-CH_2CH_2-N-(CH_3)_2$   
 $\beta$ -(Dimethylamino)ethyl acrylate
5.  $Cl-CH=CH-COO-CH_2CH_2CH_2NH-CH_2CH_3$   
3-(Ethylamino)-n-propyl- $\beta$ -chloroacrylate
- (6)  $Br-CH=CH-COO-CHCH_2-N-CH_2CH_3$   
 $CH_3$   $CH_3$   
1-(Methylethylamino)-prop-2-yl- $\beta$ -bromoacrylate
- (7)  $CH_2=C-COO-CH_2CH_2-N-(CH_3)_2$   
 $CH_3$   
 $\beta$ -(Dimethylamino)ethyl methacrylate

8.  $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2\text{CH}_2-\text{N}-(\text{CH}_2\text{CH}_3)_2$   
 $\beta$ -(Diethylamino)ethyl acrylate

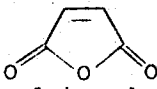


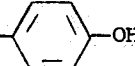
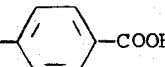
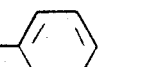
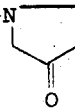
The instant water-soluble polymers may be homopolymers or interpolymers having, in addition to the repeating units defined above, any compatible repeating unit or various repeating units which are not detrimental to photographic silver halide emulsions and which allow the resultant polymer to be soluble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



- (30)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}_6\text{H}_{11}$   
N-cyclohexylacrylamide
- (31)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(\text{CH}_3)_3$   
N-tertiary octyl acrylamide
- (32)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{OH}$   
N-methylolacrylamide
- (33)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_2\text{OH}$   
N-( $\beta$ -hydroxyethyl) acrylamide
- (34)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$   
diacetone acrylamide
- (35)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}(\text{CH}_3)_2$   
N-isopropylacrylamide
- (36)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{C}_6\text{H}_5$   
N-benzylacrylamide
- (37)  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$   
methylvinyl ether
- (38)  $\text{CH}_2=\text{C}(\text{Cl})-\text{O}-\text{CH}_2\text{CH}_3$   
ethyl  $\alpha$ -chlorovinyl ether
- (39)  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{Cl}$   
 $\beta$ -chloroethyl vinyl ether
- (40)  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2-\text{OCH}_3$   
 $\beta$ -methoxyethyl vinyl ether
- (41)  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}(\text{CH}_3)_2$   
isobutyl isopropenyl ether
- (42)  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)_2$   
isooctyl vinyl ether
- (43)  $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{CH}_3$   
methylvinyl ketone
- (44)  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3$   
ethyl isopropenyl ketone
- (45)  $\text{CH}_2=\text{C}(\text{Cl})-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{CH}_3$   
n-propyl- $\alpha$ -chlorovinyl ketone

- (46)  $\text{CH}_2=\text{C}(\text{Br})-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_3$   
 $\beta$ -methoxyethyl- $\alpha$ -bromovinyl ketone
- (47)  $\text{CH}_2=\text{C}(\text{CH}_2\text{CH}_3)-\text{C}(=\text{O})-\text{CH}_2\text{CH}_2\text{OH}$   
 $\beta$ -hydroxyethyl-1-butene-2-yl ketone
- (48)  $\text{CH}_2=\text{CH}-\text{CHO}$   
acrolein
- (49)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$   
crotonaldehyde
- (50)  $\text{CH}_2=\text{C}(\text{Cl})-\text{CHO}$   
 $\alpha$ -chloroacrolein
- (51)  $\text{CH}_2=\text{C}(\text{Br})-\text{CHO}$   
 $\alpha$ -bromoacrolein
- (52)  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$   
acrylonitrile
- (53)  $\text{CH}_3\text{CH}=\text{CH}-\text{C}\equiv\text{N}$   
crotononitrile
- (54)  $\text{CH}_2=\text{C}(\text{Cl})-\text{C}\equiv\text{N}$   
 $\alpha$ -chloroacrylonitrile
- (55)  $\text{CH}_2=\text{C}(\text{Br})-\text{C}\equiv\text{N}$   
 $\alpha$ -bromoacrylonitrile
- (56)  $\text{BrCH}(\text{CH}_3)=\text{C}-\text{C}\equiv\text{N}$   
 $\beta$ -bromomethacrylonitrile
- (57)  $\text{ClCH}(\text{CH}_2\text{CH}_3)=\text{C}-\text{C}\equiv\text{N}$   
 $\beta$ -chloroethacrylonitrile
- (58)  $\text{CH}_2=\text{C}(\text{C}\equiv\text{N})-\text{COO}-\text{CH}_3$   
methyl  $\alpha$ -cyanoacrylate
- (59)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}_2$   
acrylamidoacetamide

- (60)  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}-\text{CH}_2-\text{CO}-\text{NH}_2$   
methacrylamidoacetamide
- (61)  $\text{CH}_3\text{CH}=\text{CH}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\text{CH}}-\text{CO}-\text{NH}-\text{CH}_3$   
2-crotonamido-N-methylpropionamide
- (62)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\text{CH}}-\text{CO}-\text{NH}_2$   
2-acrylamidopropionamide
- (63)  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}-\underset{\text{CH}_3}{\text{CH}}-\text{CO}-\text{NH}_2$   
2-methacrylamidopropionamide
- (64)  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CO}-\text{NH}-\underset{\text{CH}(\text{CH}_3)_2}{\text{CH}}-\text{CO}-\text{NH}_2$   
2-( $\alpha$ -chloroacrylamido)-3-methylbutyramide
- (65)  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_3$   
N-(acetamidomethyl) acrylamide
- (66)  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2\text{CH}_3$   
N-(propionamidomethyl)methacrylamide
- (67)  $\text{CH}_2=\text{C}-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2\text{CH}_2\text{CH}_3$   
N-(n-butyramidomethyl)  $\alpha$ -chloroacrylamide
- (68)   
maleic anhydride
- (69)  $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$   
maleic acid
- (70)  $\text{HOOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}_2$   
maleic acid amide
- (71)  $\text{HOOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}_2\text{CH}_3$   
N-ethylmaleic acid amide
- (72)  $\text{CH}_3-\text{OOC}-\text{CH}=\text{CH}-\text{CO}-\text{NH}-\text{CH}_3$   
N-methyl methylmaleate amide
- (73)  $\text{CH}_2=\text{CH}-\text{OOCH}$   
vinylformate
- (74)  $\text{CH}_2=\text{CH}-\text{OOC}-\text{CH}_3$   
vinyl acetate
- (75)  $\text{CH}_2=\text{CH}-\text{OH}$   
vinyl alcohol
- (76)  $\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{OOC}-\text{CH}_2\text{Br}$   
isopropenyl bromoacetate

- (77)  $\text{CH}_2=\text{CH}-\text{OOC}-\text{C}-(\text{CH}_3)_3$   
vinyl pivalate
- (78)  $\text{CH}_2=\text{CH}-\text{NH}-\text{COO}-\text{C}-(\text{CH}_3)_3$   
N-vinyl-tertiary butylcarbamate
- (79)  $\text{CH}_2=\overset{\text{COOH}}{\text{C}}-\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_3$   
ethyl-3-carboxy-3-butenate
- (80)  $\text{CH}_2=\text{CH}-$    
 $\alpha$ -vinylfuran
- (81)  $\text{CH}_2=\text{CH}-\text{COO}-\text{CH}_2-$    
 $\alpha$ -(acryloyloxymethyl)-tetrahydrofuran
- (82)  $\text{CH}_2=\text{CH}-$    
p-hydroxystyrene
- (83)  $\text{CH}_2=\text{CH}-$    
m-hydroxystyrene
- (84)  $\text{CH}_2=\text{CH}-$    
o-hydroxystyrene
- (85)  $\text{CH}_2=\text{CH}-$    
p-carboxystyrene
- (86)  $\text{CH}_2=\text{CH}-$    
m-carboxystyrene
- (87)  $\text{CH}_2=\text{CH}-$    
o-carboxystyrene
- (88)  $\text{CH}_2=\text{CH}-\text{N}$    
N-vinyl-2-pyrrolidone

The following general procedure may be used for preparing photographic emulsions using the novel polymers contemplated in the instant invention as the colloid binders.

A water-soluble silver salt, such as silver nitrate, is 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 novel polymer. The emulsion of silver halide thus-formed contains water-soluble salts, as a by-product of the double decomposition reaction, as well as any unreacted excess of the initial salts. To remove these soluble materials, the emulsion is centrifuged and washed with distilled water to a low conductance. The emulsion is then redispersed in distilled water. To an aliquot of this emulsion is 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.), is added and the emulsion is slot coated onto a base of cellulose triacetate sheet 5 mls. thick having a coating of 30 mg./sq. ft. of hardened gelatin; designated Celfa, (commercially available from Instar Supply Company, New York, N. Y.).

An alternative procedure for removing the soluble salts is to add to the emulsion a solution of polyacid, e.g., 1:1 ethylene:maleic acid; and then to lower the pH to below 5, thereby bringing about precipitation of the polyacid carrying the silver halide grains along with the precipitate, and then to wash and resuspend the resulting precipitate by redissolving the polyacid at pH 6-7.

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

The emulsions 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 amine polymer is coated with a zirconium salt, for example, zirconium sulphate, and the pH is raised to high alkalinity, wherein cross-linking occurs.

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

The emulsions of this invention may be coated and processed according to conventional procedures of the art. They may be coated, for example, onto various types of rigid or flexible supports, such as glass, paper,

metal, and polymeric films of both the synthetic type and those derived from naturally occurring products. As examples of specific materials which may serve as supports, mention may be made of paper, aluminum, polymethacrylic acid, methyl and ethyl esters, vinyl-chloride 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. These novel emulsions of the instant invention have been found to adhere to supports in a most satisfactory manner.

The polymers employed in the practice of the instant invention may contain from 5-100 mole percent of the structure which may be represented:

### AMINOALKYL-ACRYLATE

the exact amount employed depending on the desired effect. For example, the grain size distribution of the emulsion may be varied by changing the mole ratio of comonomers present in the instant copolymers. The following table summarizes grain sizes of silver halide crystals obtained from varying compositions of copolymers of acrylamide and  $\beta$ -(dimethylamino)ethyl methacrylate (DMAEM).

TABLE I

| Polymer                   | Grain Size      |                   |
|---------------------------|-----------------|-------------------|
|                           | Range ( $\mu$ ) | Average ( $\mu$ ) |
| 1:1 acrylamide : DMAEM    | 0.2 - 1.2       | 0.6               |
| 3:1 acrylamide : DMAEM    | 0.2 - 1.4       | 0.7               |
| 4.65:1 acrylamide : DMAEM | 0.3 - 1.8       | 1.0               |
| 6.41:1 acrylamide : DMAEM | 0.4 - 2.0       | 1.2               |
| 8:1 acrylamide : DMAEM    | 0.4 - 4.2       | 1.8               |
| 8.84:1 acrylamide : DMAEM | 0.3 - 5.1       | 1.8               |
| polyacrylamide            |                 | 0.8               |

It will be noted that the average grain size obtained from the AMINOALKYL-ACRYLATE copolymer tended to increase as the mole percent of acrylamide comonomer increased.

Emulsions made from the polymers of the instant invention are characterized by excellent latent image stability. For example, the latent image from an 8:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate silver halide emulsion was found to be 100 percent intact when developed after 72 hours. These polymers of the instant invention are also characterized by excellent film speed. In particular, these novel emulsions have been found to have much greater inherent speeds than gelatin emulsions. For example, a 6:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate silver halide emulsion, when processed with a processing solution and an image-receiving sheet from a Polaroid 3000 speed Land Film Pack Type 107 film assembly, was found to have an intrinsic ASA speed of 50 in addition to identical grains and size distribution as compared with the gelatin emulsion which has an intrinsic ASA speed of 3.

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 therefore, be bodied with any

water soluble polymers, overcoming the disadvantage encountered with gelatin which is only compatible with a very few polymers in a most limited pH range. As examples of specific materials which may serve as bodying polymers are polyvinyl alcohol, polyacrylamide, polyalkylacrylamides, polyvinyl pyrrolidone, poly( $\beta$ -hydroxyethyl acrylate), polyethylene imine and cellulose derivatives such as hydroxypropyl cellulose and methoxy 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. For example, when 1.0 g. of polymer of the present invention was substituted for 4.15 g. of polymer in the basic emulsion procedure described hereinafter, the same amount of silver halide with identical grain shape and size distribution was 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 consists almost exclusively of the bodying polymer.

By selecting appropriate comonomers, copolymers with desired diffusion characteristics may be prepared. For example, the following Table 2 illustrates that the rate of diffusion of alkali through an emulsion comprising one of the novel polymers may be varied by changing the polymer composition.

TABLE 2

| Polymer (at 225 mg./ft. <sup>2</sup> ) | NaOH Permeation Rate<br>mg. NaOH/<br>ft. <sup>2</sup> sec. | Time to<br>pH 10<br>(seconds) |
|----------------------------------------|------------------------------------------------------------|-------------------------------|
| Gelatin                                | 360.00                                                     | 0.09                          |
| 19:1 acrylamide:DMAEM                  | 200.00                                                     | 0.29                          |
| 19:1 N-methylacrylamide:DMAEM          | 7.00                                                       | 0.05                          |
| 19:1 N-ethylacrylamide:DMAEM           | 30.00                                                      | 0.40                          |
| 19:1 N,N-diethylacrylamide:DMAEM       | 0.40                                                       | 1.20                          |
| 19:1 N-siopropylacrylamide:DMAEM       | 0.02                                                       | 2.40                          |
| 19:1 N-vinyl-2-pyrrolidone:DMAEM       | 150.00                                                     | 0.09                          |

The instant polymers have been found to impart a black toning effect to silver obtained by physical development. Additionally, as the following Table 3 illustrates, it has been found that more silver was transferred when the emulsion layer contained one of the instant polymers than was obtained with gelatin.

TABLE 3

| Emulsion Polymer          | mg. Ag.<br>ft. <sup>2</sup> | 5 sec.<br>$\mu_{\min}$ | 5 sec.<br>$\mu_{\max}$ | 10 sec.<br>$\mu_{\max}$ | % of 10 sec. Ag.<br>transferred<br>in 5 sec. | % of 10 sec.<br>$\mu_{\max}$<br>in 5 sec. | Density<br>units per<br>mg. Ag./ft. <sup>2</sup><br>transferred<br>in 5 sec. |
|---------------------------|-----------------------------|------------------------|------------------------|-------------------------|----------------------------------------------|-------------------------------------------|------------------------------------------------------------------------------|
| Gelatin control           | 14.8                        | 0.02                   | 0.70                   | 0.90                    | 66%                                          | 78%                                       | 0.102                                                                        |
| 9:1 Acrylamide:-<br>DMAEM | 15.5                        | 0.01-<br>0.02          | 0.66                   | 0.78                    | 80%                                          | 85%                                       | 0.122                                                                        |

The instant AMINOALKYL-ACRYLATE copolymers containing acidic comonomers may be pH flocculated in order to remove the soluble salts formed as a by-product 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, a 3:1 copolymer of acrylic acid:  $\beta$ -(dimethylamino) ethyl methacrylate may be precipitated by lowering the pH below 5 and then washed and resuspended by raising the pH to between 6-7.

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

## Procedure A

A solution of 4.15 g. of the dry 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 an additional 396 ml. 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.

## Procedure B

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

The emulsion mixture was centrifuged and washed with water to a low conductance. The emulsion was then redispersed in distilled water. To an aliquot of this emulsion was added a known quantity of a solution of bodying or thickening polymer of polyvinyl alcohol having an average molecular weight of about 100,000 (commercially available from E. I. duPont de Nemours & Company, Wilmington, Del., designated Type 72-60). A surfactant such as Aerosol OT was added and the emulsion was slot coated onto a base of cellulose triacetate sheet 5 mils thick having a coating of 30 mg./sq. ft. of hardened gelatin, designated Celfa, (commercially available from Instar Supply Company, New York, N.Y.). This film so prepared was air dried, exposed on a sensitometer, and processed with a processing solution and an image-receiving sheet from a Polaroid 3,000 speed Land Film Pack Type 107 film assembly.

bly. The negative and image-receiving element were maintained in superposed position for 15 seconds, after which they were stripped apart. The photographic characteristics of the resulting positive print were measured on an automatic recording densitometer. Alternatively, the processing was effected with a processing

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solution and an image-receiving sheet from a Polaroid 200-400 speed Land Type 42 black and white roll film, or from a Polaroid 3,000 speed Land Type 20C black and white film.

The following examples are given for purpose of illustration only.

## Example I

4.7:1 copolymer of acrylamide: $\beta$ -(diethylamino) ethyl acrylate

A solution of 7.11 g. of acrylamide and 17.12 g. of  $\beta$ -(diethylamino) ethyl acrylate in 50 ml. of distilled water adjusted to pH 6 with nitric acid, was prepared in a glass tube. To this solution 0.05 g. 2,2'-azobis-[2-methylpropionitrile] catalyst was added. The tube was cooled, evacuated, flushed with nitrogen several times, sealed and placed in a 65° C. water bath for 24 hours. The solution was precipitated into acetone and the precipitate obtained was collected, washed and vacuum dried at 55° C.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability after being allowed to stand, and was free from any undesirable clumping, aggregation or sedimentation effects. From optical micrographs at a magnification of 1,000 $\times$  and from electron-micrographs at magnifications from 10,000-50,000 $\times$ , it was determined that the emulsion grains were octahedral crystals with diameters ranging from 0.2 to 1.2 microns. The average diameter was 0.6 microns.

## Example II

2.5:1 copolymer of acrylamide: $\beta$ -(diethylamino) ethyl methacrylate

A solution of 7.11 g. of acrylamide and 18.53 g.  $\beta$ -(diethylamino) ethyl methacrylate were dissolved in 50 ml. of distilled water adjusted to pH 6 with nitric acid. To this solution 0.05 g. 2,2'-azobis-[2-methylpropionitrile] catalyst was added. The solution was polymerized in a sealed tube under nitrogen and vacuum at 65° C. for 24 hours. The solution was precipitated into acetone. The precipitate was collected, washed and vacuum dried at 55° C.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed excellent stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains constituted octahedral crystals with diameters ranging from 0.2 to 1.6 microns. The average diameter was 0.7 microns.

## Example III

8.81:1 copolymer of acrylamide: $\beta$ -(tertiary butylamino) ethyl methacrylate

A solution of 7.11 g. of acrylamide and 18.53 g. of  $\beta$ -(tertiary butylamino) ethyl methacrylate were polymerized in the same manner as described in Example II.

The emulsion was prepared according to the general procedure (A) described above. The emulsion showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.4 to 1.0 microns. The average diameter was 0.5 microns.

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## Example IV

1:2 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl acrylate

A solution of 3.55 g. of acrylamide and 14.3 g. of  $\beta$ -(dimethylamino) ethyl acrylate was prepared in 200 mls. of distilled water in a flask under nitrogen. The pH was adjusted to 6.3 and 0.03 g. potassium peroxydisulfate and 0.03 g. sodium hydrogen sulfite were added.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.2 to 1.5 microns. The average diameter was 0.8 microns.

## Example V

1:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl acrylate

A solution of 42.9 g. (0.3 moles) of  $\beta$ -(dimethylamino) ethyl acrylate and 21.3 g. acrylamide were polymerized under vacuum in 65 cc. ethanol containing 0.1926 g. 2,2'-azobis-[2-methylpropionitrile]. The polymer solution obtained was diluted with ethanol, precipitated into acetone, washed in acetone and vacuum dried at 45° C. The product weighed 45 g.

The emulsion was prepared according to the general procedure (A) described above. The emulsion showed good stability and was completely free from undesirable clumping, aggregation or sedimentation. The emulsion grains were octahedral crystals with diameters ranging from 0.5 to 1.5 microns. The average diameter was 1.0 microns.

## Example VI

2:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl acrylate

A solution of 7.65 g. of  $\beta$ -(dimethylamino) ethyl acrylate and 7.11 g. acrylamide was prepared in 200 mls. of distilled water, in a flask under nitrogen. The pH was adjusted to 6.3 and 0.04 g. potassium peroxydisulfate and 0.03 g. sodium hydrogen sulfite were added.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.3 to 3.0 microns. The average diameter was 1.0 microns.

## Example VII

1:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

A solution of 7.8 g. of  $\beta$ -(dimethylamino) ethyl methacrylate and 3.55 g. of acrylamide was prepared in 150 mls. of distilled water, in a flask under nitrogen. To this solution was added 3 mls. isopropanol and the pH adjusted to 6.3 with nitric acid and 10 percent sodium hydroxide. To this solution 0.03 g. of potassium peroxydisulfate and 0.03 g. sodium hydrogen sulfite were added.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed very good stability and was free from un-

desirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.2 to 1.8 microns. The average diameter was 1.0 microns.

#### Example VIII

4:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

A solution of 7.11 g. of acrylamide and 18.53 g. of  $\beta$ -(dimethylamino) ethyl methacrylate were polymerized in the same manner as described in Example II.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.2 to 1.0 microns. The average diameter was 0.4 microns.

#### Example IX

8:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

A solution of 15.7 g. (.1 mole) dimethylamino ethyl methacrylate and 28.3 g. (.4 mole) acrylamide were dissolved in 393 ml. water and 3 ml. isopropanol containing 0.3 percent of 2,2'-azobis-[2-methylpropionitrile]. The solution was flushed with nitrogen and heated at 65° C. for 20 hours. The solution was precipitated into excess acetone, filtered and vacuum dried.

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.3 to 2.4 microns. The average diameter was 1.1 microns.

#### Example X

8.84:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

The copolymer employed contained 80 percent by weight of acrylamide and 20 percent by weight of  $\beta$ -(dimethylamino) ethyl methacrylate (commercially available from Dow Chemical Company, Midland, Michigan, designated Dow NC-1734).

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were octahedral crystals with diameters ranging from 0.2 to 2.2 microns. The average diameter was 1.0 microns.

#### Example XI

7.16:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

The copolymer employed contained 12.25 mole percent  $\beta$ -(dimethylamino) ethyl methacrylate (commercially available from Hercules Powder Company, Wilmington, Del., designated Reten-VC-2394-31A).

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The grain size diameters were within the range of 0.3 to 2.0 microns; the average grain size diameter was 1.0 microns.

#### EXAMPLE XII

6.41:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

The copolymer employed contained 13.5 mole percent  $\beta$ -(dimethylamino) ethyl methacrylate (commercially available from Hercules Powder Company, Wilmington, Del., designated Reten VC-2394-31B).

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The grain size diameters were within the range 0.4 to 2.0 microns; the average grain size diameter was 1.2 microns.

#### Example XIII

4.65:1 copolymer of acrylamide: $\beta$ -(dimethylamino) ethyl methacrylate

The copolymer employed contained 17.7 mole percent  $\beta$ -(dimethylamino) ethyl methacrylate (commercially available from Hercules Powder Company, Wilmington, Del., designated Reten-VC-2394-31C).

The emulsion was prepared according to the general procedure (A) described above. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The grain size diameters were within the range 0.3 to 1.8 microns; the average grain size diameter was 1.0 microns.

#### Example XIV

Poly  $\beta$ -(dimethylamino) ethyl methacrylate

The polymerization was carried out in carbon tetrachloride at 65° C. with 2,2'-azobis-[2-methylpropionate] catalyst. The polymer was isolated and purified by several precipitations into water-alcohol mixtures.

The emulsion was prepared according to the general procedure (A) described above except that there was no pH adjustment. The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains were mostly octagonal crystals with diameters ranging from 0.2 to 0.9 microns. The average diameter was 0.5 microns.

#### Example XV

Poly  $\beta$ -(dimethylamino) ethyl acrylate

A solution of 42.9 g. (0.3 mole) of dimethyl amino ethyl acrylate in 25 cc. water and 25 cc. (0.3 mole) concentrated hydrochloric acid was prepared. To this solution 0.13 gr. ammonium peroxydisulfate were added. The solution was flushed with nitrogen and heated to 70° C. for 1 hour. The reaction mixture was diluted with water and a solution of 13.2 gr. sodium hydroxide in 50 ml. water added. The solution was dialyzed overnight, precipitated into excess acetone and dried under vacuum.

The emulsion was prepared according to the general procedure (A). The emulsion obtained showed good stability and was free from undesirable clumping, aggregation or sedimentation effects. The emulsion grains constituted octagonal crystals. The grain size distribution ranged from 0.3 to 2.0 microns. The average diameter was 0.5 microns.

Example XVI (control)

This example shows the preparation of an emulsion by the general procedure (A), however, the emulsion binder employed was gelatin. The emulsion grains were octahedral crystals with diameters ranging from 0.2 to 1.8 microns. the average diameter was 1.0 microns.

The following table is illustrative of the densitometer readings made on samples of these emulsions.

| GRAIN GROWING POLYMER                                   | BODYING POLYMER | SILVER/POLYMER RATIO | MG. SILVER/FT. <sup>2</sup> | FORMAT         | D <sub>max</sub> | D <sub>min</sub> | ΔD   |
|---------------------------------------------------------|-----------------|----------------------|-----------------------------|----------------|------------------|------------------|------|
| 4.7:1 Acrylamide:β-(diethyl-amino)ethyl acrylate        | NONE            | ∞                    | 89.2                        | Polaroid T-20C | 0.74             | 0.32             | 0.42 |
| 3:1 Acrylamide:β-(dimethyl-amino) ethyl methacrylate    | NONE            | ∞                    | 161                         | Polaroid T-107 | 0.71             | 0.09             | 0.62 |
| 8:1 Acrylamide:β-(dimethyl-amino) ethyl methacrylate    | NONE            | ∞                    | 139                         | Polaroid T-42  | 0.85             | 0.15             | 0.70 |
|                                                         | PVA 72-60       | 1.36                 | 78.4                        | Polaroid T-20C | 1.21             | 0.04             | 1.17 |
| T-107                                                   | 1.60            | 0.13                 | 1.47                        | Polaroid       | 1.40             | 0.36             | 1.04 |
|                                                         | PVA 72-60       | 1.36                 | 55.0                        | Polaroid T-107 | 1.51             | 0.04             | 1.47 |
|                                                         |                 |                      |                             | Polaroid T-42  | 1.58             | 0.04             | 1.54 |
|                                                         |                 |                      |                             | Polaroid T-107 | 1.45             | 0.14             | 1.31 |
|                                                         |                 |                      |                             | Polaroid T-42  | 1.41             | 0.11             | 1.30 |
| 8.84:1 Acrylamide:β-(dimethyl-amino) ethyl methacrylate | PVA 72-60       | 1.36                 | 138.1                       | Polaroid T-107 | 1.22             | 0.19             | 1.03 |
|                                                         | PVA 72-60       | 2.04                 | 104.9                       | Polaroid T-42  | 1.25             | 0.27             | 0.98 |
| 7.16:1 Acrylamide:β-(dimethyl-amino) ethyl methacrylate | PVA 72-60       | 1.36                 | 125.5                       | Polaroid T-42  | 1.52             | 0.62             | 0.90 |
|                                                         |                 |                      |                             | Polaroid T-42  | 1.05             | 0.35             | 0.70 |

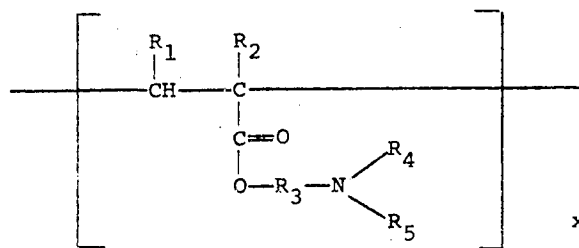
In the foregoing description, the photosensitive emulsion binder generally consisted essentially of the described water-soluble polymer. In certain photographic applications, it may be desirable to replace part, but not all, of the gelatin in the photosensitive emulsion. In view of the characteristics of these polymers described above, and further, in view of their compatability with gelatin in substantially all proportions, it will be obvious that these polymers are ideally suited for such work.

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

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

What is claimed is:

1. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises a water-soluble homopolymer having in its molecule repeating units with the general formula:



wherein:

R<sub>1</sub> is selected from the group consisting of hydrogen, lower alkyl and halogen; R<sub>2</sub> is selected from the group consisting of hydrogen, lower alkyl, halogen

and cyano; R<sub>3</sub> is selected from the group consisting of lower alkyl and lower cycloalkyl; R<sub>4</sub> and R<sub>5</sub> are each selected from the group consisting of hydrogen, lower alkyl, and lower cycloalkyl; R<sub>4</sub> and/or R<sub>5</sub> may be chemically joined with R<sub>3</sub> to form a ring structure; and x is a positive integer greater than 1.

2. The product of claim 1 wherein R<sub>4</sub> and R<sub>5</sub> are each lower alkyl.

3. The product of claim 1 wherein substantially all of said silver halide peptizer consists of said homopolymer.

4. The product of claim 1 wherein said silver halide emulsion is a silver iodobromide emulsion.

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

6. The product of claim 1 wherein said emulsion includes at least one optical sensitizing agent.

7. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises a copolymer consisting essentially of units of acrylamide and β-(dimethylamino) ethyl methacrylate.

8. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises a copolymer consisting essentially of units of acrylamide and β-(dimethylamino) ethyl acrylate.

9. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises a copolymer consisting essentially of units of acrylamide and β-(diethylamino) ethyl acrylate.

10. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises a copolymer consisting essentially of units of acrylamide and β-(diethylamino) ethyl methacrylate.

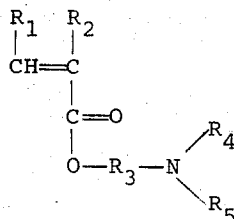
11. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises a copolymer consisting essentially of units of acrylamide and β-(tertiary butylamino) ethyl methacrylate.

12. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises poly β-(dimethylamino) ethyl acrylate.

13. A photosensitive silver halide emulsion wherein the silver halide peptizer comprises poly β-(dimethylamino) ethyl methacrylate.

14. A photographic silver halide emulsion wherein the silver halide peptizer comprises a copolymer consisting essentially of units of a first monomer of the formula:

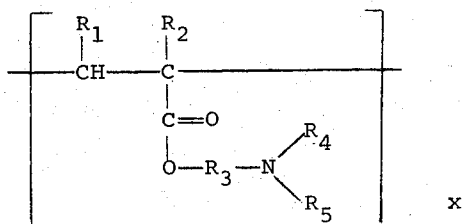
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wherein:

$R_1$  is selected from the group consisting of hydrogen, lower alkyl and halogen;  $R_2$  is selected from the group consisting of hydrogen, lower alkyl, halogen and cyano;  $R_3$  is selected from the group consisting of lower alkyl, and lower cycloalkyl; and  $R_4$  and  $R_5$  are each selected from the group consisting of hydrogen, lower alkyl and lower cycloalkyl; or  $R_4$  and/or  $R_5$  may be chemically joined with  $R_3$  to form a ring structure; and a second monomer which is an acrylamide.

15. 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 of a silver halide peptizer comprising a homopolymer having in its molecule repeating units with the general formula:



wherein:

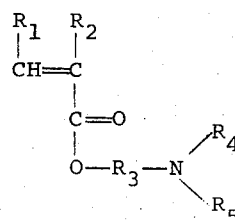
$R_1$  is selected from the group consisting of hydrogen, lower alkyl and halogen;  $R_2$  is selected from the group consisting of hydrogen, lower alkyl, halogen and cyano;  $R_3$  is selected from the group consisting of lower alkyl, and lower cycloalkyl;  $R_4$  and  $R_5$  are each selected from the group consisting of hydrogen, lower alkyl and lower cycloalkyl;  $R_3$  and/or  $R_4$  and/or  $R_5$  may be chemically joined to form a ring structure; and  $x$  is a positive integer greater than 1.

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16. The method of claim 15 wherein said peptizer is poly  $\beta$ -(dimethylamino) ethyl acrylate.

17. The method of claim 15 wherein said peptizer is poly  $\beta$ -(dimethylamino) ethyl methacrylate.

5 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 of a silver halide peptizer comprising a copolymer consisting essentially of units of a first monomer of the formula:



wherein:

$R_1$  is selected from the group consisting of hydrogen, lower alkyl and halogen;  $R_2$  is selected from the group consisting of hydrogen, lower alkyl, halogen and cyano;  $R_3$  is selected from the group consisting of lower alkyl, and lower cycloalkyl; and  $R_4$  and  $R_5$  are each selected from the group consisting of hydrogen, lower alkyl and lower cycloalkyl; or  $R_3$  and/or  $R_4$  and/or  $R_5$  may be chemically joined to form a ring structure; and a second monomer which is an acrylamide.

19. The method of claim 18 wherein said polymer is a copolymer of consisting essentially of units of acrylamide and  $\beta$ -(dimethylamino) ethyl methacrylate.

20. The method of claim 18 wherein said peptizer is a copolymer consisting essentially of units of acrylamide and  $\beta$ -(dimethylamino) ethyl acrylate.

21. The method of claim 18 wherein said peptizer is a copolymer consisting essentially of units of acrylamide and  $\beta$ -(dimethylamino) ethyl acrylate.

22. The method of claim 18 wherein said peptizer is a copolymer consisting essentially of units of acrylamide and  $\beta$ -(diethylamino) ethyl methacrylate.

23. The method of claim 18 wherein said peptizer is a copolymer consisting essentially of units of acrylamide and  $\beta$ -(tertiary butylamino) ethyl methacrylate.

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