RESEARCH DISCLOSURE

Peptizers for photographic emulsions

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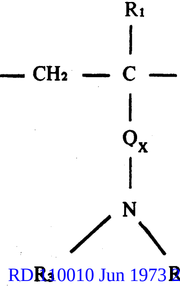
Peptizers for photographic emulsions
11010

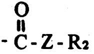
Certain polymers of tertiary amine-containing monomers and carboxylic acid monomers have been found which are excellent silver halide peptizers. Their use confers the capability of a convenient method for the coagulation, washing, and redispersion of the silver halide grains. Coagulation, washing, and redispersion of silver halide grains can be effected easily and effectively without loss of the silver halide grains by manipulating the acidity of the medium in which the silver halide grains are tested.

More specifically, these peptizers comprise polymers consisting essentially of:

A about 3 to about 35 mole percent of units of the structure


R1
CH2
C
Qx
N
R3
R4

wherein R_1 is hydrogen or a methyl radical, Q is

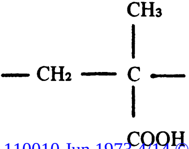


$-\overset{\overset{O}{\parallel}}{C}-Z-R_2$ - wherein Z is oxygen or =NH and R_2 is an alkylene radical of from 1 to 6 carbon atoms, x is zero or one, and R_3 and R_4 are either

(1) taken together and represent the atoms necessary to complete a 5 or 6 membered heterocyclic ring, or

(2) are independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, but only when x is equal to one;

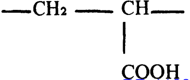
B about 30 to about 92 mole percent of units of the structure



$$-CH_2-\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}}-$$

and

C about 5 to about 65 mole percent of units of the structure

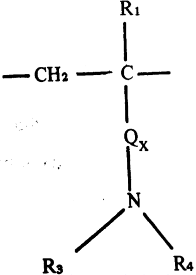


$$-\mathrm{CH_2}-\underset{\mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-$$

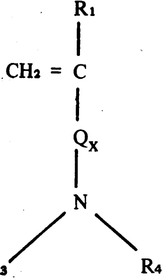
These polymers are excellent substitutes for gelatin in photographic applications, since they exhibit not only excellent salt tolerance, but also excellent photographic inertness and utility at temperatures below those at which gelatin can ordinarily be employed in the making of photographic emulsions. Further, they permit the production of silver halide grains having morphologies different from those which can be obtained with gelatin. In addition, these copolymers exhibit good compatibility with gelatin which makes it possible, if desired, to replace only a small part of the gelatin in a photographic composition, depending upon the particular combination of properties desired.

The properties which make the polymers employed in the practice of this invention suitable gelatin substitutes are very closely related to the concentration of the monomers from which the polymers are prepared. Thus, it is critical that the tertiary amine-containing units comprise from about 3 mole percent to about 35 mole percent of the polymer. Polymerized methacrylic acid units comprise from about 30 to about 92 mole percent of the polymers. The polymerized acrylic acid units which comprise the third component of the polymers are present in the range from about 5 mole percent to about 65 mole percent. Outside of the foregoing ranges for the three components, the peptization characteristics of the polymer will be significantly diminished and the advantage which they provide of allowing the use of convenient and particularly effective means of coagulation, washing and redispersion of the silver halide grains will be essentially lost.

As pointed out above, the polymers contain units having at least one tertiary amine group. These units are of the structure


R1
CH2
C
Qx
N
R3
R4

and are generally, but not necessarily, introduced into the polymer by copolymerization of the corresponding ethylenically unsaturated compound, ie


R1
CH2 = C
Qx
N
R3
R4

with acrylic acid and methacrylic acid. It would be possible of course, particularly where the tertiary amine-containing unit is an ester or an amide, to polymerize the corresponding acid, ester, or the like with the acrylic and methacrylic acids and then to form the ester or amide after polymerization, if such a procedure should be convenient and desirable in a given case.

References to various photographic silver halide emulsions, preparations, addenda, processing and systems have been published in *Product Licensing Index,* Vol 92, December, 1971, publication 9232, pages 107 - 110, Paragraphs I, III-VII and IX-XXV of this publication are applicable to the peptizers employed herein and to the emulsions, photographic elements and systems resulting from their use.

Example 1 Poly[1-vinylimidazole-co-methacrylic acid-co-acrylic acid] (Mole Ratio 1:3.5:0.5)

Polymer Preparation

A flask was charged with 56.4 g (0.60 mole) of 1-vinylimidazole, 180.6 g (2.10 moles) of methacrylic acid, 21.6 g (0.30 mole) of acrylic acid, 2.58 g of potassium persulfate, 0.86 g of sodium metabisulfite, and 1000 ml of distilled water. After purging the solution with nitrogen for 20 minutes, it was heated to 80°C with stirring for 1-1/2 hours. The system was then kept at 80°C without stirring an additional 2-1/2 hours. A small sample of the white polymer which precipitated during the course of the reaction was dried under vacuum for analysis.

Analysis Calculated for $C_{41}H_{58}N_4O_{16}$: C, 57.1; H. 6.8; N, 6.5
Found : C, 58.6; H. 7.8; N, 5.9

The inherent viscosity in 1 M NaCl (0.25 g/deciliter of solution) at 25°C was found to be 1.65.

After washing the remainder of the polymer thoroughly in distilled water, it was dissolved in water with stirring and the additition of enough dilute aqueous sodium hydroxide to bring the pH to 6.0

Silver Halide Emulsion Preparation

A silver halide emulsion was prepared in the presence of this polymer by essentially the same process described by Merrill & Perry in Example 1 of British patent 1,057,976, as follows:

A beaker was charged with a solution of 5.0 g (solids) of the above polymer, 30.37 g of potassium bromide, 0.93 g of potassium iodide and a total of 279 ml of distilled water. After adjusting the pH of the solution to 6.0, it was stirred continuously at 50°C while a solution of 35.37 g of silver nitrate in 185 ml of water was added at constant rate over 18 minutes. The smooth emulsion thus formed was then cooled to room temperature.

Emulsion Coagulation and Redispersion

A 50 ml sample of the emulsion was stirred at room temperature as the pH was lowered to about 4.3 with dilute sulfuric acid. The emulsion coagulated and settled into a compact pad at the bottom of the vessel when the stirring was stopped. After a few minutes the clear supernatant liquid was decanted and replaced with distilled water. The decanting process was convenient and effective and occurred without loss of precipitate. Upon stirring, the precipitate broke up into small discrete particles. Continuing the stirring and raising the pH back to 6.0 with dilute aqueous sodium hydroxide caused rapid reformation of a smooth dispersion which did not settle out on standing. The process of coagulation, decantation, and redispersion was repeated, and it occurred just as conveniently and effectively as the first time.

The experiment was repeated at 40°C with similar results except that the coagulation was somewhat more rapid and the precipitated pad somewhat more compact.

Example 2 Poly[1-vinylimidazole-co-methacrylic acid-co-acrylic acid] (Mole Ratio 1:2:2)

Polymer Preparation

A flask was charged with 4.7 g (0.05 mole) of 1-vinylimidazole, 8.6 g (0.10 mole) of methacrylic acid, 7.2 g (0.10 mole) of acrylic acid, 0.21 g of potassium persulfate, 0.07 g of sodium metabisulfite, and 81 ml of distilled water. After purging the solution with nitrogen for 15 minutes, it was heated at 80°C for 4 hours. A small sample of the white polymer which precipitated during the course of the reaction was dried under vacuum for analysis.

Analysis Calculated for $C_{19}H_{26}N_2O_8$: C,55.6; H, 6.4; N, 6.8
Found : C,50.9; H, 6.9; N, 4.9

The inherent viscosity of the polymer in 0.1 M NaCl (0.25 g/deciliter of solution) at 25°C was 1.64.

After washing the remainder of the polymer thoroughly in distilled water, it was dissolved in water with agitation and the addition of enough dilute aqueous sodium hydroxide to bring the pH to 6.0.

Silver Halide Emulsion Preparation

A smooth, well-dispersed silver halide emulsion was prepared in the presence of this polymer by the procedure of Example 1.

Emulsion Coagulation and Redispersion

The silver halide emulsion prepared above was tested for coagulation and redispersion by the procedure described in Example 1. This emulsion coagulated significantly more rapidly and formed a precipitated pad which was even more compact and convenient to handle than that of Example 1. Despite the compactness of the pad, it redispersed very rapidly and conveniently on change of pH.

Example 3 Poly[1-vinylimidazole-co-methacrylic acid-co-acrylic acid] (Mole Ratio 1:3:3)

Polymer Preparation

A flask was charged with 23.5 g (0.25 mole) of 1-vinylimidazole, 64.5 g (0.75 mole) of methacrylic acid, 54.0 g (0.75 mole) acrylic acid, 1.42 g of potassium persulfate, and 0.47 g of sodium metabisulfite in 568 ml of distilled water. After purging the solution with nitrogen for 15 minutes, it was heated at 80°C for 4 hours. A small sample of the white polymer which precipitated during the course of the reaction was dried under vacuum for analysis.

Analysis Calculated for $C_{29}H_{36}N_2O_{12}$: C, 57.6; H, 6.0; N, 4.6
Found : C, 53.0; H, 6.4; N, 3.9

The inherent viscosity of the polymer in 1 M NaCl (0.25 g/deciliter of solution) at 25°C was 1.05.

Silver Halide Emulsion Preparation

A smooth, well-dispersed silver halide emulsion was prepared in the presence of this polymer by the procedure of Example 1.

Emulsion Coagulation and Redispersion

The silver halide emulsion prepared above was tested for coagulation and redispersion in the manner described in Example 1. The results were essentially the same as those described in Example 1.

Example 4 Poly[2-methyl-1-vinylimidazole-co-methacrylic acid-co-acrylic acid] (Mole Ratio 1:2:2)

Polymer Preparation

A flask was charged with 108.0 g (1.0 mole) of 2-methyl-1-vinylimidazole, 172.0 g (2.0 moles) of methacrylic acid, 144.0 g (2.0 moles) of acrylic acid, 4.24 g of potassium persulfate, 1.41 g of sodium metabisulfite, and 1696 ml of distilled water. After purging the solution with nitrogen for 20 minutes, it was heated to 80°C for 5 hours. A small sample of the rubbery white polymer which precipitated during the course of the reaction was dried under vacuum for analysis.

Analysis Calculated for $C_{10}H_{14}NO_4$: C, 56.6; H 6.6; N, 6.6
Found : C, 55.8; H, 6.6; N, 6.7
Inherent Viscosity in 1 M NaCl - 1.08.

After washing the remainder of the polymer thoroughly in water, it was dissolved in distilled water with stirring and the addition of enough dilute aqueous sodium hydroxide to bring the pH to 6.0.

Silver Halide Emulsion Preparation

A smooth, well-dispersed silver halide emulsion was prepared in the presence of this polymer in the manner described in Example 1

Emulsion Coagulation and Redispersion

The silver halide emulsion prepared above was tested for coagulation and redispersion in the manner described in Example 1. The results were essentially the same as those described in Example 1.

Example 5

A high-speed silver bromoiodide (94.6) negative emulsion similar to the type of emulsion described by Trivelli and Smith (Phot J, Vol 79, 330) was prepared, using poly[1-vinylimidazole-co-methacrylic acid-co-acrylic acid] (Mole Ratio 1:2:2), prepared as described in Example 2 as the peptizer. Removal of soluble salts was accomplished by lowering the pH of the emulsion to 4.1 with dilute sulfuric acid, allowing the silver halide coagulum to settle, removing the supernatant liquid by siphoning, replacing the supernatant liquid with distilled water, redispersing the emulsion by raising the pH to 6.0 with dilute sodium hydroxide solution, and repeating the above coagulation-redispersion cycle two more times. The resulting emulsion was digested to optimum speed, dispersed in gelatin (130 g gelatin per silver mole), mixed with customarily employed adjuvants and coated on a transparent support so as to yield a silver coverage of 540 mg/ft² silver and 650 mg/ft² gelatin. Exposure (500 W, 5400°K) and development [5 minutes in 'Kodak' DK-50 developer (20°C)] yielded the following sensitometric data as compared to a similarly prepared, gelatin-peptized emulsion:

Emulsion	Relative Speed	Gamma	Net Fog Total Fog-Base & Density
Polymer-peptized	10.7	1.00	0.04
Gelatin-peptized	100	0.87	0.06

Example 6

An emulsion was prepared as described in Example 5, except that poly[1-vinylimidazole-co-methacrylic acid-co-acrylic acid] (Mole Ratio 1:3:3) was used as the peptizer. The sensitometric data obtained after exposure and processing were as follows:

*Relative speed : 11.2
Gamma : 1.25
Net Fog : 0.05

*The relative speed of a gelatin-peptized emulsion = 100.

Example 7 Silver Halide Dispersions Peptized with Poly[2-(N,N-Dimethylamino)ethyl Methacrylate-co-Methacrylic Acid-co-Acrylic Acid] (Mole Ratio 1:5:1)

A solution of 215.0 g of methacrylic acid and 36.0 g of acrylic acid in 1000 ml of water was slowly added to a solution of 78.5 g of 2-(N,N-dimethylamino)ethyl methacrylate in 2000 ml of water. The warm solution thus formed was treated with 3.3 g of potassium persulfate, 1.1 g of sodium metabisulfite, and 290 ml of water. It was then purged with nitrogen for 30 minutes and subsequently heated at 80°C with stirring for 4 hours. During that time a rubbery, sticky, white polymer gradually came out of solution in a form resembling cottage cheese. Upon cooling the aqueous supernatant was decanted and the polymer washed thoroughly with water. A small sample of the polymer was removed and dried for analysis.

Calculated for $C_{31}H_{49}NO_{14}$: 56.4% C, 7.5% H, 2.1% N
Found : 55.6% C, 7.5% H, 2.1% N

Inherent Viscosity in 0.1M NaC1: 1.45.

The rest of the polymer was dissolved in water with the addition of dilute aqueous sodium hydroxide and agitation. A clear solution resulted containing 8.9% solids and having a pH of 6.0.

A silver halide dispersion was then prepared in the presence of this polymer by essentially the same process described by Merrill and Perry in Example 1 of British patent 1,057,976, as follows:

A beaker was charged with 56.2 g of the above polymer solution, 30.37 g of potassium bromide, 0.93 g of potassium iodide, and 227 ml of water. After adjusting the pH of the solution to 6.0 it was stirred continuously at 50°C while a solution of 35.37 g of silver nitrate in 185 ml of water was added at constant rate over 20 minutes. The smooth dispersion thus formed was then cooled to room temperature.

A 50 ml sample of the dispersion was then stirred at 40°C as the pH was lowered to 4.3 with dilute sulfuric acid. The dispersion coagulated and settled into a compact pad at the bottom of the vessel when the stirring was stopped. After a few minutes the clear supernatant liquid was decanted and replaced with distilled water. The decanting process was very convenient and effective and occurred without loss of precipitate. Upon stirring the precipitate broke up into small discrete particles. Raising the pH back to 6.0 with dilute aqueous sodium hydroxide caused rapid reformation of a smooth dispersion which did not settle out on standing. The processes of coagulation, decantation, and redispersion were repeated twice more, occurring just as conveniently and effectively as the first time.

Example 8 Silver Halide Dispersions Peptized with Poly[2-(N,N-Dimethylamino)ethyl Methacrylate-co-Methacrylic Acid-co-Acrylic Acid] (Mole Ratio 1:3:1)

A polymer was prepared in the manner described in Example 7 except that it was prepared from 157.0 g of 2-(N,N-dimethylamino)ethyl methacrylate, 258.0 g of methacrylic acid and 72.0 g of acrylic acid.

Analysis Calculated for $C_{23}H_{37}NO_{10}$: 56.7% C, 7.7% H, 2.9% N
Found : 53.1% C, 7.7% H, 2.5% N
Inherent Viscosity in 0.1 M NaCl: 1.81

A sample of this polymer was used to prepare a silver halide dispersion in the same manner as that described in Example 7.

The smooth silver halide dispersion thus formed was coagulated, washed, and redispersed in the same manner as that described in Example 7. The process was very convenient and effective, and occurred without loss of silver halide grains. A similar sequence of operations was carried out on an identical sample at 25°C. Under these conditions the precipitation of the coagulated grain system is slightly slower, but is just as convenient and effective as that above and similarly occurs without loss of silver halide grains.

Example 9 Silver Halide Dispersions Peptized with Poly[2-(N,N-Dimethylamino)ethyl Methacrylate-co-Methacrylic Acid-co-Acrylic Acid (Mole Ratio 1:3.5:0.5)

A polymer was prepared in the manner described in Example 7 except that it was prepared from 157.0 g of 2-(N,N-dimethylamino) ethyl methacrylate, 301.0 g of methacrylic acid, and 36.0 g of acrylic acid.

Analysis Calculated for $C_{47}H_{76}N_2O_{20}$: 57.0% C, 7.7% H, 2.8% N.
Found : 52.7% C, 7.7% H, 3.1% N.
Inherent Viscosity in 0.1M NaCl: 1.61.

A sample of this polymer was used to prepare a silver halide dispersion in the same manner as that described in Example 7.

The smooth silver halide dispersion thus formed was coagulated, washed and redispersed in the same manner as that described in Example 7. The process was very convenient and effective, and occurred without loss of silver halide grains.

Patent applications embodying subject matter disclosed in this report may be pending in one or more countries.

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