



## Peptizers for photographic emulsions (Eastman Kodak)

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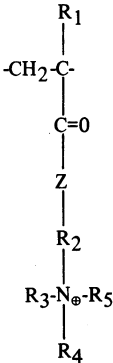
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Many attempts have been made to prepare satisfactory synthetic polymeric peptizers for silver halide emulsions. However, these materials are frequently unsatisfactory or only partially satisfactory. In certain instances, for example, when one attempts to obtain emulsions known to those skilled in the art as 'neutral emulsions' in the presence of polyacrylamide, the peptizing action of this polymer proves to be inadequate and extensive clumping of the emulsion grains occurs. Other polymers, for example poly(vinyl alcohol) or poly(vinyl pyrrolidone) provide adequate peptization but exert such potent restraint on grain growth that the emulsion grains obtained are too small for most applications.

It has now been found that certain polymers of quaternary amine-containing monomers and carboxylic acid monomers are excellent silver halide peptizers which also confer the capability of a convenient method for the coagulation, washing, and redispersion of the silver halide grains. Coagulation, washing, and redispersion can be effected easily and effectively without loss of silver halide grains by manipulating the acidity of the medium. In addition, these materials peptize effectively under both basic and neutral conditions. More specifically, these polymers are effective peptizers under the conditions generally employed for the preparation of emulsions well known in the art as ammoniacal emulsions.

More specifically, the peptizers of the present invention comprise polymers having both quaternary ammonium functionality and carboxyl functionality, said polymer consisting essentially of:

A. at least one polymerized ethylenically unsaturated compound having at least one quaternary ammonium moiety, said polymerized compound being selected from the group consisting of polymerized vinyl imidazolium compounds, polymerized vinyl pyridinium compounds and polymerized vinyl compounds which in the polymer chain have the structure:



wherein Z is oxygen or =NH,

R<sub>1</sub> is hydrogen or a methyl radical,

R<sub>2</sub> is a divalent alkylene radical of 1 to 6 carbon atoms,

R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are either

(1) independently selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(2) R<sub>3</sub> and R<sub>4</sub> taken together represent the atoms necessary to complete a 5 or 6 membered heterocyclic ring and R<sub>5</sub> is selected from the group consisting of alkyl radicals of from 1 to 8 carbon atoms, or

(3) R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> taken together represent the atoms

necessary to complete a 5 or 6 membered heterocyclic ring wherein the nitrogen atom which is attached to R<sub>2</sub> has one double bond attached thereto; and

B. at least one polymerized ethylenically unsaturated compound having at least one carboxyl radical; such that, the mole ratio in the polymeric compound of quaternary ammonium functionality to carboxyl functionality is in the range of about 1:1-15.

These novel polymers are excellent substitutes for gelatin in photographic applications, since they exhibit not only excellent salt tolerance, but they also exhibit excellent photographic inertness, utility at temperatures below which gelatin can ordinarily be employed in the making of photographic emulsions and 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 to replace only a small part of the gelatin in a photographic composition, depending upon the particular combination of properties desired.

It is significant that the properties which make the novel polymers of this invention suitable gelatin substitutes are very closely related to the concentration and nature of the monomers from which the novel polymers are prepared. Thus, it is critical that the molar ratio of quaternary ammonium functionality to carboxyl functionality be no greater than 1:1 and no less than 1:15. Outside of this range, 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 indicated above, the polymers are prepared by the polymerization of vinyl imidazolium compounds, vinyl pyridinium compounds or compounds which are the quaternary ammonium salts of alkyl amine-substituted amides or esters of acrylic acid or methacrylic acid, this polymerization being carried out in the presence of one or more polymerizable compounds having carboxyl functionality. It is not necessary that the monomers employed in the polymerization of the polymers contain the specified functional groups prior to polymerization. These groups can be added after polymerization, if desired.

Generally, the quaternary ammonium salts of this invention are prepared by reacting the corresponding tertiary amines with reagents such as alkyl p-toluenesulfonates, dialkyl sulfates, alkyl halides, propane sultone, butane sultone or the like.

The carboxylic functionality of the polymers employed in the practice of this invention can be supplied by one or more ethylenically unsaturated mono- or polycarboxylic acids.

#### Example 1

Poly[2-(methacryloyloxy)ethyltrimethylammonium Methosulfate-co-methacrylic Acid-co-acrylic Acid] (Mole Ratio 1:3.5:0.5) as a Silver Halide Peptizer

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#### Polymer preparation

A flask is charged with 198.1g (0.70 mole) of 2-(methacryloyloxy) ethyltrimethylammonium methosulfate, 210.7 g (2.45 moles) of methacrylic acid, 25.2 g (0.35 mole) of acrylic acid, 1736 ml distilled water, 4.34 g of potassium per-

sulfate and 1.45 g of sodium metabisulfite. After purging the solution with nitrogen for 20 minutes and heating to 60°C overnight, a clear, viscous dope is formed which has a pH of 2.1. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a brittle white polymer results. The inherent viscosity of the polymer is determined using a 0.25 percent solution of the polymer in 0.1 M sodium chloride at 25°C. The inherent viscosity is found to be 0.83.

The remainder of the dope is treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4. At this point the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 10.2% solids.

#### Neutral silver halide emulsion

A silver halide emulsion is prepared in the presence of this polymer in essentially the same manner as described by Merrill and Perry in Example 1 of British Patent 1,057,976:

A beaker is 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 278 ml of distilled water. After adjusting the pH of the solution to 6.0, it is stirred continuously at 50°C as a solution of 35.37 g of silver nitrate in 185 ml of water is added at constant rate over 18 minutes. The smooth dispersion thus formed is then cooled to room temperature.

A 50 ml sample of the dispersion is then stirred at room temperature as the pH is lowered to 4.4 with dilute sulfuric acid. The dispersion coagulates and settles into a compact pad at the bottom of the vessel when the stirring is stopped. After a few minutes, the clear, supernatant liquid is decanted and replaced with distilled water. The decanting process is very convenient and effective and occurs without loss of precipitate. Upon stirring, the precipitate breaks up into small discrete particles. Raising the pH back to 6.0 with dilute aqueous sodium hydroxide causes rapid reformation of a smooth dispersion which does not settle out on standing. The process of coagulation, decantation, and redispersion are repeated twice more, occurring just as conveniently and effectively as the first time.

#### Ammoniacal silver halide emulsion

An ammoniacal silver halide emulsion is also prepared in the presence of this polymer in essentially the same manner as described by Smith and Perry in Example 6 of US 3,415, 653.

A solution of 3.82 g of silver nitrate in 16 ml of water is treated with just enough ammonium hydroxide to redissolve the precipitate which forms at the beginning of the addition. The clear solution thus formed comprises 20 ml and is added to 30 ml of an aqueous solution containing 3.14 g of potassium bromide, 0.1 g of potassium iodide, and 1.0 g (solids) of the above polymer. The addition is carried out with stirring at 45°C over a period of about 85 seconds. Stirring is continued at 45°C an additional 39 minutes and then the system is cooled to room temperature. A smooth homogeneous emulsion results which fails to settle out on standing. Its pH as made is 10.1.

The ammoniacal emulsion is then tested in the same manner as the neutral emulsion above for coagulation, washing, and redispersion. It behaves similarly.

### Example 2

**Poly[2-(methacryloyloxy)ethyltrimethylammonium tosylate-co-methacrylic Acid-co-acrylic Acid] (Mole Ratio 1:3.5:0.5) as a Silver Halide Peptizer**

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#### Polymer preparation

A flask is charged with 137.2 g (0.40 mole) of 2-(methacryloyloxy)ethyltrimethylammonium tosylate, 120.4 g (1.40 moles) of methacrylic acid, 14.4 g (0.20 mole) of acrylic acid, 1088 ml of distilled water, 4.96 g of potassium persulfate, and 1.85 g of sodium metabisulfite. After purging the system with nitrogen for 20 minutes and heating to 60°C overnight, a clear, viscous dope is formed which has a pH of 2.2. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a white polymer results. The inherent viscosity as determined by the method of Example 1 is 1.06.

The remainder of the dope is treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4.5. At this point the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 9.4% solids.

### Example 3

**Poly[2-(methacryloyloxy)ethyltrimethylammonium Methosulfate-co-acrylic Acid] (Mole Ratio: 1:4) as a Silver Halide Peptizer**

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#### Polymer preparation

A flask is charged with 14.15 g (10.05 moles) of 2-(methacryloyloxy)ethyltrimethylammonium methosulfate, 14.40 g (0.20 mole) of acrylic acid, 114 ml distilled water, 0.29 g of potassium persulfate, and 0.10 g sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 60°C overnight, a clear, very viscous dope is formed. It is diluted with 172 ml of distilled water and found to have a pH of 2.2. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying, a white polymer results.

The inherent viscosity of a 0.25% solution of this polymer in 1 M sodium chloride is 1.11.

The remainder of the dope is treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4.2. At this point, the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 8.8% solids.

### Example 4

**Poly[1,2-dimethyl-5-vinylpyridinium Methosulfate-co-methacrylic Acid-co-acrylic Acid] (Mole Ratio 1:3.5:0.5) as a Silver Halide Peptizer**

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### Polymer Preparation

A flask is charged with 122.5 g (0.50 mole) of 1,2-dimethyl-5-vinylpyridinium methosulfate, 150.5 g (1.75 moles) of methacrylic acid, 18.0 g (0.25 mole) of acrylic acid, 1100 ml of distilled water, 2.91 of potassium persulfate, and 0.97 g of sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 60°C overnight, a clear, very viscous dope is formed which has a pH of 2.1. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a white polymer results. The inherent viscosity of the polymer is determined by the method of Example 1 and is found to be 1.17.

The remainder of the dope is diluted with 1700 ml of water and treated with enough dilute aqueous sodium hydroxide to raise the pH to about 4.8. At this point the polymer precipitates as a rubbery white mass. After thoroughly washing it in distilled water, the polymer is redissolved in water by stirring and the addition of enough dilute sodium hydroxide solution to bring the pH to 6.0. The resulting clear, viscous dope contains 7.5% solids.

### Example 5

Poly[1,2-dimethyl-5-vinylpyridinium Tosylate-co-methacrylic Acid-co-acrylic Acid] (Mole Ratio 1:3.5:0.5) as a Silver Halide Peptizer

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### Polymer Preparation

A flask is charged with 61.0 g (0.20 mole) of 1,2-dimethyl-5-vinylpyridinium tosylate, 60.2 g (0.70 mole) of methacrylic acid, 7.2 g (0.10 mole) of acrylic acid, 408 ml distilled water, 25 ml of ethanol, 1.27 g of potassium persulfate, and 0.42 g of sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 60°C for 8 hours, a polymer is formed which precipitates from solution. A small sample of the sticky rubbery polymer lump is washed thoroughly in water and dried under vacuum at 40°C. The inherent viscosity by the method of Example 1 is 0.40.

After washing the remainder of the polymer thoroughly in water, it is dissolved in water by stirring and the addition of enough dilute aqueous sodium hydroxide to bring the pH to 6.0. The resulting clear, viscous dope contains 10.6% solids.

### Example 6

Poly[3-methyl-1-vinylimidazolium Methosulfate-co-methacrylic Acid-co-Acrylic Acid] (Mole Ratio 1:2:2) as a Silver Halide Peptizer

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### Polymer preparation

A flask is charged with 8.8 g (0.04 mole) of 3-methyl-1-vinylimidazolium methosulfate, 6.88 g (0.08 mole) of methacrylic acid, 5.76 g (0.08 mole) of acrylic acid, 82 ml of distilled water, 0.20 g of potassium persulfate, and 0.07 g of sodium metabisulfite. After purging the solution with nitrogen for 15 minutes and heating to 80°C for 4 hours, a hazy, viscous dope forms. It is diluted with 100 ml of distilled water and is found to have a pH of 2.2. A small sample of the product is precipitated and thoroughly washed in acetone. Upon drying a sticky, rubbery polymer results.



The inherent viscosity as measured by the method of Example 3 is 0.49.

### Example 7

This example shows that the speed/fog ratio, obtainable in a high-speed negative emulsion containing gelatin-peptized grains dispersed in gelatin, can be satisfactorily matched by replacing the peptizing gelatin, used during the preparation of the emulsion, with poly[2-(methacryloyloxy)ethyltrimethylammonium methosulfate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5).

A high speed silver bromiodide (94:6) negative emulsion, similar to the type of emulsion described by Trivelli and Smith (The Photographic Journal, Vol LXXIX, May, 1939, pp 330-338) is prepared using poly[2-(methacryloyloxy)ethyltrimethylammonium methosulfate-co-methacrylic acid-co-acrylic acid] (mole ratio 1:3.5:0.5) as the peptizer. Removal of soluble salts is 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 containing 101 g potassium nitrate per silver mole, redispersing the emulsion by raising the pH to 6.4, and repeating the above coagulation-redispersion cycle two more times. The emulsion is then digested to optimum speed, dispersed in gelatin (130 g gelatin per silver mole), mixed with customarily employed in adjuvants and coated on a transparent support so as to yield a silver coverage of 540 mg/ft<sup>2</sup> silver and 650 mg/ft<sup>2</sup> gelatin. Exposure (500W, 5400°K) and development in a metol-hydroquinone developer (Kodak' DK-50 Developer) for five minutes at 20°C yielded the following sensitometric data as compared to a similarly prepared gelatin-peptized emulsion. See Table 1.

TABLE I

<u>Emulsion</u>	<u>Relative Speed</u>	<u>Gamma</u>	<u>Net Fog (Total Fog Minus Base Density)</u>
Polymer-peptized	100	1.15	0.06
Gelatin-peptized	100	0.87	0.06

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

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