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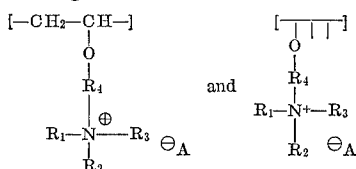
PHOTOGRAPHIC EMULSIONS

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ABSTRACT OF THE DISCLOSURE

Peptizers for silver halide dispersions in preparation of photographic emulsions are hydrophilic polymers with quaternary nitrogen atoms bonded to the polymer through ether linkages. Specific polymers of the useful class include units having formulae



wherein R_1 and R_2 are alkyl or aryl or together complete a 5 or 6 member heterocyclic ring, R_3 is alkyl, R_4 is alkylene, $\ominus \text{A}$ is acid anion, and $\text{---CH}_2\text{---CH---}$ is the repeating unit of a polysaccharide.

This invention relates to photography and more particularly to polymeric materials compatible with photographic emulsions, and methods of preparing photographic emulsions utilizing certain polymeric materials.

The initial steps in the preparation of a photographic silver halide emulsion are usually precipitation and ripening. A peptizing agent, to be effective, plays a significant role in each of these steps. Gelatin is generally used as the peptizer in commercial emulsions, but certain disadvantages are associated with its use. Gelatin is susceptible to attack by molds and bacteria. Also, as a further consequence of the natural origin of gelatin, a supply from a given source often varies in properties from time to time. Finally, the use of gelatin restricts the type of crystal irregularities obtainable by a given emulsion precipitation procedure to those types which are related to the inherent colloid-chemical nature of gelatin.

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(vinylalcohol) or poly(vinylpyrrolidone) provide adequate peptization but exert such potent restraint on grain growth that the emulsion grains obtained are too small for most applications. Various modifications of poly(vinyl alcohol) have previously been made to provide silver halide peptizers, but these derivatives have been met by only limited success.

One object of our invention is to provide new photographic emulsions of excellent stability. Another object of our invention is to provide novel silver halide dispersions of excellent stability. Still another object of our invention is to provide silver halide grains which possess photographically desirable dimensional and crystallographic properties. A further object of our invention is to provide a novel photographic element containing therein a poly-

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meric gelatin substitute. Another object of our invention is to provide a novel process for the preparation of photographic elements of high stability containing therein polymeric materials. Still another object of our invention is to provide polymeric materials which effectively peptize the silver halide formed by the double decomposition reaction from aqueous solutions of alkali halide salts and solutions of soluble silver salts, either in the presence of or absence of ammonia. Another object of our invention is to provide novel photographic emulsions which exhibit good physical development characteristics. Another object of our invention is to provide new photographic emulsions which impart a black-toning effect to silver obtained by physical development. Other objects will become obvious in the following disclosure.

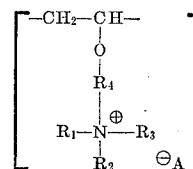
In one embodiment of our invention, light sensitive silver halide salts are peptized with a hydrophilic polymer having a plurality of quaternary nitrogen atoms chemically bonded to the polymer through ether (---O---) linkages, preferably oxyalkyl linkages such as oxymethyl. We have found that these polymers are effective silver halide peptizers which function to produce silver halide grains having photographically excellent dimensional and crystallographic properties. Silver halide grains obtained in accordance with our invention differ significantly in photographic characteristics from the silver halide grains obtained when gelatin is employed as peptizer.

Ordinarily, it is desirable to obtain crystal growth by ionic deposition to provide for a high ratio of surface to internal sensitivity in the emulsion crystals. However, for certain specific applications, a high degree of internal grain sensitivity is desirable. One such application is described in U.S. Patent No. 2,996,382 which refers to "internal image emulsions with a high degree of internal sensitivity but relatively low surface sensitivity." It is well known to those skilled in the art that a type of physical ripening known as "coalescence ripening" results in crystals of relatively high internal sensitivity. Hence, peptizers which specifically cause "coalescence ripening" are specially suited for the preparation of emulsion grains having a relatively high degree of internal sensitivity. By proper choice of the polymeric peptizers employed in our invention, it is possible to prepare various types of silver halide emulsion grains which have grown through ionic deposition as well as grains which have grown by "coalescence ripening."

In another embodiment of our invention we provide photographic silver halide emulsions containing a hydrophilic polymer having a plurality of quaternary nitrogen atoms chemically bonded to the polymer through ether linkages, preferably oxyalkyl, e.g., oxymethyl, linkages. We have found that these polymers effectively enhance physical development of silver halide emulsions in which they are incorporated, and also function as black-toning agents for the silver images.

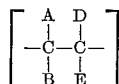
One preferred class of hydrophilic polymers employed in our invention have repeating units represented by the following general formula:

Formula 1



wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having 1 to 8 carbon atoms, such as methyl, ethyl, propyl, butyl, hexyl or octyl; an aryl group such as phenyl or naphthyl; and, R_1 and R_2 , taken together, represent the atoms, such as C, N, O or S, necessary to complete a heterocyclic ring com-

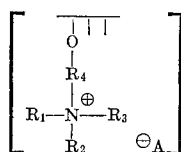
posed of 5 to 6 atoms; R_3 represents a substituent selected from the group consisting of alkyl radicals having 1 to 6 carbon atoms, such as methyl, ethyl, propyl, butyl, amyl or hexyl; R_4 represents a bivalent organic radical, e.g., an alkylene group of 1 to 5 carbon atoms, such as ethylene, propylene, butylene, pentylene and, preferably, methylene; and $\ominus A$ represents an acid anion compatible with the formation of a quaternary salt, such as p-toluene sulfonate. Preferably, the polymer is free from any substituents which might have a detrimental effect on photographic silver halide emulsions. These 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. Typical repeating units which may be present in these polymers have the following general formula:



in which two or more of A, B, D and E represent hydrogen, and the remainder, if any, each are selected from the group consisting of hydrogen; alkyl such as methyl, ethyl, propyl or butyl; aryl such as phenyl; acyl such as acetyl, propionyl, and butyryl; acyloxy such as acyloxy and propionyloxy; cyano; diacylimido; alkoxy such as methoxy, ethoxy, propoxy, and butoxy; aryloxy such as phenoxy; carbalkoxy; carbamyl; carboxy, and the like. Advantageously, the ratio of all the repeating units of the polymer to repeating units corresponding to Formula 1 above is less than 5:1, and preferably is from 4:1 to 1:1. Particularly good results have been obtained with copolymers of vinyl alcohol (which may also contain minor proportions, e.g., less than 20%, vinyl acetate) with the repeating units described in Formula 1. Preferably, these copolymers have a ratio of total repeating units to repeating units in accordance with Formula 1 of from 4:1 to 1:1.

A second preferred class of polymers employed in our invention contain repeating units having the following general formula:

Formula 2



wherein $\left[\begin{array}{c} \text{O} \\ | \\ \text{R}_4 \\ | \\ \text{R}_1-\text{N}^{\oplus}-\text{R}_3 \\ | \\ \text{R}_2 \end{array} \right]$ represents the repeating unit of a hydrophilic polysaccharide such as amylose or a far hydrolyzed cellulose ester, e.g., cellulose acetate hydrolyzed to an acetyl content of 13 to 26%; and R_1 , R_2 , R_3 , R_4 and $\ominus A$ have the same meaning given above. It is not necessary that each repeating unit of the polysaccharide contain quaternary nitrogen substituents as described in Formula 2. Further, any given repeating unit of the polysaccharide may contain more than one of the quaternary nitrogen substituents. Advantageously, in the hydrophilic polysaccharide derivatives used herein, the ratio of total repeating units to repeating units of the type described in Formula 2 is less than 5:1 and preferably is from 4:1 to 1:3. The polysaccharide derivatives employed herein are preferably free from any substituents which would exert a detrimental effect on emulsions in which they are incorporated.

The polymers employed in this invention may be prepared in any convenient manner, such as by reacting a suitable hydroxyl containing polymer with an alkoxyalkyl N,N-disubstituted amine, followed by quaternization of the amino group. The substituents on the nitrogen atom may be the same as R_1 and R_2 , defined above.

Our invention will be illustrated in the following examples. For purposes of comparison, emulsions were prepared as described in Standards I, II and III below.

STANDARD I

A "neutral" emulsion was prepared in the following manner. Twenty ml. of an aqueous solution containing 3.82 g. of silver nitrate were added over a period of 30 minutes to 30 ml. of an aqueous solution containing 3.275 g. of potassium bromide, 0.1 g. of potassium iodide and 1.0 g. of a copolymer of vinyl alcohol (87 mole percent) and vinyl acetate (13 mole percent). The reaction mixture was kept at 70° C. and stirred continuously. After complete addition of the silver nitrate, the reaction mixture was stirred continuously for an additional 30 minutes while the temperature was held at 70° C. The resulting emulsion contained a considerable number of clumps and aggregates. The grains of this emulsion were either spherical or cubical, and the average grain diameter was only 0.19 micron.

An "ammoniacal" emulsion was prepared in the following manner. Twenty ml. of an aqueous solution containing 3.82 g. of silver nitrate and an amount of ammonium hydroxide just sufficient to redissolve the precipitate formed initially on addition of ammonium hydroxide to the silver nitrate solution were added with continuous stirring over a period of 85 seconds to 30 ml. of a solution containing 3.14 g. of potassium bromide, 0.1 g. of potassium iodide and 1.0 g. of a copolymer of vinyl alcohol (87 mole percent) and vinyl acetate (13 mole percent). Stirring was continued for an additional 39-minute period. The temperature of the reaction mixture during addition and subsequent stirring was held at 45° C. The average grain diameter of the resulting emulsion, as determined 20 minutes after beginning of precipitation, was only 0.11 micron. After 40 minutes, the average grain diameter was only 0.15 micron, the mean grain area only $0.083\mu^2$, and sigma equal to $0.069\mu^2$.

STANDARD II

A "neutral" emulsion was prepared by the method described in Standard I except that the peptizer used was amylose "Nepol Q5-101," A. E. Staley Company. The emulsion obtained was completely unstable.

An "ammoniacal" emulsion was prepared as described in Standard I except that the peptizer used was amylose. The emulsion obtained was unsatisfactory due to very heavy clumping and partial sedimentation.

STANDARD III

A "neutral" emulsion was prepared as described in Standard I except that cellulose acetate was used as the peptizer. The emulsion obtained was unsatisfactory due to clumping, partial sedimentation and severe inhibition of grain growth.

An "ammoniacal" emulsion was prepared as described in Standard I except that cellulose acetate was used as the peptizer. The emulsion obtained was unsatisfactory due to very heavy clumping.

The following examples illustrate the valuable results which are obtained through practice of this invention.

Example 1.—Poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol]

(Molar ratio of the starting copoly(vinyl alcohol-vinyl acetate) to ether amine reactant 1:1.3. In the following examples, this molar ratio is indicated without any explanation.) Twenty-two grams of a copolymer of vinyl alcohol (87 mole percent) and vinyl acetate (13 mole percent) was placed in a 3-neck, one-liter flask equipped with a mechanical stirrer, a glass stopper and an 8-inch Vigreux column equipped with a take-off still head. A mixture of 87 g. of i-butoxymethylmorpholine and 500 ml. of anhydrous dioxane was added to the flask. The mixture was stirred at 150° C. (oil bath temperature) and the distillate composed of i-butyl alcohol and dioxane removed. It is important to remove the i-butyl alcohol from the reaction mixture in order to drive the equilibrium reaction to completion. The level of the reaction mixture

was maintained by the occasional addition of anhydrous dioxane. After a total of five hours' reaction time, the clear dope was cooled to 25° C. and 100 g. of methyl p-toluenesulfonate added. After 24 hours, the gel which had formed was dissolved in methanol and precipitated in ether. After drying in a vacuum desiccator, a brittle, hydroscopic polymer was obtained.

(1-A) A "neutral" emulsion was prepared with this polymer as described in Standard I. The resulting emulsion showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The emulsion consisted of tabular octahedral grains with average grain diameter equal to 0.85 micron after 40 minutes of "ripening" (hereinafter defined in terms of the time elapsed since the beginning of precipitation inasmuch as some ripening occurs immediately after some silver halide has been precipitated). The average grain diameter after 60 minutes of ripening was equal to 0.97 micron.

(1-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The resulting emulsion showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The mean grain diameter was equal to 0.50 micron after 20 minutes of ripening and 0.63 micron after 40 minutes of ripening.

Example 2.—Poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:1.3)

This polymer was prepared by a method similar to that described for Example 1 with the exception that 74 g. of ethoxymethylmorpholine was used instead of the i-butoxymethylmorpholine.

A "neutral" emulsion was prepared with this polymer as described in Standard I. After 60 minutes of ripening at 70° C., the emulsion was cooled to room temperature and coagulated by addition of 25 cc. saturated sodium sulfate solution. After separation of the coagulum from the supernatant solution by decantation, the coagulum was redispersed by addition of 19.3 ml. water and 16.4 ml. of 11 percent gelatin solution. The resulting emulsion showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with mean grain area equal to $0.764\mu^2$ and sigma equal to $0.606\mu^2$.

Example 3.—Poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:1)

This polymer was prepared by the general procedure described for Example 1 with the exception that 50 g. of methoxymethylmorpholine was used in place of the i-butoxymethylmorpholine and 77 g. of methyl p-toluene sulfonate was used for the quaternization.

(3-A) A "neutral" emulsion was prepared with this polymer as described in Standard I. After 60 minutes of ripening at 70° C., the emulsion was cooled to room temperature and coagulated by addition of 25 ml. of saturated sodium sulfate solution. After separation of the coagulum from the supernatant solution by decantation, the coagulum was redispersed by addition of 9.9 ml. of water and 16.1 ml. of an 8.4 percent solution of poly(vinyl alcohol) ("Elvanol 70-05", E. I. du Pont de Nemours and Company, low molecular weight completely hydrolyzed grade), and stirring at 40° C. The resulting emulsion showed excellent stability and was free from any undesirable clumping, aggregation or sedimentation effects. The grains of this emulsion were tabular octahedra of average grain diameter equal to 0.85 micron, mean grain area equal to $0.878\mu^2$, and sigma equal to $0.642\mu^2$.

(3-B) An "ammoniacal" emulsion was prepared as described in Standard I except that the peptizer used was

the polymer described in Example 3. After 40 minutes of ripening at 45° C., the emulsion was cooled to room temperature and the pH lowered to pH 5.8 by addition of 1 N sulfuric acid. Coagulation and redispersion were then carried out as described for the emulsion in Example 3-A. The resulting emulsion showed excellent stability and was free from any undesirable clumping, aggregation or sedimentation effects. The average grain diameter was equal to 0.52 microns, the mean grain area equal to $0.543\mu^2$ and sigma equal to $0.297\mu^2$.

Example 4.—Poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:0.69)

This polymer was prepared according to the general procedure described for Example 1 except that in this experiment 35 g. of methoxymethylmorpholine and 55 g. of methyl p-toluene sulfonate were used.

(4-A) A "neutral" emulsion was prepared with this polymer as described in Example 3. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with average grain diameter equal to 0.88 micron, mean grain area equal to $0.979\mu^2$ and sigma equal to $0.690\mu^2$.

(4-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The average grain diameter was equal to 0.52 micron after 20 minutes of ripening and 0.57 micron after 40 minutes of ripening.

Example 5.—Poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:0.46)

A copolymer of vinyl alcohol (87 mole percent) and vinyl acetate (13 mole percent) (24.6 g.) was mixed with 300 ml. anhydrous dioxane, 300 ml. anhydrous dimethylformamide and 26.2 g. of methoxymethylmorpholine. The reaction was run as described for Example 1. Sixty grams of methyl p-toluene sulfonate was used for the quaternization. The product was purified by dissolving in methanol and precipitating in ether.

(5-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with average grain diameter equal to 0.90 micron after 40 minutes of ripening and 0.96 micron after 60 minutes of ripening.

(5-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The average grain diameter was equal to 0.52 micron after 20 minutes of ripening and 0.60 micron after 40 minutes of ripening.

Example 6.—Poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:0.40)

Prepared as described for Example 1 except in this experiment 20 g. of methoxymethylmorpholine and 32 g. of methyl p-toluene sulfonate were used.

(6-A) A "neutral" emulsion was prepared with this polymer as described in Example 3. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with average grain diameter equal to 0.85 micron, mean grain area equal to $0.794\mu^2$, and sigma equal to $0.558\mu^2$.

(6-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was

free from any undesirable clumping, aggregation, or sedimentation effects. The average grain diameter was equal to 0.41 micron after 20 minutes of ripening and 0.52 micron after 40 minutes of ripening.

Example 7.—Poly[methyl(vinyloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:0.30)

Twenty-two grams of a copolymer of vinyl alcohol (87 mole percent), and vinyl acetate (13 mole percent), 15 g. of methoxy methylmorpholine and 500 ml. of anhydrous dimethylformamide were mixed at 90° under N₂. The temperature was raised to 90° (oil bath). The methanol formed was swept out by the stream of nitrogen. After five hours with stirring, the mixture was cooled to 25° C. and 21.3 g. of methyl p-toluene sulfonate were added. After two days the yellow gel was dissolved in methanol plus water, filtered, and precipitated in acetone. The product formed a dry foam in a vacuum desiccator.

A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects.

Example 8.—Poly[methyl(vinyloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:0.23)

This polymer was prepared by the general method described for Example 5. In this experiment 13 g. of methoxymethylmorpholine was used. An excess (120 g.) of methyl p-toluene sulfonate was used for the quaternization because of rapid gel formation. The final polymer was dissolved in a methanol-water mixture and precipitated in an ether-acetone mixture. An "ammoniacal" emulsion was prepared with this polymer as described in Example 1. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The emulsion consisted of predominantly two size classes: a large size class with grains typically 2 microns in diameter, and a small size class with grains typically 0.2 micron in diameter. This type of size distribution is well-known to be indicative of the fact that grain growth had occurred predominantly by a process known to those skilled in the art as "coalescence ripening." The average grain diameter was equal to 0.38 micron after 20 minutes of ripening and 0.49 micron after 40 minutes of ripening.

Example 9.—Poly[dipropylmethyl(vinyloxymethyl)ammonium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (1:1.3)

Twenty-two grams of a copolymer of vinyl alcohol (87 mole percent) and vinyl acetate (13 mole percent), 72.6 g. of methoxymethyldipropylamine and 500 ml. of anhydrous dioxane were mixed and reacted according to the method described for Example 1. The product was quaternized with 100 g. of methyl p-toluene sulfonate and isolated as in Example 1.

(9-A) A "neutral" emulsion was prepared as described in Example 3 except for the following differences: (1) The peptizer used was the polymer just described, (2) a copolymer of vinyl alcohol (87 mole percent) and vinyl acetate (13 mole percent) was used as the vehicle for the redispersed emulsion grains. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with average grain diameter equal to 0.72 micron, mean grain area equal to $0.600\mu^2$, and sigma equal to $0.394\mu^2$.

(9-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were cubic. The

average grain diameter was equal to 0.96 micron, the mean grain area equal to $1.602\mu^2$, and sigma equal to $0.833\mu^2$.

Example 10.—Morpholinomethylether methyl p-toluene sulfonate of amylose

Anhydrous amylose (16.2 g., 0.1 mole), 23.2 g. (0.18 mole) of methoxymethylmorpholine and 200 ml. of anhydrous dimethylformamide were stirred together under a stream of N₂ and at 100° for five hours. The apparatus consisted of a 3-neck flask equipped with a N₂ inlet tube, a mechanical stirrer and an 8-inch Vigreux column. During the reaction period the methanol reaction product was swept out by the N₂. After cooling the reaction mixture to 25° C., 50 g. of methyl p-toluene sulfonate was added. After 24 hours methanol was added and the yellow polymer precipitated in ether.

Analysis.—Found: N, 2.7; S, 6.4.

(10-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with average grain diameter equal to 1.0 micron after 40 minutes of ripening and 1.09 micron after 60 minutes of ripening.

(10-B) An "ammoniacal" emulsion was prepared with this polymer as described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were mostly cubic. The average grain diameter was equal to 0.56 micron after 20 minutes of ripening and 0.68 micron after 40 minutes of ripening.

Example 11.—Morpholinomethyl ether methyl p-toluene sulfate of amylose

This polymer was prepared by the method described for Example 10 except 39.3 g. (0.3 mole) of methoxymethylmorpholine and 70 g. of methyl p-toluene sulfonate were used.

Analysis.—Found: N, 3.5; S, 8.1.

(11-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were markedly deformed. Many of the grains were crescent-shaped. The average grain diameter was equal to 0.82 micron after 40 minutes of ripening and equal to 0.97 micron after 60 minutes of ripening.

(11-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were of near-spherical shape with average grain diameter equal to 0.49 micron after 20 minutes of ripening and 0.51 micron after 40 minutes of ripening.

Example 12.—Piperidinomethyl ether methyl p-toluene sulfonate of amylose

This preparation was identical with Example 10 except 25.8 g. (0.23 mole) of methoxymethylpiperidine was used in place of the corresponding morpholine derivative.

Analysis.—Found: N, 3.2; S, 7.4.

(12-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were of near-spherical shape with grain diameter equal to 0.81 micron after 40 minutes of ripening and 0.85 micron after 60 minutes of ripening.

(12-B) An "ammoniacal" emulsion was prepared with

this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were mostly cubic. The average grain diameter was equal to 0.50 micron after 20 minutes of ripening and 0.64 micron after 40 minutes of ripening.

Example 13.—Dipropylaminomethyl ether methyl p-toluene sulfonate of amylose

This preparation was similar to Example 10 except for the use of 43.5 g. (0.3 mole) of methoxymethyldipropylamine instead of the corresponding morpholine derivative.

Analysis.—Found: N, 3.1; S, 7.6.

(13-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were tabular octahedra with average grain diameter equal to 0.79 micron after 40 minutes of ripening, and 0.91 micron after 60 minutes of ripening.

(13-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were predominantly rounded-cubic. The average grain diameter was equal to 0.62 micron after 20 minutes of ripening and 0.82 micron after 40 minutes of ripening.

Example 14.—Di-n-butylaminomethyl ether methyl p-toluene sulfonate of amylose

This polymer was prepared by the method used for Example 10 with the exception that 34.6 g. (0.2 mole) of methoxymethyldi-n-butylamine was used in place of the corresponding morpholine derivative.

(14-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects.

(14-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were predominantly rounded cubes.

Example 15.—Di-n-butylaminomethyl ether methyl p-toluene sulfonate of amylose

This preparation was identical to Example 14 except for the quantity of methoxymethyldi-n-butylamine (51.9 g., 0.3 mole) and methyl p-toluene sulfonate (70 g.) used.

Analysis.—Found: N, 3.0; S, 6.8.

An "ammoniacal" emulsion was prepared with this polymer as described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were predominantly cubes with average diameter equal to 0.67 micron after 20 minutes of ripening and 0.75 micron after 40 minutes of ripening.

Example 16.—Piperidinomethyl ether methyl p-toluene sulfonate of cellulose acetate

Anhydrous water soluble cellulose acetate containing 17.6% acetyl (5.1 g.), 3.22 g. of methoxymethylpiperidine and 200 ml. of anhydrous dimethylformamide were mixed in a 300 ml., 3-neck flask equipped with a N₂ inlet tube, a Vigreux column and a mechanical stirrer. This mixture was stirred at 100° C. (oil bath temperature) and a slow stream of N₂ passed through it to sweep out the methanol reaction product. After four hours, the homogeneous

solution was cooled to 20° and 8 g. of methyl p-toluene sulfonate added. After 24 hours methanol was added, the solution filtered and poured slowly into ether. The white product was dried in vacuum.

Analysis.—Found: N, 1.9; S, 5.3.

(16-A) A "neutral" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The size distribution of the emulsion grains formed indicated that grain growth had, to a large extent, occurred by a mechanism known to those skilled in the art as "coalescence ripening." The average grain diameter was equal to 0.57 micron after 40 minutes of ripening and 0.64 micron after 60 minutes of ripening.

(16-B) An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. The grains of this emulsion were predominantly cubes with average diameter equal to 0.69 micron after 20 minutes of ripening and 0.78 micron after 40 minutes of ripening.

Example 17.—Morpholinomethyl ether methyl p-toluene sulfonate of cellulose acetate

This product was prepared as described in Example 16 except 6.6 g. of methoxymethylmorpholine was used instead of the corresponding piperidine derivative and 18 g. of methyl p-toluene sulfonate was used for the quaternization.

Analysis.—Found: N, 2.6; S, 6.5.

An "ammoniacal" emulsion was prepared with this polymer by the method described in Standard I. The emulsion obtained showed excellent stability and was free from any undesirable clumping, aggregation, or sedimentation effects. Most of the grains of this emulsion were cubic. The average grain diameter was equal to 0.71 micron after 20 minutes of ripening and 0.92 micron after 40 minutes of ripening.

It has been found that when the ratio of total repeating units in a polymer to repeating units of the type described in Formula 1 or Formula 2 is greater than about 5:1, the polymer fails to function effectively as a silver halide peptizer due to clumping, partial or total sedimentation, and restraint on the growth of the silver halide grains.

Emulsions containing the polymers of our invention demonstrate an accelerated rate of physical development over similar emulsions which do not contain such polymers. Further, the polymers employed herein have a black-toning effect on the silver obtained by physical development. Increased physical development and black-toning of silver obtained by physical development are highly desirable in various photographic elements and processes, such elements employed in diffusion transfer processes. This aspect of our invention is demonstrated in the following examples. In these examples, the polymer employed is a copolymer of vinyl alcohol, vinyl acetate and a vinyl-oxymethylamine quaternary salt. It has been found that all the other polymers of our invention, described in detail above, also function to increase physical development and as black-toning agents.

Example 18 illustrates enhanced physical development and black-toning effects in a nucleated silver halide layer which, in addition to gelatin, also contains poly[methyl-(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol]. This example demonstrates that (1) silver is formed at a faster rate if the layer contains poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] in addition to gelatin; and (2) the silver formed by physical development is black-toned.

In view of the experimental results which have been published in the scientific literature (T. H. James and W. Vanselow, *Photographic Science and Technique*, Series

II, volume 2, No. 4, pages 135-143, November 1955), it follows that if silver halide layers containing gelatin and poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] are prepared without nuclei and then subjected to a photographic process involving exposure and image development, then the ratio of physical development to chemical development would be higher than if the silver halide layer contained gelatin without any admixed polymer. Such an enhancement of physical relative to chemical development is beneficial in certain applications, for example where improvements in the acutance of the developed image are desired.

Example 18.—Initial emulsion

The following operations were all carried out under red light. An aqueous solution (20.5 ml.) containing 2.734 g. of silver nitrate and a second aqueous solution (20.5 ml.) containing 2.30 g. of potassium bromide and 0.072 g. of potassium iodide were added simultaneously with continuous stirring to 29.0 ml. of an aqueous solution containing 1.05 g. of gelatin which was kept at a temperature of 45° C. After complete addition of both solutions, stirring at this temperature was continued for an additional six minutes. The emulsion was then removed from the constant temperature bath and cooled to approximately 38° C. The pH level of the emulsion was lowered to pH 3 with 1 N sulfuric acid and a sufficient amount of saturated sodium sulfate solution added in order to coagulate the emulsion. The coagulum was then chilled and washed repeatedly with cold distilled water by decantation. The emulsion was then redispersed by warming, stirring, and addition of sufficient water and dilute sodium hydroxide to bring the emulsion weight to 24.6 g. and the pH level to pH 6. The emulsion thus obtained is hereinafter referred to as "initial emulsion."

Intermediate emulsion

To 12.3 g. "initial emulsion" there was added 0.8 ml. of water and 19.5 ml. of 9.0 percent aqueous gelatin solution. The resulting emulsion is hereinafter referred to as "intermediate emulsion."

(1) Preparation of coatings in which the only vehicle is gelatin.—A coating solution was prepared which contained 12.6 g. of the "intermediate emulsion," 1.0 ml. of a suspension of silver nuclei (containing 0.375 mg. silver nucleinate, "Silver Protein Mild," made by Mallinckrodt Chemical Works), 0.15 ml. of a 5 percent aqueous saponin solution (coating aid), and 0.55 ml. of an aqueous 0.314 percent formaldehyde solution (hardener). This emulsion was then coated on a cellulose acetate film base support and dried. The thickness of the dry coating was equal to 0.0003 inch.

(2) Preparation of coatings containing a 4:1 ratio of gelatin/poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol].—To 12.3 g. of "initial emulsion" there was added 15.6 ml. of 9 percent gelatin solution and 4.7 ml. of a 7.42 percent solution of the poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] prepared as described in Example 2. The further treatment of this emulsion, i.e., addition of nuclei etc., was carried out as described under (1) for the coating containing only gelating as the vehicle.

Strips from both coatings which had been shielded from actinic light were then developed (under red light) for different lengths of time in a developer of similar composition as the "MQ developer," described in Example 3 of U.S. Patent No. 3,068,097. After completion of the specified development period, the strips were briefly immersed in an acetic acid stop bath and then fixed in Kodak F-24 Fixer in order to remove the non-developed silver halide. After the strips had been washed in running tap water and dried, the amount of developed silver (expressed as mg. Ag/ft.²) was determined by

X-ray spectrometric analysis. Inasmuch as similarly prepared coatings from which the addition of catalytic nuclei had been omitted gave only insignificant amounts of silver when developed similarly, the formation of the developed silver is clearly associated with the catalytic nuclei present in the coatings and hence, in accordance with generally accepted scientific views, the developed silver is predominantly physically developed silver. The considerably faster rate of formation of physically developed silver in the coating containing gelatin as well as the morpholinium polymer, as compared to the coating in which gelatin is the only vehicle, is evident from the following results:

AMOUNT OF DEVELOPED SILVER FORMED, EXPRESSED AS MG. SILVER/SQUARE FOOT OF DEVELOPED COATING

Development time (seconds)	Vehicle—Gelatin (mg.)	Vehicle—4/1 mixture of gelatin/polymer of example 2 (mg.)
2.....	6.9
5.....	16.4
7.....	33
10.....	41
15.....	3.3	68
25.....	4.7	161
45.....	9.5
85.....	26
125.....	60

Furthermore, due to the toning effect of the morpholinium polymer, there was a very pronounced difference between strips from the two types of coating with regard to the tone of the developed silver. The developed silver from the coatings containing only gelatin as the vehicle had a brownish tone, while the silver from the coatings which contained the morpholinium polymer as well as gelatin was black. Also, as shown by electron microscopic studies, there were morphological differences between the silver from the two types of coatings. The developed silver in the coating containing only gelatin consisted of spherical particles of very uniform size. In the coating containing the morpholinium polymer the size distribution of the particles of developed silver was a much wider one.

Example 19

This example illustrates enhanced physical development and toning effects in a nucleated silver halide layer which, in addition to gelatin, also contained one part of poly[methyl(vinylloxymethyl)piperidinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] per 99 parts of gelatin. This polymer was prepared by the procedure described in Example 2 except 64.6 g. of methoxymethylpiperidine was used instead of the corresponding morpholine derivative.

The nucleated silver halide coatings were prepared as described in Example 18 except that the above polymer was added to the type 2 coating, and the amounts of gelatin and polymer in this coating were adjusted so as to conform to a 99/1 ratio. The coatings were processed in photographic processing solutions as described in Example 18. An estimate of the relative amount of developed silver formed after a given development time in a given strip was then obtained by determining the density at the wave length of maximum absorption (hereinafter referred to as $D_{\lambda \text{ max}}$). A plot of $D_{\lambda \text{ max}}$ versus development time for the two types of coatings then showed that the rate of formation of physically developed silver was 9.1 times faster if, in addition to gelatin, the coating had also contained the piperidinium polymer. The black toning effect exerted by this polymer was similar to the toning effect of the corresponding morpholinium polymer described in Example 18.

Example 20

This example illustrates enhanced physical development and toning effects in a nucleated silver halide layer which, in addition to gelatin, also contained one part of poly[di-n-butylmethyl(vinylloxymethyl)ammonium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] per 99 parts of gelatin. This polymer was prepared in accordance

with the procedure described in Example 3 except 86.5 g. of methoxymethyl-di-n-butylamine was used instead of the corresponding morpholine derivative.

The procedure used was the same as in Example 18 except that the above polymer was used in the type 2 coating. A plot of $D_{\lambda \max}$ versus development time for the two types of coatings then showed that the rate of formation of physically developed silver was 2.3 times faster if, in addition to gelatin, the coating had also contained the ammonium polymer. The black toning effect exerted by this latter polymer was similar to the toning effect of the morpholinium polymer described in Example 18.

Example 21

This example illustrates the increased amount of silver which can be transferred in the course of a silver halide diffusion transfer process from a silver halide layer to a nucleated receiving layer when, in addition to gelatin, poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] is also incorporated into the silver halide layer. The increased rate of solution of the silver halide grains in the silver halide layer which is brought about by the presence of this polymer then provides for a more readily available supply of silver ions which then diffuse from the silver halide layer into the receiving layer.

The preparation of the silver halide layers containing (1) gelatin only as the vehicle and (2) a 4/1 mixture of gelatin and poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol], (prepared as described in Example 1) was carried out as in Example 18 except that no nuclei were incorporated into the silver halide coatings.

Receiving layers were prepared in the following manner: To 25 ml. of 2.0 percent aqueous gelatin solution there was added 1.25 ml. of a suspension of silver nuclei containing 1.0 g. silver nucleinate/liter, 0.4 ml. of 5 percent aqueous saponin solution, and 0.5 ml. of aqueous 0.314 percent formaldehyde solution. This solution was coated on Reflection Print Support with a coating knife (clearance equal to 0.003 inch) and dried.

The amount of silver, transferred from the silver halide layer to the receiving layer during a specified contact time, was then determined in the following manner. First, the receiving layer was immersed for 20 seconds into a developer of the following composition (all quantities are expressed as g./liter):

Elon	6.25
Hydroquinone	2.5
Sodium sulfite	6.25
Sodium thiosulfate pentahydrate	7.7
Potassium bromide	1.02
Sodium carbonate monohydrate	25.0

Immediately after removal of the receiving layer from the developer solution, said receiving layer was pressed against the silver halide layer for a specified contact time. After separation of the two layers, the receiving layer was dried. The amount of silver which had transferred into this receiving layer was then determined by X-ray spectrometric analysis.

The following results show the considerably larger amounts of silver transferred into the receiving layer if the silver halide layer contains not only gelatin but also the morpholinium polymer.

MILLIGRAMS SILVER PER SQUARE FT. OF RECEIVING LAYER

Contact time (seconds)	Silver halide layer contained only gelatin as a vehicle	Silver halide layer contained a 4/1 mixture of gelatin and the polymer of Example 1 as the vehicle
20	4.1	15.5
60	10.0	

Example 22

This example illustrates the increased amount of silver which can be transferred in the course of a silver halide diffusion process from a silver halide layer to a nucleated receiving layer, if this receiving layer contains not only gelatin but also poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol]. This same example also illustrates black-toning effects which are achieved by incorporation of the polymer into the receiving layer.

The two types of receiving layers were prepared as follows: 25 ml. of coating solution containing either 5 percent gelatin, for the preparation of receiving layers containing only gelatin as the vehicle, or 4 percent gelatin and 1 percent poly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate co-vinyl acetate co-vinyl alcohol] (prepared as described in Example 1) for the preparation of receiving layers containing a 4/1 ratio of gelatin and the morpholinium polymer, 3.2 ml. of a suspension of silver nuclei (1.0 g. silver nucleinate/liter), 0.4 ml. of 5 percent aqueous saponin solution, and 0.2 ml. of 0.314 percent formaldehyde solution were coated on Reflection Print Support by means of a coating knife (clearance equal to 0.003 inch) and dried.

A strip of (unexposed) Kodak fine grain positive film was immersed for 3 seconds in the developer described in Example 21 and then pressed against the nucleated receiving layer for a specified contact time. After separation of the two layers, the receiving layer was dried. The amount of silver which had transferred into this layer was then determined by X-ray spectrometric analysis.

The following results show the considerably larger amounts of silver transferred into the receiving layer when that layer contains not only gelatin but also the morpholinium polymer.

MILLIGRAMS SILVER PER SQUARE FOOT OF RECEIVING LAYER

Contact time (seconds)	Nucleated receiving layer contained only gelatin	Nucleated receiving layer contained a 4/1 mixture of gelatin and the polymer of Example 1
20	4.6	21
60	15.8	

The black toning effects and changes in the morphology of the physically developed silver in the receiving layer containing not only gelatin but also the morpholinium polymer were similar to those obtained during physical development in a single nucleated silver halide layer, described in Example 18.

Emulsions prepared in accordance with our invention, and emulsions containing the polymers employed herein, may have incorporated therein chemical and optical sensitizers, speed increasing compounds, gelatin plasticizers and hardeners, stabilizers, coating aids and the like emulsion addenda such as described in Beavers U.S. Patent 3,039,873, col. 10 through col. 12. The emulsion may be used in various applications, such as those described in col. 12 and 13 of the above Beavers patent. The emulsions may be coated on any suitable support, such as cellulose acetate, polyester, polycarbonate, paper and polyolefin coated paper.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

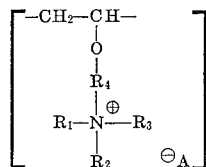
1. In the method of preparing silver halide dispersions which comprises precipitating silver halide in an aqueous solution by reacting a water-soluble silver salt with a water-soluble halide salt, the improvement which comprises incorporating in the aqueous solution, as peptizer

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for the silver halide, a hydrophilic polymer having a plurality of quaternary nitrogen atoms each chemically bonded by an ether linkage to the polymer with the oxygen of said ether linkage bonded directly to a carbon atom in the polymer chain.

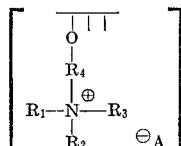
2. In the method of preparing silver halide dispersions which comprises precipitating silver halide in an aqueous solution by reacting a water-soluble silver salt with a water soluble halide salt, the improvement which comprises incorporating in the aqueous solution, as peptizer for the silver halide, a hydrophilic polymer selected from the group consisting of:

(A) polymers containing repeating units represented by the following general formula:



wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having from 1 to 8 carbon atoms, aryl radicals; and R_1 and R_2 , taken together, represent the atoms necessary to complete a heterocyclic ring composed of 5 to 6 atoms; R_3 represents an alkyl radical having from 1 to 6 carbon atoms; R_4 represents an alkylene radical having from 1 to 5 carbon atoms; and, $\ominus \text{A}$ represents an acid anion, and

(B) polysaccharides containing repeating units having the following general formula:



wherein



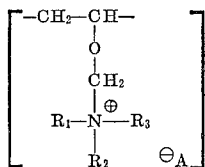
represents the repeating unit of the polysaccharide; and R_1 , R_2 , R_3 , R_4 and $\ominus \text{A}$ have the same meaning given above;

said polymers and polysaccharides having a ratio of total repeating units to repeating units having the specified general formula of less than 5:1.

3. The method of claim 2 wherein the polysaccharide is a far hydrolyzed, water-soluble cellulose acetate containing from 13 to 26% acetyl.

4. The method of claim 2 wherein the polysaccharide is amylose.

5. In the method of preparing silver halide dispersions which comprises precipitating silver halide in an aqueous solution by reacting a water-soluble silver salt with a water soluble halide salt, the improvement which comprises incorporating in the aqueous solution, as peptizer for the silver halide, a hydrophilic copolymer essentially consisting of vinyl alcohol repeating units and repeating units having the following general formula:



wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having from 1 to 8 carbon atoms; aryl radicals, and, R_1 and R_2 , taken together, represent the atoms necessary to complete a heterocyclic ring composed of 5 to 6 atoms; R_3 represents an alkyl radical having from 1 to 6 carbon atoms; 75

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and, $\ominus \text{A}$ represents an acid anion, said copolymer having a ratio of total repeating units to repeating units having the above formula of from 4:1 to 1:1.

6. In the method of preparing silver halide dispersions which comprises precipitating silver halide in an aqueous solution by reacting a water-soluble salt with a water soluble halide salt, the improvement which comprises incorporating in the aqueous solution, as peptizer for the silver halide, copoly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate-vinylalcohol-vinyl acetate] which contains less than about 20% vinyl acetate and has a ratio of total repeating units to the morpholinium sulfonate containing units of from 4:1 to 1:1.

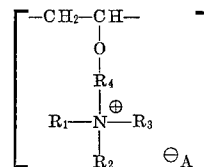
7. In the method of preparing silver halide dispersions which comprises precipitating silver halide in an aqueous solution by reacting a water-soluble silver salt with a water soluble halide salt, the improvement which comprises incorporating in the aqueous solution, as peptizer for the silver halide, an amylose derivative in which at least part of the hydroxyl groups in the repeating units have been converted to morpholinomethyl ether methyl p-toluene sulfonate groups, the ratio of total repeating units in the amylose to repeating units containing said morpholinomethylether methyl p-toluene sulfonate groups being from 4:1 to 1:3.

8. In the method of preparing silver halide dispersions which comprises precipitating silver halide in an aqueous solution by reacting a water-soluble silver salt with a water soluble halide salt, the improvement which comprises incorporating in the aqueous solution, as peptizer for the silver halide, a water-soluble, far-hydrolyzed cellulose acetate derivative in which at least part of the hydroxyl groups in the repeating units of the cellulose acetate molecule have been converted to morpholinomethyl ether methyl p-toluene sulfonate groups, said cellulose acetate containing from 13 to 26% acetyl and having a ratio of total repeating units to repeating units containing said morpholinomethyl ether methyl p-toluene sulfonate groups of from 4:1 to 1:3.

9. A dispersion of silver halide in an aqueous solution of a hydrophilic polymer having a plurality of quaternary nitrogen atoms each chemically bonded by an ether linkage to the polymer with the oxygen of said ether linkage bonded directly to a carbon atom in the polymer chain.

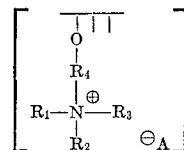
10. A dispersion of silver halide in an aqueous solution of a hydrophilic polymer selected from the group consisting of:

(A) polymers containing repeating units represented by the following general formula:



wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having from 1 to 8 carbon atoms; aryl radical, and, R_1 and R_2 , taken together, represent the atoms necessary to complete a heterocyclic ring composed of 5 to 6 atoms; R_3 represents an alkyl radical having from 1 to 6 carbon atoms; R_4 represents an alkylene radical having from 1 to 5 carbon atoms; and, $\ominus \text{A}$ represents an acid anion; and

(B) polysaccharides containing repeating units having the following general formula:



wherein $| | |$ represents the repeating unit of

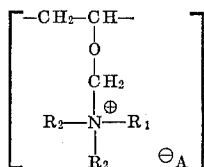
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the polysaccharide; and R_1 , R_2 , R_3 , R_4 and $\ominus A$ have the same meaning given above; said polymers and polysaccharides having a ratio of total repeating units to repeating units having the specified general formula of less than 5:1.

11. The dispersion of claim 10 wherein the polysaccharide is a far hydrolyzed, water soluble cellulose acetate containing from 13 to 26% acetyl.

12. The dispersion of claim 10 wherein the polysaccharide is amylose.

13. A dispersion of silver halide in an aqueous solution of a hydrophilic copolymer essentially consisting of vinyl alcohol repeating units and repeating units having the following general formula:



wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having from 1 to 8 carbon atoms; aryl radicals, and, R_1 and R_2 , taken together, represent the atoms necessary to complete a heterocyclic ring composed of 5 to 6 atoms; R_3 represents an alkyl radical having from 1 to 6 carbon atoms; and, $\ominus A$ represents an acid anion, said copolymer having a ratio of total repeating units to repeating units having the above formula of from 4:1 to 1:1.

14. A dispersion of silver halide in an aqueous solution of copoly[methyl(vinylloxymethyl)morpholinium p-toluene sulfonate-vinylalcohol-vinyl acetate] which contains less than about 20% vinyl acetate and has a ratio of total repeating units to the morpholinium sulfonate containing units of from 4:1 to 1:1.

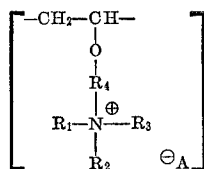
15. A dispersion of silver halide in an aqueous solution of an amylose derivative in which at least part of the hydroxyl groups in the repeater units have been converted to morpholinomethyl ether methyl p-toluene sulfonate groups, the ratio of total repeating units in the amylose to repeating units containing said morpholinomethyl ether methyl p-toluene sulfonate groups being from 4:1 to 1:3.

16. A dispersion of silver halide in an aqueous solution of a water-soluble, far-hydrolyzed cellulose acetate derivative in which at least part of the hydroxyl groups in the repeating units of the cellulose acetate molecule have been converted to morpholinomethyl ether methyl p-toluene sulfonate groups, said cellulose acetate containing from 13 to 26% acetyl and having a ratio of total repeating units to repeating units containing said morpholinomethyl ether methyl p-toluene sulfonate groups of from 4:1 to 1:3.

17. A photographic silver halide emulsion having incorporated therein, in an amount sufficient to effectively enhance physical development of the silver halide, a hydrophilic polymer having a plurality of quaternary nitrogen atoms each chemically bonded by an ether linkage to the polymer with the oxygen of said ether linkage bonded directly to a carbon atom in the polymer chain.

18. A photographic silver halide emulsion having incorporated therein, in an amount sufficient to effectively enhance physical development of the silver halide, a hydrophilic polymer selected from the group consisting of:

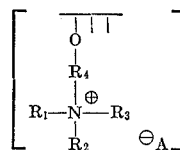
(A) polymers containing repeating units represented by the following general formula:



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wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having from 1 to 8 carbon atoms; aryl radicals, and, R_1 and R_2 , taken together, represent the atoms necessary to complete a heterocyclic ring composed of 5 to 6 atoms; R_3 represents an alkyl radical having from 1 to 6 carbon atoms; R_4 represents an alkylene radical having from 1 to 5 carbon atoms; and, $\ominus A$ represents an acid anion; and

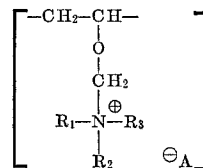
(B) polysaccharide containing repeating units having the following general formula:



wherein $\left[\begin{array}{c} | \\ | \\ O \\ | \\ R_4 \\ | \\ R_1-N^+-R_3 \\ | \\ R_2 \end{array} \right]$ represents the repeating unit of the polysaccharide; and R_1 , R_2 , R_3 , R_4 and $\ominus A$ have the same meaning given above;

said polymers and polysaccharides having a ratio of total repeating units to repeating units having the specified general formula of less than 5:1.

19. A photographic silver halide emulsion having incorporated therein, in an amount sufficient to effectively enhance physical development of the silver halide, a hydrophilic copolymer essentially consisting of vinyl alcohol repeating units and repeating units having the following general formula:



wherein R_1 and R_2 each represent a substituent selected from the group consisting of alkyl radicals having from 1 to 8 carbon atoms; aryl radicals, and, R_1 and R_2 , taken together, represent the atoms necessary to complete a heterocyclic ring composed of 5 to 6 atoms; R_3 represents an alkyl radical having from 1 to 6 carbon atoms; and, $\ominus A$ represents an acid anion, said copolymer having a ratio of total repeating units to repeating units having the above formula of from 4:1 to 1:1.

20. A reception element adapted for use in a silver halide diffusion transfer process comprising a support having coated thereon, in an amount sufficient to effectively enhance the amount of silver deposited on the support, a hydrophilic polymer having a plurality of quaternary nitrogen atoms each chemically bonded by an ether linkage to the polymer with the oxygen of said ether linkage bonded directly to a carbon atom in the polymer chain.

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U.S. Cl. X.R.

96—114; 117—161

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,425,836

February 4, 1969

Ernest J. Perry et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 26, "allkyl" should read -- alkyl --. Column 2, line 7, "alkalid" should read -- alkali --; lines 14 and 15, "obbious" should read -- obvious --. Column 3, line 13, "campatible" should read -- compatible --; line 26, "actyloxy" should read -- acetyloxy --; lines 43 to 49, to the left of the formula, "Eornula 2" should read -- Formula 2 --. Column 5, line 68, "stabilty" should read -- stability --. Column 6, line 22, "undesrable" should read -- undesirable --. Column 10, line 1, "20^o" should read -- 25^o --; line 13, "coalescene" should read -- coalescence --; line 22, "mircon" should read -- micron --. Column 12, line 63, "fater" should read -- faster --. Column 16, line 59, "radical" should read -- radicals --. Column 17, line 53, "either" should read -- ether --. Column 18, line 10, "polysaccharide" should read -- polysaccharides --; line 51, "R," should read -- R₃ --.

Signed and sealed this 24th day of March 1970.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patent