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PREPARATION OF SILVER HALIDE DISPERSIONS AND PHOTOGRAPHIC EMULSIONS USING POLYACRYLAMIDE PEPTIZERS

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This invention relates to peptizers for use in the preparation of silver halide dispersions adapted for the preparation of photographic emulsions, particularly those using polyvinyl alcohol as the vehicle.

In the making of gelatin emulsions the silver halide is formed in a gelatin solution, and this dispersion is then mixed with further gelatin to form the photographic emulsion. In the making of non-gelatin photographic emulsions, it is ordinarily desirable to first prepare a dispersion of the silver halide in a solution which has peptizing properties and which is compatible with the material which is to be employed as the carrier for the silver halide in the emulsion. Polyvinyl alcohol which is useful as a carrier for silver halide in photographic emulsions is not a satisfactory peptizer for the preparation of high-speed emulsions and, therefore, other peptizing agents are frequently desirable for the silver halide preparation instead. A number of colloids have been suggested as useful in promoting the dispersion of the silver halide upon its preparation, such as starch acetate, diethanolamine cellulose acetate, hydrolyzed gelatin and the like.

One object of our invention is to provide a method of forming silver halide dispersions which are especially useful for preparing photographic emulsions. Another object of our invention is to provide polyacrylamides which are especially useful for this purpose. Other objects of our invention will appear herein.

We have found that polyacrylamides which are water soluble are eminently suitable for use as the dispersing or peptizing material in the preparation of silver halide dispersions for use in the preparation of silver halide photographic emulsions. These polymers may be prepared by dissolving the acrylamide in water or water-alcohol so as to form a fairly dilute solution. The method of preparing these peptizing agents is described and claimed in application Serial No. 685,378 of Minsk, Kenyon, and Van Campen filed of even date, now U. S. Patent No. 2,486,191. These water-soluble polyacrylamides contain 15–20% of combined acrylimide and usually less than 1% of combined acrylic acid. These contents, however, vary to some extent in accordance with the change in details of the method which is employed in their preparation. The useful range

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of specific viscosity of these polymeric compounds is 0.09–0.225. This viscosity is determined by dissolving $\frac{1}{10}$ of a gram of the polyacrylamide in water to form 100 cc. of solution. The relative viscosity of the polymeric compound is that of the solution divided by that of a like amount of solvent without any polymers in solution therein. The specific viscosity is determined by subtracting one from the relative viscosity determined. We have also found that these polyacrylamides may first be imidized and then exhibit properties which are very useful for the purpose specified. For instance, by treating the polyacrylamide with aqueous mineral acid, such as dilute hydrobromic acid imidization of the compound occurs and the resulting compound is especially useful for peptizing purposes. We have found that not only is this compound useful for peptizing purposes, but also that is is compatible with polyvinyl alcohol and, therefore, may be mixed directly therewith in the forming of emulsions. The imidization of polyacrylamides is described and claimed in application Serial No. 685,376 of Minsk and Kenyon filed of even date, now U. S. Patent No. 2,486,190. We have found that imidized polyacrylamides can be prepared either by the acid treatment of the simple polyacrylamides or by the reaction of acetone-soluble polyacrylyl chloride with concentrated ammonia (or liquid NH_3). We have found that the imidized polyacrylamides which are useful as peptizers in accordance with our invention are found within the following ranges: combined acrylimide, 30–60%; combined acrylic acid, 4–12%; the remainder being combined acrylamide; specific viscosity .25–1.50 as determined by dissolving $\frac{1}{10}$ of a gram of the imidized polyacrylamide in water containing .25% ammonia to form 100 cc. of solution, and minimum solubility temperature, 5–100° C. The imidized polyacrylamides which are preferred for use as peptizers are those having a specific viscosity of .3 to .6%, a combined acrylimide content of 30–50%, a combined acrylic acid content of 6.5–10%, the remainder being combined acrylamide and a minimum solution temperature of 30–60° C. These water-soluble polyacrylamides each are characterized by a temperature below which its solution in water precipitates polyacrylamide. Therefore, to get solubility, some of these compounds must be dis-

solved in water at an elevated temperature. In practice, however, these compounds are employed initially for peptizing in the form of their sodium or ammonium salts and in this way they retain solubility at ordinary temperatures. We have found that these imidized polyacrylamides are especially useful as peptizing agents in that excess potassium bromide does not adversely affect the peptizing characteristics thereof as distinguished from many other colloids which may be used for peptizing, such as, for example polyvinyl alcohol in which the potassium bromide must be curtailed by adding only as needed during the formation of the silver halide, rather than in one addition. These polyacrylamides may be employed as dispersing agents in various dilutions, the usual dilution used being 1–2%. In cases, however, where fine-grained emulsions are desired, it is desirable to use a greater concentration of the polyacrylamide than in the case of emulsions in which the grains of silver halide need not be so fine.

In its broadest aspects our invention comprises the mixing together of the water-soluble silver salt and halide solutions in a dilute solution of the polyacrylamide, preferably by introducing streams of each of the reactants into the polyacrylamide solution while agitating that solution. The temperature may be elevated or not, as desired. The imidized polyacrylamides are used ordinarily in the form of the sodium or ammonium salt and, therefore, retain solubility in the water throughout the course of the reaction. A dispersion is thereby formed. The dispersion may be then thoroughly mixed with a protective colloid, such as polyvinyl alcohol, so as to form a silver halide emulsion or it may first be converted to the acid form, chilled to coagulate, washed, and then mixed with the protective colloid. Other materials, such as sensitizers, may also be incorporated. We have found that the imidized polyacrylamides not only maintain their peptizing action in the presence of an excess of potassium bromide, but also these peptizers permit Ostwald ripening and sulfur-sensitizing to proceed readily so that emulsions of relatively high photographic speed can be obtained in contrast to the characteristics of many other materials which have been found to be useful as peptizers. These polyacrylamides in the form of their sodium or ammonium salts are soluble in water as a 2½% solution at all temperatures, and, therefore, at concentrations on that order are generally useful for peptizing silver-halide preparations. The following examples illustrate the use of polyacrylamides as peptizers in the preparation of silver-halide emulsions in accordance with our invention:

Example 1.—5 grams of polyacrylamide as described herein were dissolved in 200 cc. of distilled water and the solution was adjusted to a pH of 5.5 at a temperature of 110° F. Into this solution the two following solutions, A and B, were allowed to run in fine streams, solution B being allowed to start flowing 10 seconds ahead of solution A.

A. 40 cc. of a solution of silver nitrate in water containing 20 grams of dissolved silver nitrate.

B. 15.2 grams of potassium bromide and 0.50 gram of potassium iodide dissolved in water and made up to a volume of 40 cc.

These solutions were at 80° F. and the time of the run in each case was 5 minutes. To the silver halide dispersion prepared in this way 300 cc. of a 10% solution of high viscosity polyvinyl alcohol were added with good stirring. Acetic acid was added to impart a pH of 3.5 and the emulsion was heated to 140° F. 2 grams of alpha-naphthol dissolved in 15 cc. of ethanol were stirred into the heated emulsion, and the emulsion was cooled and allowed to stand over night at 40° F. A firm gel was obtained thereby, and this gel was shredded, washed in running water until substantially free of soluble salts and melted at 140° F. It showed a pH of 5.2. The noodles were then melted. 2 grams of alpha-naphthol in 15 cc. of ethanol were added and the emulsion was coated onto glass plates. After setting by chilling and drying, it was found that these plates could be exposed and processed in normal photographic developers and fixing baths to give photographic images of good quality. It was also found that such an emulsion could be optically sensitized with the usual cyanine type of optical sensitizer and could be sulfur sensitized to improve speed and contrast by use of the types of sulfur sensitizers suitable for use in gelatin emulsions. After washing, as described, the emulsion can, if desired, be treated with boric acid and set by ammonia fuming as described and claimed in U. S. Patent No. 2,376,371, without further addition of alpha-naphthol, or it can be coated on paper without further addition of any gelling agent and after drying is suitable for the preparation of photographic prints. If desired, hardeners of the melamine-formaldehyde or urea-formaldehyde-polyvinyl alcohol type as described in U. S. Patent No. 2,367,511 and application Serial No. 497,391, now abandoned, can be added, if desired, to give papers of high melting point.

Example 2.—4 grams of a water-soluble polyacrylamide as described herein were dissolved in 200 cc. of distilled water, and the solution was adjusted to a temperature of 110° F. Into this solution solutions A and B were allowed to run in fine streams, solution B being allowed to start flowing 10 seconds ahead of solution A.

A. 40 cc. of a solution of silver nitrate in water containing 20 grams of dissolved silver nitrate.

B. 13.6 grams of potassium bromide, 0.5 gram of potassium chloride and 0.5 gram of potassium iodide dissolved in water and made up to a volume of 40 cc.

These solutions were at 80° F. and the time of the run in each case was 5 minutes. To the resulting dispersion was added 270 grams of a 11.5% solution of medium viscosity polyvinyl alcohol accompanied by good stirring. 8 milligrams of the sensitizing dye 2 3'-diethyl-4'-methyloxathiazolocarbocyanine iodide were added and 4% of melamine-formaldehyde hardener. The pH of the emulsion was adjusted to 4.1 by the addition of acetic acid. Water was added to dilute the mass and the emulsion was coated on photographic paper stock. After drying the paper was exposed, processed, washed, and dried. It showed good photographic quality, no fog, and medium contrast.

Example 3.—3 grams of an imidized polyacrylamide, such as prepared by treating polyacrylamide in aqueous alcohol solution with hydrobromic acid and having a combined acrylic imide content of 41.7%, a combined acrylic acid content of 7.91%, a combined acrylamide content of 50.4%, and a nitrogen content of 14.59% were dissolved in 200 cc. of distilled water. The solution was then adjusted to a pH of 7 with ammonia

and to a temperature of 110° F. Into this solution solutions A and B were allowed to run in fine streams, solution B being allowed to start flowing 10 seconds ahead of A. Solutions A and B are as follows:

A. 40 cc. of a solution of silver nitrate in water containing 20 grams of dissolved silver nitrate.
B. 15.2 grams of potassium bromide and 0.5 gram of potassium iodide dissolved in water and made up to a volume of 40 cc.

These solutions were at 80° F. and the run time in each case was 4 minutes. To the dispersion thus prepared 270 cc. of a 12% solution of medium viscosity polyvinyl alcohol were added with good stirring, 8 milligrams of the sensitizing dye 2,3'-diethyl-4'-methyloxathiazolocarbocyanine were added. The emulsion was diluted to the desired viscosity with water and coated on paper. After drying, the paper was exposed, developed, fixed, and dried to give a print of good photographic quality.

Example 4.—3 grams of polyacrylamide of the same type as employed in the preceding example were dissolved in 200 cc. of distilled water. The solution was adjusted to a pH of 7 with ammonia and to a temperature of 110° F. The two following solutions, A and B, were allowed to run into this solution in fine streams, the solution B being allowed to start flowing 10 seconds ahead of A.

A. 40 cc. of a solution of silver nitrate in water containing 20 grams of dissolved silver nitrate.
B. 15.2 grams of potassium bromide and 0.5 gram of potassium iodide dissolved in water and made up to a volume of 40 cc.

These solutions were at 80° F. and the run time in each case was 4 minutes. To the dispersion of silver halide so prepared, 300 cc. of a 14.7% solution of high viscosity polyvinyl alcohol were added with good stirring. The emulsion was heated to 140° F. and 2 grams of alpha-naphthol in 20 cc. of ethanol were stirred in. The emulsion was then cooled and allowed to stand over night at 40° F. A firm gel was obtained, which gel was shredded, washed in running water until substantially free of soluble salts, and melted at 140° F. The pH was adjusted to 4.5 by the addition of acetic acid. 8 milligrams of the sensitizing dye 2,3'-diethyl-4'-methyloxathiazolocarbocyanine were added, and the emulsion was coated onto paper and onto plates. On exposing this paper and these plates and processing, the resulting product showed good quality, low fog, and convenient speed for contact printing paper.

Example 5.—13½ grams of imidized polyacrylamide containing 37.6% of combined acrylimide, 54.4% of combined acrylamide, 8.04% of acrylic acid and 14.9% of nitrogen and having an M. S. T. of 42° C. were dissolved in 1125 cc. of water. 74.5 grams of potassium bromide and 1.1 grams of potassium iodide were added. After solution of all of the solid material has taken place, the pH was adjusted to 6, and the temperature was raised to 135° F. A solution of 97 grams of silver nitrate and 1125 cc. of water was run into this solution over a period of 2 minutes with rapid stirring. The emulsion was held at 135° F. for 15 minutes with stirring, and cooled to 104° F. The pH was adjusted to 6. To this emulsion 1670 cc. of a 12% solution of medium viscosity polyvinyl alcohol was added. 500 cc. of water were added to reduce the viscosity and 40 milligrams of the sensitizing dye 2,3'-diethyl-4'-methyloxathiazolocarbocyanine were also incorporated. This emulsion was coated on paper. It showed good quality, was free of fog, and had sufficient speed for use as enlarging paper.

Some imidized polyacrylamides which have been found to be useful for peptizing in accordance with our invention are the following:

Nitrogen	Amide	Imide	Acrylic Acid	M.S.T.
				°C.
14.47	48.5	43.0	8.50	47
14.19	44.1	49.0	6.9	45
13.51	39.7	47.7	11.13	83
14.59	51.4	41.5	8.88	56
14.90	54.4	37.6	8.04	42
15.58	61.7	32.3	6.96	9
15.97	62.7	30.4	6.90	29
14.59	50.4	41.7	7.91	35
15.63	58.3	36.9	4.85	5
14.94	54.9	36.8	8.32	49
13.84	43.0	48.2	8.78	59
13.77	41.3	50.2	8.49	55

It is to be understood that the preparations described in this specification are primarily for photographic purposes and, therefore, the processes are designed to be carried out under darkened conditions so that the silver halide which is prepared will not be exposed to light until used photographically, such as after haxing been coated onto paper or film.

We claim:

1. In a method of preparing silver-halide photographic emulsions in which a dispersion of the silver halide is prepared and the dispersion is then mixed with a carrier for the silver halide to form the emulsion, the step which comprises mixing together a water-soluble silver salt and a water-soluble halide in a dilute aqueous solution of a water-soluble polymer selected from the group consisting of the simple polyacrylamides having a combined acrylimide content of 15–20% and a specific viscosity of 0.09–0.225 and the imidized polyacrylamides having a combined acrylimide content of 30–60%, a combined acrylic acid content of 4–12% and a specific viscosity of .25–1.5.

2. In a method of preparing silver-halide photographic emulsions in which the silver halide is prepared in dispersion form and then mixed with a carrier for the silver halide to form the photographic emulsion, the step which comprises forming the silver-halide dispersion by mixing together a water-soluble silver salt and a water-soluble halide in a dilute aqueous solution of a simple polyacrylamide having a combined acrylimide content of 15–20% and a specific viscosity of 0.09–0.225.

3. In a method of preparing silver-halide photographic emulsions in which the silver halide is prepared in dispersion form and then mixed with a carrier for the silver halide to form the photographic emulsion, the step which comprises mixing together a water-soluble silver salt and a water-soluble halide in a dilute aqueous solution of an imidized polyacrylamide having a combined acrylimide content of 30–60%, a combined acrylic acid content of 4–12% and a specific viscosity of .25–1.5.

4. A method of forming a polyvinyl alcohol-silver halide emulsion which comprises mixing together a water-soluble silver salt and a water-soluble halide in a dilute aqueous solution of a water-soluble polymer selected from the group consisting of the simple polyacrylamides having a combined acrylimide content of 15–20% and a specific viscosity of 0.09–0.225 and the imidized

polyacrylamides having a combined acrylimide content of 30–60%, a combined acrylic acid content of 4–12% and a specific viscosity of .25–1.5 thereby forming a dispersion of the silver halide, followed by adding thereto polyvinyl alcohol as the protective colloid for the dispersed silver halide.

5. A method of forming a dispersion of silver halide adapted to the preparation of photographic emulsions which comprises mixing together a water-soluble silver salt and a water-soluble halide in a dilute aqueous solution of a water-soluble polymer selected from the group consisting of the simple polyacrylamides having a combined acrylimide content of 15–20% and a specific viscosity of 0.09–0.225 and the imidized polyacrylamides having a combined acrylimide content of 30–60%, a combined acrylic acid content of 4–12% and a specific viscosity of .25–1.5.

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