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PHOTOGRAPHIC SILVER HALIDE EMULSION

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This invention relates to photographic silver halide emulsions in which a polyvinyl propionaldehyde acetal or a polyvinyl butyraldehyde acetal is employed as the protective colloid for the silver halide therein.

Gelatin has ordinarily been employed as the protective colloid for the light-sensitive silver halides in photographic emulsions due to its ability to hold these salts in suspension, its good water permeability, its insolubility in photographic developing solutions at ordinary temperatures and its ability to form a thin coating of the light-sensitive silver halide emulsion upon a film support. Various other materials have been suggested for use as the protective colloids in photographic emulsions but in most instances the suggested materials have evidenced inferiority in one or more of the properties enumerated compared with gelatin. For instance, cellulose esters, such as cellulose nitrate, have been suggested as carriers for silver salts in photographic emulsions. The emulsion formed, however, when dry, is none too permeable to developing solution and, therefore, cellulose nitrate has not been successful with the conventional developing and fixing baths. Another disadvantage of cellulose nitrate is its insolubility in solvent mixtures containing appreciable amounts of water. This prevents the use of the water-soluble salts which are now ordinarily employed in forming light-sensitive photographic emulsions.

Various colloidal materials have been mentioned in this connection. However, many of those suggested are deficient for some reason or another, such as lack of good water permeability, inability to hold silver halide in suspension or inability to form a hard emulsion layer when coated upon a support and dried.

Gelatin, as a protective colloid for photographic silver halide emulsions, leaves much to be desired. Gelatin is susceptible to attack by organisms. For instance, under conditions of high humidity and ordinary temperatures, molds and bacteria may attack gelatin. In the tropics, gelatin is also susceptible to attack by insects. Gelatin, because of its natural source, often varies in properties from time to time and to obtain it in a highly refined condition, such as is desirable for photographic purposes, requires considerable care.

One object of my invention is to provide carriers or protective colloids for light-sensitive silver halides which can be employed instead of gelatin for photographic emulsions. Another object of my invention is to provide a carrier for silver halide in photographic emulsions that combines sufficient permeability for processing with sufficient hardness to withstand the mechanical action in the processing baths. A further object of my invention is to provide a synthesized rather than a natural product for use as the protective colloid in photographic emulsions. Other objects will appear from a further perusal of this specification.

In its broader aspects, my invention comprises the use of polyvinyl propionaldehyde acetals of approximately 45–60% vinyl alcohol content and polyvinyl butyraldehyde acetals of approximately 60–80% vinyl alcohol content for the making of photographic silver halide emulsions in place of gelatin. The acetals listed exhibit the best permeability in the higher parts of the vinyl alcohol content ranges given. For instance if an ordinary photographic fixing bath is used the propionaldehyde acetals of 50–60% and the butyraldehyde acetals of 70–80% vinyl alcohol content are preferred. These acetals are particularly suitable for emulsions for making photographic paper. For acetals in the lower part of the vinyl alcohol content range it is preferred that a fixing bath be used having good penetrating ability such as could be prepared by the adding of potassium cyanide to the fixing bath.

The following examples illustrate the preparation of acetal resins useful in preparing emulsions in accordance with my invention:

Example A

To 127 parts of polyvinyl alcohol, molecular weight 19,800, dissolved in 1500 parts of water, 103 parts of concentrated hydrochloric acid was added. 18 parts of butyraldehyde was slowly added accompanied by vigorous stirring. After a short time a gummy resin precipitated. The resin was separated from the liquid and washed in water at 60° C. The vinyl alcohol content of the resin was 75.2%, the remainder of the resin being substantially polyvinyl acetal.

Example B

A solution of 100 parts of polyvinyl alcohol in 2000 parts of water was mixed with 50 parts of concentrated hydrochloric acid and 25 parts of propionaldehyde. The resin formed was separated from the liquid and was washed in water at 60° C. until free of acid. The vinyl alcohol content of the resin was 54.5%.

The vinyl alcohol contents of the resins for use in my invention may be varied by varying the proportion of propionaldehyde or butyralde-

hyde employed in making them. Polyvinyl propionaldehyde acetals and polyvinyl butyraldehyde acetals having the vinyl alcohol content described, have the ability to hold silver halide in suspension and the emulsions prepared therewith may be easily coated out upon a support, such as paper, upon which it readily sets and dries to a hard, scratch-resistant emulsion layer. This emulsion layer may be treated with developing and fixing baths and subsequently washed thoroughly with water without dissolving.

The propionals or butals, which are useful in my invention, are those in which the propionaldehyde and butyraldehyde content of the acetal comprises substantially all of the aldehyde content thereof. It is preferred that there be no other aldehyde present and at the most no more than 10% of the aldehyde content be other than propionaldehyde and butaldehyde. The acetals, which may be employed in my invention, may be prepared by reacting propionaldehyde or butyraldehyde or their mixture with polyvinyl alcohol or they may be prepared by the hydrolysis of substantially all of the acetyl from polyvinyl acetate and reaction of part of the so-formed hydroxyl groups with propionaldehyde, butyraldehyde or their mixture. With propionaldehyde or butyraldehyde acetals having a hydroxyl content above the range specified herein, the emulsions are either undesirably soft or even soluble in the photographic processing baths which are necessary in processing the emulsion. I have found that the acetals within the range specified have a permeability and hardness which makes those materials very desirable for use as a protective carrier of photographic emulsions.

The photographic emulsions of my invention may be prepared by a process involving first dispersing silver halide in a polyvinyl propionaldehyde or butyraldehyde acetal resin as described, such as by running aqueous solutions of silver nitrate and an alkali metal halide with stirring into a solution of the resin. As the resin is not soluble in water alone, some organic solvent such as ethyl alcohol, acetone, methyl or ethyl cellosolve, or the like, must also be present. Preferably after warming to cause better dispersion and increase the speed, the mass is cooled and sensitized with a very small amount of a sensitizing dye whereupon the emulsion is ready to coat out upon a support such as paper. After drying the emulsion layer thereon, such as by a current of warm air, it may be exposed, processed, washed and dried in the usual manner and prints of good appearance result.

Instead of dispersing the silver halide directly into an aqueous solution of the resin, it is often times desirable to disperse the silver halide in some silver halide dispersing agent and subsequently mix the silver halide dispersion with an aqueous solution of the resin. I have found that the use of a silver halide dispersing agent in preparing the silver halide is particularly desirable where an increase in the sensitiveness of the emulsion is desirable. The emulsions prepared using a silver halide dispersing agent show greater contast and sensitivity to light and more speed in developing and fixing than where the silver halide is dispersed in an aqueous solution of the resin alone rather than in the solution of a material which has particularly good dispersing action on the silver halide.

My invention involves the preparation of photographic silver halide emulsions adapted to be coated on paper or upon a transparent base, such as cellulose ester film base, or glass plates to form what is normally known in the art as photographic film or photographic plates. The silver halide portion of the emulsion is ordinarily prepared by reacting together a water solution of silver nitrate and an aqueous solution of an alkali metal bromide, chloride or iodide or a mixture of any of these. The precipitation is carried out under agitated conditions so that the particle size of the precipitate is minute. Some of the silver halide dispersing agents which may be employed, if their use is desired, are some of the water-soluble synthetic resins, such as the co-polymer of maleic anhydride and vinyl acetate or its derivatives, water-soluble natural resins, such as gum arabic or carbohydrate derivatives, such as water-soluble starch acetate or ethanolamine cellulose acetate. The co-polymer of maleic anhydride and vinyl acetate and its derivatives may be prepared in accordance with the process described in U. S. Patent No. 2,047,398 of I. G. Water-soluble starch acetate is a commercial material and may be obtained from the Niacet Chemical Company or under the trade name "Accotte" from the Doe and Ingalls Company. The ethanolamine cellulose acetate may be prepared by reacting cellulose acetate, which has been hydrolyzed to a low acetyl content such as 22%, with p-toluene sulfonyl chloride and pyridine to form a cellulose acetate-p-toluene sulfonate which is then reacted with an ethanolamine. These compounds and their preparation are the invention of Kenyon and Reynolds and are described and claimed in their application Serial No. 349,222 filed of even date.

The photographic silver halide emulsions of my invention may be sensitized in the same manner as are silver halide emulsions generally. This is ordinarily accomplished with my emulsions by thoroughly incorporating a small amount of sensitizing dye after the emulsion is prepared. Examples of sensitizers, which may be employed in the emulsions described herein, are the cyanines or the sensitizing dyes disclosed in the following patents:

U. S. 2,078,233, Brooker, April 27, 1937
U. S. 2,166,736, White et al., July 18,1939
U. S. 2,186,608, Keyes, Jan. 9, 1940.
U. S. 2,165,339, Brooker, July 11, 1939.

The following examples illustrate my invention:

Example I

A solution of a polyvinyl propionaldehyde acetal resin containing 54.5% vinyl alcohol, was prepared by dissolving the resin in a 70:30 mixture of ethanol and water so as to give a concentration of 4.8%. 30 grams of this solution, diluted with 20 cc. of water and 20 cc. of acetone, was heated to 80° F. The following solutions, designated A and B, were added simultaneously over a period of three minutes accompanied by rapid stirring:

A. 10 cc. of a 50% solution of a silver nitrate in water, and

B. A mixture of 8½ cc. of 40% potassium bromide, ½ cc. 25% potassium chloride and ½ cc. of 25% potassium iodide, the solvent used being water.

70 grams of the 4.8% solution of the acetal resin was added and the emulsion was thoroughly stirred. It was sensitized by incorporating therein 2,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide. The emulsion was coated on pa-

per, dried and the resulting photographic paper was exposed and processed in the conventional developing and fixing baths. The image developed was sharp, the emulsion was sufficiently hard to withstand handling in the baths and it fixed out rapidly in the fixing bath.

Example II

A solution of a polyvinyl butyraldehyde acetal resin containing 75.2% vinyl alcohol, was prepared by dissolving it in a mixture of equal parts of ethanol and water to form a 6% solution. 10 grams of this solution was diluted with 15 cc. of water and 20 cc. of acetone and was heated to 80° F. Solutions corresponding to those designated as A and B in Example I were added simultaneously over a period of three minutes with rapid stirring. When half of A and of B had been added, 10 cc. of acetone was poured into the emulsion while continuing the addition of A and of B. At the end of the three minutes, 65 grams of the solution of the resin, prepared originally, was thoroughly incorporated. The emulsion was sensitized by incorporating 2mg. of 2,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide. The emulsion was coated on paper and dried. On processing in the conventional baths, this emulsion was found to give good results both as to physical properties and photographic quality.

Example III

A solution of a polyvinyl butyraldehyde acetal resin, containing 58% vinyl alcohol, was prepared by dissolving the resin in a 54:46 mixture of ethanol and water to a concentration of 5.7%. 30 grams of this solution was diluted with 30 cc. of water and 30 cc. of acetone and heated to 80° F. The following solutions, designated C and D, at a temperature of 80° F. were added simultaneously over a period of three minutes with rapid stirring.

C. 10 cc. of 50% silver nitrate in water.
D. 10 cc. of 40% potassium bromide and ½ cc. of 25% potassium iodide in water.

During the addition of solutions C and D, 10 cc. of acetone was added also. Then, 130 grams of the solution of the resin was diluted with 50 cc. of water and 50 cc. of acetone and this was added to the emulsion. The emulsion was then heated for 20 minutes at 45° C. and was washed by pouring into water. The excess water was pressed out and the emulsion was dissolved in a mixture of 50 cc. of water, 75 cc. of acetone and 20 cc. of ethyl cellosolve. It was sensitized with 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide. The emulsion was coated onto paper and also onto plates forming photographic paper and plates respectively.

Example IV

50 cc. of a 1% solution of diethanolamine cellulose acetate in water was heated to 80° F. and solutions corresponding to those designated as A and B in Example I were added simultaneously over a period of three minutes with rapid stirring. 100 grams of a 6% solution of polyvinyl butyraldehyde acetal resin containing 75.2% of vinyl alcohol, in equal parts of ethanol and water, was added followed by 10 cc. of ethyl cellosolve. The emulsion was sensitized with 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide. It was coated onto paper forming a photographic paper which gave good results in the usual processing baths.

Example V

50 cc. of a 2% solution of gum arabic in water was heated to 80° F. and solutions A and B were added simultaneously over a period of three minutes with rapid stirring. Polyvinyl butyraldehyde acetal resin and ethyl cellosolve were next added in the same manner as described in the preceding example. The emulsion was sensitized with 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide. The resulting emulsion was coated on paper, and dried and gave excellent results on processing.

Example VI

2 grams of the co-polymer of maleic anhydride and vinyl acetate was dissolved in 50 cc. of water and heated to 80° F. Solutions A and B were added simultaneously thereto over a period of three minutes with rapid stirring. 100 grams of a 6% solution of polyvinyl butyraldehyde acetal resin containing 75.2% vinyl alcohol in the molecule, dissolved in a mixture of equal parts of ethanol and water, was added followed by the addition of 10 cc. of ethyl cellosolve. The emulsion was sensitized with 2 mg. of 2,3'-diethyl - 4'-methyloxathiazolocarbocyanine iodide. Photographic paper was formed therefrom by coating out onto paper and drying.

Example VII

Silver halide was precipitated in a solution of the co-polymer of maleic anhydride and vinyl acetate, as described in the preceding example. 100 grams of a 4.8% solution of polyvinyl propionaldehyde acetal resin containing 54.5% vinyl alcohol dissolved in a mixture of 70 parts of ethanol and 30 parts of water, was added. The emulsion was sensitized, coated out on paper and dried as described in the preceding example.

As illustrated by the examples the acetyl resins employed in accordance with my invention are substantially entirely composed of polyvinyl alcohol and polyvinyl acetal, although the presence of a small proportion of polyvinyl ester is not deleterious.

The term "silver halide dispersing agent" as used herein is to be understood as referring to any material which (1) in dilute aqueous solution has the power of preventing the agglomeration of particles of silver halide when they form (2) is soluble either in water alone or in a mixture of a large proportion of water with an organic solvent (3) has the power of holding silver halide in suspension (4) is compatible with the polyvinyl propionaldehyde or butyraldehyde acetal resin employed and, for the best results, (5) should be sufficiently permeable to improve the permeability of the emulsion.

I claim:

1. A light-sensitive photographic emulsion comprising a silver halide and a carrier therefor selected from the group consisting of the polyvinyl propionaldehyde acetals having a combined vinyl alcohol content of approximately 45–60% and the polyvinyl butyraldehyde acetals having a combined vinyl alcohol content of approximately 60–80%.

2. A photographic silver halide emulsion comprising a finely dispersed silver halide resulting from preparing it in an aqueous solution of a silver halide dispersing agent and a protective colloid therefor selected from the group consisting of the polyvinyl propionaldehyde acetals having a combined vinyl alcohol content of ap-

proximately 45–60% and the polyvinyl butyraldehyde acetals having a combined vinyl alcohol content of approximately 60–80%.

3. A light-sensitive photographic emulsion comprising a silver halide and a carrier therefor selected from the group consisting of the polyvinyl propionaldehyde acetals having a combined vinyl alcohol content of approximately 50–60% and the polyvinyl butyraldehyde acetals having a combined vinyl alcohol content of approximately 70–80%.

4. A light-sensitive photographic emulsion comprising a silver halide and a polyvinyl propionaldehyde acetal having a combined vinyl alcohol content of 50–60%.

5. A light-sensitive photographic emulsion comprising a silver halide and a polyvinyl butyraldehyde acetal having a combined vinyl alcohol content of 70–80%.

6. A method of preparing a light-sensitive photographic emulsion which comprises dispersing silver halide in a protective colloid selected from the group consisting of the polyvinyl propionaldehyde acetals having a combined vinyl alcohol content of approximately 45–60% and the polyvinyl butyraldehyde acetals having a combined vinyl alcohol content of approximately 60–80%.

7. A method of preparing a light-sensitive photographic silver halide emulsion which comprises preparing the silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding thereto a protective colloid selected from the group consisting of the polyvinyl propionaldehyde acetals having a combined vinyl alcohol content of approximately 45–60% and the polyvinyl butyraldehyde acetals having a combined vinyl alcohol content of approximately 60–80%.

8. A method of preparing a light-sensitive photographic silver halide emulsion which comprises preparing the silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding thereto as a protective colloid an aqueous solution of a polyvinyl propionaldehyde acetal having a combined vinyl alcohol content of 50–60%.

9. A method of preparing a light-sensitive photographic silver halide emulsion which comprises preparing the silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding thereto as a protective colloid an aqueous solution of a polyvinyl butyraldehyde acetal having a vinyl alcohol content of 70–80%.

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