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PHOTOGRAPHIC SILVER HALIDE EMULSION

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This invention relates to photographic silver halide emulsions in which a water-susceptible polyvinyl ester or a polyvinyl alcohol, free of foreign materials adversely affecting water-permeability, 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 water and in photographic developing solutions at ordinary temperatures and its ability to form a thin coating of the light-sensitive silver halide emulsion upon the film base.

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 layer formed, however, when dry, is none too permeable to developing solutions 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 other colloidal materials have been mentioned in this connection. However, most of those that have been suggested heretofore are deficient for some reason or other, 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, such as photographic film base or paper, and dried.

Gelatin as a protective colloid for photographic silver halide emulsions leaves much to be desired. Gelatin is susceptible to depredation by organisms, both animal and vegetable. For instance, insects attack gelatin, particularly in the tropics. Gelatin is susceptible to the action of molds and of bacteria, particularly under conditions of high humidity and a compatible temperature. Gelatin, because of its natural source often varies in properties from time to time. Also, to obtain gelatin in a highly refined condition (as needed for photographic purposes) requires considerable care and it can be procured in limited amounts only from animal products by a slow and expensive process.

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 various photographic silver halide emulsions. Another object of my invention is to provide carriers or protective colloids for light-sensitive silver halides in photographic emulsions which possess many of the advantages but lack some of the disadvantages evidenced by gelatin. A further object of my invention is to provide a synthesized, rather than a natural, product which is controllable in its physical properties as produced and is useful as a protective colloid in photographic silver halide emulsion. Other objects will appear from a further perusal of this specification.

In its broader aspects my invention comprises the use of polyvinyl esters and polyvinyl alcohols for the making of photographic silver halide emulsions in place of gelatin. The physical properties of these materials are easily controlled in production so as to get a material of constant properties. The polyvinyl ester may be of the water-soluble type or it may be merely sufficiently water-permeable that developing of the emulsion is possible. Polyvinyl alcohol has the ability to hold silver halide in suspension, is easily coated out upon a support such as paper, readily sets and dries to a hard, scratch-resistant emulsion layer which may be treated with developing and fixing baths, because its dissolution is inhibited due to the presence of salts in the processing baths, and it may be washed thoroughly with water, after processing, without dissolving. I have found that a polyvinyl alcohol emulsion layer swells but does not dissolve when developed, fixed and washed in the usual way. After drying, it exhibits good physical properties. Where greater initial rigidity for the emulsion is desired, gelling agents may be incorporated in the emulsion as described and claimed in the McDowell and Kenyon Patents Nos. 2,249,536; 2,249,537; 2,249,538, which issued July 15, 1941, and 2,234,186, which issued March 11, 1941. The term gelling agent as used herein is used in the same sense as it is used in those applications, namely, a material which will convert polyvinyl alcohol to a gel at one temperature which gel may be converted to a sol at a higher temperature. The treatment of an aqueous solution of polyvinyl alcohol with gelling agents such as resorcinol, α-naphthol or the like in the amounts prescribed in those applications converts the

polyvinyl alcohol to a rigid gel which is thermal reversible. Thus after a silver halide has been dispersed in aqueous polyvinyl alcohol, such as 5–10% concentration, the mass, when treated with a substantial amount of a gelling agent at a slightly elevated temperature (preferably 40–90° C.) and then cooled, forms a rigid, thermal-reversible gel. This phenomena is valuable in that it makes possible the coating of the emulsion upon a support while the mass is liquid, at the elevated temperature, and then chill-setting of the emulsion. The emulsion can then be dried and forms a photo-sensitive layer on the support. The gelling agent should only be added after the formation of the emulsion to satisfactorily form a gelled product.

"Polyvinyl alcohols," which term as used herein includes also water-soluble hydrolyzed polyvinyl esters having a polyvinyl ester content of less than 5%—the remainder being polyvinyl alcohol, are particularly adapted to the preparation of unwashed emulsions and when coated on a suitable support such as paper in the form of a photo-sensitive silver halide emulsion will record images accurately and sharply, forming permanent prints when processed in the ordinary manner. Emulsions prepared in accordance with my invention may also be coated upon the usual photographic film base such as cellulose nitrate sheeting, cellulose acetate sheeting or cellulose mixed ester sheeting or upon glass plates to form photographic films or plates.

The photographic emulsions of my invention may be prepared by a process involving first dispersing silver halide in polyvinyl alcohol or a polyvinyl ester, such as by running aqueous solutions of silver nitrate and alkali metal halide into an aqueous solution of polyvinyl alcohol. Preferably after warming to cause better dispersion and increase the speed, as is well known in the art, followed by cooling and, if desired, sensitizing with a small amount of a sensitizing dye, the emulsion is ready to coat out onto 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.

While above I have referred to the polyvinyl esters as useful, the esters that may be employed are limited to those esters above included in the definition of "polyvinyl alcohols" (containing up to 5% polyvinyl ester, the remainder being polyvinyl alcohol) and to the water-susceptible polyvinyl esters, such as polyvinyl acetate, having a vinyl ester content within the range of approximately 59% to approximately 71% by weight (the remainder being polyvinyl alcohol), these water-susceptible polyvinyl esters being adapted for both washed and unwashed photographic silver halide emulsions as a protective colloid for the silver halide when processing in the usual manner is contemplated. The upper vinyl ester content (providing the rest is substantially polyvinyl alcohol) which is useful is limited only by the susceptibility to processing by photographic baths, particularly the fixing baths. For example, polyvinyl acetates, having vinyl acetate content higher than 71% (and consequently a lower polyvinyl alcohol content) may be employed for photographic emulsions if fixing baths of exceptional penetrating power are employed. Addition of potassium cyanide to a fixing bath of the usual kind will contribute to speeding up the fixing of emulsions having a high vinyl acetate content.

The hydrolyzed copolymer of vinyl acetate with a small proportion of another polymerizable compound such as vinyl chloride, styrene, an acrylic acid ester or the like might be employed to form a photographic emulsion as described herein.

To coat out silver halide emulsions of polyvinyl acetate in which the polyvinyl alcohol content is too low for water-solubility, the use of some compatible volatile organic solvent with the water in the emulsion to impart homogeneity is desirable. For instance, a small amount of acetone, ethyl alcohol, dioxan, methyl or ethyl cellosolve, or the like, may be mixed with the water employed in forming the emulsion so that a homogeneous mixture is obtained.

One further limitation upon the polyvinyl alcohols and polyvinyl esters which constitute the subject of this invention is that these alcohols and esters must have a molecular weight of not greater than 15,000. While there is some reference in the prior literature to the use of polyvinyl alcohol in photographic elements (but not in silver halide emulsions for photographic elements) none have recognized that the polyvinyl alcohol or the polyvinyl ester must have a molecular weight of 15,000 or less. After the dispersion of the slider halide in the polyvinyl alcohol has been formed, the addition of an aqueous solution of a polyvinyl alcohol of a molecular weight greater than 15,000 is not detrimental to the emulsion but its presence is undesirable until the silver halide dispersion has been prepared.

The prior literature having relation to this subject consists largely of a few patents which refer to the use of polyvinyl alcohol as a medium for photolithographic work in which polyvinyl alcohol is employed as the printing media for lithographic work. U. S. Patents 2,174,629, 2,184,288, 2,184,289, 2,184,310 and 2,184,311, for instance, refer to such usage. However, it is to be noted that consistently throughout all of these patents the polyvinyl alcohol is employed as a printing media. The polyvinyl printing media includes certain of the well-known dichromates which serve the purpose of sensitizing the printing media to the action of light. When the light is allowed to strike this printing media the polyvinyl alcohol layer is toughened in such a way that it becomes water-insoluble, whereas the unexposed portions of the printing media are of course unaffected. This printing media is then washed dissolving off the unexposed portions, leaving the exposed and toughened portions of polyvinyl alcohol to act as the final printing surface. These prior patents generally deplore the utility of polyvinyl alcohol alone for this purpose because of its low permeability to ink. Accordingly, all of these patentees require the addition to the polyvinyl alcohol printing media of certain modifying agents which increase the permeability of the printing media to ink, after it has been exposed to light. Patent No. 2,174,629 would apparently get along without any modifying agent. However, the remaining patentees referred to add such modifying agents as monocarboxylic acides, polycarboxylic acids, rubber latex or organic sulphonyl compounds such as Turkey red oil. However, the addition of these modifying agents is peculiar to the photolithographic problems involved and quite obviously do not adapt the polyvinyl alcohol for normal photographic purposes such as photographic silver halide emulsions.

Contrasted to the foregoing literature, my in-

vention is concerned with the preparation of photographic silver halide emulsions adapted to be coated upon paper or upon a transparent base such as cellulose derivative film base or glass plates to form what is normally known in the art as photographic paper, photographic film or photographic plates. In addition, I employ only polyvinyl alcohols containing no more than 5% polyvinyl ester (the remainder being polyvinyl alcohol) or I employ polyvinyl acetate in which the ester content is between 59% and 71%, the remainder being polyvinyl alcohol. In addition, the polyvinyl alcohols and esters employed by me are limited to ones having a molecular weight less than 15,000. Only by observance of these conditions have I found that an acceptable polyvinyl alcohol or polyvinyl ester silver halide emulsion without modifying agents can be successfully prepared.

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. If staining of the paper on which the emulsion is coated is objectionable an amount of sensitizing dye which is not great enough to cause staining may be employed. If a more sensitize emulsion is required and staining is not objectionable or a support which will not absorb the dye is used, a larger proportion of sensitizing dye may be incorporated. The emulsions containing the smaller amounts of sensitizing dye are ordinarily adapted for making contact prints or enlargements by projection.

The sensitizers which have been previously employed to optically sensitize silver halide emulsions may be incorporated in the emulsions of my invention to increase their sensitivity. Examples of sensitizers which may be employed in the emulsions described herein are the cyanines and the sensitizing dyes disclosed in the following patents:

U. S. No. 2,078,233, Brooker, April 27, 1937.
U. S. No. 2,166,736, White et al., July 18, 1939.
U. S. No. 2,186,608, Keyes, Jan. 9, 1940.
U. S. No. 2,165,339, Brooker, July 11, 1939.

The following examples illustrate my invention:

Example I

3.7 grams of polyvinyl alcohol was dissolved in 65 cc. of water. Solutions of 5 grams of silver nitrate in 10 cc. of water and of 3.2 grams of potassium bromide, 0.5 gram of potassium chloride and 0.12 gram of potassium iodide in 10.5 of water were run simultaneously into the solution of polyvinyl alcohol in 2–3 minutes with rapid stirring. A solution of 6 grams of polyvinyl alcohol in 50 cc. of water was then added and the emulsion was heated at 45° C. for 10 minutes. It was then cooled, sensitized with 1 milligram of 2,3'-diethyl-4'- methyloxathiazolo - carbocyanine dissolved in a little methyl alcohol and was coated on paper. The paper was dried and it was exposed, processed, washed, and dried in the usual manner for making photographic prints. A print of good appearance was obtained using the aqueous developing and fixing baths usually employed with gelatin emulsions. It is to be understood that beginning with the formation of the silver salt all of the operations in forming the photo-sensitive emulsions in this and the succeeding examples were carried out in the absence of light.

Example II

120 cc. of a 10% solution of polyvinyl alcohol was diluted with 140 cc. of water. Into this the following solutions were run with vigorous stirring, the precipitation time being five minutes, solution A: 40 cc. of a 50% solution of silver nitrate, solution B: 12.8 grams of potassium bromide, 3 grams of potassium chloride, 0.5 gram of potassium iodide and 44 cc. of water. 80 cc. of a 10% solution of polyvinyl alcohol was then added and the emulsion was stirred for 20 minutes at 50° C. 120 cc. of a 10% solution of polyvinyl alcohol was added and the emulsion was cooled. 50 grams of this emulsion was heated to 40° C. and 1.3 grams of resorcinol was added. One milligram of 2,3'-diethyl-4'-methyloxathiazolo-carbocyanine dissolved in a little methyl alcohol was added to sensitize the emulsion. The emulsion was coated on a glass plate and found to gel in 2–3 minutes at room temperature and more rapidly when chilled. The plate was exposed wet and processed. It was found to develop and fix readily.

A plate coated as before was washed by placing in cold water for 30 minutes and was then dried. On exposing and processing, the plate was found to develop and fix readily giving a clear, clean result. The emulsion was also coated on paper. It was dried by subjecting to a current of warm air. Upon exposing and processing, it was found to give a clear, clean result.

Example III

50 grams of the emulsion in the preceding example were heated to 40° C. and the following warm solution was added: 1.6 cc. ½ N potassium hydroxide, 0.125 gram of beta-naphthyl salicylamide and 5 cc. of water. The emulsion was poured out on glass plates where it set to a gel in a few minutes. The emulsion was coated on paper. It set and after drying it was processed. Developing and fixing were rapid in the normal solutions used for the processing of gelatin emulsions.

Example IV

6 grams of hydrolyzed polyvinyl acetate (71% by weight of vinyl acetate) were dissolved in 65 cc. of acetone and 44 cc. of water. 5 grams of silver nitrate was dissolved in 10 cc. of water. 5 grams of potassium bromide and .4 gram of potassium iodide were dissolved in 14 cc. of water. The solution of silver nitrate and the solution of the halide salts were run into the resin solution over a period of 2–3 minutes with rapid stirring. 2 grams additional of polyvinyl acetate dissolved in 6 cc. of acetone and 14 cc. of water was then added to the emulsion. It was heated for 20 minutes at 40° C., washed by pouring into water, pressed to a weight of 22 grams and dissolved in a mixture of 30 cc. of acetone, 50 cc. of water and 10 cc. of ethyl cellosolve. 3 cc. of monoacetin was added and the emulsion was ortho sensitized by incorporating 2,3'-diethyl-4'-methyl oxathiazolo-carbocyanine iodide therein. This emulsion was coated on paper and gave prints of good photographic quality.

Example V

6 grams of hydrolyzed polyvinyl acetate (59% by weight of vinyl acetate) were dissolved in 60 cc. of acetone and 60 cc. of water. 5 grams of silver nitrate were dissolved in 10 cc. of water. 2.4

grams of potassium bromide, 1.5 grams of potassium chloride and .1 gram of potassium iodide were dissolved in 12 cc. of water. The solution of silver nitrate and the solution of halide salts was run into the resin solution simultaneously over a period of 2–3 minutes with rapid stirring. 2 grams additional of polyvinyl acetate dissolved in 4 cc. of acetone and 16 cc. of water was added. The emulsion was heated for 20 minutes at 40° C., cooled to 20° C. and ortho sensitized with 2,3'-diethyl-4'-methyl oxathiazolo-carbocyanine iodide. It was coated on paper, dried and found to give good prints and readily developed and fixed in the usual photographic baths.

The requirements for a protective colloid for useful photographic silver halide emulsions are (1) the material must be such that the silver halide when formed does not appreciably clump or coagulate when in contact therewith in aqueous solution (2) it must coat out from its aqueous emulsion to given clear transparent films of proper strength and elasticity and (3) its dried coatings must be such that the solutions used to process photographic emulsions readily penetrate the coating and act on the silver halide grains therein.

There are very few materials which satisfy all three of these conditions. The use of cellulose nitrate in collodion emulsions is very old; this material disperses silver halides and forms satisfactory films but it does become impermeable to water upon drying and, therefore, requires specialized handling in order to develop the halide grains. Even compounds which satisfy the three requirements given are often insoluble in water or in solutions predominantly aqueous and, therefore, the usual methods which are used in aqueous systems for preparing photographic silver halide emulsions of high sensitivity are not applicable. The preparation of photographic silver halide emulsions of high sensitivity in non-aqueous systems is practically unknown as compared to the rapid negative materials of the gelatin type.

Water-susceptible polyvinyl acetates or polyvinyl alcohol as prescribed herein has been found to possess not only the three characteristics given above but also to be soluble in solutions containing a substantial percentage of water and are, therefore, particularly adapted to prepare photographic silver halide emulsions.

The hydrolyzed water-permeable polyvinyl propionates or butyrates which are most suitable for use in preparing photographic silver halide emulsions are those having a sufficient permeability to allow development of the emulsion but sufficient insolubility to resist dissolving by the processing baths. These polyvinyl propionates or butyrates may be identified by their similarity in these properties to the polyvinyl acetates having a vinyl acetate content of 59–71%.

I claim:

1. A light-sensitive photographic emulsion comprising a silver halide dispersed in a thermal-reversible gel composed of polyvinyl alcohol mixed with a gelling amount of an unsubstituted hydroxy aromatic compound selected from the group consisting of the unsubstituted polyhydric phenols and the unsubstituted dihydric naphthols.

2. A light-sensitive photographic emulsion comprising a silver halide dispersed in a thermal-reversible gel composed of polyvinyl alcohol mixed with a gelling amount of an unsubstituted polyhydric phenol.

3. A light-sensitive photographic emulsion comprising a silver halide dispersed in a thermal-reversible gel composed of polyvinyl alcohol mixed with a gelling amount of resorcinol.

4. A light-sensitive photographic emulsion comprising a silver halide dispersed in a thermal-reversible gel composed of polyvinyl alcohol mixed with a gelling amount of phloroglucinol.

5. A light-sensitive photographic emulsion comprising a silver halide dispersed in a thermal-reversible gel composed of polyvinyl alcohol mixed with a gelling amount of 2,7 dihydroxy naphthalene.

6. A method of preparing a light-sensitive photographic emulsion which comprises preparing a silver halide in an aqueous solution of a polyvinyl alcohol and subsequently adding thereto at a temperature of 40–90° C. a sufficient amount of an unsubstituted hydroxy aromatic compound selected from the group consisting of the unsubstituted polyhydric phenols and the unsubstituted dihydric naphthols to form a rigid gel at a lowered temperature.

7. A method of preparing a light-sensitive photographic emulsion which comprises preparing a silver halide in an aqueous solution of a polyvinyl alcohol and subsequently adding thereto at a temperature of 40–90° C. a sufficient amount of an unsubstituted polyhydric phenol to form a rigid gel at a lowered temperature.

8. A method of preparing a light-sensitive photographic emulsion which comprises preparing a silver halide in an aqueous solution of a polyvinyl alcohol and subsequently adding thereto at a temperature of 40–90° C. a sufficient amount of resorcinol to form a rigid gel at a lowered temperature.

9. A method of preparing a light-sensitive photographic emulsion which comprises preparing a silver halide in an aqueous solution of a polyvinyl alcohol and subsequently adding thereto at a temperature of 40–90° C. a sufficient amount of phloroglucinol to form a rigid gel at a lowered temperature.

10. A method of preparing a light-sensitive photographic emulsion which comprises preparing a silver halide in an aqueous solution of a polyvinyl alcohol and subsequently adding thereto at a temperature of 40–90° C. a sufficient amount of 2,7 dihydroxy naphthalene to form a rigid gel at a lowered temperature.

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