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PHOTOGRAPHIC SILVER HALIDE EMULSION

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This application is a continuation-in-part of my application Serial No. 318,560 entitled, "Photographic silver halide emulsions," filed February 12, 1940.

This invention relates to a method of making photographic silver halide emulsions in which the silver halide is first prepared in an aqueous solution of a silver halide dispersing agent and the dispersion is subsequently thoroughly mixed with a hydrolyzed polyvinyl acetate of 59-71%, or a hydrolyzed polyvinyl acrylate of 0.5-5% vinyl acrylate content and the emulsion prepared thereby. Gelatin has ordinarily been employed as the protective colloid for the silver halide in photographic silver halide emulsions due to (1) its ability to hold the light-sensitive silver halides in finely divided suspension, (2) its good water permeability, (3) its insolubility in water and the conventional photographic developing and fixing solutions, and (4) its ability to form a thin hard coating upon various supports.

Other materials have been suggested as substitutes for gelatin as protective colloids for the silver halides in photographic emulsions, but these previously proposed materials often evidence inferiority in one or more of the properties enumerated above with respect to gelatin. For example, cellulose nitrate has been suggested for use in this connection. This material when dry is not very permeable to the conventional aqueous developing and fixing baths. Also cellulose nitrate is insoluble in a solvent mixture containing an appreciable amount of water and, therefore, water-soluble salts cannot be used with cellulose nitrate to prepare a silver halide.

Gelatin as a protective colloid in photographic silver halide emulsions does have disadvantages. It is vulnerable to attack by animal and vegetable life. For instance, insects attack gelatin, particularly in the tropics. Also it is susceptible to the action of mold and of bacteria, particularly under high humidity conditions. Gelatin is a product of nature and is obtained from a wide variety and assortment of materials from widely scattered points, both geographical and physiological. Therefore, it is subject to considerable variation in properties from time to time. To obtain gelatin in a highly refined condition (as needed for photographic purposes) requires considerable care and it can be procured only in limited amounts from animal products by a slow and expensive process.

One object of my invention is to provide a method of making photographic silver halide emulsions of good quality in which a highly re-

finer synthetic material may be employed as the protective colloid. Another object of my invention is to provide a method of making photographic silver halide emulsions in which the silver halide is effectively dispersed therein. A further object of my invention is to prepare photographic silver halide emulsions from which pictures may be obtained comparable to those obtained with other photographic emulsions of good quality. Other objects of my invention will appear herein.

I have found that if silver halide is prepared in an aqueous solution containing a substantial amount of a silver halide dispersing agent, followed by the mixing therewith of a substantial amount of a protective colloid selected from the group consisting of the polyvinyl acetates having vinyl acetate contents of 0.5-5% and of 59-71%, an emulsion results which gives clean results and processes readily in the conventional developing and fixing baths. I have found that by preparing a photographic emulsion in this manner the silver halide is carried in the emulsion in a finely divided form, that the emulsion is easily coated onto a support and that it can readily be set and dried to a hard scratch-resistant emulsion layer which may be treated with developing and fixing baths (as is usual after exposing) and washed thoroughly with water without dissolving. Even though the polyvinyl acetate of 0.5-5% vinyl acetate content is water soluble, it does not dissolve off due perhaps partly to the action of the salts present in the processing baths. The resulting emulsion layer exhibits good physical properties. If a washed emulsion is desired with a polyvinyl acetate of 0.5-5% vinyl acetate content, it is desirable to treat the emulsion after its formation with a gelling agent as described and claimed in McDowell and Kenyon applications Nos. 318,550; 318,551; 318,552 and 318,553, filed February 12, 1940. Treatment of the emulsions with a gelling agent such as beta naphthyl salicylamide, gallic acid, resorcinol, or alpha naphthol in the manner prescribed in those applications converts the emulsion to a rigid thermo-reversible gel. For instance, after forming the photographic emulsion with the low acetyl polyvinyl acetate in which emulsion the polyvinyl acetate is present in a concentration of approximately 3-10%, a gelling agent is added thereto at an elevated temperature (preferably 40-90° C.) and the mass is then cooled to form a rigid gel. The emulsion may then be washed with water sufficiently to remove the water soluble salts resulting from the formation of the silver halide if desired, without detrimentally affecting the

polyvinyl material. If desired, the gel, washed or unwashed, can be warmed to cause the formation of a sol and can be applied in the form of a thin layer to a support for the emulsion. The emulsion layer can then be set by cooling, followed by drying in the usual manner.

The preparation of silver halide for the emulsion is carried out in a very dilute aqueous solution of a material which has the power of preventing the agglomeration of the particles of silver halide when they form. It must also be compatible with the polyvinyl acetate used as the protective colloid. Any material having these properties may be employed, these materials being referred to herein as "silver halide dispersing agents." Many materials ordinarily regarded as having dispersing powers are unsuitable for this purpose while other materials not identified ordinarily as dispersing agents are found to be useful in this connection. One of the most suitable silver halide dispersing agents is hydrolyzed starch acetate having an acetyl content of 4-15% if it resulted from the hydrolysis of a starch acetate prepared from a water-insoluble starch or having an acetyl content of 3-25% if a starch acetate prepared from a water-soluble starch was hydrolyzed to prepare it. It is desirable that the starch acetate employed be of a low viscosity type.

Another suitable silver halide dispersing agent is the co-polymer of maleic anhydride and vinyl acetate having an apparent molecular weight of the order of magnitude 30,000-200,000 (based on viscosity measurements) as described in U. S. Patent No. 2,047,398 of I. G. The condensation product of this co-polymer of maleic anhydride and vinyl acetate with aniline as described in the U. S. patent to I. G. referred to, has also been found to be useful for dispersing silver halide in accordance with the process of my invention. Water soluble lower alkyl cellulose ethers have also been found to be suitable for dispersing silver halides in my process. Ordinarily the water soluble methyl celluloses having a methoxy content of 20-30% are particularly suitable for this purpose. Other lower alkyl celluloses having corresponding alkoxy contents are suitable for this purpose. Other materials having the properties prescribed for a silver halide dispersing agent are suitable for use herein for that purpose. For instance, both gum arabic as commercially available and water-soluble urea-formaldehyde condensation products have been found quite satisfactory in preparing silver halide in a finely dispersed form, in accordance with my invention.

The silver halide dispersing agents are employed in preparing silver halide in the form of dilute aqueous solutions. For instance, a dilution of the dispersing agent in an aqueous liquid in a concentration within the range of 0.5-6% of dispersing agent is ordinarily employed. It is to be understood, however, that the proportion of silver halide dispersing agent may vary in accordance with the judgment of the individual operator. For example, if greater contrast is desired in the photographic emulsion, the proportion of dispersing agent used should be increased.

It may be stated as a general rule that the ratio of silver halide dispersing agent used to the polyvinyl acetate employed as the protective colloid should be within the range of approximately 0.5:6-4:6 (by weight). For example, in the case of water soluble methyl cellulose, the ratio to polyvinyl acetate of approximately 1:5 may be used although the addition of some solvent such

as ethyl alcohol will aid the dispersing power so that a lower ratio, such as 1:10, will give good results. In some cases the mixing of a little polyvinyl acetate with the dispersing agent may be desired but its presence in the preparation of silver halide appears to serve no useful purpose.

The polyvinyl acetates having vinyl acetate contents of approximately 0.5-5% and of 59-71% have been found to be particularly useful as the vehicles or protective colloids for the dispersed silver halide. Any of the polyvinyl esters having a vinyl acylate content of less than 5% and a viscosity of from 2-60 cps. may be employed as protective colloids for the silver halide. The moderately high viscosity esters such as of 30-50 cps. have been found quite satisfactory for this purpose. The polyvinyl acetates of 59-71% acetyl and the propionates and butyrates having corresponding properties which are useful may also be of low, medium, or high viscosity and may have viscosities corresponding to those of the low acetyl polyvinyl acetates. The useful polyvinyl acetates are derived from fully esterified polyvinyl acetates by hydrolysis and the viscosity of the polyvinyl acetate in its hydrolyzed form is governed by the viscosity of the original polyvinyl acetate.

The photographic silver halide emulsions of my invention may be prepared by a process involving first the preparation of a dispersion of silver halide accomplished by running aqueous solutions of silver nitrate and alkali metal halide into an agitated dilute aqueous solution of a silver halide dispersing agent. An aqueous solution of a polyvinyl acetate having a vinyl acetate content of 0.5-5% or of 59-71% is then added and thoroughly incorporated in the mass such as by stirring the materials together for a few minutes. As the polyvinyl acetates of 59-71% vinyl acetate content are not water-soluble, a small amount of a water-miscible solvent such as acetone, ethyl alcohol, dioxane, methyl or ethyl cellosolve which when mixed with water will accomplish the dissolution of the polyvinyl acetate must be used with water in forming the aqueous solution of the polyvinyl acetate of high acetyl content. The mass which may be termed an emulsion may, with or without warming followed by cooling, be sensitized with a small amount of a sensitizing dye. It may then be coated on a support and dried with a current of warm air to form a hard, scratch-resistant, light-sensitive emulsion layer. It may then be exposed, processed, washed and dried and good prints will result. The aqueous developing and fixing baths usually employed with gelatin emulsions are usually used for processing the emulsions of my invention. In some cases those baths might be improved by the addition of a water-miscible organic solvent, such as alcohol, acetone, cellosolve, pyridine, dioxan or morpholine to the normal developing and fixing baths.

For emulsions for coating on paper, only a small amount of a sensitizing dye should be used if staining of the paper is objectionable. These emulsions containing a small proportion of sensitizer are ordinarily adapted for making contact prints and enlargements by projection. To obtain a faster emulsion a larger proportion of sensitizing dye should be incorporated. A fast emulsion is useful in the direct photographing of objects where some speed is necessary to record the image. Those emulsions which are of high sensitivity are also useful for print-out papers and where developing is not to be employed.

The emulsions of my invention may be coated out upon a suitable support such as paper or upon the usual photographic film base such as a cellulose ester or a synthetic resin support. The usual types of cellulose ester support are cellulose nitrate sheeting, cellulose acetate sheeting, or sheeting prepared from mixed esters of cellulose. Ordinarily it is unnecessary to wash the emulsion when coating upon a paper support is contemplated. If a cellulose ester support is to be used, the coating thereon of a washed emulsion which has been sensitized gives a good quality photographic film.

Photographic silver halide emulsions may be sensitized in the same manner as are silver halide emulsions generally. Sensitizers which have been previously employed to optically sensitize silver halide emulsions may be incorporated in the emulsions described herein to increase their sensitivity. These emulsions are susceptible to sensitization by cyanine sensitizing dyes or by the sensitizing dyes which are described in the following patents: U. S. No. 2,078,233 of Brooker, dated April 27, 1937; U. S. No. 2,166,736 of White et al., dated July 18, 1939; U. S. No. 2,186,608 of Keyes, dated January 9, 1940; and U. S. No. 2,165,339 of Brooker, dated July 11, 1939, depending upon the type and range of sensitivity desired. The sensitized emulsions prepared in accordance with my invention are particularly valuable in recording the image of an object. The emulsions of my invention may be toned blue or they may be used in color processes and colored with dyes which resist diffusion. The following examples illustrate my invention:

Example 1

Twenty grams of low viscosity starch acetate having an acetyl content of 11% were dissolved in 100 cc. of water. Ten grams of this solution was taken and was diluted with 40 cc. of water. This diluted starch acetate was rapidly stirred together with solutions A and B at a temperature of 80° F. Solutions A and B are as follows:

Solution A.—10 cc. of 50% aqueous silver nitrate solution at 80° F.

Solution B.—A mixture of aqueous solutions of KBr, KCl, and KI in the following amounts and concentrations:

40% KBr	cc.
25% KCl	8.5
25% KI	0.5
	0.5

all at 80° F. after the solution.

After the solutions A and B had been thoroughly incorporated in the starch acetate solution, 60 grams of a 10% aqueous solution of high viscosity polyvinyl acetate having a vinyl acetate content of less than 5% was added and stirring was continued for five minutes. The resulting emulsion was then sensitized by adding thereto 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbo-cyanine iodide. The resulting emulsion coated and dried well on paper. Processing was satisfactory in ordinary developing and fixing baths and the photographic quality was good. The prints prepared from this solution ferrotyped easily to a high gloss. It is to be understood that in this all the succeeding examples, the preparation of the emulsion beginning with preparing the silver halide was carried out in the absence of sufficient light to detrimentally affect the light-sensitive properties of the emulsion.

Example 2

Ten grams of a cellulose ethyl ether known as Hyglin containing approximately 25-28% ethoxy, was dissolved in 190 cc. of water. Twenty grams of this solution was taken, was diluted with 40 cc. of water, heated to 80° F. and rapidly stirred while solutions A and B were run in simultaneously over an interval of three minutes. Solutions A and B were identical to those listed in the preceding example under these designations. Fifty grams of a 10% aqueous solution of high viscosity polyvinyl acetate having a vinyl acetate content of less than 5% and 25 cc. of water was added and thoroughly incorporated into the mixture. The emulsion was then sensitized by incorporating 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbo-cyanine iodide. The emulsion was then coated on paper and dried and upon exposing the emulsion was processed and was found to give prints of good quality.

Example 3

Ten grams of a low viscosity methyl cellulose having a methoxyl content of approximately 28% was dissolved in 290 cc. of water. Fifteen grams of this solution was taken, diluted with a mixture of 15 cc. of water and 15 cc. of ethyl alcohol and the resulting solution was stirred briskly and heated to 80° F. Solutions A and B (identified in Example 1) were introduced simultaneously with rapid stirring over an interval of three minutes. 50 grams of a 10% aqueous solution of high viscosity polyvinyl acetate having a vinyl acetate content of less than 5% and 20 cc. of water was added. The emulsion was sensitized by adding 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbo-cyanine iodide, and thoroughly stirring the mass. This emulsion was found to coat and dry well on paper and gave good prints upon exposure and processing in the usual manner.

Example 4

One gram of gum arabic was dissolved in 50 cc. of water at 80° F. and rapidly stirred while solutions A and B (identified in Example 1) were run in simultaneously over an interval of three minutes. At the end of this time 60 grams of a 10% aqueous solution of high viscosity polyvinyl acetate having a vinyl acetate content of less than 5% and 25 cc. of water was added. The emulsion was sensitized by incorporating therein 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbo-cyanine iodide. The emulsion was coated and dried on paper and gave prints of satisfactory quality when treated in the usual manner.

Example 5

Two grams of a resin prepared by polymerizing maleic anhydride with vinyl acetate was dissolved in 50 cc. of water at a temperature of 80° F. and rapidly stirred while solutions A and B (identified in Example 1) were run in simultaneously over an interval of three minutes. At the end of this time 60 grams of a 10% aqueous solution of high viscosity polyvinyl acetate having a vinyl acetate content of less than 5% and 25 cc. of water was added. The emulsion was sensitized by incorporating therein 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarbo-cyanine iodide. The emulsion was coated and dried on paper and gave prints of satisfactory quality when treated in the usual manner.

Example 6

0.5 gram of the condensation product of a maleic anhydride-vinyl acetate resin and aniline was dissolved in 50 cc. of water at a temperature of 80° F. and rapidly stirred while solutions A and B (identified in Example 1) were run in simultaneously over an interval of three minutes. At the end of this time 60 grams of a 10% aqueous solution of high viscosity polyvinyl acetate having a vinyl acetate content of less than 5% and 25 cc. of water was added. The emulsion was sensitized by incorporating therein 2 mg. of 2,3'-diethyl-4'-methyloxathiazolocarboxyanine iodide. The emulsion was coated and dried on paper and gave prints of satisfactory quality when treated in the usual manner.

Instead of using a polyvinyl acetate having a low vinyl acetate content, a hydrolyzed polyvinyl acetate having a vinyl acetate content of 59—71% may be employed as the vehicle in any of the preceding examples. For instance, in Example 1, instead of adding 60 grams of a 10% solution of high viscosity polyvinyl acetate of low vinyl acetate content, 60 grams of a 6% solution of polyvinyl acetate (containing 59% vinyl acetate) dissolved in a mixture of 2 parts of acetone in 3 parts of water may be employed to supply the vehicle. Instead of a polyvinyl acetate of 59% vinyl acetate, one having 71% by weight of vinyl acetate or one having a vinyl acetate content within the range of 59—71% may be employed. If desired, the emulsion may be plasticized by some compatible softening or plasticizing agent, such as monoacetin.

It is to be understood that the polyvinyl esters prescribed as useful in my emulsions have a polyvinyl acylate content of less than 5% or have a polyvinyl acetate content within the range of 59—71%, the remainder of the compound being polyvinyl alcohol.

As an alternative procedure the silver halide may be prepared and dispersed in an aqueous solution containing in addition to the silver halide dispersing agent some or all of the polyvinyl acetate. With the polyvinyl acetates having a vinyl acetate content of less than 5%, water only may be used as the solvent. In the case of polyvinyl acetates having a vinyl acetate content of 59—71% it is, of course, necessary to also use a small amount of organic solvent with the water employed as the solvent medium. As I have found, however, that the preparation of the silver halide in the dispersing agent with little or no polyvinyl acetate followed by the addition of the most or all of the polyvinyl acetate vehicle, proceeds smoothly and readily, I have ordinarily employed this procedure in preparing the emulsions of my invention.

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 for 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%. Also, vinyl derivatives which are found to have suitable properties for use as carriers in photographic emulsions such as selected from the vinyl dicarboxylates or hydroxy esters of carboxylates, the hydroxy acid esters of vinyl, or the hydrolyzed copolymer of vinyl acetate with a small propor-

tion 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.

I claim:

1. A method of preparing photographic silver halide emulsions 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 lower fatty acid esters having a vinyl acylate content of 0.5—5% and the polyvinyl acetates of 59—71% vinyl acetate content, substantially the remainder being vinyl alcohol.
2. A method of preparing photographic silver halide emulsions which comprises preparing the silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding a protective colloid thereto selected from the group consisting of the polyvinyl acetates having vinyl acetate contents of 0.5—5% and 59—71%, substantially the remainder being vinyl alcohol.
3. A method of preparing photographic silver halide emulsions which comprises preparing silver halide in an aqueous solution of a water soluble starch acetate and subsequently adding a protective colloid selected from the group consisting of the polyvinyl lower fatty acid esters having vinyl acylate contents of 0.5—5% and the polyvinyl acetates having vinyl acetate contents of 59—71%, substantially the remainder being vinyl alcohol.
4. A method of preparing photographic silver halide emulsions which comprises preparing silver halide in an aqueous solution of a water soluble lower alkyl cellulose and subsequently adding a protective colloid selected from the group consisting of polyvinyl lower fatty acid esters having vinyl acylate contents of 0.5—5% and the polyvinyl acetates having vinyl acetate contents of 59—71%, substantially the remainder being vinyl alcohol.
5. A method of preparing photographic silver halide emulsions which comprises preparing silver halide in an aqueous solution of a maleic anhydride-vinyl acetate resin and subsequently adding a protective colloid selected from the group consisting of polyvinyl lower fatty acid esters having vinyl acylate contents of 0.5—5% and polyvinyl acetates having vinyl acetate contents of 59—71%, substantially the remainder being vinyl alcohol.
6. A method of preparing photographic silver halide emulsions which comprises preparing a silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding thereto an optical sensitizer and a protective colloid selected from the group consisting of polyvinyl lower fatty acid esters having vinyl acylate contents of 0.5—5% and polyvinyl acetates having vinyl acetate contents of 59—71%, substantially the remainder being vinyl alcohol.
7. A method of preparing photographic silver halide emulsions which comprises preparing a silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding thereto a polyvinyl acetate having a vinyl acetate content of 0.5—5%, substantially the remainder being vinyl alcohol.
8. A method of preparing photographic silver halide emulsions which comprises preparing a silver halide in an aqueous solution of a silver halide dispersing agent and subsequently adding thereto a polyvinyl acetate having a vinyl ac-

tate content of 59-71%, substantially the remainder being vinyl alcohol.

9. 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 selected from the group consisting of polyvinyl lower fatty acid esters having vinyl acylate contents of 0.5-5% and polyvinyl acetates having vinyl acetate contents of 59-71%, substantially the remainder being vinyl alcohol.

10. A photographic silver halide emulsion comprising a finely dispersed silver halide resulting from its preparation in an aqueous solution of a silver halide dispersing agent, an optical sensitizer, and a protective colloid selected from the group consisting of the polyvinyl lower fatty acid esters having vinyl acylate contents of 0.5-5% and polyvinyl acetates having vinyl acetate contents of 59-71%, substantially the remainder being vinyl alcohol.

11. A photographic silver halide emulsion comprising a finely dispersed silver halide resulting from its preparation in an aqueous solution of a silver halide dispersing agent and as

the protective colloid a polyvinyl acetate having a vinyl acetate content of 0.5-5%, substantially the remainder being vinyl alcohol.

12. A photographic silver halide emulsion comprising a finely dispersed silver halide resulting from its preparation in an aqueous solution of a silver halide dispersing agent and as a protective colloid a polyvinyl acetate having a vinyl acetate content of 59-71%, substantially the remainder being vinyl alcohol.

13. A photographic silver halide emulsion comprising a finely dispersed silver halide in a mixture of a silver halide dispersing agent and a polyvinyl acetate selected from the group consisting of the polyvinyl acetates having vinyl acetate contents of 0.5-5% and of 59-71%, substantially the remainder being vinyl alcohol.

14. A photographic silver halide emulsion comprising a finely dispersed silver halide in a mixture of a water-soluble starch acetate and a polyvinyl fatty acid ester having a vinyl acylate content of 0.5-5%, substantially the remainder being vinyl alcohol.

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