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PREPARATION OF COLLOID COLOR FORMER SILVER HALIDE DISPERSIONS

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7 Claims. (Cl. 95—7)

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This invention relates to photography and, more particularly to colloid-silver halide dispersions of improved quality and to methods of preparing the same. More particularly it relates to such dispersions and methods wherein the colloid has a polymeric structure and contains dye intermediate or color-former nuclei as a part of its molecular structure.

An object of this invention is to provide improved colloid-silver halide dispersions. Another object is to provide such dispersions which are free from agglomerates of silver halide grains. Another object is to provide hydrophilic color-forming polymeric dispersions of light-sensitive silver salts which are free from soluble salts. A further object is to provide a simple, economical and effective method of making hydrophilic color-forming polymeric silver salt dispersions. A still further object is to provide synthetic hydrophilic color-former silver halide dispersions which possess good speed and sensitivity.

It has been found that improved hydrophilic color-forming polymer silver salt dispersions can be made by precipitating silver halides in aqueous colloids, especially in aqueous gelatin solutions, centrifuging the dispersion to separate out the silver halides and redispersing the silver halide particles in an aqueous solution of a hydrophilic color-forming polymer with the aid of an anionic surface active agent having a lipophilic radical of at least 6 carbon atoms and a hydrophilic radical.

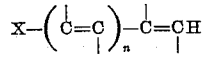
The anionic surface active agent should be added prior to the centrifuging step. This may be done advantageously by incorporating the agent with the gelatin dispersion after it has been diluted to a low gelatin concentration, e. g., about 0.1 to 5.0% by weight based on the gelatin. The anionic surface active agent can be added to the aqueous solution used for dilution or added after dilution. The silver salts can be washed in the centrifuge with water to remove any gelatin which was not thrown off during the centrifugation. The silver salts, after removal of the washing water, are then recovered from the bulk liquid for redispersion. The redispersion can be advantageously accomplished by making an aqueous paste of the recovered silver salts and mixing the paste with an aqueous solution of the hydrophilic color-forming polymer. An additional amount of the anionic surface active agent is preferably added to the silver salts recovered by centrifugation prior to redispersion.

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The initial silver halide dispersions can be made by any of the conventional methods for dispersing silver halides. For instance, an aqueous solution of a water-soluble bromide, e. g., ammonium bromide, can be added to an aqueous gelatin solution and an aqueous solution of a water-soluble silver salt, e. g., silver nitrate, added to the mixture whereupon silver bromide is precipitated. The dispersion may be ripened and further treated, if desired, to increase its sensitivity and then redispersed as described above. If a mixture of water-soluble halides, e. g., chlorides, bromides, and iodides are used a mixture of silver halides may be formed. The silver halide dispersions in the hydrophilic color-forming polymer resulting from the redispersion may be modified by the addition of various light-sensitive silver halide emulsion constituents, e. g., optical sensitizing dyes, fog inhibiting agents, sulfur sensitizers, and digested, etc., prior to coating, if desired.

The centrifuged silver salts can be redispersed in a wide variety of hydrophilic color-forming polymers. By this expression is meant organic polymeric color-formers which include in their molecular structure nuclei which are capable of forming an azomethine or quinoneimine dye on color-coupling development of silver salts and which, in the form of thin layers, e. g., 1 to 20 microns in thickness, are insoluble in water at 30° C. but are freely water-permeable. They should, moreover, be soluble to the extent of at least 5 parts by weight in 100 parts of a boiling aqueous solution containing less than 50% and, preferably, less than 25% of ethanol.

The color-former components of the hydrophilic color forming polymers have as active coupling groups a structure which may be represented by the general formula

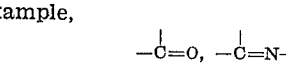


where X is an HO radical or an RHN radical; where R is hydrogen, alkyl or a substituted alkyl group, e. g., methyl, ethyl, dodecyl, betachlorethyl, betahydroxyethyl, benzyl, etc.; and n is 0 or 1. Thus X may be a primary or secondary amino group. These groups are found in reactive methylene dye intermediates or color formers and in aromatic hydroxyl and amino compounds and includes reactive ethenol, aminoethenyl, 4-hydroxy- and 4-amino-1,3-butadienyl groups. These groups occur in phenols, naphthols, anilines, naphthylamines, acylacetamides, cyano-

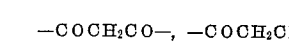
acetamides, betaketoesters, pyrazolones, homophthalimides, coumaranones, indoxyls, thioindoxyls, etc.

The reactive ethenol group represented by

occurs in phenols and naphthols which couple in the ortho positions and in the alkali soluble or enol form of most reactive methylene dye intermediates. These reactive methylene groups have a hydrogen atom rendered mobile by the proximity of certain unsaturated groups such as, for example,



and others. The —CH_2— group is usually present between two such groups, for example,

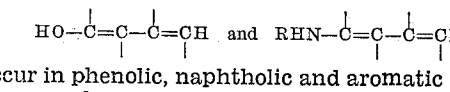


in a cyclic or acyclic system.

The reactive aminoethenyl group,

occurs in aromatic amino compounds which couple in the ortho position.

The 4-hydroxy- and 4-amino-1,3-butadienyl groups represented as



occur in phenolic, naphtholic and aromatic amino compounds which couple in the para position.

In all of these dye intermediate groups the hydrogen atoms in the coupling reactive position may be replaced by groups readily eliminated in the coupling reaction, e. g., halogen, sulfonic acid, carboxylic acid, etc.

The invention is especially useful with hydrophilic color-forming hydroxyl polymers which possess as a part of their molecular structure a plurality of aliphatic hydroxyl (viz., nonphenolic) groups and a plurality of color-former nuclei capable of forming quinoneimine or azomethine dyes on color-coupling development. In such polymers the predominant hydrophilic groups are aliphatic hydroxyl groups. They should contain at least 1 hydroxyl group to every 8 carbon atoms of the linear polymer chain, i. e., about 12.5 hydroxyl groups for every 100 chain atoms and preferably 1 to 2 hydroxyl groups for every 4 chain atoms, i. e., between 25 and 50 hydroxyl groups per each 100 chain atoms. The color former groups are attached to the polymer chain either directly or indirectly. Preferably between 1 and 35 color former nuclei should be present for every 100 chain atoms.

Suitable synthetic hydrophilic hydroxyl color forming polymers which may be used for the redispersions include those made from hydrophilic completely and incompletely hydrolyzed polyvinyl esters, e. g., the acetates, chloracetates, propionates, butyrates, and glycolates, and the completely and incompletely hydrolyzed interpolymers of such polyvinyl esters with polymerizable compounds such as ethylene, propylene, butene-1, methacrylic and acrylic acid, ethyl and methyl esters, vinyl chloride, vinyl cyanide, maleic anhydride, methyl vinyl ketone and the ethers and acetals of such compounds; and alkyd resins containing a plurality of hydroxyl groups, e. g., sorbitol-citric acid polymers. The polymer chains can be connected to the color former nuclei by various chemical groupings or linkages such as ester, carbonamide, sulfonamide, amino and imino groups, ether and acetal linkages.

A variety of anionic surface active agents of the above type are commercially available. Representative types include the alkali metal, ammonium, and strongly basic amine salts of primary and secondary monoalkyl sulfates and sulfonic acids and cycloaliphatic sulfonic acids of 8 to 18 carbon atoms, and such salts of alkyl substituted naphthalene sulfonic acids and aldehyde condensation products of naphthalene sulfonic acids and of saturated or substantially saturated aliphatic carboxylic acids of 10 to 24 carbon atoms.

The invention will be further illustrated but is not intended to be limited by the following examples wherein all parts stated are by weight, all solutions aqueous, and all temperatures centigrade unless otherwise stated. All procedures wherein light-sensitive silver salts are employed are carried out under conditions of darkness or conditions which will not expose the light-sensitive silver salts.

Example I

A gelatino-silver bromide emulsion is made by preparing an aqueous solution of 13 parts of gelatin, adding 17 parts of ammonium bromide from a 3 normal aqueous solution, admixing 15 parts of silver nitrate from a 3 normal aqueous solution and digesting the resulting dispersion at 35° for about 30 minutes. One kilogram of the solution is then diluted to 5 kilograms of solution by the addition of an aqueous solution containing sodium dodecyl sulfate in an amount sufficient to constitute 5% by weight of the gelatin. The diluted dispersion is then added to a centrifuge having two bowls, one 3 and the other 5 inches in diameter, which is actuated for 10 to 15 minutes at about 3600 R. P. M. whereby the water, soluble salts and gelatin are removed. The precipitated silver salts are removed from the bowl, washed with warm water, diluted with water and again centrifuged.

A paste of eight parts of the silver bromide is made with 50 parts of distilled water and two parts of water containing ten per cent by weight of sodium dodecyl sulfate are added. The mixture is then added to an aqueous solution of 5 parts of the hydrophilic mixed acetal of polyvinyl alcohol with salicylaldehyde and ortho sulfobenzaldehyde having a molecular weight in excess of 10,000 and containing 35 to 50 salicylacetal groups per molecule and 1.25 parts of sodium hydroxide in 100 parts of water. The resulting redispersion is coated onto a cellulose derivative film base to form a thin layer and dried. The resulting film is exposed to an object in a camera or by printing through a transparency containing a picture image and developed in a solution of the following composition:

p-Aminodiethylaniline hydrochloride

	grams	2
Sodium sulfite	do	3
Sodium carbonate	do	20
Water	liter	1

made by dissolving the chemicals in about 500 parts of water and subsequent dilution to 1000 parts. It is then washed, bleached in 4% potassium ferricyanide and fixed whereby a strong blue-green image is obtained. A baryta coated paper is coated and dried in like manner. The resulting element is exposed to light from a transparency and developed and fixed in like manner whereby a print with a blue-green image is formed.

Example II

An ammoniacal silver nitrate solution is prepared by adding concentrated ammonium hydroxide to 10 parts of an aqueous solution containing 5.5 parts of silver nitrate until the precipitate of silver hydroxide disappears. Two parts of a one per cent aqueous diethylcyclohexylamine dodecyl sulfate solution is then added. The resulting solution and a solution of 6.6 parts of ammonium bromide, 0.3 part of potassium iodide and 0.02 part of said dodecyl sulfate in 30 parts of water are added simultaneously in fine streams to a stirred solution of four parts of gelatin in 75 parts of water. The temperature is held at 45° C. during the precipitation and for a period of 20 minutes thereafter. The resulting dispersion is diluted to about two per cent gelatin strength with water and centrifuged after the manner described in Example I. The silver halide-containing material is washed with water containing about one per cent of the aforesaid dodecyl sulfate several times while being centrifuged. It is removed from the bowl, washed with water and again centrifuged. The resulting mixed silver salts are free from all but mere traces of gelatin. A paste of ten parts of the silver salts with 50 parts of water and two parts of water containing ten per cent by weight of the aforesaid dodecyl sulfate was made which was slowly added with stirring to the following solution.

	Parts
Symmetrical bis-(m-(3-methyl-5-pyrazolon-1-yl) phenyl urea-formaldehyde polymer	5
Ethanol	10
Sodium hydroxide (5 N-aqueous)	2.0
Water to make	100

The above polymer was hydrophilic and was prepared in the following manner:

Thirty-six parts of m-aminophenylmethylpyrazolone are dissolved in 300 parts of five per cent sodium carbonate solution and stirred at 5–10° C. while adding a solution of ten parts of phosgene and 50 parts of dioxan. The insoluble precipitate is filtered, extracted with 300 parts of boiling ethyl alcohol and dried. Analyses calculated for $C_{21}H_{20}H_6O_3N$=20.8%. Found: N=19.7%. Nine parts of the bis-pyrazolone urea formed was dissolved in 150 parts of water and 20 parts of 20% sodium hydroxide added. The solution was then filtered and cooled to 0° C., next mixed with three parts of 40% formaldehyde solution, and kept at 10° C. for three hours. Five parts of saturated ammonia water were then added, the mixture allowed to stand for one-half hour and then the product was precipitated by acidifying with hydrochloric acid, filtered and then dried at 60° C. The hydrophilic color former produced is soluble in 20% ethyl alcohol containing a small amount of dilute sodium hydroxide solution.

The resulting composition is coated on a cellulose acetate film base, dried and exposed and processed after the manner given in Example I whereby a strong magenta dye image is formed.

Example III

The paste containing mixed silver bromide and iodide described in Example II was slowly added to the following solution:

	Parts
Acetal of polyvinyl alcohol with allylsalicylaldehyde and phthaldehydric acid	5
Dimethyl formamide	15
Sodium hydroxide (5-N-aqueous)	1.5
Water to make	150

(The above acetal is described in United States Patent No. 2,310,943, Example X.) The resulting composition is coated onto a cellulose acetate film base and a baryta coated paper and dried. The resulting elements are exposed to an object and developed by a reversal method as follows: They are treated for a period of five minutes with intermittent agitation in a non-color forming developer of the formula:

N-methyl paraaminophenol sulfate	grams	5.0
Hydroquinone	do	7.5
Sodium sulfite	do	60.0
Potassium bromide	do	4.5
Water to	ccs	1000.0

The element was washed, re-exposed to light and developed in a solution as described in Example II. After washing for 15 minutes in running water, the film is bleached in neutral potassium ferricyanide, rinsed, fixed in plain hypo, washed and dried. A reversed dye image remains at the points where the reversed silver image was formed.

In place of the hydrophilic polymers described in the previous paragraph there can be substituted similar amounts of the reaction product of m-aminophenylmethylpyrazolone and the mixed polymerizate from vinyl chloride and maleic anhydride (described in Example I of United States Patent No. 2,178,612), the condensation product from 1,5-aminonaphthol and the mixed polymerizate from vinyl chloride and maleic anhydride (described in Example II of United States Patent No. 2,178,612), the condensate obtained from polyvinyl alcohol acetalyzed with m-aminobenzaldehyde and condensed with phenylmethylpyrazolone carboxylic acid (described in United States Patent No. 2,320,422 in Example VIII), the condensation product obtained from polyvinyl alcohol acetalized with amino-benzaldehyde and amidated with acetoacetamino phenylcarboxylic acid (described in Example IX of United States Patent No. 2,320,422), etc., with similar results. Still other useful hydrophilic polymers are described in United States Patents Nos. 2,178,612; 2,186,734; 2,310,943; 2,307,399; and 2,320,422 and in copending applications Serial Nos. 528,943, now U. S. Patent No. 2,397,865 of April 2, 1946; 528,944, now U. S. Patent No. 2,423,460 of July 8, 1947; 528,945, now U. S. Patent No. 2,397,866 of April 2, 1946; and 528,946, now U. S. Patent No. 2,415,381 of Feb. 4, 1947. The last mentioned applications, moreover, describe practical methods for linking color formers to the polymers.

Various anionic surface active agents other than those described above may be used prior to or during the centrifuging or prior to the dispersion, in place of the sodium dodecyl sulfate of the examples. Suitable additional agents include water-soluble salts of alkyl sulfates of 10 to 24 carbon atoms with bases, e. g., alkali metal hydroxides, ammonia and amines, such as the sodium, potassium, ammonium, cyclohexylamine, dimethylamine, diethylamine, salts of decylsulfate, tetradecylsulfate, hexadecylsulfate, octadecylsulfate and similar salts of the corresponding sulfonic acids; alkali metal salts of alkylated naphthalene sulfonic acid, e. g., sodium isopropylnaphthalene sulfonic acids, etc., the sodium and potassium salts of stearic, palmitic, lauric and oleic acids, fatty acids of 10 to 24 carbon atoms, e. g., lauric, stearic, etc.

In place of the water-soluble halides described

above there may be substituted one or more of the following salts to form simple or mixed light-sensitive dispersions: LiBr, KBr, KCl, KI, NaI, NaCl, NH_4Cl, NH_4I. Similarly in place of silver nitrate may be substituted other soluble silver salts, e. g., silver sulfamate, silver acetate, silver fluoride, silver phosphate and silver citrate. In place of the gelatin there can be substituted other colloids, e. g., casein, albumen, agar-agar, gum arabic, etc.

Multilayer films for three-color photography can be made by depositing three of the color yielding silver salt dispersions successively onto a base. The layers and a yellow filter layer, for example, can be so sensitized and disposed that they each record about one-third of the visible spectrum. The hydrophilic synthetic polymeric dye intermediate for the respective light-sensitive layers should form a color complementary to the utilized sensitivity of the respective layers.

Various photographic emulsion constituents can be incorporated with the hydrophilic polymer dye intermediate dispersion if desired to increase their overall sensitivity, spectral sensitivity, allylthiourea, isothiocyanate, sodium thiosulfate. Suitable optical sensitizers are described in United States Patents Nos. 2,010,383; 2,079,376; 2,202,990; 2,202,991; 2,202,992; 2,278,461; and 2,265,908.

The photographic elements obtainable by practicing the invention have various advantages. For instance, light-sensitive layers which are uniform in quality can be obtained. In addition, the layers are not subject to bacterial putrefaction or decomposition. Thinner layers, as compared with gelatin layers, can be used which is of considerable importance because the resulting films have a higher degree of definition and resolution than is obtainable by the use of gelatin-color former layers. A maximum color density is produced from the silver salt reduced. Hence, a decided saving of silver halides is attained without sacrificing the quality of the dye images. Still other advantages reside in the fact that polymers can be employed which do not permit washing after precipitation of light-sensitive silver salts, e. g., silver bromide, within the polymer itself. Thus, polymers which are not satisfactory as a medium for the precipitation of silver halides can be used. Polymer-color formers requiring solvents other than water may be employed as the binding agent of the resulting polymer. Still other advantages will be apparent from the above description of the invention.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the details described herein except as set forth in the appended claims.

What is claimed is:

1. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting said solution and admixing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides and redispersing them in a synthetic hydrophilic color-forming hydroxyl polymer which contains 25 to 50 aliphatic hydroxyl groups and 1 to 35 color former nuclei per 100 chain carbon atoms, said hydroxyl groups being directly attached to the chain carbon atoms.

2. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting to a gelatin concentration of less than 5 per cent with water containing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides and redispersing them in a synthetic hydrophilic color-forming hydroxyl polymer which contains 25 to 50 aliphatic hydroxyl groups and 1 to 35 color former nuclei per 100 chain carbon atoms, said hydroxyl groups being directly attached to the chain carbon atoms.

3. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting to a gelatin concentration of less than 5 per cent with water containing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides, making an aqueous paste of the resulting silver halides and admixing said paste with an aqueous solution of a synthetic hydrophilic color-forming hydroxyl polymer.

4. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting to a gelatin concentration of less than 5 per cent with water containing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides, making an aqueous paste of such halides with an aqueous solution containing a small amount of the aforesaid wetting agent and admixing said paste with an aqueous alkaline solution of a hydrophilic color-forming polymer.

5. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting to a gelatin concentration of less than 5 per cent with water containing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides, making an aqueous paste of such halides with an aqueous solution containing a small amount of the aforesaid wetting agent and admixing said paste with an aqueous alkaline solution of a synthetic hydrophilic color-forming polymer.

6. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting to a gelatin concentration of less than 5 per cent with water containing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides, making an aqueous paste of such halides with water and anionic dispersing agent and admixing it with an aqueous alkaline solution of a synthetic hydrophilic color-forming hydroxyl polymer.

7. The process which comprises precipitating light-sensitive silver halides in an aqueous gelatin solution, diluting to a gelatin concentration of less than 5 per cent with water containing a small amount of an anionic surface active agent containing a lipophilic group of at least 8 carbon atoms and a hydrophilic group, centrifuging off the gelatin, washing the light-sensitive silver halides, making an aqueous paste of such halides

with water and anionic dispersing agent and admixing it with an aqueous alkaline solution of a polyvinyl acetal of an aromatic aldehyde capable of coupling with a diazo compound to form an azo dye.

OTIS WILLARD MURRAY.

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