

2,752,246

PROCESS OF PREPARING A LIGHT SENSITIVE SILVER HALIDE EMULSION

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This invention relates to photography and, more particularly, to the preparation of photosensitive silver halides in a form especially well suited for use in photographic dispersions or emulsions.

In the preparation of photographic dispersions of silver halides in a polymeric colloid binder, the usual procedure has involved the formation of the silver halide crystals in an aqueous solution of the binder. Gelatin has been widely used as the binder because it possesses many desirable properties, especially its sensitizing effect on the silver halide grains and its influence on the crystal growth of the silver halides. The high sensitivity of gelatin-silver halide emulsions is believed to be partially due to the presence in the emulsions of flat, well-shaped, geometric silver halide crystals.

However, gelatin possesses some undesirable properties; for example, it is brittle, unstable, susceptible to the action of mold, bacteria, etc., especially in an atmosphere of high humidity and is a natural product and hence subject to wide variations in its properties. Therefore, attempts have been made to replace it with other types of polymeric colloid binders including water-soluble cellulose derivatives, polycarbonamides, and synthetic hydroxyl-containing polymers, e. g., polyvinyl alcohol and polyvinyl acetals. The latter have been found suitable in many respects for this purpose, and do not possess the aforementioned defects of gelatin. However, silver halide dispersions prepared in the presence of synthetic polymeric colloid binders have not contained the flat, well-shaped silver halide crystals obtainable in gelatin and photographic emulsions containing such crystals have not possessed the high sensitivity and photographic speed desired for certain types of photographic films and papers. Furthermore, preparation of silver halide dispersions in gelatin or any high molecular weight polymeric binder involves gelation or coagulation, shredding and washing or some similar time-consuming operation.

It has now been found that silver halide dispersions especially suitable for use in the preparation of photographic silver halide-protective colloid dispersions and photographic layers can be prepared by the process of this invention. This process, in its broader aspects, comprises precipitating silver halides in an aqueous solution containing from 1% to 30% of the weight of the silver halides of a non-ionic, surface-active dispersing agent containing at least 6 intralinear oxyalkylene groups of 2 to 3 carbon atoms and a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms containing an alkyl radical of at least 4 carbon atoms, and ripening the resulting dispersion of silver halides. The process is carried out in the substantial absence of actinic light and water-permeable colloids. The dispersing agent is the sole type of polymeric compound in the solution.

Suitable surface-active dispersing agents are condensation products of an alkylene oxide or a poly(alkylene oxide), wherein the alkylene radical contains 2 to 3 carbon atoms, with a water-insoluble organic compound containing an active hydrogen atom or replaceable hy-

drogen atom attached to a noncarbon atom, e. g., O, S, or N. Among such water-insoluble compounds there may be mentioned aliphatic monohydric alcohols including alkanols of 8 to 18 carbon atoms and mixtures of 2, 3 or more of such alkanols, and oleyl alcohol; fatty acids of 12 to 18 carbon atoms and mixtures of 2, 3 or more of such acids, and oleic acid; abietic acid; alkylphenols wherein the alkyl group or groups contain 4 to 18 carbon atoms, e. g., octylphenol, decylphenol, and diisobutylphenol; saturated aliphatic primary amines of 8 to 18 carbon atoms, e. g., octyl, decyl, dodecyl, tetradecyl, and octadecyl amines and mixtures thereof; and amides, e. g., lauric, stearic, palmitic, and oleic acid amides and mixtures of such amides.

In the preferred aspect of the invention, the non-ionic surface-active dispersing agents are condensation products of at least 10 moles of ethylene oxide with one mole of a monohydric alcohol of at least 10 carbon atoms, e. g., decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and oleyl alcohols or a mixture of 2, 3 or more of such alcohols, or with an alkylphenol having at least 10 carbon atoms, e. g., isobutylphenol, and diisobutylphenol, or a mixture of these.

The process of this invention is conveniently carried out by mixing a dilute aqueous solution of soluble inorganic halides, e. g., ammonium bromide, potassium iodide, and potassium chloride, or mixtures of any of these, and a condensation product of an alkylene oxide and an alcohol or phenol, etc., as defined above, with a dilute aqueous solution of a water-soluble silver salt, e. g., silver nitrate, silver sulfate, silver sulfamate, silver citrate, silver acetate, or a mixture of 2, 3 or more of such salts. After the two solutions are mixed together, the mixture is allowed to ripen at ordinary or moderately elevated temperatures, e. g., 25° C. to 50° C. until the silver halide grains develop the desired size and shape. The growth of the grains can be followed by microscopic examination. In general, ripening times of from one-half hour to four hours are sufficient to produce silver halide grains having a substantial proportion of the flat, geometric shaped grains which are similar to those formed in the presence of gelatin. In general, the longer ripening times tend to produce the larger crystals which are especially useful in high-speed photographic emulsion layers.

If desired, the precipitating solutions can contain from 1% to 20% by weight of the water of a water-miscible organic solvent, e. g., alcohols such as methanol, ethanol, etc., or glycerol.

The silver halide grains produced by the process of this invention can be separated from the aqueous medium and washed free of soluble salts by conventional methods, e. g., by decantation or centrifugation.

The washed silver halide grains can be used to prepare photographic emulsions by dispersing them in an aqueous solution of a protective colloid binder, e. g., gelatin, casein, albumin; synthetic protective colloids, e. g., polyvinyl alcohol, low-substituted polyvinyl acetals, polyvinyl acetal color formers, water-soluble polyamides, water-soluble cellulose derivatives, and the like.

Photographic emulsions can also be prepared by adding the protective colloid binder directly to the ripened dispersion of silver halides formed by the process of this invention without isolating and washing the silver halide grains. In this modification, the emulsion can be coagulated or gelled by conventional means, the resulting coagulum or gel shredded, and the shreds washed free of soluble salts with water by the usual methods.

Photographic emulsions prepared from the silver halide crystals obtained by the process of this invention have good photographic quality and are suitable for coating on conventional photographic supports, e. g., transparent

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film base, glass plates, and paper. In these emulsions the bulk of the silver halide grains range in size from 0.2 to 4.0 microns in diameter.

The invention is further illustrated by the following examples which are carried out in the absence of actinic radiations and in which proportions of ingredients are expressed in parts by volume unless otherwise noted.

Example I

A solution of 23 parts of 3 N aqueous ammonium bromide, 1.2 parts of 0.5 N aqueous potassium iodide, and 3 parts of a 10% aqueous solution of the condensation product of 1 mole of sperm oil alcohols consisting largely of C₁₄ to C₁₈ alcohols, mainly cetyl, octadecyl and oleyl alcohol, and about 20 moles of ethylene oxide is mixed with a solution of 10 parts of 3 N aqueous silver nitrate (solubilized with 20% aqueous ammonia) and sufficient water to make a total of 100 parts. The dispersion is stirred for about 10 seconds and then allowed to stand at 30° C. for a period of two hours. At the end of this time, the silver halide grains are seen to contain a substantial proportion of thin geometric shaped crystals when examined under a microscope. The halide grains after separation and washing free of soluble salts by decantation, are suitable for dispersing in a solution of a protective colloid to form a photographic emulsion for coating on paper or on a transparent film base.

Example II

The process of Example I is repeated with the exception that the dispersion is allowed to stand at 30° C. for a period of four hours. The resulting dispersion contains a higher concentration of large, flat-appearing grains.

Example III

A solution of 23 parts of 3 N aqueous ammonium bromide, 1.2 parts of 0.5 N aqueous potassium iodide, and 5 parts of a 10% solution of the condensation product of 1 mole of octylphenol with approximately 12 moles of ethylene oxide, in 100 parts of glycerol, is mixed with a solution consisting of 20 parts of 3 N aqueous silver nitrate (solubilized with aqueous 20% ammonium hydroxide) and sufficient water to make a total of 100 parts. The dispersion is stirred briefly and allowed to stand for 30 minutes at 50° C. The resulting silver halide grains contain thin-appearing grains when examined under a microscope. The silver halide crystals are separated by centrifugation and, after washing by decantation, are suitable for dispersing in a protective colloid solution for use as a photographic emulsion.

Example IV

A solution of 23 parts of 3 N aqueous ammonium bromide, 1.2 parts of 0.5 N aqueous potassium iodide, and 5 parts of a 10% aqueous solution of the condensation product of Example I is mixed with a solution of 10 parts of 3 N aqueous silver nitrate (containing sufficient 20% ammonium hydroxide to solubilize the silver nitrate) and sufficient water to make a total solution of 100 parts. After a brief stirring period, the dispersion is allowed to stand at 40° C. for five hours, then a solution of 10 parts of 3 N aqueous silver nitrate and sufficient water to make a total of 50 parts is added. After stirring for 15 minutes, the silver halide particles are well dispersed and are suitable for conversion to a photographic emulsion by the addition of an aqueous solution of a protective colloid, such as polyvinyl alcohol.

Example V

A solution of 23 parts of 3 N aqueous ammonium bromide, 1.2 parts of 0.5 N aqueous potassium iodide, and 5 parts of a 10% aqueous solution of the condensation product of approximately 15 moles of ethylene oxide with 1 mole of the amides of a mixture of coconut oil acids consisting mainly of lauric acid with minor amounts

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of myristic, palmitic and oleic acids, is mixed with a solution of 10 parts of 3 N aqueous silver nitrate (containing sufficient 20% ammonium hydroxide to solubilize it) and water to make a total of 50 parts. After stirring for 10 seconds, the dispersion is allowed to stand at 30° C. for three hours. The crystals are separated and washed by decantation and are suitable for use in the preparation of photographic emulsions.

Example VI

The process of Example V is repeated with the single exception that the dispersing agent of that example is replaced with an equal quantity of a reaction product ethylene oxide with abietic acid containing more than 9 intralinear oxyethylene groups. The resultant silver halide dispersion is essentially the same as that of Example V.

Example VII

A solution of 46 parts of 3 N aqueous ammonium bromide, 2.5 parts of 0.5 N aqueous potassium iodide, 50 parts of water and 25 parts of a 10% aqueous solution of the condensation product of 1 mole of oleyl alcohol and approximately 20 moles of ethylene oxide is stirred at 30° C. while adding a solution consisting of 20 parts of 3 N aqueous silver nitrate converted to the soluble complex with ammonium hydroxide, and 200 parts of water. The dispersion of silver halide is stirred at 30° C. for 30 minutes then treated with a solution of 20 parts of 3 N silver nitrate and 80 parts of water. Stirring is continued at 30° C. for an additional 30 minutes then the dispersion is allowed to stand without stirring for 15-30 minutes to allow the silver halide crystals to settle.

The supernatant liquid is decanted from the above precipitate of silver halide crystals and about 200 parts of a 5% aqueous solution of a mixed benzaldehyde/sodium o-sulfobenzaldehyde polyvinyl acetal containing 13% benzaldehyde groups and 7% o-sodium sulfobenzaldehyde groups is added with stirring to disperse the halides. The resulting photographic emulsion, when examined under a microscope, is seen to contain a high percentage of thin, flat, geometrically shaped silver halide grains in a highly dispersed condition. The bulk of these silver halide grains are found to range in size from 0.2 micron to 4.0 microns in diameter. This emulsion is treated with a small amount of C-cetyl betaine to improve its spreading characteristics and its viscosity is adjusted by adding water preparatory to coating in order to obtain the desired coating weight. The finished emulsion is coated on transparent film base and dried. A sample of the material is exposed photographically and developed in an aqueous solution made by diluting with two parts of water a developer of the following composition:

Water	-----cc--	500
p-Dimethylaminophenol sulfate	-----grams--	1.5
Sodium sulfite (anhydrous)	-----do----	22.5
Hydroquinone	-----do----	6.3
Sodium carbonate (anhydrous)	-----do----	15.0
Potassium bromide	-----do----	1.5
Water to make	1 liter.	

Unreduced silver halides are eliminated by treating with a 20% solution of sodium thiosulfate followed by washing. There remains a black (silver) image of good quality which is the negative of the object to which the film was exposed.

Example VIII

To the precipitated silver halides prepared as described in Example VII is added 300 parts of a 10% aqueous solution of gelatin, and the mixture is stirred to disperse the halides. The resulting photographic emulsion, when examined under a microscope, is seen to contain a high percentage of thin, flat, geometrically shaped grains in a highly dispersed condition. These halide grains are found to range predominantly in size from 0.2 micron to 3.0 microns in diameter.

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The process of this invention has been illustrated in the examples with specific mention of certain nonionic dispersing agents. However, the process is not limited to the use of these specific agents, but can be carried out with any of the above condensation products of at least 6 moles, and preferably 10 moles, of an alkylene oxide having 2 to 3 carbon atoms, i. e., ethylene and propylene oxides, with a water-insoluble organic compound having a replaceable hydrogen atom attached to a noncarbonic atom which, in turn, is attached directly to a carbon atom. Among the particularly useful condensation products which can be substituted in the examples are condensation products of 16 moles of ethylene oxide with octadecyl alcohol, 15 to 20 moles of propylene oxide with diisobutylphenol, 6 to 10 moles of propylene oxide with dodecyl alcohol, 12 moles of ethylene oxide with oleic acid, 10 to 20 moles of ethylene oxide with stearic acid, 40 moles of ethylene oxide with stearic acid, and 20 moles of ethylene oxide with propylene glycol monostearate.

Many of the surface-active dispersing agents useful in the process of this invention are available commercially. Methods for condensing the alkylene oxides with the water-insoluble compounds having active hydrogen atoms may be found in U. S. Patents 1,970,578, 2,085,706, 2,129,709, 2,454,542, and British Patent 358,114. The surface-active dispersing agents can also be obtained by reacting a lower polymer of the alkylene oxide with the alcohol, mercaptan, amine, amide or phenol instead of condensing the monomeric alkylene oxide in the presence of the alcohol, amine, amide or phenol, as described in U. S. Patent 2,069,336. Polymers obtained by condensing the reaction product of the alkylene oxide and the replaceable hydrogen-containing compound with formaldehyde are also useful in preparing silver halide dispersions.

The proportions of nonionic dispersing agent used in preparing the silver halide dispersions of this invention can vary widely, proportions ranging from 1% to 30% of the weight of the silver halides being operable. Very satisfactory results are obtained when these dispersing agents amount to from 10% to 20% of the weight of the silver halides.

This invention provides a new process of preparing silver halides for photographic purposes. The process of this invention is especially advantageous in the preparation of silver halides to be used in photographic emulsions having synthetic colloid binders, and particularly polyvinyl alcohol and polyvinyl acetals of the type described in Jennings et al. U. S. Patent 2,397,864, since ripened silver halide grains capable of giving high sensitivity are difficult to prepare in the presence of many of these particular binders. In the present process, silver halide grains having the desired shape for optimum photographic sensitivity are first prepared and then added to the particular synthetic binder desired in the photographic emulsion. The process of this invention also possesses advantages when the silver halide grains are to be used in gelatin emulsions since it simplifies the emulsion preparation. By employing this process, it is not necessary to disperse the silver halides in the gelatin, then chill the emulsion, shred it, and then wash the shreds free of soluble salts, which are time-consuming operations.

What is claimed is:

1. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent containing at least 6 intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom taken from the group consisting of O, S and N atoms to a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms containing an alkyl radical of at least 4 carbon atoms.

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2. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent containing at least 6 intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom taken from the group consisting of O, S, and N atoms to a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms containing an alkyl radical of at least 4 carbon atoms and ripening the resulting dispersion of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours.

3. A process as set forth in claim 2 wherein said process is carried out in the substantial absence of actinic light.

4. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent comprising the condensation product of ethylene oxide and octylphenol, said product containing at least 10 intralinear oxyethylene groups linked through the oxygen atom of said octylphenol, and ripening the resulting dispersion of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours, said process being carried out in the substantial absence of actinic light.

5. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent comprising the condensation product of ethylene oxide and a saturated aliphatic monohydric alcohol of 8 to 18 carbon atoms, said product containing at least 6 intralinear oxyethylene groups linked through the oxygen atom of said alcohol, and ripening the resulting dispersing of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours, said process being carried out in the substantial absence of actinic light.

6. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymer constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent comprising the condensation product of ethylene oxide and a mixture of sperm oil alcohols said product containing at least 10 intralinear oxyethylene groups linked through the oxygen atoms of said alcohols, and ripening the resulting dispersion of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours, said process being carried out in the substantial absence of actinic light.

7. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent comprising the condensation product of ethylene oxide and a mixture of amides of coconut oil acids, said product containing at least 10 intralinear oxyethylene groups linked to the nitrogen atoms of said amides, and ripening the resulting dispersion of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours, said process being carried out in the substantial absence of actinic light.

8. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent comprising the condensation product of ethylene oxide and abietic acid, said product containing at least 10 intralinear oxyethylene groups linked to the —COO— group of said acid, and ripening the resulting dispersion of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours, said

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process being carried out in the substantial absence of actinic light.

9. The process of preparing light-sensitive silver halides which comprises precipitating silver halides in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halides of a nonionic surface-active dispersing agent comprising the condensation product of ethylene oxide and oleyl alcohol, said product containing at least 10 intralinear oxyethylene groups linked to the oxygen atom of said alcohol, and ripening the resulting dispersion of silver halides at 20° C. to 50° C. for a period of ½ to 4 hours, said process being carried out in the substantial absence of actinic light.

10. The process of preparing photographic emulsions which comprises precipitating silver halide in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halide of a nonionic surface active dispersing agent containing at least 6 intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom taken from the group consisting of O, N and S atoms to a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms containing an alkyl radical of at least 4 carbon atoms, ripening the resulting dispersion of silver halide at 20° C. to 50° C. for a period of ½ to 4 hours and admixing with the ripened silver halide a protective colloid binder.

11. A process as set forth in claim 10 wherein said dispersing agent is a condensation product of ethylene oxide and octylphenol, said product containing at least 10 intralinear oxyethylene groups linked through the oxygen atom of said octylphenol.

12. A process as set forth in claim 10 wherein said dispersing agent is the condensation product of ethylene oxide and oleyl alcohol, said product containing at least 10 intralinear oxyethylene groups linked through the oxygen atom of said alcohol.

13. A process as set forth in claim 10 wherein said protective colloid is polyvinyl alcohol.

14. A process as set forth in claim 10 wherein said protective colloid is a polyvinyl acetal.

15. A process as set forth in claim 10 wherein said protective colloid is gelatin.

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16. The process of preparing photographic emulsions which comprises precipitating silver halide in an aqueous solution containing as the sole organic polymeric constituent from 1% to 30% of the weight of the silver halide of a nonionic surface active dispersing agent containing at least 6 intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom taken from the group consisting of O, N and S atoms to a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms containing an alkyl radical of at least 4 carbon atoms, ripening the resulting dispersion of silver halide at 20° C. to 50° C. for a period of ½ to 4 hours, washing the ripened silver halide grains, separating the washed grains from the aqueous medium and dispersing the washed grains in an aqueous solution containing a protective colloid binding agent.

17. A process as set forth in claim 16 wherein said dispersing agent is a condensation product of ethylene oxide and octylphenol, said product containing at least 10 intralinear oxyethylene groups linked through the oxygen atom of said octylphenol.

18. A process as set forth in claim 16 wherein said dispersing agent is the condensation product of ethylene oxide and a saturated aliphatic monohydric alcohol of 8 to 18 carbon atoms, said product containing at least 6 intralinear oxyethylene groups linked through the oxygen atom of said alcohol.

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