

## UNITED STATES PATENT OFFICE

2,688,601

## PREPARATION OF SILVER DISPERSIONS

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No Drawing. Application September 27, 1951,  
Serial No. 248,637

6 Claims. (Cl. 252—313)

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This invention relates to methods for the preparation of dispersions of silver and more particularly, to dispersions of silver absorbing light of the visible spectrum of wave lengths longer than blue light.

It is well known that silver salts, such as silver nitrate, can be readily reduced in aqueous gelatin solutions to yield colloidal dispersions of silver whose color is dependent, for the most part, upon the degree of dispersion of the silver particles. For example, silver salt reducing agents such as p-phenylenediamine and hydroquinone will readily reduce silver nitrate in aqueous gelatin solution to produce a yellow colloidal dispersion of silver. Dispersions of this type have been suggested for use in photographic materials, for example, as integral filter layers in light-sensitive multilayer photographic color films for the purpose of shielding certain emulsion layers from blue light. Such dispersions have also been suggested for use in antihalation layers on the back of multilayer color films for the purpose of preventing halation caused by the reflection of scattered rays of light from the surface of the film support. However, since yellow-colored antihalation layers, such as those containing the Carey-Lea silver dispersion, do not absorb the longer wave lengths of light, a yellow antihalation layer does not adequately protect a panchromatic photographic film from halation effects. Accordingly, dark or neutrally-colored antihalation layers are necessary for color films.

Blue or gray-colored dispersion of silver is particularly suitable for antihalation purposes on color films since it is readily removable in the photographic color process along with silver images which are customarily removed from color films to leave only the dye images. It is free from any tendency to diffuse from one layer to another, and has no harmful effect on emulsion.

As previously mentioned, the conventional method of reducing silver salts produces yellow-colored colloidal dispersions of the metal. Attempts to employ prior methods indicating the possibility of forming blue or neutral-colored silver dispersions resulted in unstable dispersions of silver. That is, when silver nitrate was reduced in aqueous gelatin solution, using hydroquinone as the reducing agent, I found that a yellow-colored dispersion was readily obtained but when I attempted to make a coarser dispersion which would be approximately neutral in color, the dispersion of silver not only gradually changed in color but the silver gradually settled out of the dispersion.

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One object of my invention is, therefore, to provide a method for preparing a stable dispersion of silver suitable for use in making photographic antihalation or filter layers.

The objects of my invention are accomplished by providing the methods by which the stable silver dispersions of blue or neutral color can be prepared.

My process involves the discovery that it is essential that the reduction of a water-soluble silver salt be carried out in the presence of gelatin, a calcium salt and an alkali-metal sulfite and that certain of the ingredients must be combined in a definite fashion.

My invention stems in part from the discovery that when gelatins prepared by different methods and from different sources were used in making silver dispersions by the reduction of silver nitrate with hydroquinone in the presence of an alkali-metal sulfite, the only stable dispersions obtained were those in which a calcium salt had been present in the original gelatin used in the reaction mixture or when the calcium salt had been intentionally added to the reaction mixture. Furthermore, I found that it was not only necessary to reduce the silver salt in the presence of sulfite, but that there should be a minimum delay between addition of sulfite and reducing agent. Presumably silver sulfite is first precipitated as a very fine dispersion, then reduced to metal, but the sulfite is unstable and should be reduced before it undergoes any change. My invention does not, of course, depend on the truth of this hypothesis. I found that it was possible to add the sulfite first to the silver nitrate-containing solution and then add the reducing agent to the solution within a period of one minute thereafter, or the reducing agent and sulfite can be added simultaneously, as in a single solution, to the silver nitrate-containing solution.

Representative methods of carrying out my invention will be understood by consideration of the following examples:

*Example 1.*—An aqueous 10 percent gelatin solution containing 228 grams of a high jelly strength non-hydrolyzed bone or hide gelatin was made. The gelatin used contained calcium salts. This solution was then adjusted to a pH of 8.0 and a solution containing 92 grams of silver nitrate in 184 cc. of water was added at 40° C. To this solution now at a pH of 5.5 and a temperature of 40° C. was then added with vigorous agitation within not more than 10 seconds, 850 cc. of an aqueous solution containing 63 grams of sodium sulfite and 45.5 grams of

hydroquinone. The reduction of the silver compound appeared to be complete within ten minutes. Upon standing, the resultant silver dispersion showed no tendency for the silver particles to settle out. The dispersion was bluish gray in color and contained a higher concentration of silver in this range of particle size than it had been possible to prepare by any known method. When the dispersion was coated so as to yield 12.5 mg. of silver per square foot, the optical density of the coating was 1.0 as measured with light of wave length 690  $m\mu$  and a density of 0.5 measured with light of wave length 460  $m\mu$ .

*Example 2.*—A 20 percent gelatin solution was made by dissolving 228 grams of a highly hydrolyzed filtered bone or hide gelatin having the physical characteristics of glue and adjusting the pH to 8.0. There was then added at 40° C. with constant stirring a solution containing 22 grams of silver nitrate in 184 cc. of water. To this solution at 40° C. was then added first a solution of 63 grams of sodium sulfite in 400 cc. of water followed within five seconds by a solution of 45.5 grams of hydroquinone in 455 cc. of a 20 percent methyl alcohol-water solution. Addition of sulfite and hydroquinone solutions were made rapidly accompanied by vigorous stirring. The resulting silver dispersion possessed absorption characteristics similar to the silver dispersion prepared as described in Example 1.

In a similar manner, when the time interval between the addition of sodium sulfite and hydroquinone solutions was increased from five seconds to one minute, the color of the resulting silver dispersion was such that the maximum density of a coating made therefrom was at a wave length of 560  $m\mu$ . When the time interval was increased to ten minutes, the resulting dispersion was yellow with a maximum density at 450  $m\mu$ .

Similarly, it was ascertained that if the gelatin was delimed, for example, by washing with acid to remove calcium salts and other acid-soluble impurities, and the reduction of the silver salt was carried out in the absence of any substantial amount of calcium salt only the yellow type of silver dispersion was obtained.

*Example 3.*—80 cc. of a 20 percent solution of a highly hydrolyzed, filtered and delimed bone gelatin was adjusted to a pH of 8.0. A solution of 6.4 grams of silver nitrate in 15 cc. of water was then added to the gelatin solution followed by one cc. of a 10 percent solution of calcium acetate. This solution was then diluted with water to 280 cc., pH 5.5, and then at 40° C. with vigorous agitation, 60 cc. of an aqueous solution containing 4.45 grams of sodium sulfite (desiccated) and 2.2 grams of hydroquinone was added. The resulting silver dispersion was found to be stable and possessed the spectral absorption characteristics similar to the silver dispersion prepared as described in Example 1.

In the above examples it is desirable to wash the soluble salts and by-products of the reaction from the silver dispersion before using the dispersion for coating photographic antihalation layers. These procedures are particularly desirable when the silver dispersion is to be incorporated into a second vehicle such as partially hydrolyzed cellulose acetate or cellulose acetate phthalate before coating the antihalation layer on to a cellulose ester support. When it is desired to wash the silver dispersion, this can be accomplished by the well known procedure of setting the dispersion, shredding, washing the

gel, and remelting it before use or by a coagulation procedure as in Example 4.

*Example 4.*—750 cc. of an aqueous solution of 75 grams of de-ashed gelatin was adjusted to pH 9.2 with sodium hydroxide and then warmed to 40° C. To this solution was then added a solution of eight grams of calcium acetate in 40 cc. of water followed by the addition of 80 grams of silver nitrate dissolved in 160 cc. of water, and the resulting solution was diluted to 1000 cc. 55 grams of anhydrous sodium sulfite were dissolved in 350 cc. of water. 40 grams of hydroquinone were dissolved in 35 cc. of boiling methyl alcohol and 40 cc. of water. The sulfite and hydroquinone solutions were then mixed and the resultant solution made up to 1000 cc. with water. A third solution was made by dissolving 25 grams of de-ashed gelatin in water, adjusting the pH to 9.2 and diluting the solution with water to a volume of 1000 cc. To this gelatin solution was then added simultaneously the silver nitrate-containing gelatin solution and the sulfite-hydroquinone solution in ten seconds with vigorous stirring, and the stirring continued for about ten minutes, during which time reduction was complete. The resulting dispersion which was neutral in color was then coagulated by adding 800 grams of anhydrous sodium sulfate and 30 cc. of concentrated hydrochloric acid in 4000 cc. of water. The coagulum was allowed to settle and was then chilled. After drawing off the supernatant liquid, the coagulum was rinsed several times with cold distilled water, drained, remelted and allowed to set. Thereafter, the coagulum was shredded and again washed with cold water, then washed with a solution of ten grams sodium sulfite and 0.3 gram of sodium hydroxide per liter, then washed with a solution of ten grams of glacial acetic acid per liter. Washing was then continued with cold distilled water until no precipitate was obtained in the wash water on addition of a solution of barium salt.

One advantage residing in the process of my invention resides in the fact that the results of the process are reproducible. That is, the procedures can be repeated in large-scale operation with the expectation that each new batch of silver dispersion will possess the physical properties set forth above.

It has been ascertained that the silver dispersions prepared as above described contained more than 50 percent of silver particles which are visible under ordinary microscopic examination and are not colloidal in the standard sense. Accordingly, the dispersions of my invention differ materially from the yellow dispersions of silver in which the greater part of the silver particles are submicroscopic in size and therefore are properly termed colloidal silver dispersions.

In the broadest aspects of my invention, as shown by the above examples, I use an amount of alkali-metal sulfite, compared to the water-soluble silver salt such as silver nitrate, equivalent to at least 0.5 mol. Thus, the amount of sulfite used should be sufficient to react with all of the silver nitrate. However, equal molecular proportions of the silver salt and the sulfite can be used to produce satisfactory dispersions. The amount of the silver salt reducing agent which is employed, such as hydroquinone, is not especially critical except that it is desirable to use an excess of the reducing agent. That is, for example, in the case of hydroquinone, satisfac-

tory results can be obtained using from about 60 to 120 grams of hydroquinone per mol of silver nitrate. Similar molecular proportions of the other silver salts and reducing agents can be employed.

The reduction of the silver salt can be carried out in the manner of my invention, above described, at a temperature from about 35 to 40° C.; however, useful results can be obtained at temperatures of operation of the order of 60° C. The process can be operated conveniently within a pH range of from about 7.5 to 10, preferably 8 to 9.5. The concentration of calcium salt present in ordinary gelatins made from limed stock is adequate, but in case a gelatin from other sources is used, it is desirable to add soluble calcium salts to produce a concentration of at least 0.0017 mol per liter of reaction mixture. The presence of compounds reacting with silver salts to give silver sulfide is also favorable to formation of a neutral or blue silver dispersion. The compounds present in an ordinary untreated gelatin frequently are sufficient to be useful: if a deashed or other gelatin of low photographic activity is used, addition of compounds like sodium thiosulfate may assist in controlling the dispersion of the silver. However, it is possible, as shown by the examples, to obtain a neutral or bluish dispersion in a deashed gelatin with addition of calcium salts only. Obviously, excessive quantities of the reducing agent, sulfite and calcium compound are to be avoided, particularly when one desires to wash a coagulum of the silver dispersion to free the dispersion of excess reactants and by-products, as in the method of Example 4. Other water-soluble silver salts besides silver nitrate can be used in the process, for example, silver perchlorate; and other calcium salts having an anion which does not precipitate a difficultly soluble silver salt, for example calcium nitrate.

I claim:

1. A method of preparing a stable dispersion of silver comprising subjecting an aqueous gelatin solution of a mixture of a water-soluble silver salt, at least one-half molecular equivalent of an alkali metal sulfite, based on the silver salt, and at least about 0.0017 mol of a water-soluble calcium salt per liter of reaction mixture, to the action of an excess of a silver salt reducing agent within approximately one minute of mixing said silver salt and alkali metal sulfite.

2. A method of preparing a stable dispersion of silver comprising subjecting an aqueous gelatin solution of a mixture of a water-soluble silver salt, at least one-half molecular equivalent of an alkali metal sulfite, based on the silver salt and at least about 0.0017 mol of a water-soluble calcium salt per liter of reaction mixture, to the

action of an excess of a silver salt reducing agent simultaneously to mixing said silver salt and alkali metal sulfite.

3. A method of preparing a stable dispersion of silver comprising subjecting an aqueous gelatin solution of a mixture of a water-soluble silver salt, at least one-half molecular equivalent of an alkali metal sulfite, based on the silver salt and at least about 0.0017 mol of a water-soluble calcium salt per liter of reaction mixture, to the action of an excess of a silver salt reducing agent within one minute after mixing said silver salt and alkali metal sulfite.

4. A method of preparing a stable dispersion of silver comprising mixing an aqueous gelatin solution containing silver nitrate and at least about 0.0017 mol of calcium acetate per liter of reaction mixture, with an aqueous solution of an excess of hydroquinone and at least one-half molecular equivalent of sodium sulfite based on the silver nitrate, the temperature of the reaction mixture being about 35-40° C. and the pH about 7.5-10.

5. A method of preparing a stable dispersion of silver comprising adding to an aqueous gelatin solution of silver nitrate containing at least about 0.0017 mol of calcium acetate per liter of reaction mixture, an aqueous solution of at least one-half molecular equivalent of sodium sulfite based on the silver nitrate, then within one minute adding an aqueous solution containing an excess of hydroquinone, the temperature of the reaction mixture being about 35-40° C. and the pH about 7.5-10.

6. A method of preparing a stable dispersion of silver comprising simultaneously adding an aqueous gelatin solution containing about 2.7 grams of calcium acetate per liter of reaction mixture and silver nitrate, and an aqueous gelatin solution containing an excess of hydroquinone and at least one-half molecular equivalent of sodium sulfite based on the silver nitrate, to an aqueous gelatin solution within a period of less than one minute, the temperature of the reaction mixture being about 35-40° C. and the pH about 7.5-10, coagulating the resulting dispersion and washing the coagulum until substantially free of excess reactants and by-products.

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