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PROCESS OF PRECIPITATING SILVER

Bela Gaspar, Beverly Hills, Calif., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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The present invention relates to the manufacture of colloidal silver and is particularly concerned with a photographic material in which such colloidal silver is utilized, for example, in a filter layer or an antihalation layer.

In the preparation of colloidal silver, chemical reducing agents are used for the purpose of reducing a silver salt to metallic silver. For many purposes such as photographic or pharmaceutical use, or for other chemical applications, for instance where such colloidal silver is used as a catalyst, the presence of residual reducing agent may have an adverse effect, and it is thus very important to remove the excess residual reducing agent from the reaction mixture, or to transform such residual reducing agent into an innocuous, non-reducing form either by decomposing or by neutralizing such reducing agent. For example, photographic colloidal silver layers which are made with the aid of reducing agents such as hydrazines, aryl hydrazines or alkaline sugar solutions generally contain residual reducing agents which have a fogging action on the adjacent photographic silver halide emulsion layers.

The chief object of this invention is the preparation of colloidal silver free of residual or excess reducing agent, and also free from reaction by-products and contaminants.

An important object is to provide a simple and economic procedure for the preparation of colloidal silver free of residual reducing agent.

A further object is to provide colloidal silver compositions and photographic colloidal silver layers free of the reducing agent employed in the preparation of the colloidal silver.

Other objects and advantages of the invention will appear hereinafter.

The above objects are achieved according to the invention by reducing a silver salt under mild reducing conditions with a salt of a borohydride in a solvent medium. The reaction is carried out in preferred manner by adding to a solution of a silver salt such as silver nitrate, a soluble salt of a borohydride, preferably an alkali metal borohydride such as sodium or potassium borohydride. In preferred practice, although not necessarily, the reduction reaction is carried out in the presence of a protective colloid such as gelatin. If desired, however, the protective colloid can be omitted provided that the silver salt is reduced with the borohydride in a sufficiently dilute solution.

After the reduction reaction is performed the excess reducing agent can be washed from the colloidal silver, or such excess reducing agent can be destroyed simply by ventilating it with air or oxygen, e.g., by permitting the solution to stand for an extended period in the air until all the residual borohydride is oxidized to a borate which has no reducing properties, or by decomposing the borohydride to hydrogen and to boric acid by acidifying it, e.g., with sulfuric, hydrochloric or acetic acid.

It will be apparent that factors such as temperature and concentration of silver salt and salt of the borohydride, and the quantity and nature of the protective colloid, when used, can be varied over a wide range. A typical procedure for preparing colloidal silver according to the invention is to add one hydrogen equivalent of a sodium borohydride to a solution of a silver salt such as, for example, silver nitrate, silver acetate, silver sulfate, or any other soluble silver salt, preferably but not necessarily, in the presence of a protective colloid such as gelatin. The equivalent weight of borohydride for reducing the silver salt is a quarter mol of borohydride based on $NaBH_4$, for each mol of silver salt. Thereafter chilling, washing and gelling, or precipitating, the colloidal silver in the solution is carried out in order to remove the residual salts. If desired, the protective colloid can also be removed by filtration, washing, centrifugation, or by chemical decomposition.

For best results in carrying out my invention I have found it desirable to use an excess of the borohydride salt solution, e.g., about 10–100% in excess of the equivalent weight for reducing the silver salt. I have found it also advantageous to use the borohydride salt solution at a high pH, usually over 11. In the preferred form of my invention and for best results, I have also found that when the silver salt employed is first transformed into a complex silver salt such as by dissolving it in excess ammonia, to form the silver ammonia salt complex, more stable colloidal silver solutions result.

The reducing reaction of the invention is preferably carried out in aqueous solution, but can also be carried out in appropriate solvents such as dimethyl-formamide, pyridine, and the like.

Instead of gelatin, other hydrophilic protective colloids such as sugar, starch, polyvinyl alcohol, interpolymers of styrene with acrylic acid, acrylic amides or substituted polyacrylic amides, gum arabic, and numerous colloids well known in the art, and including inorganic colloids such as alkali silicates, aluminum hydroxide, and the like can be used. Where a non-aqueous solvent such as the above noted dimethyl-formamide or pyridine is employed, hydrophobic water insoluble protective colloids such as polyvinyl acetate or polystyrene may be used.

The reduction reaction can also be performed in dilute solution and in the absence of a protective colloid. Under these conditions the concentrations of the reactants and solution temperature are properly adjusted in order to produce a colloidal dispersion of the reduced silver. In preferred practice of this embodiment the concentration of the silver salt and preferably also the salt of the borohydride should be in the range of about .001 to about .03 normal and temperature should be below about 20° C. The colloidal silver produced can be separated from the reaction mixture by precipitation, by centrifugation, by sedimentation, by dialysis, or ultra-filtration, as desired, depending on the nature of its final use.

The following examples illustrate practice of the invention.

Example 1 describes a typical method of making colloidal silver of high tinctorial power dispersed in gelatin and suitable for the manufacture of a filter layer in a color photographic material.

Example 1

To 320 ml. of an aqueous gelatin of 20% strength, maintained at 35° C., is added a complex silver salt solution. This salt solution was prepared by mixing a solution of 8.5 g. (0.05 mol) of silver nitrate in 42.5 cc. water, and 68 ml. of 28% ammonia solution.

To the gelatin-complex silver salt solution there was added with stirring, a solution of 0.75 g. sodium borohydride, equivalent to 0.02 mol or 0.08 equivalent, in 100 cc. water containing 1 ml. 2-normal ammonia which has been added for adjusting the pH to about 12.

The resulting mixture was stirred for 10 minutes and was left standing at 35° C. for 1½ hours. The reaction mixture was then chilled, shredded, and washed free from all soluble salts including residual sodium borohydride.

The pH of the solution was adjusted after melting to pH of 6.4 with citric acid.

When a glass plate of 108 cm.^{2} surface area was coated with gelatin solution to which 0.3 ml. of the above melted colloidal silver gelatin was added, a yellow filter layer results which has the following optical densities at various specified wavelengths:

Wavelength, mu:	Optical density
400	0.67
410	0.79
420	0.86
430	0.84
440	0.77
450	0.68
460	0.55
480	0.37
500	0.24
540	0.11
580	0.05

(The spectrum of the dried plate was determined with a Beckman DU spectrophotometer.)

Example 2

For the preparation of a colloidal filter layer on a photographic element in the form of a color photographic multilayer material, 150 cc. of the above colloidal silver gelatin of Example 1 was coated per square meter of surface to form a colloidal silver filter layer having an optical density of about 3.3 at its absorption maximum at 450 mu. This colloidal silver gelatin material can be applied alone or in combination with a filter dye added to such material.

The advantage of such colloidal silver material free of traces of borohydride reducing agent is that it is photographically completely inert, which is a substantial advantage when used in a multilayer photographic material, in that it has no fogging action with respect to the adjacent photographic layers.

Example 3

The procedure of Example 1 is repeated except that the aqueous borohydride solution is employed without addition thereto of ammonia and without adjusting the pH of such solution, and the simple silver nitrate is employed without forming the ammonia complex thereof.

Results similar to those of Example 1 are obtainable.

Example 4

A colloidal silver gelatin solution can be prepared as in Example 1, except employing 4 to 5 times the concentration of silver salt used in Example 1. The resulting colloidal silver is of darker color than that formed in Example 1, and can be coated on a photographic support to form an antihalation layer instead of a filter layer.

Example 5

The colloidal silver solution of Example 1 formed following the addition of the borohydride solution, and after standing one hour, was acidified with a sufficient quantity of dilute sulfuric acid, hydrochloric or citric acid to bring the pH of the colloidal gelatin solution to about 4. After the acid was added the excess borohydride salt decomposed with foaming. The gelatin was then chilled, shredded and washed as in Example 1. If desired, after decomposing the residual borohydride salt, the gelatin solution can be adjusted to a neutral pH with an alkaline solution such as sodium hydroxide solution.

Example 6

A .01 normal solution of silver nitrate and a .01 normal solution of sodium borohydride are each introduced into a beaker equipped with a rapidly rotating stirrer at the rate of between 30–120 cc. per minute.

Temperatures of the solutions are preferably kept under 10° C. In the resulting mixed solution a colloidal silver of very high dispersion is produced. The two solutions can also be run into a tube which is equipped with a rapidly rotating stirrer, to provide a continuous process. The solution can then be aired, or acidified, and centrifuged, or the colloidal silver can be separated by sedimentation or by dialysis, as desired.

As a further modification of the procedure described in the above Example 1, the concentration of gelatin solution employed therein can be reduced to between 0.2 and 2%. This permits the use of lower mixing temperature, down to about 28° C. When the gelatin concentration is thus reduced, the resulting reaction mixture following the reduction can be flocculated by adding solid sodium sulfate or ammonium sulfate to the dilute colloidal silver gelatin solution, which causes precipitation of a mixture of gelatin containing the suspended colloidal silver. In this manner the chilling and shredding operations are avoided and the resulting precipitate is filtered and washed free from all soluble salts essentially as described above.

For pharmaceutical purposes, in the above examples the gelatin can be replaced, e.g., by polypeptides, sugar, gum arabic or other physiologically inert substances.

For use of the colloidal silver as a catalyst, the reduction reaction can be carried out in the presence of, for example, sodium silicate or aluminum hydroxide, or in the absence of a protective colloid where the solution is properly diluted, as described above, and at relatively low temperature, and subsequently concentrating the so-formed colloidal silver by ultra-filtration, dialysis, centrifugation, or by precipitating it out of solution with neutral salts or electrolytes such as acids or bases, as described above.

From the foregoing it is seen that my invention affords a simple and economical procedure for reducing silver salts to colloidal silver, and for removing or decomposing excess or residual reducing agent and also by-products and soluble salts, such as sodium nitrate or borate, or boric acid, to produce purified colloidal silver free from traces of reducing agent. Such colloidal silver has particular value in photography for the preparation of colloidal silver filter and antihalation layers. Such colloidal silver also has utility for producing colloidal layers in the diffusion transfer process.

Although various modifications of my invention have been described for purposes of illustration, the invention is to be taken as limited only by the scope of the appended claims.

I claim:

1. The process which comprises reacting in aqueous solution a soluble silver salt with a soluble salt of a borohydride, the concentration of said silver salt and said borohydride salt in said solution being in the range of about .001 to about .03 normal, and said solution being maintained at a temperature below about 20° C., and reducing said silver salt to colloidal silver.

2. The process which comprises reacting in aqueous solution a soluble silver salt with an alkali metal salt of a borohydride, the concentration of said silver salt and said borohydride salt in said solution being in the range of about .001 to about .03 normal, and said solution being maintained at a temperature below about 20° C., the amount of said borohydride employed being about 10 to about 100% in excess of the equivalent weight required to reduce all of said silver salt, reducing said silver salt to colloidal silver, and removing residual borohydride.

3. The process which comprises reacting in aqueous solution a soluble silver ammonia complex salt with a soluble salt of a borohydride, and reducing said silver salt to colloidal silver.

4. The process which comprises reacting in aqueous solution a soluble silver ammonia complex salt with an alkali metal salt of a borohydride, in the presence of a

hydrophilic colloid, employing an amount of said borohydride in excess of that required to reduce all of said silver salt, reducing said silver salt to colloidal silver, and removing residual borohydride.

5. The process which comprises mixing an aqueous gelatin solution containing a complex silver ammonia nitrate with an aqueous alkaline solution of a sodium borohydride having a pH in excess of 11, the amount of said borohydride employed being about 10 to about 100% in excess of the equivalent weight required to reduce all of said silver salt, reducing said silver salt to colloidal silver, and removing residual borohydride.

6. The process which comprises reaching in an aqueous gelatin solution a soluble silver ammonia complex salt with an alkali metal salt of a borohydride, employing an amount of said borohydride in excess of that required to reduce all of said silver salt, reducing said silver salt to colloidal silver, and removing residual borohydride.

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DAVID L. RECK, *Primary Examiner.*

HAROLD BURSTEIN, BENJAMIN HENKIN, *Examiners.*

A. D. RICCI, H. W. CUMMINGS, N. F. MARKVA, *Assistant Examiners.*