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# [54] PROCESS FOR THE PRODUCTION OF DISPERSIONS OF COLLOIDAL SILVER

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[58] **Field of Search** ....................106/1, 137, 135; 96/84; 252/300

[56] **References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,921,914 | 1/1960 | Pechmann | 96/84 X |
| 3,459,563 | 8/1969 | Terashima | 106/1 |

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## [57] ABSTRACT

Dispersions of colloidal silver having a neutral black or slightly bluish-black color are disclosed.

The process for forming the above described dispersions in gelatin comprises mixing an aqueous alkaline gelatin solution with an aqueous solution of a water-soluble silver salt and from 0.005 to 0.7 moles of a water-soluble manganous salt per mole of said silver salt, and then reducing the silver salt by adding thereto at least 0.2 moles per mole of said silver salt of an alkali metal sulphite and an excess of a water-soluble silver salt reducing agent.

**7 Claims, No Drawings**

# PROCESS FOR THE PRODUCTION OF DISPERSIONS OF COLLOIDAL SILVER

## BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates to a process for the production of colloidal dispersions of silver, and more particularly, to dispersions of silver which absorb light in the visible spectrum having wave lengths longer than the wave length of blue light.

2. Description of the Prior Art:

It is known that black dispersions of colloidal silver can be used as antihalation layers on the back of a multilayer color film for the purpose of preventing halation caused by the reflection of rays of light from the surface of the film support. Various silver dispersions have also been suggested for use in making neutral grey optical filters, optical wedges, or yellow filter layers in light-sensitive multilayer photographic color films for the purpose of shielding certain emulsion layers from blue light.

Certain relationships are known to exist between the grain size of colloidal dispersions of silver and the spectral density thereof, for example see E. Klein: Phot. Sci. Engg. 5 5–11 (1956). Dispersions of the finest colloidal silver are stable during storage, but illustrate a color from yellow to yellowish brown. Dispersions of coarser colloidal silver are from blue to blue black in color, but the stability thereof during storage is poor.

It is desirable, for an antihalation layer used in photographic materials, in particular, for use in multilayer color films, to be neutral in color, or to have a sufficiently high reflection optical density to light of the visible spectrum, so that a panchromatic film may be adequately protected from halation effects by such layer. Such an antihalation layer should also have a sufficiently high transmission optical density to light of the visible spectrum so that a panchromatic film will also be protected from fogging by light incident to the back of the film.

Moreover, it is also desirable that the antihalation layer have no deteriorating effect, such as desensitization or fogging, upon the panchromatic emulsion layer adjacent thereto. The antihalation layer must also be capable of being completely bleached with conventional processing solutions.

Various methods have been heretofore known in the art to prepare blue dispersions of colloidal silver for antihalation layers. According to these methods, silver nitrate in an aqueous solution of gelatin is reduced with an organic reducing agent, such as hydroquinone, in the presence of an alkali metal sulphite and a water soluble alkali earth metal salt such as a calcium (U.S. Pat. No. 2,688,601), a strontium (Belgian Patent No. 630,385) or magnesium (French Patent No. 1,395,367) salt.

Although the colloidal silver dispersions prepared by these methods have little deteriorating effects on adjacent emulsion layers, and can be bleached completely by conventional processing baths, they have disadvantages. In general, the transmission optical densities of these dispersions are not neutral or the reflection densities are not high enough to make satisfactory antihalation layers from them for panchromatic films.

Dispersions of colloidal silver which are not neutral in color are neither satisfactory for neutral density grey filters nor for optical wedges.

Although black colored dispersions are particularly desirable for making antihalation layers on panchromatic films, it has not been a simple matter to produce such dispersions without creating particles which are so coarse that they settle out of the dispersions.

## SUMMARY OF THE INVENTION

It has been found that neutral black or slightly bluish-black dispersions of colloidal silver which illustrate a very high reflection and have a high transmission optical density can be produced by a process which comprises mixing an aqueous alkaline gelatin solution with an aqueous solution of a water-soluble silver salt and from 0.005 to 0.70 moles of a water soluble manganous salt per mile of said silver salt, and reducing the silver salt by adding at least 0.2 moles per mole of said silver salt of an alkali metal sulphite and an excess of a water-soluble silver salt reducing agent. The silver dispersed in the gelatin may be further coated on a support to yield a layer having a transmission optical density of at least 0.8 as measured with light having a wave length of 650 nm., 550 nm., and of 440 nm.

It is therefore an object of the present invention to provide a process for producing neutral black or slightly bluish-black dispersions of colloidal silver which have a high reflection and high transmission optical densities.

A further object of the invention is to provide a process for making such dispersions of silver in a stable and reproducible manner.

A still further object of the invention is to provide a means for producing an antihalation layer which has both high reflection and transmission optical densities and, has no deteriorating effects upon the adjacent photographic emulsion layers.

Other objects will appear from the following description of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

In accordance with the process of the invention, neutral black or slightly bluish black dispersions of colloidal silver having the heretofore described above desirable characteristics are produced by, for example, first forming a bath of a simple water soluble silver salt dissolved in an aqueous solution of a hydrophilic protective colloid, such as gelatin, and then mixing therewith a reducing agent in the presence of at least 0.2 mole of an alkali metal sulphite and from 0.005 to 0.7 mole of a water soluble manganous salt, per mole of the silver salt. It is preferred to use an excess of the reducing agent.

In order to remove from the dispersions unnecessary ions, such as nitrate ions, excess reducing agents or their oxidation products, the dispersions are then either chilled, shredded and washed with cold water, or coagulated by adding thereto suitable flocculating agents, such as those described in U.S. Pat. No. 2,982,652 and in U.S. Pat. No. 2,489,341, and finally separated from the resultant supernatant liquid and washed with cold water.

As the hydrophilic protective colloid used in the present invention, water soluble polymers ordinarily employed in the production of light-sensitive photographic silver halide emulsions, such as gelatin, polyvinyl alcohol, water soluble cellulose derivatives and so forth, may be employed.

Photographic gelatins, especially lime-processed gelatins, contain minute amounts of alkali earth metal ions such as calcium or magnesium ions. In order to eliminate the effect of these ions upon the color of the finished colloidal silver dispersions, it may be desirable to deash these gelatins, for example, by the use of ion-exchange resins.

The manganous salts which may be employed in the present invention are those capable of being dissolved in water at 20° C. at a rate of not less than 0.1 mole per liter and further which have anions, which, in the presence of silver ions, do not cause the precipitation of a sparingly soluble silver salt, for example, manganous nitrate and manganous acetate.

We have found that from about 0.005 to 0.7 mole, more preferably from 0.015 to 0.18 mole of the manganous salt per mole of water soluble silver salt is quite adequate to obtain neutral black or slightly bluish black dispersions of colloidal silver suitable for making antihalation layers. Yellow or brownish yellow dispersions are obtained when less than 0.005 mole of a manganous salt is added, whereas dispersions having low reflection optical density are often obtained when more than 0.7 mole of a manganous salt is employed.

In the preferred embodiment of the present invention, the dispersions are formed at a temperature from 40° to 65° C. and within an elevated pH range of from about 7 to 10, by use of a suitable alkali such as caustic alkali, sodium carbonate, potassium carbonate, sodium borate, sodium metaborate, potassium metaborate, sodium phosphate, etc.

The reducing agents which may be used according to our invention are those known to the art as organic developing agents, for example, hydroquinone, toluhydroquinone, catechol, monomethylaminophenol, 1-phenyl-3-pyrazolidone, paraphenylenediamine, ascorbic acid and so on.

The black dispersions of silver obtained according to the present invention may further have added thereto, preferably prior to the washing procedure, thiol compounds or compounds capable of readily forming thiol compounds through decomposition thereof, in order to improve the stability on storage of the finished dispersions. Suitable compounds are 2-mercaptoimidazole, 2-mercaptobenzoimidazole, 2-mercaptobenzoxazole, 5-carboethoxy-2-mercapto-4-methylthiazole, 3-mercapto-1,2,4-triazole, 2-mercapto-5methylthiadiazole, and 1-phenyl-5-mercaptotetrazole.

The black dispersions of colloidal silver obtained according to the present invention may be used for making antihalation layers for color negative films, color reversal films, color print films, color positive films, color paper, and so forth, by uniformly coating and drying said dispersions onto a support which has previously been given a subcoating, the thickness of the antihalation layers being in the range of from about 1 to 10 microns.

To make silver dispersions according to the present invention, various procedures may be adopted. In these procedures, the reducing agent is added to a freshly or simultaneously formed mixture of a soluble silver salt and an alkali metal sulphite in an aqueous solution of a hydrophilic protective colloid, in the presence of a suitable amount of manganous ions and within an elevated pH range of from about 7 to 10. The following examples are of methods which illustrate, but do not limit, the present invention.

## EXAMPLE 1

To 100 parts of a 24 percent aqueous solution of lime-processed inert bone photographic gelatin there were added 5 parts of a 1 molar aqueous solution of sodium carbonate with stirring and keeping the temperature in the range of 35°–40° C. When the aqueous sodium carbonate solution was completely mixed with the gelatin solution, 3 parts of a 1 molar aqueous solution of manganous nitrate was added thereto. Then, 50 parts of a 10 percent aqueous solution of silver nitrate were added at a constant rate for 30 seconds. After addition of silver nitrate, a mixture of 3 parts of sodium sulphite, 17 parts of sodium metaborate and 3 parts of a 10 percent methanolic solution of 1-phenyl-3-pyrazolidone with 95 parts of water were added thereto within 1 minute. After 3 minutes, 10 percent of a 0.3 percent methanolic solution of 2-mercaptobenzoimidazole was added and, after a further 5 minutes, a 10 percent solution of aqueous sulfuric acid was added until a pH value of 4.5 was reached. The resulting dispersions of colloidal silver in gelatin were then chilled, shredded into pieces, and washed repeatedly with cold water until the amount of sulfate ions was negligible. One hundred parts of the resulting black dispersion of colloidal silver in gelatin gel were then remelted and 2 parts of a 5 percent aqueous solution of chromium acetate and 1 part of a 4 percent aqueous solution of saponin were added. The mixture was thereafter coated onto a transparent film support and dried to a thickness of 1–10 microns.

The transmission optical density was about 1.38 at all wave lengths of 420 - 700 nm. when coated at a concentration of 0.7 grams of silver per square meter and the reflectance was about 3.8 percent to all wave lengths of light in the visible spectrum.

## EXAMPLE 2

A 5 % aqueous solution of lime-processed inert bone photographic gelatin was passed through mixed beds of ion exchange resins, Amberlite IR–120 and IRA–400, at 38° C., to remove substantially all of the contaminating metallic or other ions therefrom. To 200 parts of the gelatin solution were added 10 parts of 1 molar aqueous solution of sodium carbonate and 10 parts of a 1 molar aqueous solution of caustic soda while mixing vigorously. Then, 4 parts of 1 molar aqueous solution of manganous nitrate was added thereto. After mixing to insure complete contact, 25 parts of a 20 percent aqueous solution of silver nitrate was added thereto, and 90 parts of a solution of 40 parts of sodium sulphite and 14 parts of hydroquinone in 1000 parts of water were added within 1 minute. After the reduction was completed, 10 parts of a 0.3 percent methanol solution of 2-mercaptobenzoimidazole and a further 25 parts of a 5 percent aqueous nitric acid solution were added and the mixture cooled. The thus resulting black dispersion of colloidal silver in gelatin were chilled, shredded, and washed repeatedly with cold water until any sulfate ions were barely detectable. One hundred parts of the resulting black dispersion of colloidal silver in gelatin gel were then remelted, and 2 parts of a 5 percent aqueous solution of chromium acetate and 1 part of a 4 percent aqueous solution of saponin were added thereto. The mixture was then coated onto a transparent film base and dried to a thickness of 1–10 microns.

For comparison with the dispersion produced by a known method, such as that described in U.S. Pat. No. 2,688,601, dispersions of colloidal silver were prepared in a like manner as mentioned above with the exception that 4 parts of a 1 molar aqueous solution of calcium nitrate was added in place of the manganous nitrate of Example 2. This mixture was coated onto a transparent film base at a concentration of 0.70 gram of silver per square meter.

The transmission optical density and reflectance of the dispersions of colloidal silver are tabulated below.

TABLE 1

| | Optical density | | | Reflectance | | |
|---|---|---|---|---|---|---|
| | 650 nm | 550 nm | 440 nm | 650 nm | 550 nm | 440 nm |
| Using Mn of the invention | 1.22 | 1.22 | 1.20 | 3.2% | 3.2% | 3.2% |
| Using Ca for comparison | 1.54 | 1.18 | 0.72 | 6.2% | 6.4% | 6.6% |

## EXAMPLE 3

To 200 parts of a 20 percent aqueous solution of inert bone photographic gelatin were added, while stirring vigorously and keeping the temperature at 35°–40° C., 8 parts of a 1 molar aqueous solution of sodium carbonate and 7 parts of a 1 molar aqueous solution of caustic potassium. To this, from 0.5 to 20 parts of a 1 molar aqueous solution of manganous nitrate and 25 parts of a 20 percent aqueous solution of silver nitrate were added simultaneously. After 30 seconds, a reducing solution which consisted of 3.5 parts of sodium sulfite and 1.3 parts of hydroquinone in 90 parts of water was added. After 2 minutes, 10 parts of a 0.3 percent methanol solution of 2-mercaptobenzoimidazole was further added together with 10 parts of a 10 percent aqueous sulfuric acid, followed by cooling and setting. The obtained gelatin gel containing black dispersions of colloidal silver were finely shredded and washed with cold water, the washing being continued until any sulfate ions were barely detectable. The resulting colloidal silver dispersions were coated onto film supports as in Example 1 and dried.

The transmission optical density and reflectance are tabulated below.

TABLE 2

| Manganous nitrate | Mol/Mol $AgNO_3$ | Optical density | | | Reflectance | | |
|---|---|---|---|---|---|---|---|
| | | 650nm | 550nm | 440nm | 650nm | 550nm | 440nm |
| 0.25 part | $8.5\times10^{-3}$ | 0.50 | 0.87 | 1.85 | 7.8% | 5.4% | 3.2% |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 0.5 part | $1.7\times10^{-2}$ | 0.87 | 1.00 | 1.25 | 3.0% | 3.0% | 2.9% |
| 2.5 parts | $8.5\times10^{-2}$ | 1.30 | 1.30 | 1.27 | 3.4% | 3.4% | 3.4% |
| 5.0 parts | $1.7\times10^{-1}$ | 1.48 | 1.25 | 0.9 | 4.9% | 5.0% | 5.0% |
| 20 parts | $6.8\times10^{-1}$ | 1.00 | 1.08 | 0.62 | 9.8% | 9.5% | 9.2% |

Generally the amount of silver salt reducing agent is not critical and desirable amounts are from 0.25 to 1.50 moles per mole of silver salt.

All parts in the examples are parts by weight.

What is claimed is:

1. A method of preparing a black dispersion of silver in gelatin which comprises mixing an aqueous alkaline solution of gelatin with an aqueous solution of silver nitrate and a manganese salt in a ratio of from 340 to 1,360 grams of gelatin per mole of silver nitrate, and from 0.005 to 0.7 mole of said manganese salt per mole of said silver nitrate, said manganese salt being capable of being dissolved in water at 20° C. at a rate of not less than 0.1 mole per liter and wherein the anion of said manganese salt does not cause the precipitation of a sparingly soluble silver salt in the presence of silver ions; and reducing the silver nitrate by adding to the resulting mixture at least 0.2 mole, per mole of silver nitrate, of an alkali metal sulfite and from 0.25 to 1.5 moles, per mole of silver nitrate of a water-soluble organic compound capable of reducing the silver nitrate to silver colloid.

2. The method as in claim 1 wherein the water soluble organic compound capable of reducing silver salt to silver colloid is hydroquinone, toluhydroquinone, catechol, monomethylaminophenol, 1-phenyl-3-pyrazolidone, paraphenylenediamine or ascorbic acid.

3. The method as claimed in claim 1 wherein the alkali metal sulfite is sodium sulfite.

4. The method as claimed in claim 1 wherein the manganese salt is manganese nitrate.

5. The method as claimed in claim 1 wherein the gelatin is deashed to an extent that the reduction mixture does not contain more than 0.001 gram ion of any alkali earth metal ions.

6. A method of preparing a black dispersion of silver in gelatin which comprises mixing an aqueous alkaline solution of gelatin with an aqueous solution of silver nitrate and a manganese salt selected from the group consisting of manganese nitrate and manganese acetate in a ratio of from 340 to 1360 grams of gelatin per mole of silver nitrate and from 0.005 to 0.7 mole of said manganese salt per mole of silver nitrate; and reducing the silver nitrate by adding to the resulting mixture at least 0.2 mole, per mole of silver nitrate, of an alkali metal sulfite and from 0.25 to 1.5 moles, per mole of silver nitrate, of a water-soluble reducing agent selected from the group consisting of hydroquinone, toluhydroquinone, catechol, monomethylaminophenol, 1-phenyl-3-pyrazolidone, paraphenylenediamine and ascorbic acid, at a temperature of from 40° to 65° C. and within a pH range of from about 7 to 10.

7. A supported stable silver dispersion in gelatin prepared by the method as claimed in claim 1 wherein when said dispersion is coated on a support so as to yield a layer containing from about 0.65 to about 0.75 grams of silver per square meter, said layer having a transmission optical density of at least 0.8 as measured with light having wave lengths of the group consisting of 650 nm., 550 nm. and 440 nm.

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