Higher rates of silver deposition from silvering compositions such as ammoniacal silver nitrate solutions are achieved by employing as a reducer an aldonic acid having 4 – 7 carbon atoms, or a salt or lactone thereof. Preferred reducers are gluconic acid, sodium gluconate, sodium glucoheptonate or glucono delta lactone. Since the reducer is stable in the strong base normally employed in silvering, it can be added to the strong base prior to admixing the strong base with the silvering solution.
**Fig. 1.**

Relative rates of deposition of silver by various reducers.

**Fig. 2.**

Deposition of silver at various reducer concentrations.

**Legend:**
- Glucono-delta-lactone
- Dextrose
- Fructose
- Invert sugar
- Arabinose

**Graph 1:**
- X-axis: Reducer concentrations (moles/l. x 10^2)
- Y-axis: Deposition of silver (mg/sq. ft.)

**Graph 2:**
- X-axis: Reducer concentrations (moles/l. x 10^2)
- Y-axis: Deposition of silver (mg/sq. ft.)

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ELECTROLESS SILVERING COMPOSITION AND METHOD

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of application Ser. No. 98,716 filed Dec. 16, 1970, now abandoned.

This invention relates to methods and compositions for the electroless deposition of metallic silver on various substrates.

In the electroless deposition of silver, as in the manufacture of mirrors, vacuum bottles and Christmas tree ornaments, mild reducing agents such as formaldehyde, glucose or invert sugar have been employed with silver compounds or complexes such as ammoniacal silver nitrate to produce metallic silver. However, under the conditions of high alkalinity normally required in the reaction mixtures containing the silver compound or complex and the reducer, careful attention must be given to control of temperature, concentrations of reactants, and techniques of admixing and applying the reaction mixtures to substrates for the deposition of silver thereon since silvering solutions are short-lived and the reducing agents tend to be unstable, often evolving hydrogen or decomposing to form sludge or interfering products.

Practice of such methods is also complicated by the fact that solutions of silver-nitrogen compounds or complexes such as ammoniacal silver nitrate, in the presence of the strong base normally employed to provide the desired high alkalinity, tend to form explosive compositions on standing. Furthermore, the strong base tends to separate out of solution at lower temperatures and the rates of silver deposition are limited by the costs which can be tolerated in heating up the solutions to temperatures providing improved rates.

The electroless deposition of silver, due to the relatively high cost of silver and the instability of silvering solutions, requires a high rate of deposition as compared to most other metals. It is therefore highly desirable to employ silvering solutions which are not unduly sensitive to temperature reductions, high alkalinity and decomposition such that the rates of deposition are lowered and reaction is otherwise inefficient.

Accordingly, although the known reducing agents are inexpensive and available in high purity, the known methods of silvering have been greatly restricted in variability of conditions and economy due to the aforementioned problems.

OBJECTS AND SUMMARY OF THE INVENTION

An object therefore of the present invention is to provide new and improved silvering solutions and silvering methods which are less sensitive to process conditions such as high alkalinity, temperature lowering, and sequence of admixture of the reactive ingredients.

Another object is to provide new and improved silvering solutions and silvering methods which are more economical in the use of silver.

Another object is to provide new and improved silvering solutions and methods based upon a new class of reducing agents which are stable in highly alkaline medium.

A still further object of the invention is to provide new and improved methods of preparing silvering solutions, especially from concentrates of the ingredients, which take advantage of the stability of the reducers of the invention in strongly alkaline solutions, and which are not subject to the explosive tendencies of known methods.

Still other objects, features and advantages of the invention will in part be obvious and will in part be apparent from the specification which follows.

The invention accordingly comprises a composition of matter possessing the characteristics, properties and relation of components, as well as methods which comprise one or more steps and the relation of such steps, which composition and methods will be exemplified as hereinafter described, and the scope of the invention will be indicated in the claims.

Briefly, an electroless silvering method of the invention comprises reactively contacting a water soluble silver composition, which contains silver in the ionic state, and a reducing agent which comprises an aldonic acid having 4 to 7 carbon atoms, or a salt or lactone of such aldonic acid, or mixtures of two or more of such acids, salts or lactones. In another aspect, the invention pertains to a silvering solution comprising an aqueous medium containing a water soluble silver composition, in which silver is present in the ionic state, where also being present in the solution the aforementioned aldonic acid, salt, lactone or mixture, in an amount effective to induce reduction of the silver composition to metallic silver. In still another aspect, the invention includes methods of mixing the silvering solutions in which, contrary to usual practice, the reducing agent may be pre-mixed with one or more other reactants such as alkali before the final silvering solution is formed.

DETAILED DESCRIPTION

The aldonic acid, salts and lactones of the invention are known compounds containing 4 to 7 carbon atoms inclusive. As acids the compounds may be represented by the following structure:

\[ \text{HOC}_\text{n}(\text{CHOH})_{\text{m}}\text{COOH} \]

where \( n \) is 2 to 5 inclusive. These acids are readily prepared by the cautious oxidation of the corresponding aldoses in a known manner. For example, the aldote tronic acids, the aldopentonic acids and the aldohexonic acids, are prepared from the corresponding aldolotetoses, aldopenotoses and aldohexoses as in the fermentative oxidation of glucose to gluconic acid. The aldonic acids and lactones include the alpha and beta forms, where they exist, as well as the various optical isomers. Thus, the aldopentonic acids include the D and L forms of arabinonic, ribonic, xylonic and lycytic acids. Similarly, the aldohexonic acids include the D and L forms of gluconic, monnonic, galactonic, talonc, altronic, allonic, gulonic, and idonic acids. The preferred salts of the acids are the water soluble salts including the alkali metal salts and ammonium or amino salts, such as sodium, potassium, and ammonium gluconate. Salts which have lesser degrees of water solubility are useful although surfactants may be required to improve their dispersability.

Of the foregoing acids, the aldohexonic and aldopheptonic acids are preferred. Particularly preferred is gluconic acid, including its highly water soluble salts such as sodium gluconate, and its lactones such as glucono delta lactone and glucono gamma lactone. Gluconic and glucoheptonic acids, their sodium salts, and especially glucono delta lactone, are commercially avail-
able in high purity, such purity being an important consider-

ation in the deposition of silver, for avoidance of streaks and the like. Moreover, since the salts and/or lactones of the aldonic acids exist along with the acids in aqueous solution, the relative proportions being depend-

ent on pH, the reducing agents of the invention in-
clude mixtures of one or more of such acids, salts and lactones.

Any silver composition in which silver in present in the

ionic state, and which is sufficiently water soluble for reactive contact with the reducing agent of the in-
vention, is suitable, although not all to the same extent.

Thus, any of the well known silver compounds or salts, inclu-
sion complexes, coordination compounds (Wer-
ner complexes), and the like, will be effective provided the compositions have the requisite water solubility and interfering reactions are avoided. Among the useful compositions may be mentioned the soluble silver salts such as silver nitrate and the like. The preferred ionic silver composition, however, is one in which the silver ion is complexed since not only is the solubility of the silver compound improved thereby, but also the ten-
dency to precipitation of silver oxide with increase of

pH is reduced. Ammonia is the preferred complexing agent for these purposes and forms with silver nitrate the silver diammine ion, Ag\((\text{NH}_3)_2^+\). If desired, surfac-
tants may be employed to further improve the water

solubility of the silver composition.

In the present method, as in nearly all industrial proc-
esses for the electrolecs deposition of silver, a highly al-
kaline medium is desirable for acceptable rates of reac-
tion. A pH of at least about 12 will be suitable and prefer-
ably about 12.7 or higher. Since it is observed that the rate of reaction is proportionate to the alkalinity of the reaction medium, it is believed that the highly alka-
line medium facilitates the transfer of electrons from the reducer to the silver ion. The alkalinity is provided

by any suitable means and preferably by the presence of a strong base such as an alkali metal hydroxide of
which sodium hydroxide is representative.

The relative proportions of reactants in the silvering

solutions of the invention may vary over a wide range. Preferably, however, the molar ratio of the reducer to the silver compound, such as silver nitrate, will be about 1:1 to about 2:1. Below this range the quantity of silver deposited begins to decrease rapidly and above this range the quantity deposited is only marginally in-
creased.

Likewise, the ratio of silver salt to the other reactants

may vary widely. Preferably, the weight ratio of strong

base such as sodium hydroxide to silver salt such as sil-

ver nitrate is about 1:1. On a molar basis, the preferred

ratio of hydroxyl ion to silver diammine ion is at about 4:1. An amount of concentrated ammonia (28%) su-

fficient to form the silver diammine complex is also pre-
ferred to be present in the reaction mixture.

Except for the sequences of admixture of the react-

ants, the other conditions for the preparation of the silvering solutions of the invention and the deposition of silver therefrom are not critical and may be varied

as desired for optimum effects. Such conditions include the manner of forming the silver diammine complex and the provision of the highly alkaline reaction me-

dium. For example, the complex may be formulated by precipitating silver oxide from a solution of a soluble silver salt, such as silver nitrate, by reaction with a strong base such as sodium hydroxide, and then adding

concentrated ammonium hydroxide (28%) until the last of the silver oxide passes into solution. A slight ex-

cess of ammonium hydroxide is added in order to com-
pensate for evaporative losses which may occur prior to use of the silver solution. Alternatively, the silver diammine complex may be formed directly from a sil-

"ver salt by mixing the solution containing a soluble sil-

ver salt with the appropriate amount of concentrated ammonium hydroxide. The strong base, such as sodium hy-

droxide, may then be added to the solution or may be otherwise admixed as further explained below.

Various other considerations of the reaction are

within the skill of the art and may be varied accord-
ingly. These include the absolute concentrations of the

various reactants, the total hydroxyl ion concentration

in the reaction mixture, temperature and duration of
reaction, and the manner in which the silvering solution

is applied to the substrate.

However, the stability of the new reducers of the in-
vention in strong alkali makes possible several new ways of forming the component mixtures of the silvering

solution as well as the final silvering solution itself. For example, in the conventional method, the reducer

comprises a separate solution which is added to a previ-
ously prepared solution of sodium hydroxide and am-

moniacal silver nitrate shortly before or simultaneously

with application of the final reaction mixture to the

substrate upon which it is desired to deposit a silver

film.

In one of the new methods provided by the invention,

the ammoniacal silver nitrate may comprise a first solu-
tion and the strong base and reducer may comprise a

second solution. The two solutions are then admixed as

required to deposit the silver. A variation on this

method is to provide a portion of the reducer in the first

solution and the remainder in the second solution.

In another new method of the invention, the reducer

may be provided in a first solution with silver nitrate,

and a second solution may contain the strong base and

ammonium hydroxide complexing reagent. These two

solutions are then admixed when it is desired to deposit

the silver. Similar to the first method, a portion of the

reducer may be present in each of these two solutions

prior to admixture.

In still another method of preparing the reaction mix-
tures, a known reducing agent for the electrolecs depo-
sition of silver may be employed in conjunction with the

reducers of the invention. For example, the conven-
tional techniques for admixture of the reactants may be

utilized with the exception that the known reducer,

such as a carbohydrate compound, is present in the so-
lution of the reducer of the invention. Alternatively,

one solution may contain the conventional carbohy-
drate reducer, a second solution may contain the strong

base and reducer of the invention, and a third solution

may contain the silver diammine reactant. In either

case, upon admixture of the three solutions, silver is de-

posited as a coating.

In any case the component solutions after their prep-

aration are brought together just before contact with

the substrate to be silvered. This may be achieved in a

variety of ways known to those skilled in the art. For

example, the component solutions may be poured or

pumped such that they meet just before contact with

the substrate. Alternatively, the component solutions

may be air-atomized prior to or simultaneously with in-
termixing at the surface of the substrate. Normally,
also, the component solutions are first formulated as concentrates, to be stored and later diluted at time of use.

As pointed out above, transfer of electrons from the reducing compound to the silver compound is facilitated by high hydroxyl ion activity in the reaction mixture. But if any of the commonly employed aldosreductors are dissolved in a solution with such concentrations of alkali, and hence hydroxyl ions, then within a very short time the solution becomes yellow, then orange-brown, and finally a deep dark brown, indicating drastic chemical changes of the original aldo structure. The specific nature of the decomposition products is not known. However, what is clearly evident is: (a) the power to reduce is destroyed, and (b), it requires only a small volume percent of such products, when added to a normally active silvery solution, to "poison" the reaction, that is, to prevent the deposition of silver.

By contrast, the behavior of the reducers of the invention, in the presence of concentrations of alkali which decompose the commonly used reducers, is vastly different. For example, even at temperatures as high as 160°F, and at 50 percent sodium hydroxide, the reducers of the invention are stable for long periods of time, 30 days or more in the case of gluconic acid. Under the same conditions, the known aldo reducers decompose in minutes.

A wide variety of optional ingredients may be added to the silvery solution of the invention which essentially comprises the aqueous medium containing a water soluble ionic silver composition and reducing agent. As indicated, it is preferred to enhance the rate of deposition by the addition of a strong base such as an alkali metal hydroxide, of which sodium hydroxide is representative. For example, it is often desirable to add to the reaction mixture, modifiers for the purpose of buffering the solution, controlling the odor of the reaction mixture, or for preventing the deposition of sludge on the surface to be silvered. The problem of preventing deposition of sludge, however, is different in silverying processes than in the deposition of other metals such as copper and nickel. The reason for this is that reaction mixtures for the deposition of silver are far more reactive and difficult to control than reaction mixtures for the deposition of most other metals. For example, it is known to use various complexing or chelating agents in concentrates for the electroless deposition of copper or nickel in order to prevent dispersion of colloidal aggregates of the metal throughout the entire reaction mixture since this would prevent deposition of the metal on the surface to be plated. Such techniques are not normal in silverying due to the extreme reactivity of the solutions.

The following examples are intended as further illustration of the invention but are not necessarily limitative except as set forth in the claims. All parts and percentages are by weight unless otherwise indicated. These examples should be considered in conjunction with the accompanying drawing in which:

FIG. 1 is a chart comparing the amount of silver deposited using various reducing agents; and

FIG. 2 is a graph comparing the amount of silver deposited using various reducing agents at different concentrations.

EXAMPLE 1

In the first of two separate tanks of 400 liters each is prepared an aqueous (distilled water) reducer solution containing glucono delta lactone at a concentration of 2.25 grams per liter. In the second tank is prepared an aqueous (distilled water) silver solution containing the ingredients and at the concentrations set forth in Table I:

<table>
<thead>
<tr>
<th>Table I</th>
<th>Tank 1: Reducer Solution</th>
<th>Tank 2: Silver Solution</th>
<th>Ammonia (28%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gluconolactone</td>
<td>Sodium Hydroxide</td>
<td>Silver Nitrate</td>
<td>9.5 cc/l</td>
</tr>
<tr>
<td>2.25 g/l or</td>
<td>5 g/l</td>
<td>5 g/l</td>
<td>or 3800 cc/l/tank</td>
</tr>
<tr>
<td>900 g/tank total</td>
<td>or</td>
<td>or</td>
<td>or 2000 g/tank</td>
</tr>
<tr>
<td>or 2000 g/tank total</td>
<td></td>
<td>or 2000 g/tank total</td>
<td></td>
</tr>
</tbody>
</table>

The silver solution of Table I may be prepared in several ways. The first method can be used by operators who prepare their own chemicals. In this procedure, the 2,000 grams of silver nitrate are added with vigorous agitation to about 90 gallons of distilled water. Then a solution of the 2,000 grams of sodium hydroxide dissolved in about 5 gallons of distilled water is added, again with vigorous agitation. This causes precipitation of the silver ions in the form of silver oxide, which must under no circumstances be permitted to settle, before concentrated ammonia is poured in slowly until the last of the silver oxide just passes into solution. The resulting "silver solution" is then topped off at 400 liters with distilled water. The two solutions may then be flowed by gravity to the surface upon which it is desired to deposit the metallic silver. The two solutions are permitted to mix and react either just before application to the surface or at the point of application to the surface. The application can be in the form of "pour," a technique formally in wide use for silverying of mirrors, or the flows may be air-atomized such that they meet at the point of application to the surface. Normally, it is preferred to mix the two solutions before contact with the surface to be silvered when the surface is a vacuum flask or ornamental surface, as in the case of the silverying of Christmas tree ornaments.

This first method is a practical technique for the determination of the correct volume of concentrated ammonia to use with given concentrations of silver and sodium hydroxide, whatever the specific concentration of the ammonia.

In silverying techniques employing reducers of the prior art, if splashes of silver solution which contains the suspension of silver oxide get on the floor, and drops of concentrated ammonia get to such splashes, explosive silver azide AgN₃ will form. With the reducers of the present invention, however, the silver solutions are stabilized against these hazards, at least at the reactant proportions normally employed in silverying.

EXAMPLE 2

The reducer and silver solutions of Example 1 are again prepared but the silver solution is formed in accordance with a second method as follows:

The 2,000 grams of silver nitrate are first dissolved in about 300 liters of water. To this solution is then added concentrated ammonia, in the amount determined by
the procedure of Example 1. This forms the silver complex ion first. Then the appropriate weight of sodium hydroxide, dissolved in 100 liters of pure water is added with stirring, to complete the solution. The two solutions are then applied to the surface to be silvered substantially as described above.

The concentrations set forth in Table I may be varied widely, depending on the nature of the surface to be silvered and other conditions, but for best results in most applications, the ratios of Table I should be approximately maintained. Some types of silvering are favored by a higher ratio of sodium hydroxide to silver nitrate than unity, in which case a determination of the volume of concentrated ammonia by the method described in Example 1 would be advisable to establish a formulation.

With regard to the use of higher concentrations of silver nitrate and alkali, and the appropriate volume of concentrated ammonia, there are upper limits beyond which there is a rapidly increasing danger of forming an explosive. For example, a concentration of 32 grams per liter of silver nitrate, 25 grams of sodium hydroxide, and about 50 cc of concentrated ammonia, each per liter of final reaction mixture, is dangerous. However, except for accidental attainment of such concentrations, the usual practice in the electrolysis deposition of silver employs concentrations very much below these proportions, as in Table I, and therefore are quite safe.

EXAMPLE 3

This Example illustrates additional mixing methods made possible by the reducers of the invention.

If the four basic chemicals required for the electrolytic deposition of silver include a prior art reducer, and only two tanks are to be employed from which the two solutions flow in equal amounts to the work, it is obvious that the only way to form the solutions is as illustrated in Table I. If there exists for some purpose an advantage in placing these same chemicals in three tanks and from which they would flow to the surface to be silvered in three equal amounts, then again only one possibility exists for doing this, namely, reducer in the first tank, alkali in the second tank, and the silver nitrate and ammonia in the third tank. A somewhat trivial variation is placement of some ammonia with the alkali.

But since the reducers of the invention can be incorporated in the alkali without the decomposition produced by the solutions of the known aldehyde reducers in alkali, the present invention offers new ways of mixing the four essential components, with attendant special benefits.

Table II below compares the alternative methods B, C and D, made available by the reducers ("new") of the present invention, with method A, to which the practitioner is limited by use of the known reducers ("old"):  

<table>
<thead>
<tr>
<th>Method</th>
<th>Reducer (new)</th>
<th>NaOH, NH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 tanks</td>
<td>AgNO₃, NH₃</td>
<td>NaOH</td>
</tr>
</tbody>
</table>

\[3,776,740\]

It will be noted that new method D permits use of combined reducers, such as a known aldehyde carbohydrate type reducer, in tank 1, and a reducer of the invention, in tank 2.

The above solutions are then applied to the substrate to be silvered in substantially the same fashion as described above.

A special benefit resulting from the use of new method C concerns the manufacture of "antique" mirrors, since this method permits silvering patterns not possible with a standard mix. Methods B, C and D provide special advantages in the manual application of solutions for the deposition of silver on Christmas tree ornaments, in that these methods do not require an operator to mix sodium hydroxide with ammoniacal silver nitrate. Hence, the preparation of the solutions is very much less likely to produce accidental explosions.

EXAMPLE 4

The rate of deposition of silver from a reacting solution containing silver diammine ions, sodium hydroxide and a reducer was measured for a number of reducers. The variables were held constant throughout the experiments and only the reducer was varied. In each case, the following variables were maintained constant at the values recited:

| Silver diammine concentration | 5 x 10⁻⁵ moles/liter |
| Sodium hydroxide concentration | 5 x 10⁻⁵ moles/liter |
| Reaction time | 120 seconds |
| Reaction temperature | 25.0°C |
| Reducer concentration | 5 x 10⁻⁵ moles/liter |

The reducers tested were glucono delta lactone, as representative of the invention, dextrose (a commercial form of glucose), fructose, invert sugar (equimolar amounts of glucose and fructose) and arabinose.

The amount of silver deposited from the reacting solution expressed in milligrams of silver per square foot of surface was determined in each case and the results charted. The charted results are reproduced in FIG. 1. It will be seen from the results shown in FIG. 1, that glucono delta lactone produces a higher rate of deposition of silver than conventional aldehyde-type carbohydrate reducers.

EXAMPLE 5

The deposition of silver from a reacting solution containing silver diammine ions, sodium hydroxide and a reducer was measured for a number of reducers at different concentrations. With the exception of the concentration and nature of the reducer, the variables were held constant throughout the tests. The following is a list of the values of the variables held constant:

| Silver diammine concentration | 5 x 10⁻⁵ moles/liter |
| Sodium hydroxide concentration | 4 x 10⁻⁵ moles/liter |
| Reaction time | 120 seconds |
| Reaction temperature | 25°C |

Glucono delta lactone was employed as a reducer exemplifying the present invention and dextrose and invert sugar were employed as reducers exemplifying the prior art.
The deposition of silver, expressed as milligrams per square foot of surface, at the various concentrations of reducer was determined and the results reproduced in the form of the graph lines appearing in FIG. 2. It will be seen from these results that the rate of deposition of silver increased rapidly to a maximum and then declined in the case of dextrose and invert sugar, whereas in the case of glucono delta lactone, the rate rose less rapidly to a maximum value which then was maintained over the range of concentrations tested. Therefore, not only does the glucono delta lactone provide improved deposition rates compared to the prior art, but also maintains the higher rates over a wide range of reducer concentrations.

EXAMPLE 6

The rate of deposition experiment of Example 4 was repeated in all essential respects except that the reducer tested was sodium heptagluconate, obtained from The Belzak Corporation of Clifton, N.J., as an aqueous solution wherein the major proportion of the heptagluconate was in the beta isomer form. The test showed that the reducing efficiency by this reducer was similar to that of glucono delta lactone, while providing substantially the same advantages as glucono delta lactone in other respects, such as stability in the highly alkaline medium. The heptagluconate may be used in various other forms, many of which are commercially available, including the acid form (gluheptonic acid) and various salt forms, such as crystalline sodium glucoheptonate alpha isomer, and aqueous solutions of sodium heptagluconate of various activities, containing essentially only the alpha or beta forms, or various mixtures of these isomers. Since the heptagluconate at the present time is somewhat cheaper than the corresponding forms of gluconic acid, the heptagluconate may be preferred to gluconic acid (or its salt or lactone) for some reducer applications. It is also within the scope of the invention to employ admixtures of gluconic acid and heptagluconic acid (including their salts and lactones) in varying proportions in accordance with the reducer efficiencies and economies desired.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in providing the above compositions and in carrying out the above methods without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A method according to claim 1 wherein said compound is gluconic acid, sodium gluconate, or glucono delta lactone.

2. A method according to claim 1 wherein said compound is an aldohexonic or aldoheptonic acid, or a salt or lactone thereof.

3. A method according to claim 1 wherein said compound is gluconic acid, sodium gluconate, or glucono delta lactone.

4. A method according to claim 1 wherein said silver composition comprises ammoniacal silver nitrate.

5. A method according to claim 1 wherein said reducer compound is heptaconic acid or sodium heptagluconate.

6. A method according to claim 1 wherein said compound is gluconic acid, said silver composition comprises ammoniacal silver nitrate, and the deposition is effected in the presence of a strong base.

7. A method according to claim 6 wherein said strong base is sodium hydroxide.

8. In a silvering solution comprising an aqueous alkaline medium containing a water soluble ionic silver composition capable of reduction to metallic silver and a reducer for said composition, the improvement which comprises providing as said reducer an effective amount of a compound selected from an aldonic acid having 4-7 carbon atoms, a salt of said aldonic acid, and a lactone of said aldonic acid.

9. A silvering solution according to claim 8 wherein said compound is an aldohexonic or aldoheptonic acid, or a salt or lactone thereof.

10. A silvering solution according to claim 8 wherein said compound is gluconic acid, sodium gluconate, or glucono delta lactone and said silver composition comprises ammoniacal silver nitrate.

11. A silvering solution according to claim 1 having a pH of at least 12.

12. A silvering solution according to claim 8 containing sodium hydroxide and silver nitrate, and having a pH of about 12 to about 12.7, wherein said silver composition is silver diammine nitrate, said compound is gluconic acid, heptagluconic acid or the sodium salt thereof, the molar ratio of said compound to said silver nitrate is about 1:2 to about 1:1, the weight ratio of sodium hydroxide to silver nitrate is about 1:1, and the molar ratio of hydroxyl ion to silver diammine ion is at least about 4:1.

13. A method of preparing a silvering solution which comprises:

   a. admixing in water a silver salt and an amount of a complexing agent effective to render the silver salt soluble and to reduce the tendency of the silver solution to precipitate silver oxide with increase of pH, to form a first aqueous solution containing a completed silver salt.

   b. admixing in water an alkali metal hydroxide and a reducer compound selected from an aldonic acid having 4-7 carbon atoms, a salt of said aldonic acid, and a lactone of said aldonic acid to form a second aqueous solution, and

   c. mixing said first and second solutions, wherein the amounts of said complexed silver salt, alkali metal hydroxide and reducer are effective for deposition of metallic silver from said silvering solution.

14. A method of preparing a silvering solution which comprises:

   a. admixing in water a silver salt and a reducer compound selected from an aldonic acid having 4-7 carbon atoms, a salt of said aldonic acid, and a lactone of said aldonic acid, to form a first aqueous solution,

   b. admixing in water an alkali metal hydroxide and ammonia to form a second aqueous solution, and

   c. admixing said first and second solutions, wherein the amounts of said silver salt, reducer compound, alkali metal hydroxide and ammonia are effective to deposit metallic silver from said silvering solution.

* * * * *