

SPECIFICATION

Compositions and Method for Inhibiting Formation of Explosive Compounds and Conditions in Silvering Concentrates for Electroless Deposition of Silver

This invention relates to the inhibition of formation of explosive compounds and conditions which can result from contacting concentrates of ammoniacal silver salts and strong alkali, which are normally utilized in dilute form, in simultaneous admixture with a reducer to effect electroless deposition of silver. A serious and inherent hazard encountered in shipment and use of ammoniacal silver salts, particularly in concentrated forms, is the danger of accidental or negligent admixture or contacting of the ammoniacal silver composition with a strongly alkaline material or a concentrated alkali solution, for example sodium hydroxide, potassium hydroxide or the like.

It is well known that upon such contact, without suitable safeguards or inhibitors, explosive conditions and compounds, often referred to as fulminating silver, can form and result in detonation, which can be quite violent and dangerous. This hazard is particularly prevalent in situations where for reasons of economy and commercial preferences many industrial firms utilizing these materials utilize concentrated solutions involving separate shipment and handling of materials. Although the risk of formation of explosive compounds or conditions upon inadvertent or accidental admixture could be minimized by use and shipping of dilute solutions of ammoniacal silver salts and strong alkali, or by carefully controlling the admixture of the same together with a reducer to effect the desired electroless deposition, the safety hazard still remains, since shipping and plant personnel may not be fully informed regarding the dangers and human error is an ever present factor in any industrial endeavor.

It has long been known in the art that metallic silver can be electrolessly deposited by appropriate use of combinations of (1) ammoniated silver salts, hereinafter also referred to as "ammoniacal silver salts", (2) strong alkali, (i.e. metal hydroxides of Group 1A which are strong electrolytes) such as sodium hydroxide and (3) a reducer for the ammoniacal silver salts, such as carbohydrates, e.g. invert sugar, formaldehyde, as well as more recently developed reducers such as aldonic acids and polyhydric alcohols, which will be discussed hereinafter in greater detail. It was soon discovered that explosions could occur with detonation resulting from even very slight mechanical or thermal stimulus in a mixture which could result from contacting concentrates of ammoniacal silver salts and strong alkali.

In the prior art it was recognized that such explosions were produced from reactions between silver diammine and hydroxyl ions, when brought into contact in aqueous solution. These ions are believed to react a first form silver amide, then silver imide and finally silver nitride. These substances are all black and rather insoluble in aqueous solution.

Of the foregoing compounds, the nitride is the most unstable and is capable of spontaneous explosion, as well as detonation upon the slightest mechanical or thermal stimulation, with the silver imide readily detonated by the explosion of the silver nitride. It is also known that formation of these explosive compounds is promoted by high alkalinity in the reaction medium and by increases in temperature. While it is possible to minimize the formation of such explosive compositions and conditions by maintaining either or both of the ammoniacal silver salt and a strong base in a highly diluted state, such dilute concentrations are not commercially economical, particularly with regard to the shipment of the materials from the supplier to the end user who utilizes the same to deposit metallic silver.

The sensitivity to explosion of the mixture formed by contacting an ammoniacal silver salt and strong caustic varies with time and temperature. However, it has been found that at normal room temperature, the critical concentration below which explosion is generally not likely to occur is about 45 g/l each of ammoniacal silver salt and strong alkali. Typical concentrates supplied for commercial use contain 250 g/l of ammoniacal silver and 200 g/l of sodium hydroxide, so that these materials must be diluted 5.5 and 4.4 times, respectively, in order to reach the 45 g/l critical level. Even at this critical level there would be no guarantee that explosion will not occur if the materials were admixed. Thus, further dilution would be recommended to provide a margin of safety. Such further dilution would be utterly impractical, however, because of high cost of transportation of the same weight of chemicals in up to ten times the amount of water now generally used.

Commercially, industrial use of ammoniacal silver salts and strong alkali is directed to concentrates of such solutions, which, if contacted, would result in a mixture having a concentration of perhaps 5 to 10 times the aforementioned critical concentration for avoidance of explosion simply on the basis of dilution. Accordingly, these solutions are manufactured, shipped, stored and handled in concentrated form until such time as they are prepared for appropriate reaction by simultaneous admixture to effect electroless deposition of silver on an appropriate workpiece surface.

In the event that ammoniacal silver salt and strong alkali are brought into contact in a mixture in which they are present above the aforementioned critical concentration, formation of explosive compounds and conditions can occur spontaneously, or over varying degrees of time, depending upon the resulting hydroxyl ion concentration (pH), the concentration of silver diammino ion and the temperature. For example, if one cc each of a 250 g/l solution of ammoniacal silver nitrate and a 200 g/l solution of sodium hydroxide are admixed, a black precipitate forms rapidly and a sharp explosion

sufficient to disintegrate a test tube containing the mixture will occur rapidly, depending upon temperature.

Accordingly, there is substantial need for improved methods and compositions which will inhibit formation of such explosive compounds and conditions and allow concentrates of such solutions to be safely shipped, stored and utilized without risk of explosion.

The earliest known reducers for the electroless deposition of silver, e.g. carbohydrates, such as invert sugar, dextrose, fructose or arabinose will prevent formation of explosive compounds and conditions when admixed with an ammoniacal silver salt and strong alkali, because the silver salt is rapidly reduced to elemental silver and other non-explosive compounds. However, such reducers cannot be made available in the reaction medium by first being admixed with either the concentrated ammoniacal silver salts or the strong alkali, because such reducers in the presence of hydroxyl ions are catalytically converted to non-reducers and/or, in the presence of ammoniated silver, produce amounts of reduced silver sludge, only minute quantities of which would render the solution commercially unfit.

However, in U.S. Patent No. 3,776,740 of Sivertz *et al* and Canadian Patent No. 945,307 a method for electroless deposition of silver and method for inhibition of the formation of fulminating silver are disclosed, utilizing a class of reducing agents comprising aldonic acids having 4 to 7 carbon atoms. The preferred reducers disclosed by Sivertz *et al* are gluconic acid, sodium gluconate, sodium glucoheptonate or glucono-delta-lactone. This class of reducers, it was disclosed, could be included either with the ammoniacal silver salt, with the strong alkali, or a portion of the reducer with each of the concentrated solutions of ammoniacal silver salt and strong alkali. These reducers were found to be not only useful for deposition of metallic silver upon simultaneous combination of the solutions containing ammoniacal silver salts and strong alkali, respectively, but they were also found to have other properties, not in any known way related to their reducing capabilities, namely to resist the action of hydroxyl ions to destroy their effectiveness as reducers of silver ions. These reducers are also stable in combination with each of the various components.

As further disclosed in Canadian Patent No. 945,307, this class of reducers, as a result of being stable in both concentrated solutions of ammoniacal silver salts and strong alkali could be added to the same to inhibit the formation of explosive fulminating silver upon accidental or inadvertent contacting, because the presence of the reducer would cause the silver salts to be rapidly reduced, thereby avoiding formation of explosive compounds or conditions in the mixture.

U.S. Patent No. 3,983,266 discloses the utility of a broad class of polyhydric alcohols having from 3 to 8 carbon atoms as reducers of ammoniacal silver salts. The preferred polyhydric alcohol is sorbitol. However, while U.S. Patent No. 3,983,266 recognized that such polyhydric alcohols could be used as reducers for ammoniated silver, its use as disclosed in that patent was specifically restricted to the long prior-established techniques for old conventional reducers, such as glucose, which required that such reducers must be applied from separate containers and in streams of spray entirely separate from the alkali and ammoniated silver. Accordingly, one skilled in the art was taught by this patent that three concentrates were to be used, one of which was ammoniated silver, one sodium hydroxide and one reducer. Consequently, they would know that it was still necessary to deal most cautiously with the first two members of the three-part system, which are well known to be capable of producing explosives. U.S. Patent No. 3,983,266 refers to Sivertz Patent No. 3,776,740 and discusses the same as prior art, yet does not disclose or suggest that its own novel polyhydric alcohol reducers could be utilized in a two-part silvering system, such as that disclosed in the Sivertz patent for use with its aldonic acid reducers. In fact, U.S. Patent No. 3,983,266 teaches against incorporation of sorbitol in strong alkali, thus precluding use of the reducer in the manner disclosed by Sivertz *et al*.

The present invention is particularly directed to the situation in which, though generally accidental or inadvertent, concentrated solutions of ammoniacal silver salt and a strong alkali come into contact, resulting in the formation of a mixture of potentially explosive compounds, such as fulminating silver, or explosive conditions. In accordance with the present invention, not only is a method for inhibiting formation of such explosive compounds and conditions provided, but also an improved multi-part silvering system utilizing ammoniacal silver and strong alkali in conjunction with a suitable conventional reducer, is provided. This multi-part silvering system is protected against the formation of such explosive compounds and conditions as a result of inadvertent or accidental contacting of the materials, no matter in what proportion the concentrated solution of strong alkali and ammoniated silver happen to be mixed.

The following definitions are provided to assist in the understanding of the description herein and will be utilized accordingly:

"Concentrated solution" is a solution having a concentration of soluble components indicated, which concentration is greater than the concentration at which said solution is normally utilized to effect electroless deposition of silver.

"Strong alkali" refers to basic compounds formed by elements of Group 1A of the Periodic Table, including but not limited to sodium hydroxide and potassium hydroxide.

"Extraneous ammonium ions" refers to a source of ammonium ions rather than those normally existing in ionic form in an aqueous solution of ammoniacal silver salt and refers to both ammonium ions provided from an additional source, such as by addition of an ammonium salt, or which are

generated *in situ* as a result of effecting a change in chemical balance, pH or the like in an aqueous solution of an ammoniacal silver salt, whereby additional ammonium ions are generated therein.

"Reducer" refers to any compound which is capable of effecting reduction of ammoniacal silver salts to elemental silver to produce electroless deposition of silver.

5 "Fulminating silver" refers to a mixture of various forms of silver amide/imide/nitride compounds, 5 which are explosive and susceptible to detonation by mechanical or thermal stimulus.

The present invention is predicated upon the discovery that the formation of explosive conditions and compounds in a mixture resulting from contact of a concentrated aqueous solution of ammoniacal silver salts and strong alkali can be inhibited by including an effective amount of explosion inhibitor 10 comprising a polyhydric alcohol having 4 to 6 carbon atoms, preferably sorbitol, mannitol or xylitol. The 10 explosion inhibitor is preferably included in the concentrated aqueous solution of ammoniacal silver salt, in which case it is preferable to also provide in the solution of ammoniacal silver salts sufficient extraneous ammonium ions to stabilize the explosion inhibitor and prevent deterioration of the solution. It is also fully within the purview of the present invention that the explosion inhibitor can, 15 alternatively, be combined with the strong alkali solution, or that a portion of the explosion inhibitor 15 could be combined with both the solution containing ammoniacal silver salt and the strong alkali solution.

According to the present invention therefore there is provided a method for inhibiting formation of explosive conditions or compounds in a mixture resulting from contact of concentrated aqueous 20 solutions of an ammoniacal silver salt and a strong alkali, which comprises providing an effective 20 amount of an explosion inhibitor comprising a polyhydric alcohol having 4 to 6 carbon atoms, said explosion inhibitor being admixed either with (1) said concentrated aqueous solution of ammoniacal silver salt preferably together with sufficient extraneous ammonium ions to stabilize said explosion inhibitor therein (2) said concentrated aqueous solution of strong alkali, or (3) both of solutions (1) and 25 (2), prior to formation of said mixture. 25

The present invention also provides an improved multi-part silvering system for electroless deposition of silver by simultaneous admixture of the system components, wherein the system components are protected from formation of explosive compounds and conditions. The multi-part silvering system of the present invention comprises (A) a concentrated aqueous silvering solution 30 comprising ammoniacal silver salt, (B) a concentrated aqueous solution of strong alkali and (C) an 30 effective amount of reducer for the ammoniacal silver salt, with an effective amount of an explosion inhibitor comprising a polyhydric alcohol having 4 to 6 carbon atoms, which may be either included in component (A), (B), or a portion thereof in both (A) and (B). It is within the purview of the present invention that the conventional reducer for the ammoniacal silver salt may be provided either in system 35 component (A), (B), or a portion thereof in both (A) and (B), provided the conventional reducer is 35 compatible therein. Furthermore, it is within the purview of the invention that if a sufficient amount of said explosion inhibitor is provided, it can also serve as reducer, so that use of other conventional reducers may not be required.

It has now been discovered that polyhydric alcohols having 4 to 6 carbon atoms, preferably 40 sorbitol, mannitol or xylitol, can be utilized to provide a novel and improved method and compositions 40 for inhibiting formation of explosive conditions and compounds, frequently referred to as fulminating silver. In addition, since compounds in this class of polyhydric alcohols are known to have utility as reducers for ammoniacal silver salt in the presence of sufficient strong alkali, the invention provides a novel method and compositions whereby these materials can be utilized as reducers in a manner not 45 previously disclosed or suggested by the prior art, with the added benefit of providing protection 45 against the danger of explosion in the event of inadvertent or accidental contact of concentrated ammoniacal silver salt and strong alkali.

In particular, it has been discovered that the polyhydric alcohols of the invention can be combined with either concentrated ammoniacal silver salt and/or strong alkali solutions, so that their 50 performance for purposes of electroless deposition of silver is not adversely affected and the 50 polyhydric alcohol does not decompose or is not adversely affected in its capacity to serve as an explosion inhibitor upon simultaneous combination of the three system components; namely, the ammoniacal silver salt, the strong alkali and a conventional reducer.

In the event that a concentrated solution of ammoniacal silver salt or strong alkali, having the 55 explosion inhibitor of the present invention present therewith, should come into contact, the materials 55 will react to produce a colloidal material (generally referred to as "silver mud"), which, while resulting in an amorphous form rather than a crystalline form of silver, nevertheless interferes with the reactions between these materials which could lead to formation of explosive silver compounds and conditions. The reaction involving formation of the "silver mud" is preferred and occurs at a faster rate than the 60 reactions leading to formation of explosive compounds, such as fulminating silver. Furthermore, the 60 concentrations of ammoniacal silver salt and strong alkali are decreased by the reduction reaction either completely, or at least below the critical concentration above which explosion is likely to occur.

It has been discovered that the explosion inhibitors of the present invention are better and more efficient than the reducers disclosed in U.S. Patent No. 3,776,740. The polyhydric alcohols utilized as 65 explosion inhibitors are non-ionic and therefore do not act as complexing agents which can desensitize 65

an activated glass surface, causing premature sludging, or removal of sensitizer therefrom, causing a void in the plating. Furthermore, these polyhydric alcohols are more efficient with regard to the electron transfer required for reduction of the ammoniacal silver salt, since they contain more potential free electrons than the aforesaid reducers disclosed in U.S. Patent No. 3,776,740.

Furthermore, it has been discovered that explosion can be effectively inhibited with substantially less polyhydric alcohol than would be expected simply to effect reduction of silver to its colloidal form, accompanied by dilution of the admixture constituents. While at present it is not fully understood why this occurs, nevertheless the phenomenon has been observed and indeed is of beneficial and advantageous utility. It makes it possible to achieve effective protection against explosion utilizing substantially less polyhydric alcohol, than would be required to utilize its reducing capability in a multi-part silvering system. Of course, it is fully within the purview of the invention that one may also add quantities of these polyhydric alcohols sufficient to also effectively reduce the ammoniacal silver to effect deposition of a silver film, as hereinafter discussed in detail.

The method for inhibiting formation of explosive conditions or compounds in a mixture which could result from contact of an ammoniacal silver salt in concentrated aqueous solution and a strong alkali, comprises providing an effective amount of an explosion inhibitor comprising a polyhydric alcohol having 4 to 6 carbon atoms. The explosion inhibitor is preferably admixed with the concentrated solution of ammoniacal silver salt, preferably in conjunction with sufficient extraneous ammonium ions to stabilize the explosion inhibitor in the concentrated solution of ammoniacal silver salt. The extraneous ammonium ions may be provided either by addition of an ammonium salt, such as ammonium nitrate or ammonium citrate, as well as other ammonium salts which are compatible with the ammoniacal silver salt being used and which will not interfere with the reduction thereof to elemental silver. When ammonium nitrate is used, about 10—200 g/l and, preferably, between about 16—80 g/l should be added to the concentrated solution of ammoniacal silver salt.

It is also possible and fully within the purview of the present invention that any extraneous ammonium ions required to stabilize the explosion inhibitors of the present invention can be generated *in situ*, while leaving a sufficient excess of free ammonia, as required for the system of silver deposition described herein. These extraneous ammonium ions are generated *in situ* by addition of an acid which is compatible with the ammoniacal silver salt and will not lead to formation of precipitates with the same, nor interfere with its eventual reduction to metallic silver. Such acids include but are not limited to citric acid, tartaric acid, acetic acid, nitric acid. In one method citric acid is provided in the range 5—100 g/l and preferably 5—20 g/l.

Without being restricted to any single mechanism or theory, since such is not yet fully understood, it is nevertheless believed that extraneous ammonium ions are generated *in situ* in a solution of ammoniacal silver salt by the following mechanism.

In order to prevent precipitation of silver oxides and hydroxides when the silver salt is ultimately reacted with alkali to effect electroless deposition of silver, an excess of ammonia is added to and is present in the aqueous solution of ammoniacal silver salt. Each mole of silver salt will only complex with two ammonia molecules and the remainder or excess of which is termed "free ammonia". Generally, ammoniacal silver salt solutions used commercially are provided with about 10% in excess of the free ammonia required to prevent silver oxide or hydroxide formation.

It is well known that an equilibrium is established between the ammonium ions and free ammonia, having an equilibrium constant.

$$K = \frac{(\text{NH}_4^+) (\text{OH}^-)}{(\text{NH}_3^*)} = 1.8 \times 10^{-5}$$

wherein

K is the equilibrium constant, at 25°C

(NH_4^+) is the molar concentration of ammonium ions,

(OH^-) is the molar concentration of hydroxyl ions, and

(NH_3^*) is the molar concentration of free ammonia, which is calculated as the total ammonia

added to the silver salt to form ammoniacal silver salt less 2 times the molar concentration of silver salt.

Upon admixture of an acid, as aforementioned, to a solution of ammoniacal silver salt, a corresponding molar amount of free ammonia, NH_3^* , will be consumed and form an ammonium acid salt, thereby increasing the concentration of ammonium ions, NH_4^+ . Since the equilibrium constant, K, remains the same the concentration of hydroxyl ions, OH^- , will decrease and effect a corresponding lowering of pH.

Alternatively, addition of extraneous ammonium ions, in the form of ammonium nitrate or the like, also causes a decrease in hydroxyl concentration and reduced pH. It makes no difference whether these extraneous ammonium ions are added as ammonium salts or whether they are generated *in situ*.

It is a preferred feature, however, that sufficient extraneous ammonium ions be provided to effect a decrease in the pH of the ammoniacal silver salt solution in order to stabilize the explosion inhibitors of the present invention. Otherwise, the pH will be too high and premature reduction of some of the silver

will occur resulting in formation of a silver "mud" and consuming, if not totally depleting, the silver salt available for electroless deposit to metallic silver.

For purposes of the invention, it is preferred to provide sufficient extraneous ammonium ions, generally ranging from between 0.2 to 1.0 moles per liter and preferably about 0.33 moles per liter, to stabilize the explosion inhibitor in the aqueous solution of ammoniacal silver salt and prevent deterioration of the same, which may be accompanied by formation of silver mud. While the resulting pH in the ammoniacal silver salt solution will vary, depending upon the amount of free ammonia provided therein, for a typical solution having 3.5 moles per liter of free ammonia, the pH should be below about pH 11.7 to 11.5. The pH need not be much lower to effectively stabilize the explosion inhibitor and will only result in surplus ammonium ions and reduced commercial economies.

The polyhydric alcohols which have been found to be useful as explosion inhibitors in accordance with the invention are those polyhydric alcohols having between 4 to 6 carbon atoms. These polyhydric alcohols include, but are not limited to, sorbitol and mannitol, which are preferred, as well as arabitol, ribitol and xylitol. However, it is fully within the purview of the present invention that other polyhydric alcohols having the required characteristics may be utilized. Furthermore, various known isomers, including stereoisomers, can be utilized as explosion inhibitors in accordance with the present invention.

The ammoniacal silver salts within the purview of the present invention are those silver salts which may be derived from any silver compound that can be complexed with ammonia and which are capable of being reduced to metallic silver to effect electroless deposition of silver on an appropriate surface. Such a surface may be, for example, a glass surface which is sensitized with stannous salts, such as chlorides or fluorides. Most commonly, the silver salts utilized are those which are sufficiently water soluble to provide an aqueous medium and preferably include silver nitrate, preferably in the range 100—500 g/l or salts formed by reacting silver oxide with mineral acids such as sulfuric acid, or with organic acids such as acetic acid, carbonic acid, or oxalic acid to form corresponding sulphates, acetates, carbonates, oxalates.

For the purposes of the invention, any strong alkali may be utilized, such as sodium hydroxide, potassium hydroxide, or any compound, which is a "strong electrolyte" (i.e. a metal salt of Periodic Group 1A).

In the preferred embodiment of the present invention, it is particularly advantageous to combine the explosion inhibitor with the concentrated solution of ammoniacal silver salt, because this protects against the formation of explosive conditions or compounds, regardless of the source of strong alkali contamination. This provides an additional safety factor, since during shipment and handling, it is quite possible that the concentrated solution of ammoniacal silver salt may come into contact with a strong alkali from a source other than that intended to be ultimately utilized therewith in a multi-part system for electroless deposition of silver.

Alternatively, in another embodiment of the invention, the explosion inhibitor can be admixed with the strong alkali solution of a multi-part system for electroless deposition of silver. When combined with a strong alkali, the explosion inhibitors of the present invention do not require further stabilization.

In yet a further embodiment of the invention, a portion of the explosion inhibitor can be provided in both the concentrated ammoniacal silver salt and strong alkali solutions.

Furthermore, in accordance with the present invention, an improved multi-part system for electroless deposition of silver upon simultaneous admixture of the two components is provided and is protected against the formation of explosive conditions or compounds, such as fulminating silver. This improved multi-part system preferably comprises the following compositions:

Solution A—a concentrated aqueous silvering solution of ammoniacal silver salt and an explosion inhibitor comprising a polyhydric alcohol having 4 to 6 carbon atoms and sufficient extraneous ammonium ions to stabilize the polyhydric alcohol and prevent deterioration thereof, and

Solution B—an aqueous solution of strong alkali.

As an alternative embodiment of the improved multi-part system of the invention, the following combinations may be utilized:

Solution A—a concentrated aqueous silvering solution comprising ammoniacal silver salt, and Solution B—an aqueous solution of strong alkali and an explosion inhibitor of the present

invention.

A further embodiment of the multi-part system of the invention may be provided as follows:

Solution A—a concentrated aqueous silvering solution comprising ammoniacal silver salt and a portion of the explosion inhibitor of the present invention together with sufficient extraneous ammonium ions to stabilize the explosion inhibitor and prevent its deterioration, and

Solution B—an aqueous solution of strong alkali and a second portion of the explosion inhibitor of the present invention.

In accordance with the present invention, about 10—200 g/l and preferably 25—200 g/l of explosion inhibitors comprising a polyhydric alcohol is utilized to inhibit formation of explosive compounds and conditions upon admixture of concentrated ammoniacal silver salt and strong alkali. If between about 10—60 g/l, and preferably 25—60 g/l, of the explosion inhibitor is used, it is generally

necessary to utilize a conventional reducer for the ammoniacal silver salt, so as to achieve a commercially acceptable rate and quality of electroless deposition of silver. Conventional reducers, such as those discussed previously, may either be combined with the concentrated ammoniacal silver salt, or the strong alkali solution, provided of course that such reducers are compatible therewith. If the conventional reducer is not compatible, then it must be added separately in admixture with the ammoniacal silver nitrate and strong alkali components to effect electroless deposition of silver, as is well recognized in the prior art.

However, if between about 60 to 200 g/l of the explosion inhibitor is utilized in accordance with the foregoing, an additional reducer or reducers for the ammoniacal silver salt may not be required, in order to effect deposition of metallic silver upon admixture of the solutions containing ammoniacal silver salt and strong alkali. Although it is not economically advantageous to utilize greater amounts of these polyhydric alcohols, it would be fully within the purview of the present invention to do so. In this case, instead of three only two concentrates contain all the essential chemicals whereby, among other benefits, shipping costs are substantially reduced.

These multi-part silvering systems are utilized by appropriate dilution, generally ranging from 10—50 times below their concentrated strength, and simultaneous admixture of these diluted solutions just before contact with the substrate upon which a metallic silver film is to be applied. The less dilute solutions give a faster rate of deposition and require a shorter reaction time, while the more dilute solutions yield slower rates of deposition and necessitate a longer reaction period.

Simultaneous admixture of these diluted system "parts" 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 so that they meet just before contact with the substrate. Alternatively, the component solutions may be air-atomized prior to or simultaneously with intermixing at the surface of the substrate.

A wide variety of optional ingredients may be added to the silvering solutions of the invention for their various known advantages and utilities. For example, conventional additives, such as brighteners, hardeners and retarders may be utilized.

The following examples are intended as further illustrations of the invention, but are not necessarily limited except as set forth in the claims. All parts and percentages are by weight unless otherwise indicated and concentrations are molar, expressed as moles per liter (m/l), unless otherwise specifically indicated.

Example 1

A concentrated aqueous solution of ammoniacal silver salt was prepared using 1.47 m/l of silver nitrate and 6.17 m/l of ammonium hydroxide. A concentrated strong alkali solution was prepared using 5.0 m/l of sodium hydroxide and 2.87 m/l of ammonium hydroxide. A series of potentially explosive mixtures were prepared by contacting these concentrated solutions of ammoniacal silver salt and strong alkali in various proportions to provide a 6 cc sample which was subsequently tested for explosion after 48 hours at room temperature. After this period the likelihood of explosion decreases. Each of the various mixtures was placed in a 250 cc Pyrex-type glass beaker ("Pyrex" is a Registered Trade Mark), which was then sealed in a plastic bag of the "zip-close" type as an added safety precaution. However, a small slit was provided in the bag to allow a glass or metal rod of approximately 1/4 inch in diameter to be inserted. The mixture was then tested after 48 hours by prodding lightly with the rod in an attempt to detonate the same. Once detonation was achieved, the explosive components would detonate completely, so that further prodding would not produce any further explosion.

In order to evaluate the violence of explosion, an arbitrary Violence Scale was established:

45	Violence	Description	45
	0	No explosion, even after multiple prodding for 5 minutes.	
	1	Explodes, but glass vessel not broken and plastic bag not ripped; slight "pop" sound.	
	2	Explodes, glass vessel broken, but plastic bag not ripped.	
50	3	Explodes, glass vessel broken and plastic bag slightly ripped.	50
	4	Explodes, glass vessel broken and plastic bag ripped about bottom only.	
	5	Explodes, glass vessel broken into small fragments, plastic bag extensively ripped by fragments, and substantial noise produced.	

The results of this series of experiments is set forth in Table 1, which indicates final concentrations of the potentially explosive mixtures produced by contacting the concentrated ammoniacal silver nitrate solution and sodium hydroxide solutions, as well as the violence rating produced by attempted detonation.

Table 1

	Volume Ratio Silver: Hydroxide Solutions	Silver Nitrate (m/l)	Ammonium Hydroxide (m/l)	Sodium Hydroxide (m/l)	Explosion Violence Rating	
5	1:21	0.06	3.01	4.97	0.5	5
	1:11	0.13	3.14	4.59	1.0	
	1:5	0.25	3.42	4.17	3.0	
	1:2	0.49	3.97	3.33	4.0	
10	1:1	0.74	4.53	2.50	5.0	10
	2:1	0.98	5.07	1.67	3.0	
	5:1	1.22	5.67	0.83	2.0	
	11:1	1.35	5.87	0.35	0	
	21:1	1.41	6.03	0.20	0	

15 As is indicated in Table 1, explosions occurred at various ratios of concentrated ammoniacal silver nitrate and sodium hydroxide. 15

Example 2

20 In accordance with the preferred embodiment of the invention, sorbitol was added to the concentrated aqueous solution of ammoniacal silver nitrate, together with ammonium nitrate to provide sufficient extraneous ammonium ions to stabilize the solution, as indicated in Table 2. 20

25 Thereafter, the concentrated solutions of ammoniacal silver nitrate into which sorbitol was added as an explosion inhibitor and concentrated solution of sodium hydroxide were admixed to provide potentially explosive mixtures. These mixtures were then tested for explosion potential in the same manner as in Example 1. The results are set forth in Table 2, which indicates that explosion was successfully inhibited in each instance. 25

Table 2

Table 2									
30	Volume Ratio Silver: Hydroxide Solutions	Silver Nitrate (m/l)	Ammonium Hydroxide (m/l)	Sodium Hydroxide (m/l)	Sorbitol		Ammonium Nitrate (m/l)	Explosion Violence Rating	30
					(m/l)	— (g/l)			
	1:5	0.25	3.42	4.17	0.05	9.6	0.05	0	
	1:2	0.49	3.97	3.33	0.11	21.0	0.10	0	
	1:1	0.74	4.53	2.50	0.17	32.5	0.16	0	
35	2:1	0.98	5.07	1.67	0.22	42.1	0.21	0	35
	5:1	1.22	5.67	0.83	0.28	53.5	0.26	0	

Example 3

40 Example 2 was repeated substituting mannitol for sorbitol and using exactly the same amounts of all materials for identical combinations of concentrated ammoniacal silver nitrate solution and concentrated sodium hydroxide solution. Again as was set forth in Table 2 for Example 2, the explosion violence in this series of experiments was again zero in all cases, since no explosions occurred. 40

Example 4

45 A series of potentially explosive mixtures of concentrated ammoniacal silver nitrate and sodium hydroxide solutions was prepared along the same lines as in Examples 2 and 3. However, in accordance with an alternative embodiment of the present invention sorbitol was first combined with the concentrated sodium hydroxide solution, rather than the ammoniacal silver nitrate solution prior to admixture thereof. Once again, the final concentrations of the resulting mixtures were tested for explosion potential. The results are set forth in Table 4. 45

Table 4

	Volume Ratio Silver: Hydroxide Solutions	Silver Nitrate (m/l)	Sodium Hydroxide (m/l)	Sorbitol		Explosion Violence Rating	
50	1:5	0.25	4.17	0.28	53.5	0	50
	1:2	0.49	3.33	0.22	42.1	0	
	1:1	0.74	2.50	0.17	32.5	0	
55	2:1	0.98	1.67	0.11	21.0	0	55
	5:1	1.22	0.83	0.05	9.6	0	

Example 5

Example 4 was repeated substituting mannitol for sorbitol as the explosion inhibitor, again providing the same in the concentrated solution of sodium hydroxide, prior to admixture with the concentrated solution of ammoniacal silver nitrate. The same series of reactive mixtures was prepared as in Example 4 and once again the value Explosion Violence Rating was zero in all cases, as no explosions could be produced.

Example 6

A two-part silvering system for deposition of metallic silver on a glass surface was prepared using sorbitol as the explosion inhibitor of the invention, combined with the concentrated solution of ammoniacal silver nitrate.

First, a concentrated aqueous solution containing 250 grams/liter (g/l) 1.47 m/l of silver nitrate and 417 cc/liter (6.17 m/l) of 28% w/v ammonium hydroxide was prepared. To this solution 60 g/l (0.31 m/l) of sorbitol and 25 g/l (0.31 m/l) of ammonium nitrate were added in accordance with the invention.

A second solution was prepared containing 200 g/l (5.0 m/l) of sodium hydroxide and 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide. Each of these concentrated solutions was diluted equally about 25 times with water prior to use. In normal industrial applications, each of these concentrated solutions are diluted between 10—50 times with water prior to use. The diluted solutions were then fed through separate nozzles which were directed so as to provide admixture of the materials in spray form upon a glass surface, which was passed through the spray and thereby deposited with a film of metallic silver.

Example 7

A two-part silvering system for deposition of metallic silver on a glass surface was prepared using sorbitol as the explosion inhibitor of the invention, combined with the concentrated aqueous solution of caustic.

A concentrated aqueous solution of ammoniacal silver nitrate was prepared by admixing 250 g/l (1.47 m/l) of silver nitrate and 417 cc/l (6.17 m/l) of 28% w/v ammonium hydroxide. A concentrated aqueous caustic solution was prepared by admixing 200 g/l (5.0 m/l) of sodium hydroxide, 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide and 60 g/l (0.31 m/l) of sorbitol.

Each of these concentrated solutions was diluted equally about 25 times with water prior to use and then fed through separate nozzles which were directed so as to provide admixture thereof in spray form upon a glass surface which was passed through the spray. A reflective silver film was deposited on the glass surface.

Example 8

A three-part silvering system for deposition of metallic silver on a glass surface was prepared in which sorbitol was utilized as the explosion inhibitor of the invention and a conventional reducer; namely, dextrose, was used to effect deposition at an acceptable commercial rate.

A first concentrated aqueous solution was prepared by admixture of 250 g/l (1.47 m/l) of silver nitrate, 417 cc/l (6.17 m/l) of 28% w/v ammonium hydroxide, 25 g/l (0.13 m/l) of sorbitol and 25 g/l (0.31 m/l) of ammonium nitrate in water.

A second concentrated aqueous solution was prepared by admixture in water of 200 g/l (5.0 m/l) of sodium hydroxide and 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide.

A third concentrated aqueous solution of 11 g/l (0.56 m/l) of dextrose in water was also prepared. Invert sugar can be substituted for the dextrose, if desired.

Each of these concentrated solutions was then diluted equally about 25 times with water prior to use. The three diluted solutions were fed through separate nozzles directed so as to provide admixture of the solutions in a spray applied to the glass surface to be coated. As the glass surface was passed through the spray, a reflective silver film was deposited thereupon.

Example 9

A three-part silvering system similar to that set forth in Example 8 was prepared. However, the first concentrated aqueous solution was prepared by admixture of 25 g/l (1.47 m/l) of silver nitrate and 417 cc/l (6.17 m/l) of 28% w/v ammonium hydroxide in water. The second concentrated aqueous solution was prepared by admixture of 200 g/l (5.0 m/l) of sodium hydroxide, 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide and 25 g/l (0.13 m/l) of sorbitol in water. The third concentrated solution was prepared as in Example 8, above.

These three solutions were then diluted and applied as in Example 8 and a reflective film of silver was deposited on the target glass surface.

Claims

1. A method for inhibiting formation of explosive conditions or compounds in a mixture resulting from contact of (1) a concentrated aqueous solution of an ammoniacal silver salt and (2) a



Example 5

Example 4 was repeated substituting mannitol for sorbitol as the explosion inhibitor, again providing the same in the concentrated solution of sodium hydroxide, prior to admixture with the concentrated solution of ammoniacal silver nitrate. The same series of reactive mixtures was prepared as in Example 4 and once again the value Explosion Violence Rating was zero in all cases, as no explosions could be produced.

Example 6

A two-part silvering system for deposition of metallic silver on a glass surface was prepared using sorbitol as the explosion inhibitor of the invention, combined with the concentrated solution of ammoniacal silver nitrate.

First, a concentrated aqueous solution containing 250 grams/liter (g/l) 1.47 m/l of silver nitrate and 417 cc/liter (6.17 m/l) of 28% w/v ammonium hydroxide was prepared. To this solution 60 g/l (0.31 m/l) of sorbitol and 25 g/l (0.31 m/l) of ammonium nitrate were added in accordance with the invention.

A second solution was prepared containing 200 g/l (5.0 m/l) of sodium hydroxide and 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide. Each of these concentrated solutions was diluted equally about 25 times with water prior to use. In normal industrial applications, each of these concentrated solutions are diluted between 10—50 times with water prior to use. The diluted solutions were then fed through separate nozzles which were directed so as to provide admixture of the materials in spray form upon a glass surface, which was passed through the spray and thereby deposited with a film of metallic silver.

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A two-part silvering system for deposition of metallic silver on a glass surface was prepared using sorbitol as the explosion inhibitor of the invention, combined with the concentrated aqueous solution of caustic.

A concentrated aqueous solution of ammoniacal silver nitrate was prepared by admixing 250 g/l (1.47 m/l) of silver nitrate and 417 cc/l (6.17 m/l) of 28% w/v ammonium hydroxide. A concentrated aqueous caustic solution was prepared by admixing 200 g/l (5.0 m/l) of sodium hydroxide, 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide and 60 g/l (0.31 m/l) of sorbitol.

Each of these concentrated solutions was diluted equally about 25 times with water prior to use and then fed through separate nozzles which were directed so as to provide admixture thereof in spray form upon a glass surface which was passed through the spray. A reflective silver film was deposited on the glass surface.

Example 8

A three-part silvering system for deposition of metallic silver on a glass surface was prepared in which sorbitol was utilized as the explosion inhibitor of the invention and a conventional reducer; namely, dextrose, was used to effect deposition at an acceptable commercial rate.

A first concentrated aqueous solution was prepared by admixture of 250 g/l (1.47 m/l) of silver nitrate, 417 cc/l (6.17 m/l) of 28% w/v ammonium hydroxide, 25 g/l (0.13 m/l) of sorbitol and 25 g/l (0.31 m/l) of ammonium nitrate in water.

A second concentrated aqueous solution was prepared by admixture in water of 200 g/l (5.0 m/l) of sodium hydroxide and 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide.

A third concentrated aqueous solution of 11 g/l (0.56 m/l) of dextrose in water was also prepared. Invert sugar can be substituted for the dextrose, if desired.

Each of these concentrated solutions was then diluted equally about 25 times with water prior to use. The three diluted solutions were fed through separate nozzles directed so as to provide admixture of the solutions in a spray applied to the glass surface to be coated. As the glass surface was passed through the spray, a reflective silver film was deposited thereupon.

Example 9

A three-part silvering system similar to that set forth in Example 8 was prepared. However, the first concentrated aqueous solution was prepared by admixture of 25 g/l (1.47 m/l) of silver nitrate and 417 cc/l (6.17 m/l) of 28% w/v ammonium hydroxide in water. The second concentrated aqueous solution was prepared by admixture of 200 g/l (5.0 m/l) of sodium hydroxide, 195 cc/l (2.87 m/l) of 28% w/v ammonium hydroxide and 25 g/l (0.13 m/l) of sorbitol in water. The third concentrated solution was prepared as in Example 8, above.

These three solutions were then diluted and applied as in Example 8 and a reflective film of silver was deposited on the target glass surface.

Claims

1. A method for inhibiting formation of explosive conditions or compounds in a mixture resulting from contact of (1) a concentrated aqueous solution of an ammoniacal silver salt and (2) a



* C L M S *

concentrated aqueous solution of a strong alkali, which comprises providing an effective amount of an explosion inhibitor comprising a polyhydric alcohol having 4 to 6 carbon atoms in at least one of said concentrated aqueous solutions (1) or (2).

2. The method of claim 1, wherein said polyhydric alcohol is any one of sorbitol, mannitol, arabitol, ribitol and xylitol.

3. The method of claim 1 wherein said explosion inhibitor is provided in said concentrated aqueous solution of ammoniacal silver salt together with sufficient extraneous ammonium ions (as hereinbefore defined) to stabilize said explosion inhibitor therein.

4. The method of claim 1 or 2 wherein said polyhydric alcohol is sorbitol or mannitol provided in the range of 25—200 g/l.

5. The method of claim 4 wherein the range is 25—60 g/l.

6. The method of claim 4 wherein the range is 60—200 g/l.

7. The method of any of the preceding claims wherein said source of extraneous ammonium ions is provided by addition of ammonium nitrate or ammonium citrate to said aqueous solution of ammoniacal silver nitrate.

8. The method of claim 7 wherein said ammonium nitrate is provided in a range of 10—200 g/l.

9. The method of claim 8 wherein the range is 16—80 g/l.

10. The method of claim 3 wherein said source of extraneous ammonium ions is provided by addition to said concentrated aqueous solution of ammoniacal silver nitrate of an effective amount of citric acid, tartaric acid, acetic acid, or a mineral acid compatible with said ammoniacal silver nitrate, whereby said extraneous ammonium ions required to stabilize said polyhydric alcohol are generated *in situ*.

11. The method of claim 10 wherein citric acid is provided in a range of 5—100 g/l.

12. The method of claim 11 wherein the range is 5—20 g/l.

13. The method of any of the preceding claims wherein a conventional reducer for said ammoniacal silver salt is included either with (a) said concentrated aqueous solution of ammoniacal silver salt, (b) said concentrated aqueous solution of strong alkali, or (c) both of solutions (a) and (b), provided said conventional reducer is compatible therewith, so as to facilitate reduction of said ammoniacal silver salt to effect electroless deposition of silver upon contacting the solutions containing said ammoniacal silver salt and strong alkali.

14. A multi-part system for electroless deposition of silver by simultaneous admixture of diluted portions thereof on a work surface, which system is protected against formation of explosive compounds or conditions upon contacting the system components, said system comprising the following compositions:

(A) a concentrated aqueous silvering solution comprising ammoniacal silver salt,

(B) a concentrated aqueous solution of strong alkali, and

(C) an effective amount of a reducer for the ammoniacal silver salt,

and wherein either in solution A or in solution B or in both there is provided sufficient explosion inhibitor comprising a polyhydric alcohol having 4 to 6 carbon atoms to effect said deposition of silver and sufficient extraneous ammonium ions to stabilize said polyhydric alcohol in said aqueous silvering solution and thereby prevent deterioration of the same.

15. The system of claim 14 wherein a conventional reducer for said ammoniacal silver salt is included either in solution A, solution B, or a portion of said conventional reducer is included in each of solutions A and solution B, provided said conventional reducer is compatible therewith, or if said conventional reducer is not compatible therewith, said reducer is provided in a separate solution C which is simultaneously admixed with said solutions A and B, said conventional reducer being included in an amount effective to improve depositions of metallic silver on said work surface upon admixture of solutions A and B.

16. The multi-part silvering system of claim 14 or 15 wherein said ammoniacal silver salt is ammoniacal silver nitrate, said polyhydric alcohol is selected from sorbitol, mannitol, arabitol, ribitol, and xylitol and said extraneous ammonium ions are provided in said solution A by (1) addition of ammonium nitrate or ammonium citrate, or (2) by generation of said extraneous ammonium ions *in situ* by addition of citric acid, or mineral acids compatible with said ammoniacal silver salt.

17. The multi-part silvering system according to any of claims 14—16 wherein said ammoniacal silver nitrate is provided in the range of 100—500 g/l of silver nitrate, said polyhydric alcohol is provided in the range of 25—200 g/l, said ammonium nitrate is provided in the range of 10—200 g/l, and said citric acid is provided in the range of 5—100 g/l.

18. The multi-part silvering system of claim 14 wherein said polyhydric alcohol is provided in a range of 25—60 g/l.

19. A method for inhibiting formation of explosive conditions or compounds in a mixture resulting from contact of concentrated aqueous solutions of an ammoniacal silver salt and a strong alkali substantially as herein described with reference to any one of Examples 2—9.



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20. A multi-part system for electroless deposition of silver substantially as herein described with reference to any one of Examples 2—9.

21. A multi-part system as claimed in claim 14 wherein said polyhydric alcohol serves as the reducer.

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