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3,672,939

ELECTROLESS PROCESS FOR FORMING THIN METAL FILMS

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No Drawing. Filed June 2, 1969, Ser. No. 829,755
Int. Cl. B44d 1/08; C03c 17/10

U.S. Cl. 117—54

20 Claims

ABSTRACT OF THE DISCLOSURE

The invention described herein relates to an electroless process for forming thin metal films, particularly transparent films, on a reactive substrate. It particularly relates to a method of spraying two alkaline solutions—one containing a chelated metal salt and the other containing a reducing agent—onto a reactive substrate to form a metal film by reduction of the metal salt. More particularly, the invention relates to an electroless process for forming metal films of metals contained in Groups Ib and VIII of the Periodic Table, especially iron, cobalt, and nickel, by forming an alkaline solution of soluble chelated salts of said metals in an aqueous media, preferably including boric acid, and spraying said solution on a reactive substrate at substantially the same time that an alkaline solution of a boron-containing reducing agent, especially alkali metal borohydrides, is sprayed on the substrate. The invention has been found to be particularly useful for forming transparent films of cobalt, nickel, iron, and the like on sensitized transparent substrates such as glass and plastic.

BACKGROUND

Techniques of electroless plating of metal films on various types of substrates are well known in the art. Electroless plating of metals such as nickel, cobalt, iron, and the like on metallic substrates or on sensitized non-metallic substrates is an important process in the electrochemical industry. An electroless process generally involves an aqueous media having dissolved therein a metal salt and an appropriate reducing agent. A metallic article or a sensitized non-metallic article is immersed in an electroless plating bath whereupon a metal film is deposited upon the article by an autocatalytic mechanism.

Although the electroless process is an old and established one, improvements are constantly being sought. For example, Brenner and Riddell discovered in 1944 that nickel could be autocatalytically deposited upon metallic substrates from a nickel salt solution containing sodium hypophosphite. U.S. Pats. 2,532,283 and 2,532,284 were issued to Brenner and Riddell upon their discoveries. The Brenner process, however, proceeds satisfactorily only at elevated temperatures which is disadvantageous for certain substrates such as the thermoplastic organic polymeric materials. Recent improvements in electroless immersion plating involve the use of boron-containing reducing agents which are effective at room temperature. U.S. Pat. 3,140,188 and U.S. Pat. 3,045,334 are representative of improved electroless plating processes of this type.

Although immersion plating of the so-called catalytic metals, that is, iron, platinum, silver, nickel, gold, cobalt, palladium, and copper, on sensitized non-metallic materials, as for example, materials sensitized in accordance with the method described in U.S. Pat. No. 2,702,253, are quite efficient for certain purposes, such processes do have disadvantages. An immersion process is not especially adaptable to coating extremely large articles. Also, the composition of the plating bath changes during use, thereby requiring frequent chemical analysis and addition of

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materials to maintain a constant bath composition. If a constant bath composition is not maintained, the metal films formed therein are non-uniform.

Furthermore, immersion processes are not especially adaptable to forming transparent films inasmuch as the rate of deposition is difficult to control and film non-uniformity results since a heavier coating is deposited upon that portion of the article which is the first to enter and last to leave the plating bath.

Some of the above-mentioned objections can be overcome with a spraying process. One type of spraying process is described in U.S. Pat. 2,956,900 of Carlson et al. wherein two separate solutions are sprayed upon substrates to form nickel coatings. This process uses sodium hydro-sulfite and sodium hypophosphite as reducing agents. One disadvantage of the process is the sulphurous fumes which are emitted when hydrosulfite reducing agents are utilized. Another disadvantage is the inability of the process to form uniform, transparent films upon a sensitized glass or plastic substrate.

Although considerable effort has been expended in the development of an electroless process for deposition of metal coatings, there is no described process which is entirely satisfactory for the formation of uniform, thin films, especially transparent films, upon reactive substrates.

INVENTION

It has now been discovered that uniform, thin films, particularly transparent films, can be developed by spraying upon a reactive substrate an alkaline solution of a chelated metal salt, preferably containing boric acid and an alkaline reducing solution containing a boron-containing reducing agent, preferably an alkali metal borohydride.

This process has been found to be effective over a broad temperature range for coating any of the so-called catalytic metal substrates or non-catalytic substrates sensitized in a manner to promote deposition of continuous, adherent metal films. Catalytic substrates and processes for rendering inert substances catalytic are well known.

Both opaque and transparent films may be produced by the method of this invention. Best uniformity of transparent films is achieved when films are deposited to a thickness having light transmission of 30 percent or less. The films produced by this invention are continuous and adherent to the substrate.

Sheets of glass filmed with transparent metal films of this invention, especially nickel, cobalt, and iron films, are useful as solar control windows, reflecting much of the solar radiation impinging thereon. Opaque metal films can be utilized on metal or other substrates as mirrors or to provide corrosion resistance.

METAL SALT SOLUTION

A solution containing a metal of Groups Ib and VIII consists generally of a chelated metal salt of an inorganic or organic acid, preferably the latter, especially acetic acid, a small amount of an organic or inorganic acid, preferably boric acid, and sufficient alkaline material, preferably ammonium hydroxide, to maintain the pH above 7. The preferred metals are nickel, cobalt, and iron although copper, lead, antimony, tin, bismuth, and noble metals such as palladium, platinum, osmium, gold, silver, and the like and alloys of the above may be utilized according to the practice of this invention.

As mentioned above, various metal salts of inorganic and organic acids soluble in aqueous solutions may be utilized. Metal salts having only slight solubility in aqueous solutions may be utilized inasmuch as active concentrations of metal range from about 0.1% by weight to about 20% by weight of the solution. A preferred

concentration is about 0.5% by weight to about 10% by weight of the metal per unit weight of solution. Furthermore, the valence state of the soluble metal ion is unimportant; for example, cobaltous or cobaltic salts are equally effective.

Typical metal salts useful in this invention include: nickel chloride, nickel bromide, nickel iodide, nickel sulphate, cobalt bromide, cobalt chloride, cobalt fluoride, iron chloride, iron bromide, iron sulphate, and the like. Also useful are the halides, especially chlorides, nitrates, and like salts of copper, lead, antimony, tin, bismuth, and the above-mentioned noble metals.

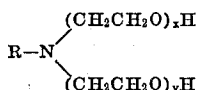
Typical salts of organic acids useful in this invention include: nickel acetate, nickel propionate, nickel fluoroborate, nickel citrate, nickel tartrate, nickel maleate, cobalt acetate, cobalt citrate, cobalt itaconate, and the like. Similar organic salts of copper, lead, tin, antimony, bismuth, and the above-mentioned noble metals are also useful.

Although the pH of the metal solution is maintained above 7, for transparent films it is desirable to operate from pH 7 to pH 11, and preferably from pH 7.2 to pH 7.6. The presence of a small quantity of an inorganic or organic acid, preferably boric acid, is essential. The formation of transparent films of metals such as nickel, cobalt, iron, and the like has been found to be greatly facilitated by the presence of boric acid. Other acids may also be utilized, for example, acetic acid, propionic acid, citric acid, tartaric acid, and the like. Boric acid has been found to promote film uniformity and to reduce the tendency of the metal film to peel from the substrate during drying. For best results, it is desirable to include boric acid in the metal-containing solution even though additional acids may be present.

The metal-containing solution may contain a wetting agent. Wetting agents which have been found particularly effective in a spray process for deposition of transparent films of metals, for example, nickel, cobalt, iron, and the like are non-ionic and cationic wetting agents which are known not to precipitate heavy metals from solution. Wetting agents particularly useful for this purpose include:

Cationic agents such as:

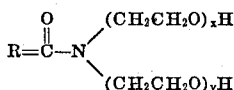
- (1) quaternary ammonium salts, for example tetramethyl ammonium chloride dipropyl dimethyl ammonium chloride,
- (2) alkylene oxide condensation products of organic amines, for example



wherein R is a fatty alkyl group preferably having about 12 to 18 carbon atoms and x and y represent whole numbers from 1 to about 20, typical products of this type being ethylene oxide condensation products of cocoamines, soybean amines, and the like, having an average molecular weight of about 200 to about 3,000.

Non-Ionic agents such as:

- (1) alkylene oxide condensates of amides, for example hydrogenated tallow amides having a molecular weight of about 200 to about 300, and oleyl amines wherein a typical structure is



wherein R, x, and y have the same significance as set forth immediately above for organic amine condensates;

- (2) alkylene oxide condensates of fatty acids.

Wetting agents of the above types are useful in promoting film uniformity. Of particular utility are the

alkylene oxide condensation products of organic amines which have been found to promote substantially-mottled-free transparent films of nickel, cobalt, iron and the like formed by the spray process described herein. Cocoamine-ethylene oxide condensates having a molecular weight of greater than about 300 have been found especially effective for this purpose. Typical cocoamines are Ethomeen C-15 and Ethomeen C-20 of Armour and Company, described hereinafter in the examples.

A chelating agent is essential in the alkaline metal salt solution to prevent precipitation of the metal salt. The preferred chelating agent is gluconic acid, or an alkali metal salt thereof, especially sodium gluconate; however, known chelating agents such as citric acid, glycolic acid, sodium ethylenediamine, lactic acid, aminotetracetic acid, and the like are useful. The formation of transparent metal films of good optical characteristics is enhanced by the utilization of gluconic acid or sodium gluconate.

The quantity of chelating agent utilized should be that which is sufficient to maintain the metal salt in solution at the operating temperatures. Generally, chelating agents are utilized in a mole-to-mole ratio for each mole of metal ion present although it has been found that lesser quantities are effective with the dilute coating solutions of this invention. Good coatings are produced from metal solutions having a molar ratio of 1:4 of chelating agent to metal ion, and a molar ratio of between about 1:2 and 1:1 is preferred for deposition of transparent metal films.

The metal salt solution is preferably formed by dissolving a desired quantity of nickel salt in water and adding the desired amount of chelating agent. Boric acid is preferably added next and then the pH of the solution is adjusted to about pH 7 or greater with an alkaline material, preferably a hydroxide. Boric acid may be added before the chelating agent, but the chelating agent preferably precedes the addition of any alkaline materials.

The alkalinity of the metal salt solution should be maintained between a pH of 7 and 9.5, and preferably between 7.2 and 7.6. Alkaline materials generally may be used for pH control although hydroxides such as sodium, potassium, and ammonium hydroxide are preferred, with best results being achieved with ammonium hydroxide.

The temperature of the metal salt solution should be maintained between about 40° F. and 200° F. for general coating purposes and between about 60° F. and 100° F., preferably 70° F. to 80° F., for deposition of uniform, transparent films.

REDUCING SOLUTION

The reducing solution comprises an aqueous solution of a boron-containing reducing agent, said solution having a pH greater than 7 and preferably above 9. Best quality transparent films are formed when the reducing solution is maintained at a pH of about 11 to 12.5. The boron-containing reducing agent may be present in solution as about 0.01% by weight to about 5% by weight of the solution. While boron-containing reducing agents are effective in the aforementioned range, a preferred concentration of 0.05% by weight to about 2% by weight is preferred. Exceptionally useful boron-containing reducing agents are the alkali metal borohydrides such as sodium borohydride, lithium borohydride, and potassium borohydride. Other boron-containing reducing agents, however, are effective although frequently unavailable in commercial quantities. Exemplary boron-containing reducing agents other than borohydrides are the boron-containing compounds listed in U.S. Pat. No. 3,140,188 of Zirngiebl et al., incorporated herein by reference. Amine boranes such as diethylamine borane, trimethylamine borane, triethylamine borane, and pyridine borane may also be used. Other effective boron-containing compounds include substituted borohydrides such as sodium trimethoxy borohydride and the like.

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The reducing solution is preferably alkaline inasmuch as boron-containing reducing agents oxidize very rapidly in acid and neutral solutions. It is preferred that the pH of the intermixed solution, that is, the solution formed by the impingement of the two spray solutions at the surface of the object to be coated, be at least 7.

PROCESS

The metal-containing solution and reducing solution are each passed through separate spray nozzles so that the sprays intermix and contact the surface of the article to be coated. Single nozzle guns may be also used where the solutions intermix in the gun or outside the gun. The flow rates of each solution may be approximately equal or may vary greatly. The flow rates of the respective solutions are not critical; however, it is desirable to maintain a weight ratio of reducing agent to metal contained in the metal-containing solution of about 10:1 to about 1:2000 parts per weight reducing agent to parts per weight of metal. The temperature of the article to be coated is not material although the temperature of the article should be uniform in order to promote film uniformity. The process is quite effective at room temperature, although a preferred temperature range is from 40° F. to about 200° F.

The substrate must be receptive to metal deposition. For the deposition of films of nickel, cobalt, iron, and the like, it is preferred to have a reactive metal substrate, for example, in the formation of a transparent article, an appropriate substrate is a transparent glass article coated with a transparent metal film of copper, aluminum, tungsten, cobalt, platinum, silver, boron, thallium, vanadium, titanium, nickel, gold, germanium, silicon, chromium, molybdenum, iron, tin, palladium, lead, indium, cadmium, zinc and the like. For example, a transparent copper film could be deposited on a transparent glass or plastic substrate by means of vacuum deposition or sputtering and thereafter sprayed according to the teaching of this invention with a transparent coating of nickel, cobalt, iron, or the like.

A further method of preparing the substrate for electrodeless deposition according to this invention may be accomplished in accordance with the teaching of U.S. Pat. 2,702,253 or U.S. Pat. 3,011,920, the teachings therein being incorporated herein by reference.

EXAMPLE I

A commercial soda-lime-silica glass sheet was washed with a commercial detergent until the glass was completely and uniformly wetted by water. The sheet was rinsed with tap water and then rinsed with demineralized water.

The glass surface was then contacted with a dilute solution of stannous chloride (about 0.1% by weight SnCl_2). The glass was thoroughly rinsed with demineralized water and then contacted with a dilute solution of palladium chloride (about 0.025% by weight PdCl_2). The glass was completely rinsed with demineralized water.

The glass was hand sprayed with two sprays—one of nickel solution, the other of reducing solution—to form a nickel film. The sprays intermingled at the glass surface. Each spray had a flow rate which ranged from 50 to 500 milliliters per minute; however, the rates were maintained in a balanced condition.

Nickel solution composition

Nickel chloride—5 grams
Boric acid—2.5 grams
Gluconic acid (50% solution in water)—13 milliliters
Sodium hydroxide (50% aqueous solution)—added until pH 7.5

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Ethomeen C-15¹—2 drops
Water added to form 1 liter solution

Nickel chloride was dissolved in water, the chelating agent (gluconic acid) and boric acid were then added in that order followed by sodium hydroxide and C-15. The remaining water was added to bring solution volume to 1 liter.

Reducer solution composition

Sodium borohydride—0.75 gram
C-15¹—1 drop
Water added to form 1 liter solution

The pH of the reducer solution was about 9.5. The temperature of each solution was about room temperature.

The above solutions were sprayed substantially simultaneously in equal volumes upon a sensitized glass plate. Film formation was rapid. After spraying for about 1 minute, a nickel film was formed having a light transmission of 20%. The film was very uniform in appearance and very adherent to the substrate.

EXAMPLE II

A nickel acetate solution was utilized to form a transparent nickel film.

Nickel solution composition

Nickel acetate—5 grams
Boric acid—2.5 grams
Sodium gluconate—9.0 grams
Water added to 1 liter
Ammonium hydroxide—added to pH 7.5
C-20 surfactant²—2 drops

Reducing solution composition

Sodium borohydride—0.5 gram
Water added to 1 liter
Sodium hydroxide (50% aqueous solution) added to pH 11.5
Ethomeen C-20 surfactant²—1 drop

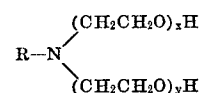
The processing conditions were similar to those set forth in Example I.

The resulting nickel film formed after spraying for 1 min. 15 seconds had a light transmission of about 20%. The film was very uniform and adherent.

The nickel acetate solution was utilized to prepare several samples. The results were very reproducible. Uniform films of a desired light transmission could be produced in continuous fashion.

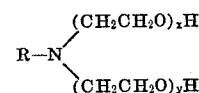
The reducing solution was found to be exceptionally stable when adjusted to a pH of 11.0 to 12.5. The reducing solution of this example had a shelf life of 15 hours as compared with 3 to 4 hours for an unadjusted solution.

¹ Ethomeen C-15 (trademark of Armour and Company) is a cocoamine having an average molecular weight of 422 and the following generalized formula:



wherein R is derived from a cocoamine and $x+y$ equals 5.

² Ethomeen C-20 (trademark of Armour and Company) is a cocoamine having an average molecular weight of 645 and the following generalized formula:



wherein R is derived from a cocoamine and $x+y$ equals 10.

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EXAMPLE III

Cobalt films were formed electrolessly from the following solutions:

Cobalt solution composition

Cobalt acetate—5 grams
Boric acid—2.5 grams
Sodium gluconate—9.0 grams
Water added to form 1 liter
pH adjusted to between 7.2 and 7.6 with ammonium hydroxide
Surfactant (C-20)—2 drops

Reducer solution composition

Sodium borohydride—0.5 gram
Water added to form 1 liter
pH adjusted to between 11.0 and 11.5 with 50% aqueous sodium hydroxide

The above solutions were sprayed in equal volumes through a double nozzle spray gun onto glass which had been cleaned and sensitized in the manner described in Example I. After spraying at a rate of 75 to 120 milliliters per minute per nozzle for about 1 minute, 20 seconds, a transparent adherent cobalt film was formed on the glass. The film had a luminous transmittance of about 20%.

EXAMPLE IV

An iron film was formed electrolessly from the following solutions:

Iron solution composition

Ferrous ammonium sulfate—5.0 grams
Boric acid—9.0 grams
Water added to form 1 liter
pH adjusted to between 7.0 and 7.5 with ammonium hydroxide
Surfactant (C-20)—2 drops

Reducing solution composition

Sodium borohydride—0.50 gram
Water added to form 1 liter
pH adjusted to between 11.0 and 16.5 with 50% aqueous sodium hydroxide

The above solutions were sprayed onto pre-sensitized glass in the manner described in Example III. A transparent iron film having a light transmission of about 20% to 25% was formed after spraying for about 1 minute to 1½ minutes. The film must be rinsed immediately with demineralized water to prevent oxidation. Of course, oxidation could be prevented by using methanol, ethanol, or similar polar organic solvents to form the metal salt and reducer solutions.

EXAMPLE V

A gold film was formed electrolessly from the following solutions:

Metal solution composition

Chlorolauric acid—1.0 gram
Sodium carbonate—5.0 grams
Water added to form 1 liter
Surfactant (C-20)—2 drops
No pH adjustment required

Reducing solution composition

Sodium borohydride—0.5 gram
Water added to form 1 liter
pH adjusted to between 11.0 and 11.5 with 50% aqueous sodium hydroxide
Surfactant (C-20)—1 drop

The above solutions were sprayed in equal volumes onto a glass surface that had been thoroughly cleaned, sensitized with stannous chloride, and rinsed with distilled water.

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A bright, transparent gold film was formed on the glass after spraying for about 1 to 2 minutes at a rate of about 25 to 50 milliliters per minute per nozzle.

EXAMPLE VI

Copper films were formed electrolessly from the following solutions:

Copper solution composition

Copper fluoroborate—5.0 grams
Ethylene diamine tetracetic acid—13 grams
Boric acid—2.5 grams
Water added to form 1 liter
pH adjusted to between 7.6 and 8.0 with 50% aqueous sodium hydroxide
Surfactant (C-20)—2 drops

Reducing solution composition

Sodium borohydride—0.5 gram
Water added to form 1 liter
Surfactant (C-20)—1 drop

Equal volumes of the above solutions were sprayed onto glass which had been cleaned, sensitized with stannous chloride, and super-sensitized with palladous chloride. A transparent copper film was formed after spraying for about 1 to 2 minutes at a rate of about 60 milliliters per minute per nozzle.

Although specific embodiments of the instant invention have been set forth hereinabove, the invention is not intended to be limited thereto but includes all of the modifications and variations falling within the scope of the following claims.

What is claimed is:

1. A process for forming thin metallic films of metals of Group VIII and Group Ib of the Periodic Table on a sensitized substrate comprising contacting said substrate substantially simultaneously with a spray of a metal salt solution having a pH of greater than 7 and a spray of a reducing solution having a pH greater than 7
 - (a) said metal salt solution comprising water, a chelated metal salt of an organic or inorganic acid and an effective amount of boric acid to provide for the deposition of a uniform film, and
 - (b) said reducing solution comprising water and a boron-containing reducing agent.
2. The method of claim 1 wherein the metal salt is selected from the class of salts of nickel, cobalt, and iron and mixtures thereof.
3. The method of claim 1 wherein the metal salt solution contains a sufficient amount of an alkaline material to maintain a solution pH about 7 to 11.
4. The method of claim 3 wherein the reducing solution contains a sufficient amount of an alkaline material to maintain a solution pH of greater than 9.
5. The method of claim 2 wherein the boron-containing reducing agent is an alkali metal borohydride.
6. The method of claim 2 wherein the metal salt is a nickel salt.
7. The method of claim 1 wherein the chelated metal salt is formed from reaction with a chelating agent selected from the class consisting of gluconic acid, citric acid, glycollic acid, sodium ethylenediamine, aminotetracetic acid.
8. The method of claim 1 wherein the metal films and the reactive substrate are transparent.
9. The method of claim 1 wherein the process is carried out at a temperature of about 40° F. to 200° F.
10. The method of claim 2 wherein the metal salt is a metal acetate.
11. A method of forming a transparent film of a metal selected from the class consisting of nickel, cobalt, iron and mixtures thereof on a glass substrate by
 - (a) contacting said substrate with an aqueous stannous chloride sensitizing solution;

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(b) contacting said sensitized substrate with an aqueous super-sensitizing solution of a noble metal selected from the group consisting of salts of palladium, platinum and mixtures thereof;

(c) contacting said super-sensitized substrate substantially simultaneously with a spray of an aqueous metal salt solution having a pH of about 7.2 to about 7.6 and a spray of an aqueous reducing solution having a pH of about 11 to about 12.5, said solutions intermixing at the glass surface to form a coating solution having a pH of about 8 to about 9;

(1) said metal salt solution comprising chelated salts of metals selected from the class consisting of nickel, cobalt, and iron, and mixtures thereof, and an effective amount of boric acid to provide for the deposition of a uniform film, and

(2) said reducing solution containing an alkali borohydride.

12. The method of claim 11 wherein the metal salt is a metal acetate.

13. The method of claim 12 wherein the metal acetate is nickel acetate.

14. The method of claim 11 wherein the pH of the metal salt solution is adjusted with ammonium hydroxide.

15. The method of claim 11 wherein the chelated salts of metals are formed by reaction with gluconic acid.

16. The method of claim 11 wherein the temperature of the metal salt solution is maintained at about 70° F. to about 80° F. and the temperature of the reducer solution is maintained at about 65° F. to about 70° F.

17. The method of claim 11 wherein the metal salt solution and reducer solution are each sprayed at substantially the same rate.

18. The method of claim 11 wherein the metal salt solution comprises about 1 to about 50 parts nickel ace-

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tate, about 1 to about 50 parts boric acid, sufficient gluconic acid or sodium gluconate to maintain the nickel acetate in solution and about 1,000 parts of water, said nickel acetate to boric acid ratio ranging from about 1:1 to about 5:1, and said reducer solution comprising about 0.1 part to about 10 parts sodium borohydride and about 1,000 parts of water.

19. The method of claim 18 wherein each 1,000 liters of the metal salt solution and reducer solution contains about 0.5 to about 5 drops of a wetting agent.

20. The method of claim 19 wherein the wetting agent is a cocoamine-ethylene oxide condensate having a molecular weight of about 645.

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U.S. Cl. X.R.

117—35 S, 47 R, 50, 105.5, 124 C, 130 E