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3,671,291

ELECTROLESS PROCESS FOR FORMING THIN METAL FILMS

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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 solutions, one, an acidic solution containing a metal salt and the other, an alkaline solution containing a boron 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 Group Ib and Group VIII of the Periodic Table, especially iron, cobalt, and nickel, by forming a solution of soluble salts of said metals in an acidic, 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 electro-chemical 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 auto-catalytically deposited upon metallic substrates from a nickel salt solution containing sodium hypophosphite. U.S. Patents 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. Patent 3,140,188 and U.S. Patent 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. Patent 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, there-

by requiring frequent chemical analysis and addition of 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. Patent 2,956,900 of Carlson et al. wherein two separate solutions are sprayed upon substrates to form nickel coatings. This process uses sodium hydrosulfite 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 can be developed by spraying upon a reactive substrate, an acidic metal salt solution, 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 largely independent of temperature and is effective 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 substrates 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 the film is deposited to a thickness having light transmission of about 30% 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 of the Periodic Table consists generally of a metal salt of an inorganic or organic acid and a small amount of an organic or inorganic acid, preferably boric acid, to maintain a solution pH of less than 7. When an acid other than boric acid is used to adjust solution pH, boric acid is to be included in the solution as well and is to be employed in an amount which is effective to promote film uniformity. 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 aque-

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ous 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 ion 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.

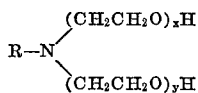
Typical salts of organic acids useful in this invention include: nickel acetate, nickel propionate, nickel fluoroborate, nickel citrate, nickel tartrate, nickel maleate, cobalt acetate, cobalt citrate, cobalt itaconate, and the like. Similar organic salts of a copper, lead, tin, antimony, bismuth, and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

As mentioned hereinabove, the metal containing solution contains sufficient quantity of an acid to maintain a pH of less than 7. Although a pH range of 1 to 7 is effective, a preferred pH range is from about 4 to about 5. Numerous acids, of course, can be utilized to maintain an effective pH range, for example, inorganic acids such as hydrochloric, nitric, sulphuric, boric, and carbonic acids, and the like, may be utilized as well as organic acids such as acetic acid, propionic acid, citric acid, tartaric acid, and the like, may be utilized. Although the above acids are effective in maintaining a proper pH range, it has been found that boric acid is preferred in maintaining a pH range of between 4 and 5. Moreover, boric acid has been found to promote film uniformity and to reduce the tendency of the metal film to peel from the substrate during spraying. These features are especially desirable in the formation of transparent metal films. In order to obtain improved film uniformity boric acid is essential in the metal containing solution even though additional acids may be utilized and to aid in pH control.

The metal-containing solution may contain an appropriate wetting agent. Wetting agents which have been found particularly effective in a spray process for deposition of transparent films of 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

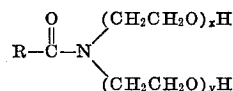


wherein R is a fatty alkyl group preferably having about 12 to 18 carbon atoms and x and y represent whole numbers from 1 to about 20, typical products of this type being ethylene oxide condensation products of coco amines, soybean amines, and the like, having an average molecular weight of about 200 to about 3000.

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 amides wherein a typical structure is

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where R, x and y have the same significance as set forth immediately hereinabove 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 mottle-free transparent films of nickel, cobalt, iron and the like formed by the spray process described herein. Coco amine-ethylene oxide condensates having a molecular weight of greater than about 300 have been found especially effective for this purpose. A typical coco amine is Ethomeen C-15 of Armour and Company, described hereinafter in the examples.

REDUCING SOLUTION

The reducing solution comprises an aqueous solution of a boron-containing reducing agent, said solution having a pH of 7 to 14, and preferably of about 8 to 10. 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. Patent 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.

The reducing solution is preferably alkaline inasmuch as boron-containing reducing agents oxidize very rapidly in acid and neutral solutions. The alkalinity of the reducing solution should not be so great that the pH of the intermixed metal-containing solution and reducing solution is above 7. 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 7 or less.

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 also be 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 ap-

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. These metals are known as catalytic metals for electroless deposition of films of cobalt, nickel, iron, 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 electroless deposition according to this invention may be accomplished in accordance with the teaching of U.S. Patent 2,702,253 or U.S. Patent 3,011,920, the teachings therein being incorporated herein by reference.

Example I

A 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.

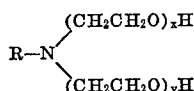
The glass surface was then contacted with a dilute solution of stannous chloride (about 0.1 percent by weight of SnCl_2). The glass was thoroughly rinsed with demineralized water and then contacted with a dilute solution of palladium chloride (about 0.025 percent by weight of PdCl_2). The glass was completely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

The glass was contacted 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 ml./min., however, the rates were maintained in a balanced condition.

Nickel solution composition:

$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ —5.0 grams
Boric acid—2.5 grams
Water—1 liter
Ethomeen C-15—2 drops

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 plus y equals 5.

Reducing solution composition:

Sodium borohydride—0.5 grams
Water—1 liter
Ethomeen C-15—1 drop
Adjusted pH to 9–10 with NaOH

The nickel coated glass has a light transmission of about 12 percent after being contacted for about 1 min. at a flow rate of about 70 milliliters/min. Film formation occurred in about one to two minutes and the film was clear, uniform and substantially mottle-free.

Example II

A glass sheet was coated with cobalt in substantially the same manner as in Example I, being cleaned, sensitized, and super-sensitized in the same manner as Example I.

The cobalt solution was identical to Example I with 5 grams cobaltous chloride replacing the nickel chloride. The reducing solution had the same composition. The spray rates were also the same.

A 12" x 12" glass sample was coated with cobalt metal. The film had a slight brownish tint but was uniformly transparent and had light transmission of 10 per-

cent after spraying for two minutes at a flow rate of about 60–70 milliliters/minute for each solution.

Example III

To illustrate the effectiveness of reducing agents in the spraying process of this invention, a nickel film was formed in the following manner:

Glass was cleaned in the manner described in Example I. A dilute stannous fluoride was utilized as the sensitizing agent while platinum chloride was used in dilute solution as the supersensitizing agent.

Nickel solution composition:

$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ —7.5 grams
 H_3BO_3 —5.0 grams
Water—1 liter
pH—4.0–5.0 (no adjustment necessary)

Reducing solution composition:

Sodium borohydride—0.5 gram
Water—1 liter
pH adjusted to 9–10 with aqueous NaOH solution of about 0.1 N

A nickel film was formed having a transmission of 14 to 30 percent at a flow rate of 60 to 70 milliliters per minute after one minute. A non-uniform film having good adhesion was formed.

When nickel sulfate was substituted for nickel chloride in the above examples, comparable films are obtained.

When potassium borohydride was substituted in the above examples, comparable results are obtained.

Example IV

To determine the effectiveness of acids other than boric acid, an experiment was conducted where the following nickel containing solution was utilized:

NiSO_4 —25 grams
Sodium tartrate—25 grams
Water—1 liter
pH adjusted to 5 with NaOH solution

A standard sodium borohydride reducing solution of the type described in Example I was utilized; only a trace of nickel film was formed on the glass.

In another variation of this experiment, 10 grams of sodium hypophosphite was added to the nickel solution but no film was formed.

Example V

When citric acid was substituted in the above experiment for sodium tartrate, a trace film was formed.

Example VI

Test tube experiments were conducted to determine the effectiveness of the following compounds for reducing nickel ions:

Hydrazine tartrate
Hydrazine sulfate
Hydroxyl ammonium sulfate
Sodium hydrosulfite

The only reducing agent which reduced nickel ion to nickel metal was sodium hydrosulfite.

The following solutions were admixed on a glass surface to determine the type of nickel film which might result:

Nickel solution composition:

NiSO_4 —20 grams
Citric acid—10 grams
Sodium hypophosphite—10 grams
NaOH—8 grams
Water—1 liter
pH—8

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Reducing solution composition:

10 grams per liter of water of sodium hydrosulfite (sodium dithionite)

The above solutions gave no film when simultaneously sprayed upon cleaned, sensitized, supersensitized glass.

The sodium hydrosulfite solutions were found to be unstable; stability was enhanced by addition of zinc sulfate and sodium tetraborate.

Sodium formaldehyde sulfoxalate (20 grams per liter) was found to reduce nickel salts, but did not give a nickel film when used in a spray formulation.

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

We claim:

1. A process for forming thin metallic films of metals of Group VIII and Group Ib of the Periodic Table on a catalytic sensitized substrate comprising contacting said substrate substantially simultaneously with a spray of a metal salt solution of the selected metal of Groups VIII and Ib having a pH of less than 7 and a spray of a reducing solution having a pH greater than 7:

(a) said metal salt solution comprising water, a metal salt of an organic or inorganic acid, and an effective amount of boric acid to provide an observably uniform metallic film on the substrate; 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 2 wherein the metal salt is a nickel salt.

4. The method of claim 1 wherein the boron-containing reducing agent is an alkali metal borohydride.

5. The method of claim 1 wherein the metal films and the substrate are transparent.

6. The method of claim 1 wherein the process is carried out at a temperature of about 40° F. to 200° F.

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7. A method of forming transparent metal films of nickel, cobalt, and iron on a glass substrate by

(a) contacting said substrate with an aqueous stannous chloride sensitizing solution;

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

(c) contacting said super-sensitized substrate substantially simultaneously with a spray of an aqueous metal salt solution having a pH of less than 7 and a spray of an aqueous reducing solution having a pH greater than 7 said solution intermixing at the glass surface to form a coating solution having a pH of less than 7;

(1) said metal salt solution comprising salt of metals selected from the class consisting of nickel, cobalt, and iron, and mixtures thereof, and an effective amount of boric acid to provide an observably uniform metallic film on the substrate, and

(2) said reducing solution containing an alkali borohydride.

8. The method of claim 7 wherein the metal salt solution contains from about 0.5 to about 10 percent by weight of metal ion based on the weight of the metal salt solution.

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