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ETCHING COMPOSITION PREPARATORY TO NICKEL PLATING

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ABSTRACT OF THE DISCLOSURE

Aluminum metals having nickel coatings plated directly thereon may be prepared by electroless deposition of nickel from an aqueous plating solution containing nickel ions, dimethylaminoborane, a carboxylic acid complexing agent and a stress reducer. Nickel plated magnesium metals and beryllium metals may be similarly prepared. The metal surface is rendered susceptible to plating by initially contacting it with a novel activating solution containing ammonium bifluoride and either dimethylaminoborane or nitric acid, and then rinsing if nitric acid is used. Where dimethylaminoborane is used in the activating solution, the metal surface is thereafter stabilized with an aqueous stabilizing solution of dimethylaminoborane. Electroless plating is then carried out, producing a stress free hermetically sealed nickel coating of substantially uniform thickness directly on the aluminum metal, magnesium metal, or beryllium metal surface. Once such a coating is established, further plating with copper, nickel or other metals may be effected by electrolytic or electroless means. The nickel coated surface is preserved in a proper state for any such additional plating by holding it in an aqueous preservative solution of dimethylaminoborane.

This application is a division of the earlier filed copending application Ser. No. 8,014 filed Feb. 2, 1970 now U.S. Pat. No. 3,667,991 issued June 6, 1972.

This invention lies in the field of electroless nickel plating and more particularly relates to aluminum metals, magnesium metals, and beryllium metals having nickel coatings electrolessly plated directly thereon after activation of the metal surfaces with a novel aqueous activation bath and to processes for plating such metals.

Plating of nickel directly onto the surface of aluminum metals would provide numerous beneficial results. Corrosion protection of the metal surface can, of course, be provided by such a coating. A nickel coating also serves as an excellent substrate for receiving a coating of another metal which may be deposited by either electroless or electrolytic means.

Prior to the present invention, however, no method had been known by which nickel could be plated directly onto aluminum metals. Direct electrolytic methods are ineffective since hydrogen ions are reduced preferentially to nickel ions at an aluminum metal cathode, thus liberating hydrogen rather than depositing nickel. Compositions for electroless plating of nickel have been known for some time, but have not heretofore been useful for plating aluminum metal. Methods were known to the prior art by which nickel was indirectly plated on aluminum by first laying down an intermediate metal layer upon which the nickel is deposited. The principal process employed heretofore is a complex one involving chemical deposition of zinc followed by a so-called copper strike. The aluminum metal surface must first be oxidized, e.g. with nitric acid. The surface is then contacted with an alkaline zincate solution to chemically deposit the zinc layer. Next, the zinc layer is electrolytically coated with a thin layer of copper from a solution such as copper cyanide. Nickel may then be plated on the copper layer by electrolytic

means. This process involves several steps and does not, in any event, provide a nickel coating plated directly onto the aluminum metal surface but rather a nickel coating separated from the aluminum surface by layers of two other metals. It may be noted, moreover, that since the nickel is ultimately deposited electrolytically, it is difficult to properly plate surfaces of complicated shape by this process. A uniform thickness of nickel plate is not achieved when complicated shapes are electrolytically plated and in order to insure a coating of adequate thickness at all points on the surface, some points receive a coating which is unnecessarily and in some cases undesirably thick.

By whatever process nickel may be deposited directly or indirectly on aluminum metals, certain properties of the nickel coating are important. It is desirable in most cases that the nickel deposit be stress free. It is also desirable in most instances that the nickel deposit be hermetically sealed. If the nickel deposit is not so sealed, but rather has pinholes therein, the plated article may be defective. Moreover, if another metal is to be electrolytically plated onto the nickel deposit, not only would the presence of such a pinhole prevent electrodeposition at that point, but the pinhole might well be enlarged by the tearing action of hydrogen gas formed during electrolysis at the exposed aluminum metal surface.

There has thus been an unfulfilled need in the art for a practical means for plating a coating of nickel directly onto aluminum, particularly means which produces a plated metal of uniform thickness, provides a hermetic seal, and a plated product essentially free of internal stresses.

Among the objects of the present invention, therefore, may be noted the provision of an article of manufacture having nickel plated directly onto an aluminum, magnesium or beryllium metal surface; the provision of a process for the electroless plating of nickel directly onto such metals; the provision of a process of the type indicated for depositing nickel of substantially uniform thickness onto the surfaces of such metals; the provision of a process for depositing a hermetically sealed coating of nickel on the above-noted metals; the provision of a process for depositing a substantially stress free coating of nickel onto such metals; the provision of a process for depositing a nickel coating of substantially uniform thickness on aluminum metal surfaces of complicated or irregular configuration; and the provision of compositions useful for activating the surfaces of the aforementioned metals, rendering them receptive to electroless plating of nickel. Other objects and features will be in part apparent and in part pointed out hereinafter.

The present invention is thus directed to a process for plating nickel directly onto the surface of metals selected from the group of aluminum metals, magnesium metals, or beryllium metals. The surface of the metal is first activated by contacting it with an aqueous activating solution containing ammonium bifluoride and dimethylaminoborane. Alternately, the activating solution may contain ammonium bifluoride and nitric acid. The metal surface is then either rinsed, if nitric acid has been used in the activation bath, or further contacted with an aqueous stabilizing solution containing dimethylaminoborane if dimethylaminoborane has been used in the activation bath. The metal surface is thereafter contacted with an aqueous plating solution containing nickel ions, dimethylaminoborane, a carboxylic acid or amino carboxylic acid compound as a complexing agent, and a stress reducer. A deposit of nickel is thereby chemically deposited on the surface of the metal. The invention is further directed to the additional step wherein the nickel plated metal surface is prepared for further plating operations by removing it from contact with the plating solution and immersing it in an aqueous preservative solution contain-

ing dimethylaminoborane and holding it in contact therewith until such time as such further plating operations are to be conducted. The invention also includes compositions useful for activating the surface of a metal object to render the metal surface subject to the chemical deposition of nickel from a solution containing nickel ions. The activating composition comprises an aqueous solution of ammonium bifluoride and either nitric acid or dimethylaminoborane. The invention further comprehends an article of commerce comprising a metal selected from the group consisting of aluminum metals, magnesium metals, or beryllium metals, having a coating of nickel plated directly thereon.

In accordance with the present invention, it has been found that a coating of nickel may be plated directly onto the surface of aluminum, magnesium and beryllium metals by electroless deposition from a solution containing nickel ions, dimethylaminoborane, a carboxylic acid or amino carboxylic acid complexing agent and a stress reducer. Nickel is deposited from the plating solution by chemical reduction with the dimethylaminoborane serving as the reducing agent. The nickel coating thus formed on the metal surface is of very high quality, being not only of substantially uniform thickness, but also substantially stress free and hermetically sealed. Thus, an object having such a nickel coating is well adapted for further plating by either electroless or electrolytic means from either alkaline or acid baths to produce various commercially useful plated articles.

The terms aluminum metals, magnesium metals, and beryllium metals as used herein, include not only essentially pure aluminum, magnesium and beryllium but also various alloys thereof known to the art.

Electroless deposition of nickel onto aluminum metals, which had not been possible heretofore, is made feasible through the present invention by activation of the metal surface with the novel activating solutions of this invention. Two aqueous activating solutions may be used. The preferred activating solution contains ammonium bifluoride and dimethylaminoborane. Alternatively, a solution containing ammonium bifluoride and nitric acid may be used. Without being bound to any particular theory, we attribute the activating effect of these solutions to the apparent removal of the oxide film normally present on aluminum metals. The activating bath containing dimethylaminoborane is preferred because it not only cooperates with the ammonium bifluoride in removing the oxide film, but protects the pure metal surface from subsequent oxidation to which it is so highly susceptible. Since nitric acid is a powerful oxidizing agent it is surprising to find it is also useful in an activation bath whose presumed function is to remove oxides. Apparently the nitric acid, functioning as an acid, cooperates with the ammonium bifluoride in removal of the "thick" or "hard" oxide film normally on the metal, but in the presence of the ammonium bifluoride acts as an oxidizing agent to reform only a "thin" oxide layer. The thin oxide layer thus reformed is subject to reduction by the dimethylaminoborane in the plating bath. The presence of the reformed oxide film is evidenced by an induction period between the time an activated metal surface is contacted with the plating solution and the time electroless deposition of nickel begins. Its "thinness" is evidenced by the fact that plating does, after several minutes, begin. Ammonium bifluoride, though an effective acid pickling agent in its own right, has not been found to be effective by itself in activating an aluminum metal surface for electroless nickel plating. Even the presence of dimethylaminoborane in the plating bath will not render active an aluminum metal surface pretreated with ammonium bifluoride only. But in cooperation with a reducing agent, dimethylaminoborane, on the one hand, or with an oxidizing agent, nitric acid, on the other, ammonium bifluoride has been found effective in so preparing the aluminum metal surface for electroless plating.

In the practice of the present invention, the aluminum metal surface is initially vapor degreased by any convenient method. Vapor degreasing with such solvents as methyl ethyl ketone, ethyl butyl ketone, trichloroethylene or the various fluorochloromethanes or fluorochloroethanes (sold under the trade designation "Freon" by E. I. du Pont de Nemours & Co.) has been found effective. It will be understood that other solvents which provide a clean, grease-free surface may also be used. It is also desirable to use an air hose to remove any solid particles from the metal surface. After degreasing, the metal surface is dried.

The cleaned, degreased and dried metal surface is then contacted with one of the novel activating solution compositions of this invention, as by immersion therein. The activating solution should possess the requisite properties to render the metal surface subject to the electroless deposit of nickel thereon without appreciably attacking the said metal surface. The aforementioned compositions of this invention meet these criteria. Though a wide range of concentrations of the components of these compositions are effective in activating the aluminum metal surface, we prefer to use an activating solution containing between about 20 and 100 grams per liter of ammonium bifluoride and, when dimethylaminoborane is used, between about 2 and about 10 grams per liter of dimethylaminoborane. The pH of the activating solution is preferably maintained on the acid side but above about 3.0. Below this pH, the aluminum metal surface is attacked and the dimethylaminoborane tends to decompose instantaneously. This lower pH limit defines the maximum concentration of nitric acid when that compound is used. The metal surface is contacted with the activating solution for a period of about 15 seconds to 2 minutes. The temperature of the activating solution is conveniently room temperature, i.e. between about 20° C. and 30° C. The temperature of the activating solution should not exceed approximately 40° C. if dimethylaminoborane is used, since above that temperature, this compound tends to decompose.

After activation, if dimethylaminoborane is used in the activating solution, the aluminum metal is contacted with an aqueous stabilizing solution containing dimethylaminoborane. The purpose of contacting the metal surface with the stabilizing solution is to insure that the surface is coated with a thin layer of dimethylaminoborane to protect it from oxidation before it is contacted with the plating solution. A very wide range of dimethylaminoborane concentrations is effective in the stabilizing solution. We prefer to use a dimethylaminoborane concentration of about 2% to 5% by weight, but concentrations of less than 1% or more than 10% would also serve to provide effective protection of the metal surface from oxidation. The temperature of contact of the metal surface with the stabilizing solution is conveniently room temperature, i.e. about 20° C. to 30° C. Again, temperatures in excess of 40° C. should be avoided because they may cause decomposition of the dimethylaminoborane. Typically, a contact time of about 3 to 5 minutes is adequate.

If the metal surface has been activated by the use of a solution containing ammonium bifluoride and nitric acid instead of a solution containing ammonium bifluoride and dimethylaminoborane, the stabilizing solution is not used. Rather, the activated aluminum metal surface is prepared for electroless plating by simply rinsing with water at room temperature.

Following a water rinse or treatment with the stabilizing solution, as the case may be, the metal surface is contacted with the aqueous plating solution. When the solution is in contact with an aluminum metal surface, the nickel ions contained therein react with the dimethylaminoborane thereby depositing a nickel coating on the aluminum metal substrate.

$$3OH^- + Ni^{++} + (CH_3)_2NH_2B \rightarrow Ni^o + (CH_3)_2NH + H_2 + H_2BO_3^-$$

The plating solution bath adapted for use in the process of this invention is adapted to provide proper deposition of nickel without attacking, etching, or corroding the surface of the aluminum metal. The plating solution bath we prefer to use contains between about 8 and about 12 grams per liter of nickel ions and between about 2 and about 3.5 grams per liter of dimethylaminoborane. As the source of nickel ions, any soluble nickel salt such as nickel sulfate and nickel acetate may be employed. The plating solution also contains a stress reducer and a complexing or chelating agent. The stress reducer typically may be a compound such as 2-mercapto benzothiazole, 2,3-dimercapto propanol or other divalent sulfur compounds known to the art. The concentration of the stress reducer may be widely varied, preferably ranging between about 0.05 and about 0.5 parts per million. The complexing or chelating agent may be a carboxylic acid or amino carboxylic acid compound such as citric acid, glutamic acid or the water soluble salts thereof, including alkali metal salts of glutamic acid (e.g., monosodium glutamate) and alkaline earth metal salts of glutamic acid. The complexing agent should be present to the extent of about 10 to 50 grams per liter of solution. Plating solutions of this type are commercially available, one particularly useful bath being sold under the trade designation "727XP" by Service Chemical Co.

As deposition of nickel on the aluminum metal surface proceeds, an alkaline material such as ammonia, preferably in the form of ammonium hydroxide, is added to the plating solution in order to maintain the pH of the solution in the desired range of about 8.5 to 10. If the total surface area plated is sufficient to significantly deplete the nickel ion and dimethylaminoborane concentration, it may be necessary to replenish the plating solution during plating by adding a solution of a soluble nickel salt, such as nickel sulfate, and dimethylaminoborane to the solution. The temperature of the bath during the plating operation is preferably maintained in the range of about 50° C. to 70° C. The time required to deposit a satisfactory nickel plating varies between about 20 and about 60 minutes, depending upon the temperature at which plating operations are conducted.

After the aluminum metal has been contacted with the plating solution under the above-noted conditions for a sufficient period of time, a stress free, hermetically sealed nickel deposit of uniform thickness is formed on the aluminum metal surface. An article of manufacture consisting of aluminum, magnesium or beryllium metal having a nickel coating plated directly on the surface thereof is thereby produced. Such an article of manufacture is commercially useful for many purposes. As noted, such an article is particularly useful as an intermediate product from which articles having an additional thickness of nickel or having a laminate of nickel and other metals may be produced by further conventional electrolytic or electroless processes. Thus, for example, the nickel plated articles of the invention may be additionally plated with copper from a copper sulfate bath, with cadmium from a cadmium cyanide bath, with tin from a tin sulfate bath, etc.

To preserve the nickel plated metal surface for additional plating operations, it may be held in contact with an aqueous preservative solution containing dimethylaminoborane. A wide range of dimethylaminoborane concentrations may be used for this purpose. We prefer to use a concentration of between about 2% and 5%, but this is not critical. The temperature of the preservative solution is conveniently room temperature, i.e., about 20° C. to 30° C. The temperature of this solution should not exceed 40° C., however, since above that temperature decomposition of diethylaminoborane commences.

The practice of the invention may be further illustrated by means of the following examples:

EXAMPLE 1

Several mandrels fabricated from 2S aluminum and weighing about 1.58 grams each were vapor degreased. Solid particles on the surface of the mandrels were removed with an air hose and the surfaces were dried.

After drying, the degreased aluminum mandrels were immersed in an aqueous activating solution bath containing 20 grams per liter ammonium bifluoride and 5 grams per liter dimethylaminoborane for 60 seconds at room temperature. The weight loss from the aluminum mandrels averaged 0.35 milligram after 30 seconds, and 0.65 milligram after 60 seconds.

Upon removal from the activating bath, the aluminum mandrels were soaked at room temperature in an aqueous stabilizing solution containing 2% dimethylaminoborane for several minutes.

The mandrels were then removed from the stabilizing solution and immersed in an aqueous plating solution. The plating solution used was that sold under the trade designation "727XP" by Service Chemical Co. This plating solution contained about 10 grams per liter of nickel ions, about 3 grams per liter of dimethylaminoborane, about one-tenth part per million of a stress reducer, and a carboxylic acid compound of the aforementioned type as a complexing agent. The aluminum mandrels were each held in the plating solution for about 60 minutes at 60° C. with occasional stirring. The pH of the plating solution was maintained between about 8.5 and 9.5 by intermittent addition of ammonium hydroxide. As the nickel ion content of the plating solution fell to about 8 grams per liter, it was raised back to about 12 grams per liter by addition of nickel sulfate. Similarly, dimethylaminoborane was added to the solution whenever its concentration in the solution fell to about 2 grams per liter. Sufficient dimethylaminborane was added on each addition to bring its concentration in the plating solution up to about 3.5 grams per liter.

Upon removal from the plating solution, each mandrel was found to have a uniform, adherent coating of nickel. The nickel coated mandrels were soaked in a 20% sodium hydroxide solution for 16 hours to test the integrity of the hermetical seal of the nickel coatings. No hydrogen was evolved at any time during the 16-hour period, indicating a hermetically sealed coating of nickel covered the surface of each mandrel.

As soon as each mandrel was removed from the plating solution, it was placed back in the stabilizing solution (functioning in this respect as a preservative solution) and held there in readiness for copper plating.

The nickel coated aluminum mandrels were then electrolytically plated with copper from an acid copper sulfate bath. No hydrogen evolution was observed from the nickel plated aluminum surface during electrolysis.

EXAMPLE 2

Example 1 was repeated using aluminum alloy 6061 mandrels. Again, an adherent, uniform, hermetically sealed nickel coating was laid down on each mandrel. No hydrogen was evolved either during soaking with 20% sodium hydroxide or during copper plating of the nickel plated aluminum.

EXAMPLE 3

Example 1 was repeated except that the activation solution contained 100 grams per liter of ammonium bifluoride and 10 grams per liter of dimethylaminoborane. Immersion time in the activation solution was 15 seconds. An adherent, uniform, hermetically sealed nickel coating was again laid down on each mandrel. No hydrogen was evolved either during soaking with 20% sodium hydroxide or during copper plating of the nickel plated aluminum metal.

EXAMPLE 4

Example 1 was repeated except that the activating solution contained 10 grams per liter of ammonium bi-

fluoride and 2 grams per liter of dimethylaminoborane. Immersion time in the activating solution was 2 minutes. An adherent, uniform, hermetically sealed nickel coating was laid down on each mandrel. No hydrogen was evolved either during soaking with 20% sodium hydroxide or during copper plating of the nickel plated aluminum mandrel.

EXAMPLE 5

Example 1 was repeated except that the stabilizing solution contained 5% of dimethylaminoborane. The same results were achieved with respect to uniformity, adherency, hermetical sealing, and passivity to sodium hydroxide solution and to any form of attack during copper plating.

EXAMPLE 6

Example 1 was repeated except that aluminum alloy 2024 mandrels were used. The same results were achieved with respect to uniformity, adherency, hermetical sealing, and passivity to sodium hydroxide and to any form of attack during copper plating.

EXAMPLE 7

Example 3 was repeated except that aluminum alloy 5052 mandrels were used. The same results were achieved with respect to uniformity, adherency, hermetical sealing, and passivity to sodium hydroxide and to any form of attack during copper plating.

EXAMPLE 8

Example 1 was repeated except that a magnesium mandrel was used. The same results were achieved with respect to uniformity, adherency, hermetical sealing, and passivity to sodium hydroxide and to any form of attack during copper plating.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above methods and products without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A composition useful for activating the surface of a metal selected from the group consisting of aluminum metals, magnesium metals, and beryllium metals to render the metal surface subject to the chemical deposition thereon of nickel from a solution containing nickel ions, the said composition comprising an aqueous solution of ammonium bifluoride and dimethylaminoborane.

2. The composition useful for activating the surface of a metal selected from the group consisting of aluminum metals, magnesium metals, and beryllium metals to render the metal surface subject to the chemical deposition thereon of nickel from a solution containing nickel ions, the said composition comprising an aqueous solution of ammonium bifluoride and dimethylaminoborane wherein a liter of the said composition contains between about 20 and about 100 grams of ammonium bifluoride and between about 2 and about 10 grams of dimethylaminoborane.

3. A water soluble concentrate useful for preparing an aqueous solution with which the surface of a metal selected from the group consisting of aluminum metals, magnesium metals, and beryllium metals may be contacted to activate the metal surface, thus rendering the surface subject to the chemical deposition thereon of nickel from a solution containing nickel ions, said concentrate comprising a mixture of ammonium bifluoride and dimethylaminoborane.

4. A water soluble concentrate useful for preparing an aqueous solution with which the surface of a metal selected from the group consisting of aluminum metals, magnesium metals, and beryllium metals may be contacted to activate the metal surface, thus rendering the surface subject to the chemical deposition therein of nickel from a solution containing nickel ions, said concentrate comprising a mixture of ammonium bifluoride and dimethylaminoborane wherein ammonium bifluoride is present in an amount sufficient to constitute between about 67 and about 98% by weight of the said composition, the balance dimethylaminoborane.

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