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METHOD OF CHEMICALLY PLATING BASE LAYERS WITH PRECIOUS METALS OF THE PLATINUM GROUP

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The present invention relates to a method of chemically plating non-metallic or metallic base layers, such as glass, carbon, stainless steel, iron, titanium and nickel with a precious metal of the platinum group such as platinum, palladium, rhodium, iridium, osmium, ruthenium or alloys thereof.

One of the known ways of thermochemically coating a noble metal onto a base is by dissolving salts of precious metals in an organic solvent, such as acetone, alcohol or glycol, adding an organic reducing agent thereto, such as anise oil or oil of lavender, spreading the resulting mixture over the article to be plated and then heating the article by means of a flame or in a furnace whereupon the precious metal is deposited on the base layer. The adherence of the thus applied precious metal coating can be improved by effecting the plating operation in an inert atmosphere, e.g. an atmosphere of helium, or by carrying out a secondary heat treatment in such an atmosphere.

One disadvantage in this and similar thermochemical methods of plating which are known is that the reduction of the precious metal salts takes place at such a high temperature that, before said temperature is reached, the organic reducing agent which is added has either entirely or largely evaporated. It is true that the reduction can still be effected by means of the carbon originating from carbonization of the reduction agent, e.g. oil of lavender, but experience has shown that in such case, a shinning, properly adherent coating of precious metal cannot be obtained.

Another disadvantage of carrying out the reduction at elevated temperatures is that, as a rule, the reduction is carried out in an oxygen-containing atmosphere with the result that the base metal is strongly oxidized. This also detracts from the usability of this method.

The principal object of the present invention is to provide certain improved methods for plating a base with precious metal whereby the abovementioned difficulties are obviated. A more specific object of the invention is the provision of a method of plating with compounds of precious metals such as iridium, rhodium and platinum, wherein the reduction of said compounds can be effected at temperatures which are many hundreds of degrees lower than those conventionally used whereby the base, e.g. stainless steel, titanium, is not damaged and an improved adherence is obtained. Other objects will also be apparent from the description which follows.

Broadly stated, the present invention involves first cleaning the surface or surfaces of the base to be plated and in the case where the base is a metal, the surface should be degreased and cleaned of rolling mill scale and oxide film in known manner. The thus cleaned base is then covered, according to the invention, with a solution of a precious metal salt in an organic solvent and heated in the presence of a reducing agent in a reasonably closed furnace into which a gas having an alkaline reaction is passed. There is no necessity for flushing out the furnace with this gas as the process may be carried out in the presence of air or oxygen as long as

sufficient alkaline-reacting gas is used (e.g. more than 5% by volume of this gas based on the total atmosphere). The reducing agent may be an organic reducing agent which is dissolved or otherwise incorporated into the organic solvent or, if desired, it may be in the form of a gas admixed with the alkaline-reacting gas. Alternatively, a combination of these two reducing means may be used, i.e. some of the reducing agent may be included with the solvent and the balance supplied with the alkaline-reacting gas. Normally a large excess of reducing agent is used, e.g. the four fold excess or more, based on the weight of the precious metal salt, to ensure the complete reduction thereof.

Preferably, the article covered with the solution of a precious metal salt is dried and preheated, usually in the range of 250 to 500° C. for 10 seconds to 10 minutes, e.g. 350° C. for 20 seconds and only thereafter the ammonia and the reducing gas are passed into the furnace.

The solution of the precious metal salt in the solvent can be applied to the base layer by brushing or dipping. The conditions for heating the thus treated base layer in the presence of the reducing agent and alkaline-reacting gas will vary depending on other factors, e.g. the nature of the base, but usually the temperatures and times selected will correspond with those referred to above in connection with preheating, i.e. 250 to 500° C., not in excess of 600° C., for from 10 seconds to 10 minutes.

If a thick coating of precious metal is desired and if for said purpose a number of thinner coatings of precious metal are formed, this may be effected at relatively low temperatures, for example, up to 350° C., and the ammonia and reducing gas (if any), may be supplied only during the final treatment which is carried out at the necessary reducing temperature of e.g. 350° C.

A typical plating solution may comprise a precious metal chloride dissolved in a mixture of isopropyl alcohol and linalool (e.g. 1 to 5 parts by weight of alcohol and 5 to 1 parts of linalool). Such a solution is used in the following examples but different solvents such as acetone and/or other ketones and alcohols may also be effectively used. Furthermore, the reducing agent linalool (i.e. coriandrol) may be replaced by etherical oils, such as anise oil, oil of lavender or bergamot oil, without affecting the results of the invention.

If it is desired to use a plate of a base metal, particularly titanium, coated with a thin layer of precious metal, as anode in electrolytic processes, the coated product is preferably subjected to an after-treatment as soon as possible but at any rate within 10 hours after the coating treatment is completed. This after-treatment takes place in an ordinary closed furnace in which the air can circulate to a limited extent. The definite heat-treatment takes place between 400 and 500° C., but on the whole, 400° C. will be sufficient. Higher temperatures will cause the platinum metals to darken, and tend to cause these metals to diffuse into the titanium, which affects the electric conductivity of the product, with the result that fewer amperes per square unit will pass into an electrolyte at some given voltage than in the case of this diffusion not having taken place.

The time of this treatment depends again on the requirements set for the electrode (anode) subsequently. On the whole, the longer the heat treatment the more resistent the electrode will become. The minimum duration of this heat treatment is 4 hours, the optimum efficacy being at 150 hours. An average treatment of 90 hours will, in most cases, give the desired result.

The coated article may be introduced into the heated furnace, but it is to be preferred to introduce the article into the furnace at room-temperature, and after heating it in the furnace during the required time, allowing it to

cool to room temperature in the furnace, before removing it.

It has been found that the addition of ammonia to the air circulating in the furnace during the heat treatment, prevents the layer of platinum metal (or its alloys) from getting darker, so that the articles maintain their bright appearance after the treatment.

While all of the examples herein show the use of precious metal chlorides, it should be noted that other halides e.g. iodides or bromides may also be satisfactorily used. Similarly, while ammonia is used as a suitable example of an alkaline gas useful herein, other gaseous bases such as amines (e.g. amines containing 1 to 4 carbon atoms such as methyl amine, ethyl amine, dimethyl amine and butyl amine) may be used in lieu of, or in addition to, ammonia gas.

Where the reducing agent is used in gaseous form together with the alkaline-reacting gas, town gas (i.e. a gas mixture consisting of 3–6% CO_2, 35–45% H_2, 10–18% N_2, 12–22% CO, 18–24% CH_4 and 2–5% heavy hydrocarbons e.g. 5.2% CO_2, 38% H_2, 16.4% N_2, 15.2% CO, 21.2% CH_4 and 4% heavy hydrocarbons) has proven advantageous because of its ready availability but it may be replaced by methane, carbon monoxide or hydrogen.

It is preferred to so arrange the furnace that the gas introduced cannot be ignited by the source of heat. Additionally, it is desirable that the gases introduced, such as, for example, ammonia and town gas are preheated (e.g. from 200 to 500° C.) before they enter the furnace and contact the article to be plated.

The treatment according to the invention can be carried out not only with the precious metals and their alloys mentioned hereinbefore, but also with other precious metals such as palladium, ruthenium, osmium or alloys of said precious metals in any desired ratio.

As will be appreciated, the invention provides a technically easily realizable method of converting precious metal compounds into the metallic form at much lower temperatures than hitherto possible to obtain bright metallic coatings which adhere very well to nonmetallic or metallic base layers. The coatings formed may be extremely thin or they can be given the desired thickness by a repeated application.

Products manufactured according to the invention represent a significant advance in all those fields where it is desired to provide thin coatings of precious metals for their properties of corrosion resistance, mechanical strength, good electric contact and conductivity. Examples of such products are anodes having a base metal core coated with a thin layer of precious metal. These anodes may be used in electrolytic processes, e.g. brine electrolysis, particularly if the core metal is titanium. Cathodes having a core of stainless steel or nickel coated with precious metal can also be prepared according to the present process for use in electrolytic processes. Additionally, the invention is useful for preparing glass locally coated with precious metal for use in distributing switches in the electronic and in the radio industry; glass coated with alloys of precious metals for use in the optical industry; and carbon, silicagel and like materials coated with precious metals for use as catalysts.

The invention is further described in the following examples. These examples, however, are given only for purposes of illustration and are not intended to limit the invention in any respect.

Example I

A plate of titanium which had previously been thoroughly cleaned was brushed with a liquid plating mixture composed of 5 cc. of isopropyl alcohol, 5 cc. of linalool and 1 gram of iridium chloride. Thereafter, the thus coated plate of titanium was suspended in a vertical tubular furnace heated to a temperature of about 380° C., and through which a mixture of ammonia gas and town gas was passed, the treatment lasting thirty seconds. As a result of this treatment, it was found that the plate of titanium was covered with a coating of metallic iridium having a metallic lustre which adhered to the titanium plate very well. The coated plate was eminently suitable as an electrical conductor.

An identical plate brushed with a like plating mixture was placed in the furnace under the same conditions, but the gas-ammonia mixture was not passed through the furnace, and only the reducing properties of the liquid plating mixture were relied on to coat the titanium plate. It was found that even when this plate of titanium was heated to 800° C. or higher an adhering metallic layer of iridium on the titanium was not obtained. Additionally, the resultant coating of iridium was black and only poorly conductive. It was also noted that the temperature of 800° C. was too high for the titanium to withstand and the base became brittle due to the action of the oxygen and the nitrogen from the air. Furthermore, the titanium was covered with a thick layer of titanium oxide and/or nitride. As a result, this titanium was useless as a conductor for electricity.

The cleaning of the plates of titanium may effectively be carried out as follows:

Two plates of titanium are degreased in any known manner, then placed in chemically pure concentrated hydrochloric acid, and connected to a source of alternating current. The current is passed through the liquid at a current density of 5 amps/dm.^{2} and a voltage of 1 volt for a period ranging from 1 minute to 1 hour, for example, 15 minutes. After the supply of current has been discontinued the plates are allowed to remain in the hydrochloric acid for about 5 minutes. The plates are then removed from the bath, rinsed with distilled water, and dried in the air at about 70° C.

According to the present invention, the thermo-chemical conversion of the metal salt when coating titanium can be effectively carried out below 500° C. It will be appreciated from the foregoing that this offers very significant advantages and meets an urgent need in the art. If only ammonia is used (i.e. the town gas is excluded), some improvement over prior techniques is realized because the precipitate on the titanium has a metal gloss whereas without ammonia and town gas, the precipitate, insofar as this is visible, is black. The adherence is poor, however, and the electric conductivity is also appreciably inferior to that obtained when both ammonia (or other alkaline-reacting gas) and town gas are passed through the furnace together. Usually, the proportion of alkaline-reacting gas to town gas should fall within the range of 5 to 50% by volume of alkaline-reacting gas based on the total volume of gas, although other proportions may also be used.

After applying the coating of iridium the plate may be subjected to the after-treatment mentioned hereinbefore.

Example II

A glass plate was thoroughly cleaned and subsequently brushed with a mixture made of 10 cc. of isopropyl alcohol and 1 gram of rhodium chloride. The plate covered with this mixture was first dried at a temperature of 80° C. and the dried plate was subsequently suspended in a vertical tubular furnace and heated to a temperature of 390° C. Ammonia and town gas were introduced into the furnace and after 30 seconds a properly adhering lustrous metallic layer of rhodium had deposited on the glass.

A glass plate brushed with the same mixture was also heated in the furnace without the addition of ammonia and town gas. The glass plate was heated up to 810° C. (the softening point of the glass) without the black precipitate which was formed changing into an electricity conducting layer having a metallic lustre. When only one gas, either town gas or ammonia, was passed through the furnace, the color of the precipitate was somewhat lighter, but there was no adherence of the rhodium to the glass.

Example III

A plate of stainless steel was cleaned in known manner and was subsequently brushed with a mixture composed of 2.5 cc. of isopropyl alcohol, 2.5 cc. of linalool, and 1 gram of platinum chloride. This plate was suspended in a vertical tubular furnace through which, as in the preceding examples, ammonia and town gas were passed after the plate had been heated to 255° C. A firmly adhering coating of platinum was obtained on the stainless steel plate. When a like plate was brushed in the same manner and heated to 310° C. with either the town gas or ammonia omitted, a metal coating was obtained, but the adherence of this coating was poor.

Example IV

Thoroughly cleaned tantalum was brushed with a mixture of 0.5 gram of iridium chloride and 1 gram of platinum chloride in 10 cc. of isopropyl alcohol and 10 cc. of linalool. When the tantalum was heated to 350° C. and town gas and ammonia were passed through the furnace, as in the preceding examples, the metals precipitated as an alloy containing 70% of platinum and 30% of iridium and a complete conversion and good adherence were obtained. However, when similarly brushed tantalum was heated and town gas and ammonia were omitted, good results could not be obtained even at temperatures above 800° C.

Example V

Thoroughly cleaned titanium was brushed with a mixture of a total of 1 gram of platinum chloride and rhodium chloride in a proportion of 2:1 in 10 cc. of isopropyl alcohol. When the titanium was placed in a furnace heated to 350° C. and town gas and ammonia were passed through the furnace as in the preceding examples, complete conversion to an alloy of 70% of platinum and 30% of rhodium was obtained. Strong adherence of the alloy to the titanium was obtained.

However, with a similarly heated plate when the town gas and ammonia were omitted, good adherence could not be obtained even at temperature above 850° C. and the resulting precipitate did not resemble a metal. When only town gas or only ammonia was used, a partial conversion occurred but the adherence of the resulting coating was poor.

Example VI

Activated carbon was first thoroughly freed of dust and subsequently sprayed with a mixture of 20 cc. of isopropyl alcohol, 20 cc. of linalool and 1 gm. of palladium chloride. This carbon was heated to 260° C. in a furnace into which ammonia was passed and a firmly adhering metallic impregnation was obtained. When similarly sprayed carbon was heated but the ammonia was omitted, it was necessary to heat the carbon up to 430° C. to convert the palladium chloride, and this temperature impaired the mechanical strength and the activity of the carbon. In contrast, the palladium impregnated activated carbon obtained by heating the carbon to 260° C., in an atmosphere of ammonia formed an excellent catalyst mass.

It will be appreciated that various modifications may be made within the scope of the invention as defined in the following claims, wherein I claim:

1. A process for coating a base with a precious metal selected from the group consisting of platinum and alloys thereof, which consists essentially of the steps of applying to said base a reducible salt of at least one of said precious metals, and heating said base in a gaseous mixture consisting essentially of a gaseous reducing agent and a gas having an alkaline reaction, said heating being at a temperature sufficient to reduce said precious metal salt and form a firmly adherent coating of platinum metal on said base, said temperature being above the temperature at which the salt decomposes and below the temperature at which the base will be damaged.

2. The process of claim 1 wherein said base comprises titanium and the heating step is carried out at a temperature between 250° C. and 600° C.

3. The process of claim 1 wherein said gaseous reducing agent is a hydrocarbon containing gas and said gas having an alkaline reaction is ammonia gas.

4. A process for coating a base with a precious metal selected from the group consisting of platinum and alloys thereof, which consists essentially of the steps of applying to said base an organic solvent solution of a reducible salt of at least one of said precious metals, drying the solution to form the dried salt, heating the base in a gaseous mixture consisting essentially of a gaseous reducing agent and a gas having an alkaline reaction, said heating being at a temperature sufficient to reduce said precious metal salt and form a firmly adherent coating of platinum metal on said base, said temperature being above the temperature at which the salt decomposes and below the temperature at which the base will be damaged.

5. The process of claim 4 wherein said organic solvent solution includes an organic reducing agent, said gaseous reducing agent being in addition to the reducing agent of said solution.

6. The process of claim 1 wherein said heating step is carried out at a temperature between 250 and 600° C. for 10 seconds to 10 minutes.

7. The process of claim 1 wherein said precious metal salt is a halide.

8. The process of claim 1 wherein the base is preheated before heating in the presence of said alkaline-reacting gas and reducing gas.

9. A process for plating titanium with a platinum group metal which consists essentially of the steps of covering a surface of said titanium with a solution of a chloride of at least one platinum group metal in an organic solvent therefor, heating said titanium to remove the solvent and then continuing the heating in the presence of an organic reducing agent, in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas above a decomposition temperature for the chloride salt and below about 500° C. whereupon said chloride is reduced and a lustrous, adherent coating of the platinum group metal is deposited on said titanium.

10. A process for plating titanium with a platinum group metal which consists essentially of the steps of covering a surface of said titanium with a solution of a chloride of at least one platinum group metal in an organic solvent therefor, heating said titanium to remove the solvent and then continuing the heating in the presence of an organic reducing agent in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas at a temperature above the decomposition temperature of the chloride salt and below about 500° C. whereupon said chloride is reduced and a lustrous, adherent coating of the platinum group metal is deposited on said titanium, and within 10 hours completing the process by heating the plated titanium in air at a temperature ranging from 400 to 500° C. for a period of from 4 to 150 hours.

11. A process for plating titanium with at least one platinum group metal which consists essentially of the step of covering a surface of said titanium with a plating mixture composed of isopropyl alcohol, linalool and a chloride salt of the platinum group metals, heating said titanium to remove the solvent and then continuing the heating in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas at a temperature of about 380° C. for 30 seconds, whereupon said chloride is reduced and a lustrous, adherent coating of the platinum group metal is deposited on said titanium.

12. A process for plating titanium with an alloy of platinum group metals, which consists essentially of the steps of covering a surface of said titanium with a plating mix-

ture composed of isopropyl alcohol and a mixture of chloride salts of the platinum group metals, heating said titanium to remove the solvent and then continuing the heating in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas at a temperature of 350° C., whereupon said chlorides are reduced and a lustrous, adherent coating of an alloy of the platinum group metals is deposited on said titanium.

13. A process for plating glass with a platinum group metal, which consists essentially of the steps of covering a surface of the glass with a plating mixture composed of isopropyl alcohol and a chloride salt of the platinum group metals, heating said glass to remove the solvent and then continuing heating the glass plate in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas at a temperature of 390° C. for 30 seconds, whereupon said chloride is reduced and a lustrous, adherent coating of an alloy of the platinum group metal is deposited on said glass.

14. A process for plating stainless steel with a platinum group metal, which consists essentially of the steps of covering a surface of the stainless steel with a plating mixture composed of isopropyl alcohol, linalool, and a chloride salt of the platinum group metals, heating said stainless steel to remove the solvent and then continuing heating the stainless steel in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas at a temperature of 255° C., whereupon said chloride is reduced and a lustrous, adherent coating of the platinum group metal is deposited on said stainless steel.

15. A process for impregnating activated carbon with a platinum group metal, which consists essentially of the steps of spraying a surface of said carbon with a plating mixture composed of isopropyl alcohol, linalool and a chloride salt of the platinum group metals, heating said carbon to remove the solvent and then continuing heating the activated carbon in the presence of ammonia at a temperature of 260° C., whereupon said chloride is reduced and an adherent metallic impregnation of activated carbon is obtained.

16. A process for coating a metallic base with a precious metal selected from the group consisting of platinum and alloys thereof, which consists essentially of the steps

of applying to the base a reducible salt of at least one of said precious metals, and heating said base in a gaseous mixture consisting essentially of a gaseous reducing agent and a gas having an alkaline reaction, said heating being at a temperature sufficient to reduce said precious metal salt and form a firmly adherent coating of precious metal on said base, said temperature being above the temperature at which the salt decomposes and below the temperature at which the precious metal begins to diffuse into the metal of the base.

17. A process as claimed in claim **10** in which ammonia is added to the air in which the completion heating step is carried out.

18. A process for plating glass with a platinum group metal which consists essentially of the steps of covering a surface of the glass with a plating mixture comprised of isopropyl alcohol and a chloride salt of the platinum group metals, heating said plate to remove the solvent and then continuing heating the glass in a gaseous mixture consisting essentially of ammonia gas and a hydrocarbon containing reducing gas at a temperature sufficient to reduce the chloride salt and form a firm, lustrous, adherent coating of the metal on the glass, said temperature being above the temperature at which the salt decomposes and below a temperature at which the glass will soften.

References Cited by the Examiner

UNITED STATES PATENTS

1,236,383	8/1917	Fahrenwald	117—130
1,583,268	5/1926	Bart	117—35.5
1,954,353	4/1934	Ernst	106—1
2,285,277	6/1942	Henke	252—447
2,328,101	8/1943	Rosenblatt	117—130
2,511,472	6/1950	Kmecik	117—35.5
2,873,216	2/1959	Schnable	117—130
2,915,406	12/1959	Rohda et al.	117—130
2,979,424	4/1961	Whitehurst et al.	117—160
3,112,215	11/1963	Ruosch et al.	117—160
3,117,023	1/1964	Tirrell	117—130
3,133,829	5/1964	Cupery et al.	117—127

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