

UNITED STATES PATENT OFFICE

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METHOD FOR SECURING ADHESION OF
ELECTROPLATED COATINGS TO A
METAL BASE

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The invention described herein may be manufactured and used by or for the Government for governmental purposes without the payment of any royalty thereon.

This invention relates to a method for improving the nature of electrodeposited metals and alloys, and it has particular reference to methods for improving the adhesion of electroplated coating to the surface of the underlying metal base.

Broadly stated, a principal object of our invention is to provide improved adhesion of electrodeposits to the underlying surfaces.

A more specific object is to improve the adhesion to a metal base of an electroplated metal coating.

Another object is to provide improved adhesion of electrodeposited alloys of two or more metals to the underlying metal base surfaces.

Still another object is to improve the adhesion to steel of metals and alloys which are electrodeposited thereon.

A further object is to improve the adhesion of electrodeposited metals or alloys to "strike" deposits.

Electroplaters have long sought for methods of improving the adhesion of electroplated coatings to the metal base or object being plated. Numerous means or techniques have accordingly been evolved by the prior art to accomplish this purpose. A certain measure of success has been achieved in improving the adhesion of electroplated metals; however, there has been considerable difficulty in making electrodeposited alloys adhere firmly to a base so coated.

Our invention has made possible, with almost unqualified assurance, that most electrodeposited alloys as well as metals will remain positively adherent to surfaces upon which they are plated without peeling or becoming otherwise impaired upon application of any stress or through the effect of time and wear.

Our invention, in its very broad aspects, consists in the use of a pre-plating treatment with alternating current (A. C.) prior to the normal electroplating operation. Although A. C. current has been used by electroplaters for other purposes, e. g., A. C. current superimposed on D. C. (direct current) for obtaining more ductile deposits, better anode corrosion, and a faster rate of plating, the use of A. C. current for securing the improved adhesion of electrodeposits has never before been known to the prior art. It should be understood that our novel A. C. treatment does not result in any metal from the

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electrolyte plating on the surface being treated. Instead, it is our understanding that the A. C. treatment renders the surface of the base metal (or a "strike" coating thereon) either more reactive or freer from oxide so that the subsequent conventional D. C. plating operation will result in a tenaciously adherent coating not normally obtainable without the A. C. pretreatment.

The striking virtues of using this pre-plating A. C. treatment were discovered by us while practicing the invention of Abner Brenner, Polly Burkhead and Clara A. Sentel, which invention they have described in co-pending application Serial No. 708,566; filed on even date herewith, entitled "Method of and Bath for Electrodepositing Tungsten Alloys," and in an article by said Brenner, Burkhead and Emma Seegmiller published in the Journal of Research of the National Bureau of Standards, vol. 39, October 1947, page 351 et seq. During the course of our experiments we found that, although the said invention of Brenner-Burkhead-Sentel provided a convenient means for obtaining electroplated alloys of tungsten with cobalt, iron and nickel, the resulting alloy deposit would be considerably improved by the use of our novel A. C. treatment prior to the actual plating operation which they have invented.

Incidental to these other experiments, we have found that our unique A. C. treatment also serves to improve the adhesion of "plain," unalloyed deposits of cobalt or nickel to a tungsten alloy. Improvements over the adhesiveness of the deposits obtained by existing plating methods may be similarly obtained in the plating of cobalt upon cobalt, nickel on nickel, cobalt on nickel, and nickel on cobalt.

In applying the adherent deposits which our invention now makes possible, it is sometimes preferable although not altogether necessary to plate the desired coating on a basis metal such as upon a "strike" deposit. "Strike" deposits are well known to the prior art, conventionally consisting of a special bath used in addition and prior to the main plating bath and operation. A "strike" deposit is obtained by employing special conditions such as a bath containing a low concentration of the metal to be plated therefrom and is used merely to get the first coating of that metal on the object to be plated, after which additional amounts of the metal are built up on the object in the "regular" plating solution.

If a "strike" deposit is employed, the thus coated metal base is thereafter subjected to our

novel A. C. treatment and subsequently plated in any desired manner.

The following procedure, which has particular application to improving the adhesion of a tungsten-cobalt alloy to gun steel, is set forth as a typical example of a plating procedure wherein our inventive process may be employed:

1. The steel is cleaned and polished (preferably electropolished) if necessary.

2. The thus cleaned steel is made the anode in an electrolytic bath containing 70% sulphuric acid and etched for two minutes at a current density of 25 amperes per square decimeter of the steel's immersed surface.

3. The steel object is then rinsed and dipped for 15 seconds in a dilute (1:4) solution of hydrochloric acid.

4. A "strike" deposit of cobalt is plated upon the steel from an acid cobalt bath for three minutes at a current density of 20 amperes per square decimeter. A bath suitable for this purpose typically contains 25 grams per liter of cobalt as the chloride, and has a pH of 0.7.

5. The cobalt coated steel is dipped in a 1:1 solution of hydrochloric acid for a few moments and then rinsed.

6. At this point our inventive process is employed. The steel object, treated as above described, is placed in a regular tungsten-cobalt alloy bath and ordinary 60 cycle A. C. current is applied for five seconds at a current density of $\frac{1}{4}$ ampere per square decimeter. Immediately thereafter a switch is made to the conventional D. C. plating current. This switch may actually be made before the A. C. current is disconnected, or immediately after disconnecting the same.

7. Plating of the alloy (in our illustrative example, tungsten-cobalt alloy) upon the steel object is then carried out as usual. Such "usual" plating techniques may satisfactorily follow the aforementioned invention disclosed by Brenner-Burkhead-Sentel and covered by their co-pending patent application.

It will be obvious, of course, that all the steps which preceded our novel A. C. treatment in the above outlined process are not necessary to the practice of our invention, and may be modified to suit the individual needs or desires of a particular operator. For example, where nickel or cobalt is being plated upon a nickel surface, improved adhesion of the coating may be had by merely electropolishing the nickel surface in 70% sulphuric acid at 25 amperes per square decimeter, thereafter rinsing in strong hydrochloric acid, and following with our unique A. C. treatment just before plating. Other modifications might include use of alternating currents of various frequencies, the only condition being that the cycle must change at least once during the coating operation. Standard current frequencies, as from 25 to 60 cycles per second, are preferable, however.

The amount of A. C. current necessary for securing the above described benefits of our invention depends on the nature of the bath employed and the type of metal to be plated, but is not a critical factor. For example, in plating tungsten-cobalt alloy we have successfully used current densities from 0.5 to 1 ampere per square decimeter, and periods of A. C. pre-plating treatment from several minutes to as little as five seconds. We have found it preferable to use longer periods of treatment when lower current densities are employed.

Examples of tungsten alloy baths which may be employed with the present invention are more fully disclosed in the aforementioned co-pending application of Brenner-Burkhead-Sentel. However, the composition of those baths may briefly be set forth herein as follows:

For electrodepositing nickel-tungsten alloy, a suitable bath may consist of 26 grams/liter nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$); 70 grams/liter sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$); 100 grams/liter sodium citrate; and the remainder consisting of water. In some cases, where the alkalinity of the bath requires adjustment, certain materials such as ammonium hydroxide may help make up the balance of the bath instead of just plain water.

A suitable cobalt-tungsten alloy bath may preferably consist of the following amounts per liter: 70 grams sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$); 28 grams cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$); 100 grams Rochelle salt, 50 grams ammonium chloride; and the remainder substantially all water except for such supplemental material as ammonium hydroxide which may be required for adjusting the alkalinity of the bath.

For electrodepositing iron-tungsten alloy metal we have found a satisfactory plating bath to comprise the following amounts per liter: 70 grams sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$); 8 grams of iron in the form of sulphate or chloride; 100 grams sodium citrate; 50 grams ammonium chloride; and the remainder substantially all water except for a sufficient quantity of ammonium hydroxide or the like which may be necessary to adjust the pH of the bath.

With regard to the electrolytes which are usable, it may be well to show the broad applications of our invention by making reference to the U. S. Patent 811,759 issued February 6, 1906 to W. C. Arsem for "Electrodeposition." Arsem's patent teaches the use of an alternating current under conditions which will result in a coating of metal being deposited from an electrolyte. He states that his process is limited to use with an electrolyte containing metal (such as platinum) which is not easily corroded by the acid radical of the plating baths, or which is substantially inactive as an anode in the electrolyte used. As an example of an instance wherein his method is inapplicable Arsem cites the plating of copper from a solution of copper sulphate, pointing out that the reversing A. C. current will in one half of its cycle corrode or redissolve the copper deposit formed in the other half of the cycle. There are no such limitations in the practice of our invention, as our A. C. treatment is not intended to result, nor in fact does it result, in deposition of metal from the electrolyte. Consequently, a wide choice of electrolytes may be employed.

Although we have definitely shown that the use of an A. C. pre-plating treatment improves the adherence of electrodeposited metal to the base material, it is of interest to note that in certain applications particular caution must be exercised in order to get the full benefits of our invention. For example, in the plating of a cobalt or cobalt alloy on steel we have found that the use of our A. C. treatment applied with high current densities, say in excess of 10 amperes per square decimeter, will result in a non-adherent deposition of the cobalt on the steel. As far as we have been able to determine, the cause of this action seems to be a chemical replacement of the steel by the cobalt. Apparently,

the effect of the A. C. current is simply to activate the steel so that the chemical replacement thereof can proceed at an appreciable rate.

Although the just described result of using our novel A. C. treatment with high current densities indicates that for best results with our invention lower current densities should be employed, the relative increase of time that is required is comparatively small and will be found to be no objection when employed in commercial electroplating practice. In fact, expenditure of the small amount of extra time which is required in applying our invention in addition to that required by conventional plating processes, is well compensated for by the resulting greatly enhanced adhesion of the coating to the base material.

Other advantages of our invention will readily become apparent to electroplaters and others skilled in this art. Such advantages may be seen in comparing techniques for plating nickel upon nickel or nickel upon cobalt, etc., plated by conventional methods, with similar electroplating work done with the additional aid of our A. C. pre-plating treatment.

As an example of such advantages, a further comparison could be made of the results of the best known prior art method of securing adhesion of nickel or cobalt to a nickel base with the results obtained when our invention is employed. The prior art method referred to consisted of electropolishing the nickel base with 70% sulphuric acid, followed by an etching treatment for several minutes in a nickel chloride bath with reverse current prior to the regular plating operation. The advantages thereover which are obtained by using our novel A. C. current method are (1) that it does not remove or etch the surface upon which plating is to be done, and (2) it does not dissolve off any of the metal base surface to form metal salts which would contaminate the plating bath.

From the foregoing it will thus be seen that our invention has provided a simple and highly effective method for improving the adhesion of electrodeposits to the underlying surfaces; that we have provided improved adhesion of electrodeposited alloys of two or more metals to the underlying metal base surfaces; that we have improved the adhesion to a base metal of an electroplated metal coating; that we have improved the adhesion to steel of metals and alloys which are electrodeposited thereon; and that we have improved the adhesion of electrodeposited metals or alloys to "strike" deposits.

As earlier pointed out, although a number of possible applications of our invention have been described, it will be quite obvious to those generally skilled in the art that a number of other applications thereof are possible such applications may be made independently or in combination with many varied methods of electroplating without departing from the spirit and intent of our invention.

Our invention is therefore extensive in its adaption and is not to be restricted to the form here disclosed by way of illustration.

We claim:

1. The method of improving the adhesion to a cobalt base of an electrolytically codeposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the cobalt base an electrode in an electrolytic bath from which one of said tungsten alloys can be plated upon

said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the alloy from said bath upon said base by passage of direct current through the bath and through the base.

2. The method of improving the adhesion to a cobalt base of an electrolytically codeposited coating of tungsten and iron, which method comprises the steps of making the cobalt base an electrode in an electrolytic bath from which the tungsten-iron alloy can be plated upon said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the tungsten-iron coating from said bath upon said base by passage of direct current through the bath and through the base.

3. The method of improving the adhesion to a cobalt base of an electrolytically codeposited coating of tungsten and nickel, which method comprises the steps of making the cobalt base an electrode in an electrolytic bath from which the tungsten-nickel alloy can be plated upon said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the tungsten-nickel coating from said bath upon said base by passage of direct current through the bath and through the base.

4. The method of improving the adhesion to a cobalt base of an electrolytically codeposited coating of tungsten and cobalt, which method comprises the steps of making the cobalt base an electrode in an electrolytic bath from which the tungsten-cobalt alloy can be plated upon said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the tungsten-cobalt coating from said bath upon said base by passage of direct current through the bath and through the base.

5. The method of improving the adhesion to a metal base having a surface coating of cobalt of an electrolytically codeposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the metal base a cathode in a first electroplating bath containing a "strike" plating solution of cobalt, passing direct current through said first bath to provide a "strike" electrodeposit of cobalt upon said metal base, thereafter making the cobalt-coated base an electrode in a second electroplating bath from which one of said tungsten alloys can be plated upon said base, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive codeposit upon the said cobalt-coated base of the alloying metals in said bath.

6. The method of improving the adhesion to a metal base having a surface coating of cobalt of an electrolytically codeposited alloy of tung-

sten and iron, which method comprises the steps of making the metal base a cathode in a first electroplating bath containing a "strike" plating solution of cobalt, passing direct current through said bath to provide a "strike" electrodeposit of cobalt upon said metal base, thereafter making the said cobalt-coated base an electrode in a second electroplating bath from which the tungsten-iron alloy can be deposited, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive deposit of the tungsten-iron alloy upon the said cobalt-coated base.

7. The method of improving the adhesion to a metal base having a surface coating of cobalt of an electrolytically codeposited alloy of tungsten and nickel, which method comprises the steps of making the metal base a cathode in a first electroplating bath containing a "strike" plating solution of cobalt, passing direct current through said bath to provide a "strike" electrodeposit of cobalt upon said metal base, thereafter making the said cobalt-coated base an electrode in a second electroplating bath from which the tungsten-nickel alloy can be deposited, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive deposit of the tungsten-nickel alloy upon the said cobalt-coated base.

8. The method of improving the adhesion to a metal base having a surface coating of cobalt of an electrolytically codeposited alloy of tungsten and cobalt, which method comprises the steps of making the metal base a cathode in a first electrolytic bath containing a "strike" plating solution of cobalt, passing direct current through said bath to provide a "strike" electrodeposit of cobalt upon said metal base, thereafter making the said cobalt-coated base an electrode in a second electroplating bath from which the tungsten-cobalt alloy can be deposited, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive deposit of the alloy upon the said cobalt-coated base.

9. The method of improving the adhesion to a nickel base of an electrolytically codeposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the nickel base an electrode in an electrolytic bath from which one of said tungsten alloys can be plated upon said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the alloy from said bath upon said base by passage of direct current through the bath and through the base.

10. The method of improving the adhesion to a nickel base of an electrolytically codeposited

coating of tungsten and iron, which method comprises the steps of making the nickel base an electrode in an electrolytic bath from which the tungsten-iron alloy can be plated upon said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the tungsten-iron coating from said bath upon said base by passage of direct current through the bath and through the base.

11. The method of improving the adhesion to a nickel base of an electrolytically codeposited coating of tungsten and nickel, which method comprises the steps of making the nickel base an electrode in an electrolytic bath from which the tungsten-nickel alloy can be plated upon said base and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the tungsten-nickel coating from said bath upon said base by passage of direct current through the bath and through the base.

12. The method of improving the adhesion to a nickel base of an electrolytically codeposited coating of tungsten and cobalt, which method comprises the steps of making the nickel base an electrode in an electrolytic bath from which the tungsten-cobalt deposit can be plated upon said base and passing alternating current at a current density of about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the tungsten-cobalt coating from said bath upon said base by passage of direct current through the bath and through the base.

13. The method of improving the adhesion to a metal base having a surface coating of nickel of an electrolytically codeposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the metal base a cathode in a first electroplating bath containing a "strike" plating solution of nickel, passing direct current through said first bath to provide a "strike" electrodeposit of nickel upon said metal base, thereafter making the nickel-coated base an electrode in a second electroplating bath from which one of said tungsten alloys can be plated upon said base, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive codeposit upon the said nickel-coated base of the alloying metals in said bath.

14. The method of improving the adhesion to a metal base having a surface coating of nickel of an electrolytically codeposited alloy of tungsten and iron, which method comprises the steps of making the metal base a cathode in a first electroplating bath containing a "strike" plating solution of nickel, passing direct current through said bath to provide a "strike" electrodeposit of nickel upon said metal base, thereafter making the said nickel-coated base an electrode in a second electroplating bath from which the tungsten-iron deposit can be plated upon said base, passing alternating cur-

rent through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive deposit of the tungsten-iron alloy upon the said nickel-coated base.

15. The method of improving the adhesion to a metal base having a surface coating of nickel of an electrolytically codeposited alloy of tungsten and nickel, which method comprises the steps of making the metal base a cathode in a first electroplating bath containing a "strike" plating solution of nickel, passing direct current through said bath to provide a "strike" electrodeposit of nickel upon said metal base, thereafter making the said nickel-coated base an electrode in a second electroplating bath from which the tungsten-nickel deposit can be plated upon said base, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive deposit of the tungsten-nickel alloy upon the said nickel-coated base.

16. The method of improving the adhesion to a metal base having a surface coating of nickel of an electrolytically codeposited alloy of tungsten and cobalt, which method comprises the steps of making the metal base a cathode in a first electrolytic bath containing a "strike" plating solution of nickel, passing direct current through said bath to provide a "strike" electrodeposit of nickel upon said metal base, thereafter making the said nickel-coated base an electrode in a second electroplating bath from which the tungsten-cobalt deposit can be plated upon said base, passing alternating current through said electrode and second electroplating bath at a current density of from about 0.25 to 1 ampere per square decimeter for from about five seconds to several minutes, and thereafter passing direct current through said electrode and through said second electroplating bath to obtain an adhesive deposit of the alloy upon the said nickel-coated base.

17. The method of improving the adhesion to a metallic base of an electrolytically co-deposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the metallic base an electrode in an electrolytic bath from which one of said tungsten alloys can be plated upon said base, and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to codepositing the alloy from said bath upon said base by passage of direct current through the bath and through the base.

18. The method of improving the adhesion of an electrolytically codeposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt to a base material constituting a metal of the group consisting of cobalt and

nickel, which method comprises the steps of making said metallic base material an electrode in an electrolytic bath from which one of said tungsten alloys can be plated upon said base, and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about five seconds to several minutes immediately prior to co-depositing the alloy from said bath upon said base by passage of direct current through the bath and through the base.

19. The method of improving the adhesion to a cobalt base of an electrolytically co-deposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the cobalt base an electrode in an electrolytic bath from which one of said tungsten alloys can be plated upon said base, and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about 5 seconds to several minutes immediately prior to co-depositing the alloy from said bath upon said base by passage of direct current through the bath and through the base.

20. The method of improving the adhesion to a nickel base of an electrolytically co-deposited alloy of tungsten and a metal of the group consisting of iron, nickel and cobalt, which method comprises the steps of making the nickel base an electrode in an electrolytic bath from which one of said tungsten alloys can be plated upon said base, and passing alternating current at a current density of from about 0.25 to 1 ampere per square decimeter through said bath and through said base for from about 5 seconds to several minutes immediately prior to co-depositing the alloy from said bath upon said base by passage of direct current through the bath and through the base.

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