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PLATING PLATINUM METALS ON CHROMIUM

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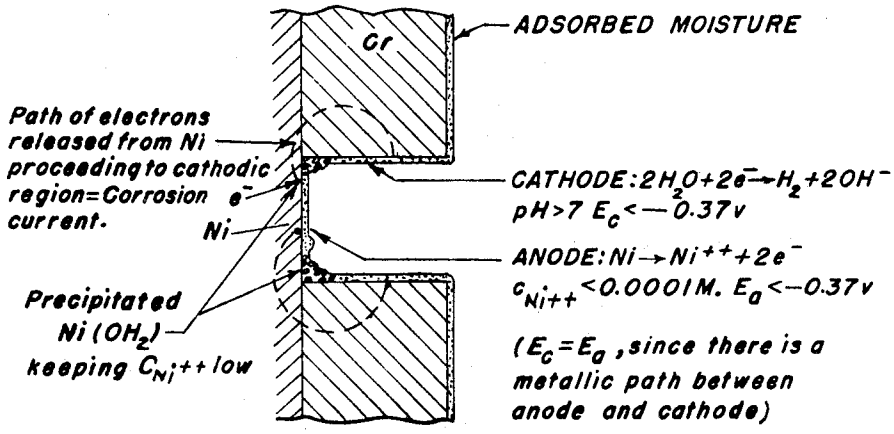


FIG. 1. IDEALIZED REPRESENTATION OF CORROSION IN PORE IN CHROMIUM-PLATED NICKEL

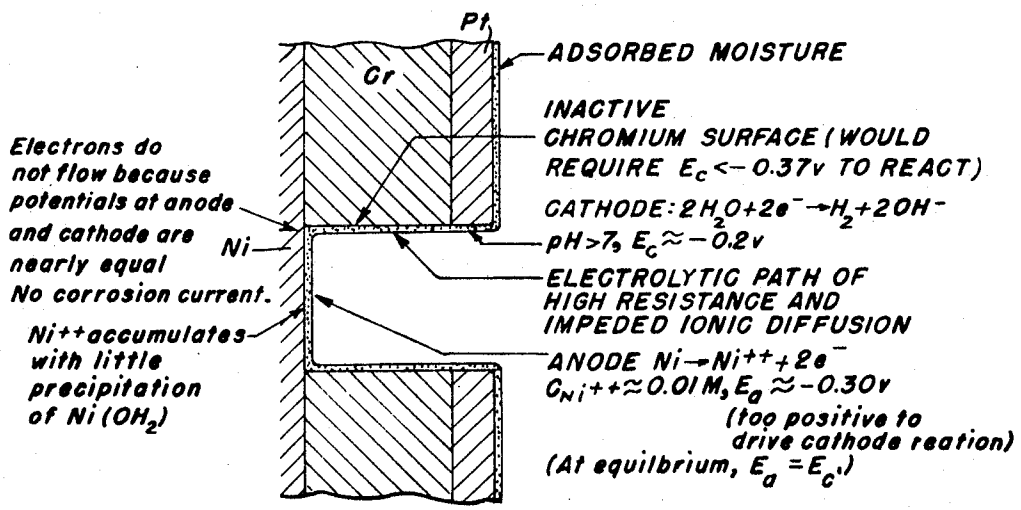


FIG. 2. IDEALIZED REPRESENTATION OF CORROSION IN PORE IN PLATINUM-CHROMIUM-PLATED NICKEL

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PLATING PLATINUM METALS ON CHROMIUM

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Continuation-in-part of application Ser. No. 493,560, Oct. 6, 1965. This application Oct. 24, 1966, Ser. No. 589,087

Int. Cl. C23b 5/50, 5/30, 1/04

U.S. Cl. 204—32 21 Claims

This application is a continuation-in-part of application Ser. No. 493,560, filed Oct. 6, 1965, now abandoned, which was a continuation-in-part of application Ser. No. 181,478, filed Mar. 21, 1962, now abandoned.

This invention relates to improvements in the plating of platinum, palladium, and rhodium. More particularly, it relates to novel self-passivating corrosion-resistant duplex metal coatings, and to methods for producing such coatings.

The platinum metals are characterized by their attractive, silvery color, their resistance to tarnish and corrosion, their catalytic activity, and their good surface properties for electrical contacts. However, they are very expensive; consequently many efforts have been made to apply them in coatings thin enough to be relatively low in cost, while providing their excellent surface properties.

However, it has been found that thin coatings, by whatever method they are applied, are penetrated by microscopic and submicroscropic holes, pores, cracks, and other discontinuities. The substrate metal is exposed to corrosive atmospheres through these openings. Corrosion products derived from the substrate spread over the surface, and the article is tarnished; furthermore, the catalytic activity and contact conductance is impaired because the surface is partly or wholly covered with corrosion products. Because of the low hydrogen overvoltage on platinum metals, corrosion of the substrate appears to be more rapid than in their absence. What is even worse, corrosion of the substrate metal undermines the top coating of precious metal, which falls off and is lost.

I have found that if the platinum metals are applied over a thin undercoating of chromium, the tendency for tarnishing of the substrate is remarkably suppressed, and the desirable surface properties of the platinum metals is retained for extended periods. Furthermore, as a coating system, such duplex coatings are unexpectedly effective in preventing corrosion. In this respect they resemble closely the duplex coating system of gold on chromium, as described in my copending application Ser. No. 589,088, filed Oct. 24, 1966.

The phenomena of this invention are concerned with the passivation and depassivation of chromium. Like certain other metals, chromium may assume a passive state in which ordinary corrosion or tarnishing processes are practically extinguished, and the passivated metal surface remains in its initial condition for an indefinite period. With some metals, passivity is quickly lost, unless it is maintained by appropriate chemical or electrochemical treatment; this is true of ordinary carbon steels. But with chromium, passivity is often spontaneously established and maintained.

Heretofore a standard corrosion-resistant coating has been a duplex electroplated coating of chromium on nickel. The chromium surface attains passivity and remains untarnished, although corrosion of the nickel undercoating through unavoidable cracks in the bright chromium electroplate is accelerated by the presence of the chromium. In the absence of depassivating agents, nickel-chromium coatings maintain a bright surface finish for a number of years. Early corrosion of such finishes has usually been attributed to the presence of chlorides. The

duplex coating of the present invention shows resistance to corrosion greatly superior to nickel-chromium coatings, even in extended immersion in hydrochloric acid.

One object of the present invention is to provide a protective coating that can be plated on metal surfaces, and which assumes and retains passivity even in the presence of some depassivating agents, so that tarnishing and corrosion are suppressed.

Another object of the invention is to provide a non-tarnishing, self-passivating plated coating which affords relatively permanent protection to a metal substrate even though employing thinner coatings than those of the common copper-nickel-chromium coating systems.

Another object is to provide a non-tarnishing, self-passivating plated coating which does not accelerate corrosion of the substrate metal through openings in the protective coating.

Another object is to provide a non-tarnishing, self-passivating plated coating which has the desirable surface properties of platinum, palladium, and rhodium, while requiring only small quantities of these metals.

Another object of this invention is to provide methods and baths for applying these new duplix coatings in a way that results in true adhesion of the platinum metal to the chromium.

The term "adhesion" is used as has long been established in the art, namely, to mean that the coating is adhered so strongly to the substrate that it cannot be dislodged or separated by mechanical forces, such as might be exerted by vigorous rubbing, by application of a chisel, by large variations in temperature, or by bending of the plated article. According to Electroplating Engineering Handbook (A. K. Graham, editor, Reinhold Publishing Co., New York, 1955, page 65), "There needs to be an atomic lattice continuity at the interface between the coating and the basis-metal in order to obtain true adhesion." "True adhesion" is equivalent to what I mean herein by "adhesion" and "adherence." I am speaking of adhesion in the sense in which H. B. Linford used the term in Plating 41, 1954, page 283, when he said "the adhesion should be of the same order of magnitude as the tensile strength of the metals themselves." Another investigator, C. L. Faust, Monthly Rev. Am. Electroplaters' Soc., March 1946, page 266, says, "Adhesion should be considered as solely a matter of workmanship in plating, and like that, is either good or bad. Adhesion of a degree should not be accepted. If adhesion is not perfect, the preparation and plating process are either not under proper control or are improperly selected for the job."

If a coating can be rubbed off by repeated rubbing with a soft cloth to which pressure is applied, or if it can be lifted off by affixing adhesive tape and then removing the tape, its adhesion is unsatisfactory; it is not an adherent coating, as I use the term herein and as the term is characteristically used in the electroplating art. In other words, physical adsorption by van der Waal forces is *not* adhesion, in the present sense.

Other objects, advantages and features of the invention will appear from the more detailed description that follows.

In the drawings:

FIG. 1 is an idealized representation of corrosion in a pore in chromium-plated nickel.

FIG. 2 is an idealized representation of corrosion in a pore in platinum-chromium plated nickel, illustrating some of the advantages of the present invention.

Like other plated coatings, the thin platinum metal top-coat (it may be platinum or paladium or rhodium) is undoubtedly penetrated by submicroscopic pores, fissures, and other openings, exposing the underlying chromium to corrosive attack. However, chromium becomes

passive spontaneously, and this effect is further reinforced by the fact that active chromium would be anodic to the platinum metal, and thus would immediately be passivated. In the passive state, it is not tarnished or corroded appreciably. Since the platinum metal is intrinsically proof against tarnish and corrosion, and the chromium where exposed is likewise tarnish-free, the duplex coating is not noticeably corroded.

However, microscopic examination indicates that many discontinuities in the platinum metal fall immediately over the cracks which form a network in the underlying chromium. Accordingly, the substrate of base metal is exposed through these openings. Why is corrosion of the base metal exposed through these openings strongly suppressed?

It might be thought that the accumulation of corrosion products in these pores stifles the corrosion reaction, as was suggested by Lukens in connection with gold coatings on stainless steel. However, in studies of nickel-chromium coatings, it has been found that the nickel undercoat is corroded steadily (though slowly) through the pores in chromium. See, for example, W. E. Lovell, E. H. Shotwell and J. Boyd, Tech. Proc. Amer. Electroplaters' Soc. 47, 215 (1960); E. J. Seyb, ibid. 47, 209; W. H. Safranek and R. W. Hardy, Plating 47, 1027 (1960). The corrosion products do not stifle the corrosion reaction in these coatings, and it seems unreasonable to suppose that they would do so simply because 0.000,005" of a platinum metal is applied over the chromium.

It is generally accepted that nearly all corrosion reactions arise from electrolytic cells comprising anodic and cathodic regions which are contiguous, or nearly so, in the corroding metal. At the anode, the metal dissolves and produces ions. The cathode reaction is usually the discharge of hydrogen from water. The electrolyte is a film of moisture adsorbed on the metal surface, ordinarily too thin to be visible. Corrosion seldom occurs in the absence of moisture.

In the submicroscopic pores under consideration, the dimensions of the exposed substrate are assumed to be too small for contiguous anodic and cathodic regions to coexist within the substrate metal surface. Consequently, the cromium apparently functions as cathode, when no precious metal coating is applied. Considering the ordinary nickel-chromium coatings, the anode reaction is: $Ni \rightarrow Ni^{++} + 2\ e^-$; and the cathode reaction is:

$$2H_2O + 2\ e^- \rightarrow H_2 + 2OH^-$$

The question then arises whether the potentials prevailing at these electrodes are sufficient to account for the observed corrosion. According to the Nernst equation, and the accepted standard potential of nickel, the anode potention is given by $E_a = -0.250 + 0.03 \log c_{Ni}{}^{++}$. The cathode potential is $E_c = 0.00 - 0.06\ pH + 0.06 \log p_{H_2}$. Assuming an effective partial pressure of 10^{-7} atm. for hydrogen in the adsorbed electrolyte, and a pH of about 7, $E_c = 0.00$ v. These assumptions can be varied over a wide range without affecting the conclusions significantly.

To these static potentials, the effective overpotentials must be added. The corrosion data suggest a corrosion current of the order of a microampere per square centimeter; the nickel overpotential is therefore negligible. The hydrogen overpotential can be calculated from data given by G. Milazzo ("Electrochemistry," Elsevier Publishing Co., New York, 1963, p. 230) for chromium, using the Tafel law, which is believed to hold for this electrode. At 1μ amp./cm.^{2}, it is 0.37 v.

For the corrosion reaction to proceed, the anode potential must be more negative than the cathode potential; that is, it must be more negative than 0.00–0.37 v. Setting $E_a = -0.37$ v., it is found that the equilibrium value of $C_{Ni}{}^{++}$ is 0.0001 M. Therefore, corrosion apparently proceeds as long as the concentration of nickel ions in the film of electrolyte adsorbed on the nickel substrate does not exceed about 0.0001 M. The passive chromium will function as cathode. This state is shown schematically in FIG. 1.

From the solubility product of nickel hydroxide, which is 2×10^{-16}, according to F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, New York, 1962, p. 733, it is calculated that any hydroxide ion concentration greater than 10^{-6} M. is sufficient to cause nickel ions to precipitate as $Ni(OH)_2$. As the cathodic half of the corrosion reaction produces hydroxide ions, as shown in the equation given above, the hydroxide ion concentration will generally exceed this limiting value; nickel ions will be removed from the electrolyte in the precipitate, the nickel ion concentration will be less than 0.0001 M., and consequently the anode potential will be sufficiently negative to cause the corrosion reaction to proceed. This conclusion is in agreement with observations.

However, if a coating of a platinum metal overlies the chromium, the situation is altered as shown in FIG. 2. The hydrogen overvoltage on the platinum metal is far lower than that on chromium. Consequently, the cathodic reaction is shifted from chromium to the platinum metal. The nickel ions produced at the anode, and the hydroxide ions produced at the cathode, are now separated by an intervening face of passive chromium, which apparently takes no part in the corrosion process.

In order to precipitate $Ni(OH)_2$, the ions must diffuse across the chromium face. As the passive film on this face is hydrophobic, the film of moisture thereon will tend to be discontinuous. If moisture were completely repelled by the passive chromium, the corrosion cell would lack electrolytic contact, and corrosion would stop; this is quite conceivable. But more generally, there will be a thin, irregular film through which ionic diffusion is very slow. Because of this impediment to diffusion, nickel ions will tend to accumulate at the anode. The concentration may exceed 0.0001 M., especially in view of the very minute quantity of electrolyte involved. Consequently the potential of the nickel anode would become too positive to cause the corrosion reaction to proceed. The high ohmic resistance to be expected in the film of electrolyte lying on the passive chromium would also be an important factor. My current thinking is that the corrosion reaction is strongly inhibited in this manner.

In summary, the peculiar inhibition of corrosion observed when a platinum metal is deposited on chromium is apparently due to the fact that the cathodic and anodic regions are separated by a passive chromium face which impedes both ionic diffusion and electrolytic conduction, shifting the corrosion potentials to levels which are insufficient for corrosion to proceed. The hydrophobicity of passive chromium also tends to interrupt couple action between substrate and the platinum metal coating by causing the electrolyte film to fail.

A major difficulty in producing the duplex coatings was that in conventional baths used for electroplating platinum metals, the reduction potential of the noble metal is so positive, and that of activated chromium is so negative, that the platinum metal was plated out by displacement upon immersion of the chromium-plated surface into the bath. Such deposits are loose and black, and interfere with the adhesion of any compact coating subsequently deposited on them.

I have found that the difficulties are solved by use of complex ions of the noble metals with smaller dissociation constants than those used in prior art plating baths, so that the noble metal reduction potential approaches the value of chromium. Although a large number of platinum metal complexes are known, most of them are extremely slow to react (are not labile), and hence cannot yield the metal at a rate sufficient to form a sound metallic coating.

I have found that suitable baths can be prepared from iodo complexes, provided that a large excess of a soluble

iodide, that is, the iodide of one of the alkali metals (sodium, potassium, lithium), or of ammonium, or of magnesium is used. Other soluble metal iodides which do not form an insoluble complex salt of the noble metal can be used. Although the iodo complexes of the platinum metals are, in general, not very soluble, nevertheless workable plating baths can be prepared, particularly in the presence of highly concentrated iodides, in which the complexes appear to have enhanced solubility. Of the various iodides, lithium appears to be especially effective, at concentrations nearing saturation.

Plating doubtless occurs from such complex ions as tetraiodoplatinate (II), tetraiodopalladate (II), and tetraiodorhodate (III), or possibly the hexacovalent ion of the last metal. It should be especially noted that in these baths platinum is deposited from the divalent state, whereas in other platinum plating baths, it is found in the tetravalent state. On chromium, satisfactory electroplates are not obtained from tetravalent platinum. Divalent palladium is also used in the baths of this invention. The iodide ion apparently stabilizes the divalent state of these metals, though with chloride, the tetravalent state is the more stable, at least in he case of plainum. Furthermore, the only chloride bath suitable for electroplating of platinum is one containing strong HCl, in which chromium would be dissolved almost instantaneously—long before a metal deposit could be made on it.

With iodide ions in the electrolyte, difficulties arise at the anode. The platinum metals are not dissolved, owing perhaps to their ready passivation and the relatively low oxidation potential of the iodide. Instead, iodine is liberated, and as it is an oxidizing agent, it can readily repassivate the chromium surface so that any subsequent deposit is nonadherent.

This difficulty is avoided by placing the anode in a separate compartment, having electrolytic communication with the cathode compartment through a porous medium such as unglazed porcelain or fritted glass. The anode can then be made of any conductive material which is not attacked by the anolyte. Platinum metal, platinum-coated titanium or tantalum, graphite, or iron containing 8–16% silicon, can be used in anolytes consisting of dilute sulfuric or phosphoric acid, or other nonoxidizable acids. Basic anolytes, such as KOH, NaOH, or LiOH, can be used with anodes of nickel or stainless steel, though in general, acidic anolytes are preferred.

The porous diaphragm prevents ready diffusion of oxidizing substances such as molecular oxygen, hydrogen peroxide, or free radicals into the catholyte; it also prevents ready diffusion of iodide and precious metal into the anolyte. Ions are transferred, however, as required by the electrochemical reactions: hydrogen ions will move from the anolyte into the catholyte, and a small amount of iodide ions (or chloride ions, by preferance, if these are present, on account of their greater mobility) from the catholyte into the anolyte.

The oxidation of iodide can be prevented without the complication of a diaphragm by adding to the bath some substance which is more readily oxidized at the anode than iodide. Ferrocyanides and methanol are examples, but they may have an effect on the electroplate.

During the plating operation, the precious metal is lost from the catholyte, and it is not replenished from the anode. This, however, is the rule in precious metal plating. After most of the precious metal has been deposited, the catholyte is removed and treated to recover the metal which remains. If the anolyte is acidic, then the acidity of the catholyte is more or less maintained, and it can be regenerated by adding the iodide salt of the precious metal (for example, PtI_2).

Because of these and other complications, and especially because of the relatively low current efficiency, it may be desirable to apply only a very thin, or "strike" coating of the precious metal from the iodide bath. If a thicker coating is desired, the article may then be transferred to a conventional precious metal plating bath, and the remainder of the desired coating deposited in the usual way.

The presence of chlorides is permissible in the iodide bath, for the iodo complexes are in general more stable than chloro complexes, and are therefore formed even in the presence of chlorides.

On a substrate of 0.000,02 inch of chromium, coatings of platinum or rhodium with an estimated thickness of 0.000,003 inch appear to be completely resistant to warm, strong nitric acid. This is not true if the coatings are deposited on a nickel, copper, or brass substrate, without the chromium undercoating. No doubt the thin precious metal coating is somewhat porous, but chromium exposed through the pores becomes passive and fails to corrode or tarnish.

This is strong evidence that thin precious metal coatings on a chromium undercoating will resist tarnish or corrosion indefinitely in ordinary atmospheres.

The chromium itself is deposited directly on the substrate, or on an undercoating of copper or copper-nickel or of nickel, made in the conventional manner. Any suitable chromium plating process may be used. The current density, temperature, and time of plating are preferably chosen to give a coating thickness of 0.000,02 inch.

After the chromium-plated surface is thoroughly rinsed, it is depassivated by dipping it for 2–150 seconds in dilute hydrochloric, sulfuric, or acetic acid. Typical times are 5 to 30 seconds in 5 to 10% hydrochloric acid at room temperature. It may be helpful to pass current through the depassivating bath, making the chromium-plated surface cathodic, typically at current densities of 10 to 100 amperes per square foot. The electric current makes the chromium surface cathodic, hastens depassivation, and helps to prevent excessive dissolution of the chromium by the acid, for as soon as the chromium is depassivated, it is actively attacked by the acid.

The depassivation treatment should be regulated so that the thickness of the chromium coating is not greatly diminished. A treatment of 5 seconds in 15% by volume hydrochloric acid at room temperature, with 30–40 amperes per square foot cathodic current, is usually satisfactory.

It is also possible to use 5–10% sulfuric acid, 15–25% phosphoric acid, or 10–30% acetic acid. In fact, these last acids are preferred to hydrochloric, since they do not attack the chromium quite as rapidly.

After depassivation, the surface is kept wet with a rinse solution of 0.1–0.5% acid, to prevent repassivation by air when the article is transferred to the plating bath.

In the following, Examples 3–8 give composition ranges for suitable baths to be used after depassivation of the chromium as in Examples 1 and 2.

EXAMPLE 1

A. Depassivation.

	Preferred	Permissible Range
Hydrochloric acid	8% (by wt.)	4–20%.
Temperature	75° F	65–95° F.
Time	4 sec	2–20 sec.

(Temperature and time are adjusted to suit the concentration of the acid.)

B. Rinsing.

	Preferred	Permissible Range
Hydrochloric acid	0.3%	0.01–1.0%.

C. Platinum metal plating (i.e. platinum or palladium or rhodium).

EXAMPLE 2

A. Depassivation.

	Preferred	Permissible Range
Sulfuric acid	5%	3–20%.
Temperature	90° F.	70–100° F.
Time	6 sec.	2–20 sec.
Current density	30 amp./sq. ft.	10–100 amp./sq. ft.

B. Rinsing.

	Preferred	Permissible Range.
Sulfuric acid	0.5%	0.01–1.0%.

C. Platinum metal plating.

EXAMPLE 3

	Range	Preferred
Platinum (II) iodide, PtI_2	5–15 g./l.	10 g./l. or saturation.
Potassium iodide, KI	400–600 g./l.	85% saturation.
Hydrocholoric or hydriodic acid, HCl or HI, concd	10–40 ml./l.	15 ml./l.

EXAMPLE 4

	Range	Perferred
Platinum (II) iodide, PtI_2	5–15 g./l.	12 g./l or staturation.
Lithium iodide, LiI	600–750 g./l.	85% saturation.
Hydrochloric or hydriodic acid, HCl or HI, concd	10–40 ml./l.	15 ml./l.

EXAMPLE 5

	Range	Preferred
Palladium (II) iodide, PdI_2	5–15 g./l.	12 g./l. or saturation.
Lithium iodide, LiI	600–750 g./l.	85% saturation.
Hydrochloric or hydriodic acid, HCl or HI, concd	10–40 ml./l.	15 ml./l.

EXAMPLE 6

	Range	Preferred
Palladium (II) chloride, $PdCl_2$	5–15 g./l.	12 g./l.
Ammonium iodide, NH_4I	700–900 g./l.	85% saturation.
Hydrochloric or hydriodic acid, HCl or HI, concd	10–40 ml./l.	15 ml./l.

EXAMPLE 7

	Range	Preferred
Rhodium (III) chloride, $RhCl_3$	5–15 g./l.	12 g./l.
Sodium iodide, NaI	650–850 g./l.	85% saturation.
Hydrochloric or hydriodic acid, HCl or HI, concd	10–40 ml./l.	15 ml./l.

EXAMPLE 8

	Range	Preferred
Rhodium (III) iodide, RhI_3	5–15 g./l.	12 g./l. or saturation.
Magnesium iodide, MgI_2	800–1,100 g./l.	85% saturation.
Hydrochloric or hydriodic acid, HCl or HI, concd	10–40 ml./l.	15 ml./l.

In the above, the iodides mentioned are apparently interchangeable. The precious metal can be added as chloride as well as iodide; it becomes an iodo complex with the excess of alkali iodide. No published values are available for the saturations cited. Eighty-five percent saturation is obtained by saturating 850 ml. of water, and then adding 15% water. Working conditions for Examples 15–20 are:

	Range	Preferred
Temperature	35–90° C.	50° C.
Current density	5–50 amp./sq. ft.	15 amp./sq. ft.

EXAMPLE 9

To prepare on iodide plating bath, 0.5 g. of PtI_2 was added to a solution of 10 g. of KI in 25 ml. water. After the solution was boiled for 20 minutes, most of the black PtI_2 had dissolved to give a very dark red-brown solution. It was estimated that about 10–20% of the PtI_2 remained undissolved; it was left suspended in the bath. The soltuion was acidified with 2 ml. concentrated HCl.

The cathodes were brass panels, of which 1 x ½ inch was exposed in the bath. They had previously been plated with 0.0002 inch of bright nickel and 0.000,02 inch of chromium. After being degreased in a hot alkaline cleaning bath, they were rinsed and activated by cathodizing them for 10 seconds, at 30 amp./sq. ft. in HCl, 8% by weight. Most cathodes were plated without further rinsing; certain were dipped into concentrated HCl until bubbling ceased, indicating that the chromium had been removed.

A rod of graphite was used as an anode. It was placed in a porous porcelain cup containing 10% H_3PO_4 as an electrolyte. This arrangement prevented the oxidation of iodide ion to free iodine at the anode during the plating operation.

Plating was carried out with vigorous cathode agitation, a current of 0.15 amp., and at 40–70° C. for 10 minutes. A bright, smooth coating of platinum was produced. Platinum was also deposite on the brass exposed on the obverse face; this finish was matte, corresponding to the unpolished state of the substrate.

During the plating operation gas was vigorously evolved. The current efficiency was not determined, but was estimated to be about 20–40%. On some samples, the platinum coating could be rubbed off by vigorous abrasion with wet linen; when this occurred, the addition of 1 ml. of concentrated HCl, and warming the bath to 50° C., resulted in a bright coating with good adhesion. In all cases, the coated specimens withstood bend tests, and could be heated in a gas flame without the production of blisters.

A series of samples was produced by the standard procedure given above for testing in corrosive environments.

EXAMPLE 10

The bath was prepared exactly as in Example 9, but 26 g. of KI were used instead of 10 g. The results were about identical, but nearly the entire quantity (0.5 g.) of PtI_2 dissolved. The plating range at 50° C. extended from 0.11 to 0.45 amp. The plated specimens were indistinguishable from those produced in the first experiment.

EXAMPLE 11

The bath was prepared exactly as in Example 9, but 27 g. of LiI were used instead of KI. The entire portion of PtI_2 (0.5 g.) dissolved. The plating range at 50° C. extended from 0.15 to 0.60 amp. A number of specimens were plated, and excellent adhesion was obtained in each case, although no additions of HCl were made after the bath was originally prepared.

EXAMPLE 12

The bath was prepared and samples were plated exactly as in Example 11, except that $PdCl_2$ was used in place of PtI_2. All of the palladium salt dissolved. The plating range extended from 0.05 to 0.55 amp., and all of the specimens showed good adhesion.

EXAMPLE 13

The bath was prepared and samples were plated exactly as in Example 11, except that 0.5 g. of $RhCl_3$ were employed instead of the PtI_2. The precious metal salt dissolved readily, giving a deep red solution. The plating range extended from 0.1 to 0.7 amp. at 50° C., and no trouble with adhesion was observed on any of the cathodes.

EXAMPLE 14

Specimens from all of the preceding experiments were tested by placing a drop of concentrated HCl on the noble metal coating and heating the specimen very gently over a gas flame utnil the acid evaporated, which took 5–10 minutes. The results were as follows:

Metal	With Chromium Undercoat	Without Chromium Undercoat
Pt	No noticeable effect	Flaking of Pt, with formation of green salts.
Pd	do	Flaking of Pd, with formation of green salts.
Rh	do	Extensive peeling of Rh, formation of green salts.

Apparently the HCl prevented passivation of the nickel substrate, and since this was anodic to the precious metal, it dissolved out from under the top coating, allowing it to flake or peel.

EXAMPLE 15

The tests of Example 14 were repeated, using concentrated HNO_3 in place of HCl. The results were as follows:

Metal	With Chromium Undercoat	Without Chromium Undercoat
Pt	No noticeable effect	Extensive peeling of Pt with formation of green salts in 2 minutes.
Pd	Slow attack on Pd; green salts visible after 12 minutes.	Extensive peeling of Pd with formation of green salts visible after 90 secs.
Rh	No noticeable effect	No noticeable effect.

The excellent resistance to hot nitric acid indicates that these coating systems will not undergo visible tarnish when exposed to the air. Furthermore, since the chromium undercoating acts to block diffusion of substrate metals, especially copper or silver, to the precious metal, whether it is gold, platinum, palladium, or rhodium, the accumulation of sulfides or oxides on the surface is prevented.

EXAMPLE 16

When immersed in warm sodium polysulfide solution, the three plating systems (Cr-Pt, Cr-Pd, Cr-Rh) were unaffected after 3 hours.

The process produces non-tarnishing coatings with minimal thickness of precious metals, and therefore imparts the appearance and tarnish-resistance of these metals at very low cost. Furthermore, the chromium undercoating blocks the diffusion of substrate metals, especially silver or copper, through the precious metal top-coating. In some cases this diffusion has led to the formation of sulfides or oxides on the surface which give relatively high resistances to electrical contacts.

It is suggested to compare these results with those obtained with chromium-gold duplex coatings as set forth in my copending application Ser. No. 589,088, filed Oct. 24, 1966. Apparently in these duplex coatings, gold and the platinum metals function similarly with respect to corrosion reactions, and it is presumed that the more extensive experiments with chromium-gold duplex coatings may be taken to indicate the behavior of chromium-platinum metal duplex coatings as well.

EXAMPLE 17

A suitable plating schedule for coating steel objects with platinum metals is:

	Inch
Copper	0.0001
Nickel	0.0002–0.0005
Chromium	0.000,02–0.000,08
Platinum, palladium, or rhodium	0.000,001–0.000,05

The heavier the nickel and copper undercoats, it is to be expected that the more pronounced the ultimate corrosion resistance will be. For a brass object, the copper may be omitted. For white metal, it is desirable to use at least 0.0002 inch copper.

The thickness of the platinum metal applied depends on the intended use. For ornamental coatings for indoor exposures, about 0.000,002 inch is adequate. But if the finished object is likely to be subjected to wear, as are doorknobs or tableware, or is to be used outside where an occasional burnishing will be applied to remove accumulated soils, substantially thicker coatings are advisable, e.g., up to 0.005 inch or so. Heavier platinum metal coatings may be applied over the preliminary platinum metal coating from conventional type baths. The thinner duplex coatings, if not supplemented, are not serviceable where the surface is subject to considerable abrasive wear, or where they are apt to be nicked or otherwise damaged mechanically.

The invention thus includes these significant features: (a) depassivation of the chromium coating; (b) prevention of repassivation by use of an acid rinse and an acidic plating bath; and (c) formulation of the bath so that the precious metal complex ion does not give displacement deposits on depassivated chromium. In the case of gold, the addition of alloying metals to inhibit displacement is of important assistance.

To those skilled in the art to which this invention relates, many changes in construction and widely differing embodiments and applications of the invention will suggest themselves without departing from the spirit and scope of the invention. The disclosures and the description herein are purely illustrative and are not intended to be in any sense limiting.

I claim:

1. A process for plating a chromium surface to provide a corrosion-resistant adherent precious metal coating, comprising the steps of

(a) depassivating said chromium surface by cathodizing it in an acid bath,

(b) rinsing the depassivated surface with a weak acid bath,

(c) plating on said depassivated surface from an aqueous acidified solution of an alkali iodide containing a salt chosen from the group consisting of PtI_2, PdI_2, $PdCl_2$, $RhCl_3$, RhI_3 and mixtures thereof with each other.

2. The process of claim 1 wherein the salt is one of the iodides named therein; wherein the anode and cathode are kept separated during the step of electroplating while providing electrolytic communication through a porous diaphragm.

3. The process of claim 2 wherein the anode is immersed in an electrolytically conductive anolyte and said anode comprises any conductive material not attacked by said anolyte.

4. The process of claim 3 wherein said anolyte is chosen from the group consisting of the non-oxidizable acids.

5. The process of claim 4 wherein said anode is chosen from the group consisting of a platinum-group metal, titanium coated with a platinum-group metal, tantalum coated with a platinum-group metal, graphite, and iron containing 8–16% silicon.

6. The process of claim 3 wherein said anolyte is chosen from the group consisting of KOH, NaOH, and LiOH and said anode is chosen from the group consisting of nickel and stainless steel.

7. A process for plating platinum on a chromium surface, comprising the steps of

(a) depassivating said chromium surface by cathodizing it in an acid bath,

(b) rinsing the depassivated surface in a weak acid solution, and

(c) electroplating platinum from an aqueous acidified bath comprising a strong solution of an alkali iodide containing platinum (II) iodide in an amount of 5 to 15 grams per liter.

8. The process of claim 7 wherein said strong solution of alkali iodide is a solution of 400 to 600 grams per liter of potassium iodide.

9. The process of claim 7 wherein said strong solution of alkali iodide is a solution of 600 to 750 grams per liter of lithium iodide.

10. The process of claim 7 carried on at 35 to 90° C. at a current density of 5 to 50 amperes per square foot.

11. A process for plating palladium on a chromium surface, comprising the steps of

(a) depassivating said chromium surface by cathodizing it in an acid bath,

(b) rising the depassivated surface in a weak acid solution, and

(c) electroplating palladium from an aqueous acidified bath comprising 5 to 15 grams per liter of palladium halide dissolved in a strong iodide solution.

12. The process of claim 11 wherein said acidified palladium plating bath comprises 5 to 15 grams per liter of palladium (II) iodide dissolved in 600 to 750 per liter of lithium iodide aqueous solution.

13. The process of claim 11 wherein said acidified palladium plating bath comprises 5 to 15 grams per liter of palladium (II) chloride dissolved in 700 to 900 grams per liter of ammonium iodide aqueous solution.

14. The process of claim 11 carried on at 35° to 90° C. at a current density of 5 to 50 amperes per square foot.

15. A process for plating rhodium on a chromium surface, comprising the steps of

(a) depassivating said chromium surface by cathodizing it in an acid bath,

(b) rising the depassivated surface in a weak acid solution,

(c) electroplating rhodium from an aqueous acidified strong iodide solution containing 5–15 grams per liter of a rhodium halide.

16. The process of claim 15 wherein said acidified solution contains 5–15 grams per liter of rhodium (III) chloride in an aqueous solution of 650–850 grams per liter of sodium iodide.

17. The process of claim 15 wherein said acidified solution contains 5–15 grams per liter of rhodium (III) iodide in an aqueous soltuion of magnesium iodide.

18. The process of claim 15 carried on at 35° to 90° C. at a current density of 5–50 amperes per square foot.

19. A plating bath for plating platinum on chromium, comprising an aqueous solution of about 80 to 90% saturation of an iodide chosen from the group consisting of the iodides of lithium, sodium, potassium, ammonium, and magnesium, 5–15 grams per liter of PtI_2 dissolved therein, and acid to obtain a pH of 2.5 to 4.

20. A plating bath for plating palladium on chromium, comprising an aqueous solution of about 80% to 90% saturation of an iodide chosen from the group consisting of the iodides of lithium, sodium, potassium, ammonium, and magnesium, 5–15 grams per liter of PdI_2 or $PdCl_2$ dissolved therein, and acid to obtain a pH of 2.5 to 4.

21. A plating bath for plating rhodium on chromium, comprising an aqueous soltuion of about 80% to 90% saturation of an iodide chosen from the group consisting of the iodides of lithium, sodium, potassium, ammonium, and magnesium, 5–15 grams per liter of trivalent rhodium halide dissolved therein, and acid to bring the pH to 2.5 to 4.

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