United States Patent Office

3,186,925
Patented June 1, 1965

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3,186,925
CHROMIUM PLATING PROCESS WITH A PURE NICKEL STRIKE

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No Drawing. Filed Nov. 1, 1960, Ser. No. 66,417
3 Claims. (Cl. 204—41)

This invention pertains to electroplating and more particularly to the forming of a decorative chromium plated part having improved durability.

Among the plating sequences currently being commercially used to produce decorative chromium plated parts is that involving the use of a dual layer nickel coating immediately subjacent the chromium coating. Although the dual layer nickel coating may be applied directly onto a basis metal, a more frequent commercial practice includes applying a thin preliminary coating of a metal, such as copper, to the basis metal and then applying the dual layer nickel and chromium coatings. More specifically, the latter sequence involves initially applying a layer of copper to the surface of the basis metal. A layer of semi-bright nickel is then applied to the copper layer; a layer of full-bright nickel is applied to the semi-bright nickel layer, and then an overlay of decorative chromium is applied to the full-bright nickel layer.

A not uncommon problem present in either of the above-mentioned sequences lies in obtaining satisfactory adhesion of the semi-bright nickel layer to the surface upon which it is applied. This problem is especially significant when the semi-bright nickel layer is applied to a copper plated surface. The nature of the semi-bright plating bath and its inherent method of use are believed to be the cause of the poor adhesion of the nickel to a basis metal such as copper or steel. The poor adhesion contributes to unsatisfactory durability, particularly unsatisfactory corrosion resistance, of the finished part. Although various explanations as to the cause of the unsatisfactory adhesion have been offered heretofore, not one has provided a solution by which satisfactory adhesion can be consistently obtained under commercial production conditions.

Principal objects of the invention are to provide an improved decorative chromium plated part which has improved durability due to improved adhesion of the dual layer nickel coating and to provide an improved method of forming a decorative chromium plated part.

The invention comprehends applying an extremly pure layer of nickel to the surface of the part immediately prior to applying a conventional dual layer nickel coating. It is essential to the invention that the nickel layer be pure in the sense that there are relatively no codeposited substances in the nickel layer, as is true in conventional commercially applied nickel layers. It is also of importance that no current be passed through a pure nickel plating bath solution while the part is being immersed therein.

It is believed that bipolar effects, inorganic contaminants in the semi-bright nickel plating bath, organic additives such as wetting agents, brighteners and the like in the semi-bright nickel plating bath all contribute to codeposition of other substances with the nickel to cause poor adhesion of the semi-bright nickel layer to a basis metal such as copper or steel. All of these undesirable factors are obviated by electrodepositing a pure nickel layer onto the basis metal immediately before the layer of the semi-bright nickel is deposited.

An extremely adherent, uniform pure nickel layer can be obtained by immersing the part to be plated into a suitable nickel plating bath without current on, in contradistinction to immersion into a semi-bright nickel plating bath with current on.

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The specific bath composition which is preferred to apply the pure nickel layer may vary, depending upon the apparatus used, preferred plating times, temperatures, composition of the part being plated, size and configuration of the part being plated, etc. However, for most applications, particularly for copper plated parts, a Watt's-type bath solution, such as that having the following composition, can be used:

Bath I

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	oz./gal.	40
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	oz./gal.	4
Boric acid	oz./gal.	5
pH		3–3.5
Temperature	° F.	130
Cathode current density	amps./sq. ft.	10–60

The bath is operated with air agitation and an anode to cathode area ratio of about 1:1. The purity of the bath is maintained with constant recirculating filtration through an active carbon pack and periodic dummying. It is preferred that the pH of the bath solution be maintained at approximately 2.0 to 4.0 for best results. However, in some instances, a pH as high as approximately 5.2 may be preferred.

As previously indicated, the bath is used to apply an extremely pure nickel coating. The bath therefore contains no materials other than as formulated above and, therefore, contains no wetting agents or brighteners of any sort. Although a Watt's-type bath, such as Bath I, is the most generally satisfactory bath which can be used to apply my pure nickel layer, in some instances it may be preferred to employ other baths to obtain the pure nickel coating. A high chloride bath such as follows can be used:

Bath II

Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	oz./gal.	32
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	oz./gal.	12
Boric acid	oz./gal.	4–5
pH		2.5
Temperature	° F.	130
Cathode current density	amps./sq. ft.	10–60

As indicated in connection with Bath I, Bath II is used as described above without conventional addition agents and its purity is maintained by constant recirculating filtration through an active carbon pack and periodic dummying. Hence, substantially all impurities introduced into the bath by drag-out from preceding baths are substantially continuously removed. Since the bath is formulated so as to be substantially free of contaminants, obviously the only contaminants introduced into it would be from drag-out of baths used in preceding treatments, e.g., cleaning or copper plating. An anode to cathode area ratio of 1:1 is preferred and air agitation can be used.

Other nickel plating solutions which might be employed to attain satisfactory results in certain instances would be as follows:

Bath III

Nickel chloride ($NiCl_2 \cdot 6H_2O$)	oz./gal.	32
Boric acid	oz./gal.	4
pH		0.9–1.1
Temperature	° F.	130
Cathode current density	amps./sq. ft.	50–100

Bath IV

Nickel fluoborate ($Ni(BF_4)_2$)	oz./gal.	29.3
Boric acid	oz./gal.	4
pH		3.0–4.5
Temperature	° F.	130
Cathode current density	amps./sq. ft.	50–100

Mild agitation, such as air agitation, can be used. An anode to cathode area ratio of 1:1 can be used for the lower current density depositions while a ratio of 3:1, respectively, is preferred for higher current density depositions. Baths III and IV, like Baths I and II, are used as described without conventional addition agents and while maintaining purity through constant recirculation through an activated carbon pack and periodic dummying.

The pH of Baths I and II is preferably adjusted with HCl or H_2SO_4 while the pH of Bath III is preferably adjusted with HCl. The pH of Bath IV can be adjusted with HCl, H_2SO_4 or HF. Since it is the presence of foreign metal salts and organic additives which principally cause impurities in the coating to result, any of the common mineral acids will at least be generally satisfactory for adjusting the pH of the bath solution.

The specific manner in which the purity of the nickel plating baths is maintained is not particularly critical and the purity can be maintained in the known and accepted manner for purifying plating solutions. As indicated above, constant recirculating filtration through an activated carbon pack can be used to remove organic contaminants. Periodic additions of hydrogen peroxide can be used for the same purpose. Inorganic contaminants can be precipitated chemically but it is more feasible to remove them under commercial production conditions by periodic dummying of the bath.

As a specific example of the practice of my invention a metal part, such as one made from SAE 1010 steel, is polished and cleaned to form a suitable surface for subsequently applied electrodeposited coatings. The particular manner in which the metal part is cleaned is only as material to my invention as it is to any general electroplating procedure and may, therefore, be varied considerably.

In one method of cleaning, the workpiece is immersed for four minutes to five minutes in an alkaline soak cleaner containing two ounces per gallon to six ounces per gallon of the following mixture, by weight:

	Percent
Sodium metasilicate	30
Trisodium phosphate	50
Soda ash	13
Sodium resinate	7

Up to 4%, by weight, sodium sulfite can be added to prevent etching if the mixture is to be used to clean zinc base alloy die cast parts.

After the soak cleaning, the workpiece is subjected to an alkaline spray cleaner, such as an aqueous solution containing three ounces per gallon of sodium metasilicate, and then immersed again in the above-mentioned soak cleaner for about two minutes. The workpiece is then removed from the soak cleaner, subjected to another alkaline spray rinse, such as described above, and subjected to an anodic electrocleaning in a solution made up as follows:

	Oz./gal.
Sodium orthosilicate	8
Tetrasodium pyrophosphate	1
Sodium carbonate	1

Using a bath temperature of approximately 160° F. to 180° F. the workpiece is subjected to an anodic potential for about 30 seconds to 45 seconds with an anode current density of approximately 15 amperes per square foot to 100 amperes per square foot. After the anodic cleaning, the part is thoroughly rinsed in cold water and then immersed for approximately 30 seconds in a room temperature aqueous bath containing 0.2% to 0.5% sulfuric acid, by volume.

Thereafter the part is removed from the sulfuric acid solution, thoroughly rinsed and placed in a copper strike bath, such as one having the following composition:

Copper cyanide, CuCN	4 oz./gal.
Sodium carbonate, Na_2CO_3	2 oz./gal.
Rochelle salts	3 oz./gal.
pH	About 11.5.
Free sodium cyanide	0.9 oz./gal. to 1.6 oz./gal.
Temperature	125° F.

Using this bath a copper coating of approximately 0.00005 inch in thickness is deposited in about two minutes when using a cathode current density of about 60 amperes per square foot.

After the desired thickness of copper is deposited in the strike solution, the workpiece is removed therefrom and directly placed in a copper plating bath having the following composition:

Copper cyanide, CuCN	8 oz./gal. to 10 oz./gal.
Sodium cyanide, NaCN (free)	1.3 oz./gal. to 2.5 oz./gal.
Caustic potash	4 oz./gal.
Wetting agent (liquid)	6 cc./gal. to 10 cc./gal.
Brighteners	As needed.

A copper coating approximately 0.0005 inch to 0.0008 inch in thickness is deposited with both mechanical and air agitation of the bath under a cathode current density of about 10 amperes per square foot to 30 amperes per square foot and a bath temperature of about 160° F.

Thereafter the part is removed from the copper plating bath, rinsed in cold water and cleaned for approximately one-half minute in the above-identified anodic electrocleaning solution. It is then removed from the electrocleaning solution, rinsed in cold water and dipped in an aqueous solution containing about 1% to 3%, by volume, sulfuric acid. The workpiece is then rinsed in water, preferably de-ionized water.

From the rinse the workpiece is directly immersed without current on into a solution for plating a pure nickel layer. A Watt's-type bath solution, such as Bath I can be used. The pure nickel layer is deposited as described in connection with Bath I to form a coating approximately 0.00001 inch in thickness.

After the desired thickness has been obtained, the part is rinsed in cold water and directly immersed, with current on, into a solution for plating a semi-bright nickel layer having a columnar microstructure. A solution which can be used to obtain such a coating is as follows:

$NiSO_4 \cdot 6H_2O$	g./l.	300
$NiCl_2 \cdot 6H_2O$	g./l.	40
H_3BO_3	g./l.	40
Sodium lauryl sulfate	g./l.	0.5
Coumarin	g./l.	0.25
H_2O to make one liter.		
pH		3.5
Temperature	° F.	140
Cathode current density	a.s.f.	50

The nickel is deposited until a thickness of approximately 0.0007 inch is obtained. It is preferred to both introduce the workpiece into the solution as well as remove it therefrom with the current on. In general I have found best results to be obtained if the semi-bright bath contains sulfur-free brighteners.

After the workpiece is removed from the semi-bright nickel plating solution it is rinsed and immersed, with current on, into a full-bright nickel plating solution, such as one having the following composition:

$NiSO_4 \cdot 6H_2O$	g./l.	300
$NiCl_2 \cdot 6H_2O$	g./l.	40
H_3BO_3	g./l.	40
Sodium lauryl sulfate	g./l.	1
Coumarin	g./l.	0.3
Benzene mono-sulfonate	g./l.	10
H_2O to make one liter.		
pH		3.2
Temperature	° F.	130
Cathode current density	a.s.f.	30

For both nickel plating solutions cast carbon anodes bagged in nylon can be employed. After nickel plating, if desired, the parts can be cathodically cleaned, rinsed and dipped in an aqueous solution containing 30%, by weight, hydrochloric acid.

The workpiece is then rinsed in cold water and immersed in a chromium plating bath to apply the chromium coating onto the dual layer nickel coating. A chromium plating bath that can be used to provide excellent results is one containing 32 ounces per gallon chromic acid (CrO_3) and in which the chromic acid to sulfuric acid ratio is about 100:1. The bath is operated at a temperature of approximately 118° F. and a cathode current density of approximately 180 amperes per square foot. Sufficient chromium is deposited to apply an overlay of at least 0.000015 inch. As is typical for chromium deposition, no agitation is required during the deposition and an anode to cathode area ratio of about 1:1–2:1, respectively, can be used.

The chromium overlay can also be accomplished in accordance with the invention described in the previously filed United States patent application serial No. 833,672, now abandoned, in the names of Frederick L. Brower and Robert C. Miller and which is assigned to the assignee of the present invention. The invention described in the referenced United States patent application entails employing a pulsating current density to apply the chromium overlay. The cathode current density is periodically raised and lowered in cyclic fashion repeatedly during the chromium deposition to obtain a more uniform coverage on the surface of the part.

As previously indicated, a steel part such as one made from SAE 1020 steel can be decoratively chromium plated without the use of an initial copper layer. In such instance my pure nickel layer is directly applied to the steel, preferably using Bath II in the manner described. The part is then rinsed in cold water and the conventional dual layer nickel coating and chromium overlay applied in the same manner as hereinbefore indicated in detail.

The pure nickel layer which is used need only have an average thickness which is sufficient to produce a continuous coating on the surface being plated. Even on parts having complex surface contours, a continuous coating can generally be achieved with a pure nickel layer having an average thickness of about 0.0001 inch. In some instances, however, it may be preferred to employ a pure nickel layer having a greater average thickness.

It is to be understood that although the invention has been described in connection with certain specific examples thereof no limitation is intended thereby except as defined in the appended claims.

What is claimed is:

1. In a method of decorative chromium plating which includes the steps of treating a workpiece in at least one bath solution to prepare the workpiece surface for reception of a nickel strike, electrodepositing a nickel strike to the workpiece surface, electrodepositing a semibright nickel coating onto the nickel strike, electrodepositing a bright nickel coating onto the semibright nickel coating and electrodepositing an overlay of chromium onto the bright nickel coating, the improvement which comprises electrodepositing the nickel strike from a bath which consists of at least one inorganic nickel ion-producing salt, an inorganic pH adjusting agent and water and which is maintained substantially free of organic and other inorganic materials introduced into the bath by drag-out from any preceding surface preparation baths by substantially continuous purification means.

2. The method as defined in claim 1 wherein the workpiece is immersed in the nickel strike bath without current on and the nickel strike is deposited after the workpiece is fully immersed.

3. In a method of decorative chromium plating which includes the steps of treating a workpiece in at least one bath solution to prepare the workpiece surface for reception of a nickel strike, electrodepositing a nickel strike to the workpiece surface, electrodepositing a semibright nickel coating onto the nickel strike, electrodepositing a bright nickel coating onto the semibright nickel coating and electrodepositing an overlay of chromium onto the bright nickel coating, the improvement which comprises immersing the workpiece without current on in a nickel strike bath which consists of nickel sulfate, nickel chloride, boric acid and water and which is maintained substantially free of organic and other inorganic materials introduced into the bath during its use by substantially continuous purification means and the nickel strike is electrodeposited after the workpiece is fully immersed.

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