

March 15, 1960

W. G. LEE ET AL
PROCESS OF CHEMICAL NICKEL PLATING OF AMPHOTERIC
ELEMENTS AND THEIR ALLOYS
Filed Nov. 27, 1957

2,928,757

FIG 1
10

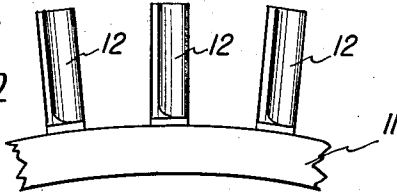


FIG 2

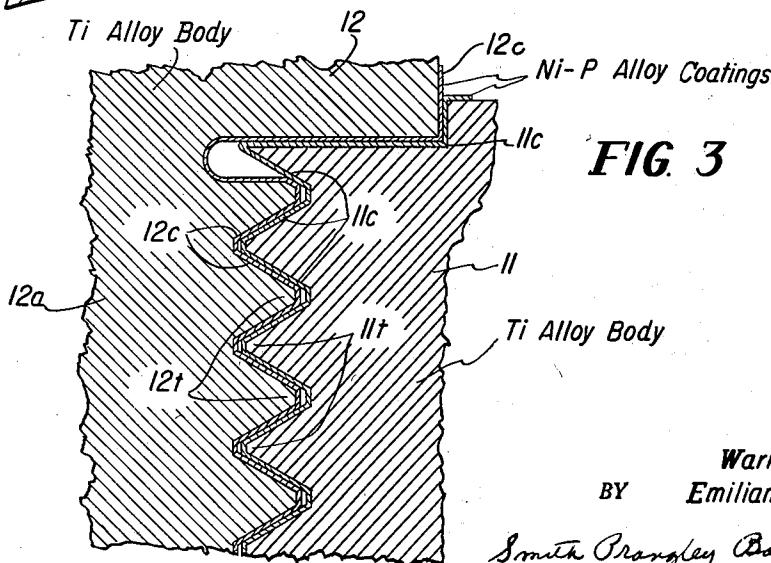
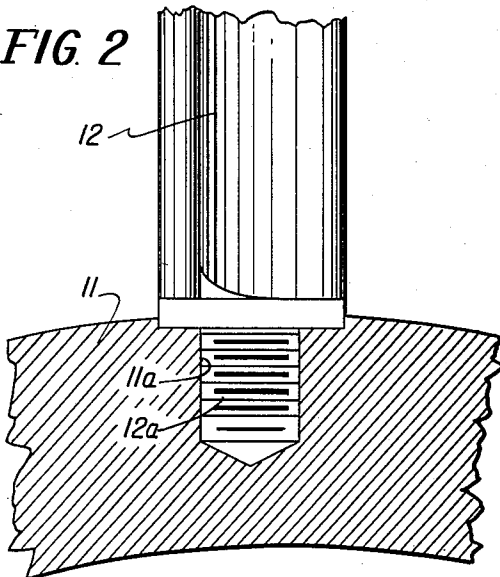


FIG 4

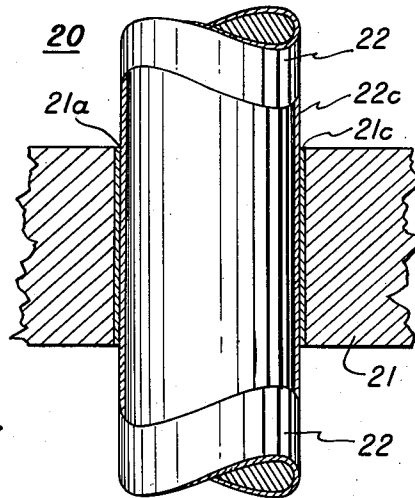


FIG 3

INVENTOR.

Warren G. Lee

BY Emilian Browar

Smith, Pringley, Baird & Clayton
Attys.

1

2,928,757

PROCESS OF CHEMICAL NICKEL PLATING OF AMPHOTERIC ELEMENTS AND THEIR ALLOYS

Warren G. Lee, East Chicago, and Emilian Browar, Gary, Ind., assignors to General American Transportation Corporation, Chicago, Ill., a corporation of New York

Application November 27, 1957, Serial No. 699,373

9 Claims. (Cl. 117—50)

The present invention relates to chemical nickel plating of the amphoteric metals of group VI B of the periodic systems of elements, and their alloys, and to processes of effecting such plating with aqueous chemical nickel plating baths of the nickel cation-hypophosphite anion type.

Heretofore the chemical nickel plating of workpieces having surfaces formed essentially of the amphoteric metals of group IV B and their alloys, has been of little practical utility, as such coatings as have been produced thereon readily flake-off, since the coatings are not intimately bonded thereto. This statement is particularly applicable to the important amphoteric element titanium, although it is applicable to the other elements of this group that consists of: titanium, zirconium and hafnium.

The principal reason for this lack of adhesion between the amphoteric metal surface and the coating is that such a surface is extremely sensitive to hydrolysis and immediately films over upon contact with the aqueous chemical nickel plating bath; whereby there is a film layer at the interface between the amphoteric metal surface and the coating of nickel-phosphorus alloy that is inherently produced by a plating bath of this type. Of course, this prevents initiation of the plating and intimate bonding between the amphoteric metal surface and the coating, with the result that the coating exhibits no substantial adhesion to the surface carrying the same.

Accordingly, it is a general object of the invention to provide a process of chemical nickel plating of a workpiece having an amphoteric metal surface, wherein the coating produced is intimately bonded to the surface and exhibits great adhesion thereto.

Another object of the invention is to provide a process of preparing the amphoteric metal surface of a workpiece for plating with a chemical nickel plating bath so that the subsequently produced coating carried thereby is intimately bonded to the prepared surface.

A further object of the invention is to provide a process of the character noted, that is expressly adapted for use in the chemical nickel plating of titanium and its alloys.

A further object of the invention is to provide a process of the character noted that involves a heat-treatment step following the nickel plating of the amphoteric metal surface, whereby a diffusion reaction is produced between the amphoteric metal surface and the nickel-phosphorus alloy coating, whereby the interface is alloyed to produce an intimate bond therebetween.

Further features of the invention pertain to the particular arrangement of the steps of the method, whereby the above-outlined and additional operating features thereof are attained.

The invention, both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawing, in which:

Figure 1 is a fragmentary end elevational view of a compressor rotor that is made in accordance with the process of the present invention;

2

Figure 2 is an enlarged fragmentary view, partially in section, of a portion of the compressor rotor, shown in Fig. 1, illustrating the manner in which one of the blades is detachably secured to the associated support and involving a threaded connection therebetween;

Figure 3 is a greatly enlarged sectional view of the threaded connection or joint between the root of the blade and the support, illustrating the protective coatings respectively carried by these two parts and preventing galling therebetween; and

Figure 4 is a fragmentary vertical sectional view of another machine that is made in accordance with the process of the present invention.

Referring now to the drawing, there is illustrated in Fig. 1 a fragmentary portion of a compressor rotor 10 that may comprise a part of the air compressor that co-operates with an associated gas turbine in a jet engine, or the like. More particularly, the rotor 10 comprises a support 11 of substantially drum-like configuration, and a plurality of annular rows of blades 12 disposed about the outer surface thereof. The rotor 10 is housed in an associated casing or stator, not shown, and mounted for rotation at high speed therein so that the annular rows of blades 12 co-operate with other annular rows of blades carried internally of the stator, so as to provide a multi-stage centrifugal air compressor. In the rotor 10, the support 11 and each of the blades 12 is formed of a suitable titanium alloy, and each of the blades 12 is detachably secured to the support 11 to accommodate replacement and overhaul in a ready and simple manner.

As best shown in Fig. 2, each of the blades 12 terminates at the base thereof in a threaded root 12a that is normally arranged in threaded relation with a co-operating threaded opening 11a provided in the support 11; and as illustrated in Fig. 3, the threads carried by the root 12a are designated 12t and the threads carried by the wall of the support 11 about the opening 11a therein are designated 11t. Also, as shown in Fig. 3, the threads 12t and the root 12a and the adjacent shoulder provided on the base of the blade 12 carry a unitary coating 12c, and the threads 11t and the surface of the support 11 adjacent to the opening 11a therein carry a unitary coating 11c; whereby the coatings 12c and 11c are in direct frictional engagement with each other.

The coating 12c is intimately bonded to the root 12a, including the threads 12t, and has a substantially uniform thickness normally in the general range 1/2 to 1 mil; and similarly, the coating 11c is intimately bonded to the support 11, including the threads 11t, and has a substantially uniform thickness normally in the general range 1/2 to 1 mil. Each of the coatings 11c and 12c essentially comprise nickel-phosphorus alloy of the composition inherently produced by chemical nickel plating from an aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type; and such alloy essentially comprises 89% to 97% nickel and 3% to 11% phosphorus, by weight.

The arrangement of the coatings 11c and 12c in direct engagement with each other is very advantageous as these coatings prevent galling that would otherwise take place between the parts 11 and 12 formed essentially of titanium, with the resulting freezing of these parts together so that subsequently it would be impossible to remove the blade 12 from the support 11, as is the usual case where titanium alloy parts are arranged in pressure engagement with each other. However, the coatings 11c and 12c do not exhibit galling therebetween, whereby the titanium alloy parts 11 and 12 may be readily disassembled and reassembled at will, without damage thereto.

This anti-galling characteristic thus imparted to the titanium alloy parts 11 and 12 by the protective nickel-

3

phosphorus alloy coatings 11c and 12c is totally foreign to the nature of titanium alloys and now affords an exceedingly large scope of utilization of such parts.

In the construction of the rotor 10, the support 11 and the blades 12 may be formed of any one of a number of commercially available titanium alloys, including that manufactured by the Republic Steel Corporation and sold under the name "C-130AM"; which alloy contains the following principal components:

	Percent
Al	4
Mg	4
Ti	Remainder

These titanium alloys normally contain titanium in the general range 90% to 95% and other alloying elements in the range 5% to 10%. Another typical titanium alloy of this character contains the following principal components:

Al	3.18
Cr	4.68
Fe	0.22
Ti	Remainder

Still another typical titanium alloy of this character contains the following principal components:

Cr	2.84
Fe	1.43
Ti	Remainder

A further typical titanium alloy of this character contains the following principal components:

Mn	7.8
Ti	Remainder

The composition of the titanium alloy is in no way critical with respect to the present process, since any such alloy containing in excess of 90% titanium exhibits the previously mentioned amphoteric characteristic rendering it impossible to obtain an intimately bonded nickel-phosphorus alloy coating thereupon, without special treatment in accordance with the present process.

In the foregoing description of the rotor 10 it was explained that the elements 11 and 12 are provided with the respective coatings 11c and 12c, and while this is the preferred construction, it will be appreciated that really only one of the coatings 11c or 12c is essential to prevent the titanium-upon-titanium contact and resulting galling therebetween. More particularly, there is no galling of a titanium alloy upon a nickel-phosphorus alloy of the character described.

Referring now to Fig. 4, a fragmentary portion of a machine or device 20 is illustrated that comprises a support or plate 21 having an opening 21a formed therein into which a shaft or bar 22 is mounted and arranged for relative movements with respect thereto, the shaft 22 being mounted for rotation about its longitudinal axis or longitudinal sliding movement, or both. The plate 21 and the shaft 22 are formed of suitable titanium alloys and respectively carry chemically deposited nickel-phosphorus alloy coatings 21c and 22c arranged in engagement with each other, so as to prevent galling between the elements 21 and 22, as previously explained. This bearing arrangement is very advantageous as the nickel-phosphorus coatings 21c and 22c resist wear and may be lubricated with any light oil, or the like.

In the foregoing description of the machine 20 it was explained that the elements 21 and 22 are provided with the respective coatings 21c and 22c, and while this is the preferred construction, it will be appreciated that really only one of the coatings 21c or 22c is essential to prevent the titanium-upon-titanium contact and resulting galling therebetween.

Considering now the process of the present invention, the work-piece formed essentially of titanium, and nor-

4

mally comprising an alloy thereof, as previously noted, is first subjected to a conventional vapor degreasing step in order to effect substantial and ordinary cleaning thereof. Next the work-piece is subjected to alkaline cleaning (such as Enthone #160, or equivalent) to remove therefrom buffing compounds, etc., that may have been employed in the machining thereof; and normally a hot aqueous solution of the alkaline cleaner is employed at a temperature of about 195° F. throughout a time interval of about 2 to 5 minutes. The work-piece is then rinsed in cold water.

Next the work-piece is pickled by immersion thereof for about 10 to 15 seconds in a special pickling solution described hereinafter; and then the work-piece is again rinsed with cold water. The two last-mentioned steps are repeated so that the work-piece is again subjected to the pickling step for about 10 seconds and thereafter rinsed with cold water for about 10 to 15 seconds. At this time, the surface of the work-piece has been conditioned or prepared for chemical nickel plating, as explained more fully subsequently.

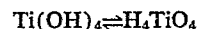
Turning now to the composition of the pickling bath, it essentially comprises an aqueous solution of hydrochloric acid, hydrofluoric acid and a mild oxidizing agent, both the hydrochloric acid concentration and the hydrofluoric acid concentration being high. Specifically, the pickling bath may be composed from 900 cc. $\pm$ 10 cc. hydrochloric acid (18° Bé.) and 100 cc. $\pm$ 2 cc. hydrofluoric acid (70%), together with the mild oxidizing agent, such, for example, as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the approximate range 25 to 100 gms. This pickling bath thus comprises about 8 mole/liter of hydrochloric acid, about 4½ mole/liter of hydrofluoric acid and about 0.1 to 0.4 mole/liter of ferric chloride. Specifically, in formulating the plating bath, the following proportions are recommended:

900 cc. HCl solution (18° Bé.)
100 cc. HF solution (70%)
50 gm. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

In preparing the pickling bath the two acid solutions are mixed, and the required amount of ferric chloride is melted in a steam bath and then added to the acid mixture under agitation.

While ferric chloride is preferred as the mild oxidizing agent, because of the simplicity and economy thereof, other suitable oxidizing agents may be employed, such, for example, as the water soluble salts of iron: ferric sulfate, ferric acetate, etc.; and the water soluble salts of manganese: manganese chloride, manganese sulfate, manganese acetate, etc.

Apparently, the fundamental modulus of this pickling bath is dependent upon this high concentration of hydrochloric acid in combination with this high concentration of hydrofluoric acid, since with this composition of the pickling bath there is removed the amphoteric film that immediately forms upon the surface of the titanium work-piece incident to contact thereof with the aqueous chemical nickel plating bath, and as a result of hydrolysis. It is postulated that this film that normally forms upon the surface of the titanium work-piece involves the equilibrium:



In any case, the film that is present upon the surface of the titanium work-piece is effectively removed by this pickling bath, so that the subsequently applied coating of the nickel-phosphorus alloy in the chemical nickel plating bath is continuous and intimately bonded thereto.

A number of suitable plating baths are available for the present purpose, as disclosed in U.S. Patent No. 2,532,283, granted on December 5, 1950, to Abner Brenner and Grace E. Riddell, in U.S. Patent No. 2,658,841, granted on November 10, 1953, to Gregoire Gutzeit and Abraham Krieg, and in U.S. Patent No. 2,658,842, granted on November 10, 1953, to Gregoire Gutzeit and Ernest

J. Ramirez, as well as in the copending application of Gregoire Gutzeit, Serial No. 376,977, filed August 27, 1953, the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 478,492, filed December 29, 1954, and in the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 569,815, filed March 6, 1956, now Patent No. 2,822,294, granted February 4, 1958.

A chemical nickel plating bath of this type essentially comprises an aqueous solution of nickel cations and hypophosphite anions, the nickel cations being derived from nickel sulfate, nickel chloride, nickel hypophosphite, etc., and the hypophosphite anions being derived from hypophosphorous acid, sodium hypophosphite, potassium hypophosphite, nickel hypophosphite, etc. Preferably, such a plating solution comprises an absolute concentration of hypophosphite anions within the range 0.15 to 1.20 moles/liter, a ratio between nickel cations and hypophosphite anions expressed in molar concentrations within the range 0.25 to 1.60, and a pH in the range 4.5 to 11. The plating bath disclosed in the Gutzeit, Talmey and Lee application, Serial No. 569,815, is particularly advantageous and comprises, in addition to the nickel cations and the hypophosphite anions, lactic anions and propionic anions, and having a pH in the acid range 4.4 to 5.6; and specifically this plating bath comprises an absolute concentration of the hypophosphite anions within the range 0.15 to 1.20 moles/liter, a ratio between nickel cations and hypophosphite anions expressed in molar concentrations within the range 0.25 to 1.60, an absolute concentration of lactic anions within the range 0.25 to 0.60 mole/liter, and an absolute concentration of propionic ions within the range 0.025 to 0.060 mole/liter. A typical plating bath of this type has the following composition:

Nickel ion (as nickel sulfate) -----m.p.l.	0.08
Hypophosphite ion (as sodium hypophosphite) -----m.p.l.	0.225
Lactic ion (as lactic acid) -----m.p.l.	0.30
Propionic ion (as propionic acid) -----m.p.l.	0.03
pH (adjusted with H ₂ SO ₄ and NaOH) -----	4.7

In the plating step, the work-piece is immersed in the chemical nickel plating bath, while the plating bath is at a relatively high temperature, normally in the general range 94° C. to 98° C., throughout an appropriate time interval depending upon the thickness of the nickel plating required. For example, the particular plating bath set forth above has a normal plating rate of about 1 mil/hour; and of course, as previously noted, the coating that is inherently produced by a plating bath of this type essentially comprises a nickel-phosphorus alloy containing about 89% to 97% nickel and about 3% to 11% phosphorus, by weight. In this step, the work-piece is suspended in the plating bath by an insulating line (Dacron etc.) and out of contact with any metallic part, so as to avoid any galvanic action, and the resulting surface blemish or discontinuity.

Following this chemical plating step, the work-piece is subjected to heat-treatment that merely constitutes elevating the temperature thereof to about 425° C., whereby a diffusion reaction takes place at the interface between the surface of the titanium work-piece and the nickel-phosphorus alloy coating. The diffusion reaction mentioned occurs at the temperature 421° C. (800° F.); whereby there is probably formed in the interface a ternary alloy of titanium and nickel and phosphorus. This ternary alloy in the interface intimately bonds the nickel-phosphorus alloy coating to the titanium work-piece; and the resulting coating is highly corrosive-resistant, smooth and bright, and prevents the normal galling of titanium-upon-titanium, as previously explained.

In the foregoing description of the present process, the work-piece has been described as being formed essentially of titanium or a suitable titanium alloy. How-

ever, the process has been carried out successfully precisely in the manner described when the work-piece has been formed of the other of the amphoteric elements of group IV B including: zirconium alloys and hafnium alloys. For example, the heretofore experienced difficulty in the chemical nickel plating of the zirconium alloy surface of a work-piece has resided in the circumstance that this amphoteric metal (like titanium) is subject to the formation of a film upon the outer surface thereof due to hydrolysis upon immersion in the aqueous chemical nickel plating solution. However, in accordance with the present process, the film mentioned is removed from the outer surface and the re-formation of this film thereupon is inhibited; whereby upon contact with the aqueous chemical nickel plating solution, the plating reaction takes place directly upon the zirconium alloy surface of the work-piece, without the interfering film at the interface. Of course, in this example, and following the chemical nickel plating of the zirconium surface of the work-piece, the heat-treatment step at the elevated temperature of about 425° C. is employed, so as probably to produce a ternary alloy at the interface comprising zirconium and nickel and phosphorus.

In view of the foregoing, it is apparent that there has been provided an improved process of chemical nickel plating of work-pieces having amphoteric metal surfaces, as well as an improved subcombination in the process with respect to the preparation of the surfaces noted for the subsequent chemical nickel plating of the coatings thereupon. Also the process is productive of an improved article of manufacture and particularly in an assembly of two parts formed essentially of titanium and completely devoid of galling therebetween.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. The process of plating with nickel the metal surface of a work-piece, wherein said metal surface essentially comprises an amphoteric element selected from the group consisting of titanium, zirconium and hafnium; said process comprising cleaning said metal surface by contact with a suitable cleaning bath, then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a mild oxidizing agent, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter, the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter, then contacting said metal surface with a chemical plating bath of the nickel cation-hypophosphite anion type throughout a sufficient time interval to obtain a nickel plating upon said metal surface, and then heating said work-piece to a temperature at least as high as about 425° C. so as to effect a diffusion reaction at the interface between said nickel plating and said metal surface.

2. The process of plating with nickel the metal surface of a work-piece, wherein said metal surface essentially comprises an amphoteric element selected from the group consisting of titanium, zirconium and hafnium; said process comprising cleaning said metal surface by contact with a suitable cleaning bath, then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a soluble salt of iron, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter, the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter, then immersing said work-piece in a chemical plating bath of the nickel cation-hypophosphite anion type throughout

a sufficient time interval to obtain a nickel plating upon said metal surface, and then heating said work-piece to a temperature at least as high as about 425° C. so as to effect a diffusion reaction at the interface between said nickel plating and said metal surface.

3. The process of plating with nickel the metal surface of a work-piece, wherein said metal surface essentially comprises a titanium alloy, said process comprising cleaning said metal surface by contact with a suitable cleaning bath, then conditioning said metal by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a mild oxidizing agent, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter, the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter, then contacting said metal surface with a chemical plating bath of the nickel cation-hypophosphite anion type throughout a sufficient time interval to obtain a nickel plating upon said metal surface, and then heating said work-piece to a temperature at least as high as about 425° C. so as to effect a diffusion reaction at the interface between said nickel plating and said metal surface.

4. The process of plating with nickel the metal surface of a work-piece, wherein said metal surface essentially comprises a titanium alloy, said process comprising cleaning said metal surface by contact with a suitable cleaning bath, then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a soluble salt of iron, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter, the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter, then immersing said workpiece in a chemical plating bath of the nickel cation-hypophosphite anion type throughout a sufficient time interval to obtain a nickel plating upon said metal surface, and then heating said work-piece to a temperature at least as high as about 425° C. so as to effect a diffusion reaction at the interface between said nickel plating and said metal surface.

5. The process of preparing the metal surface of a work-piece for plating thereon by a chemical plating bath of the nickel cation-hypophosphite anion type, wherein said metal surface essentially comprises an amphoteric element selected from the group consisting of titanium, zirconium and hafnium; said process comprising cleaning said metal surface by contact with a suitable cleaning bath, and then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a mild oxidizing agent, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter and the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter.

6. The process of preparing the metal surface of a work-piece for plating thereon by a chemical plating bath of the nickel cation-hypophosphite anion type, wherein said metal surface essentially comprises an amphoteric element selected from the group consisting of titanium, zirconium and hafnium; said process comprising cleaning said metal surface by contact with a suitable cleaning

bath, and then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a soluble salt of iron, wherein one liter of said pickling bath contains the substantial equivalent of 900±10 cc. hydrochloric acid (18° Bé.) and 100±2 cc. hydrofluoric acid 70%.

7. The process of preparing the metal surface of a work-piece for plating thereon by a chemical plating bath of the nickel cation-hypophosphite anion type, wherein said metal surface essentially comprises an amphoteric element selected from the group consisting of titanium, zirconium and hafnium; said process comprising cleaning said metal surface by contact with a suitable cleaning bath, and then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and ferric chloride, the absolute concentration of ferric chloride in said pickling bath being in the general range 0.09 to 0.36 mole/liter, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter, and the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter.

8. The process of preparing the metal surface of a work-piece for plating thereon by a chemical plating bath of the nickel cation-hypophosphite anion type, wherein said metal surface essentially comprises a titanium alloy, said process comprising cleaning said metal surface by contact with a suitable cleaning bath, and then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and a mild oxidizing agent, the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter and the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter.

9. The process of preparing the metal surface of a work-piece for plating thereon by a chemical plating bath of the nickel cation-hypophosphite anion type, wherein said metal surface essentially comprises a titanium alloy; said process comprising cleaning said metal surface by contact with a suitable cleaning bath, and then conditioning said metal surface by contact with a pickling bath, wherein said pickling bath essentially comprises an aqueous solution of hydrochloric acid and hydrofluoric acid and ferric chloride, the absolute concentration of ferric chloride in said pickling bath being in the general range 0.09 to 0.36 mole/liter the absolute concentration of hydrochloric acid in said pickling bath being about 8 mole/liter, and the absolute concentration of hydrofluoric acid in said pickling bath being about 4½ mole/liter.

References Cited in the file of this patent

UNITED STATES PATENTS

2,717,218	Talmey et al. -----	Sept. 6, 1955
2,774,688	Girard -----	Dec. 18, 1956
2,825,682	Missel et al. -----	Mar. 4, 1958

OTHER REFERENCES

Brenner et al.: Part of Journal of Research of the Nation Bureau of Standards, Research Paper RPI, 835, volume 39, pp. 385-395, November 1947.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,928,757

March 15, 1960

Warren G. Lee et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 30, after "surface" insert -- by --.

Signed and sealed this 30th day of August 1960.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents