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PROCESSES OF CHEMICAL NICKEL PLATING OF AMPHOTERIC AND LIKE MATERIALS

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The present invention relates to chemical nickel plating of metals characterized by the rapid formation of passive films upon the surfaces thereof upon contact with air and water, and more particularly, to improved processes of the general character disclosed in U.S. Patent No. 2,928,757, granted on March 15, 1960, to Warren G. Lee and Emilian Browar.

The production of satisfactory nickel coatings upon amphoteric metal surfaces, utilizing chemical nickel plating baths of the nickel cation-hypophosphite anion type is difficult to achieve, as explained in the Lee and Browar patent mentioned, by virtue of the rapid formation upon these metal surfaces of passive films incident to contact with air and water. These passive films are apparently caused by the great tendency toward oxide formation of these amphoteric metals by contact with moist air.

Not only do these passive films interfere with the continuity and the uniformity of the coatings that are produced upon such metal surfaces, but they are responsible for the usual lack of adhesion of such coatings upon such metal surfaces.

While the amphoteric elements of group IVB (titanium, zirconium and hafnium) comprise classical examples of metals possessing the previously-described characteristic of "rapid filming over" upon contact with air and moisture, the total class involved further comprises many other industrial metals upon which it is highly desirable to provide sound nickel coatings utilizing chemical nickel plating baths of the type mentioned. More particularly, this total class of "film-forming" metals comprises, in addition to the amphoteric elements, titanium, zirconium and hafnium, and their alloys, nickel-copper alloys, nickel-chrome alloys, nickel steels and high-alloy steels containing an element selected from the group consisting of chromium, molybdenum, tungsten, vanadium and columbium. Specifically, it is virtually impossible to obtain chemical nickel plating upon stainless steel and inconel alloys by virtue of the rapid formation upon the surfaces of these metals of passive films upon contact with moist air.

While the previously mentioned Lee and Browar process is entirely satisfactory for the production of chemical nickel coatings upon the amphoteric elements of group IVB, and the allows thereof, this process is not satisfactory for the production of such chemical nickel coatings upon the other metals of this total "film-forming" class, including nickel-copper alloys, nickel-chrome alloys, nickel steels, and high-alloy steels containing an element selected from the class consisting of chromium, molybdenum, tungsten, vanadium and columbium.

Accordingly, it is the principal object of the present invention to provide a process of chemical nickel plating, utilizing an aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, that is generally applicable to the total group of "film-forming" metals, whereby substantially the same procedural steps may be carried out in the preparation of such metal, preceding the chemical nickel plating step, regardless of the exact specification of such metal that is characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water.

Another object of the invention is to provide a process

of chemical nickel plating of nickel-copper alloys, nickel-chrome alloys, nickel steels and chrome steels.

A further object of the invention is to provide a process of chemical nickel plating of high-alloy steels that contain an element selected from the class consisting of chromium, nickel, molybdenum, tungsten, vanadium and columbium.

A still further object of the invention is to provide an improved process of pretreating a metal surface that is characterized by the rapid formation of a passive film thereon upon contact with air and water, so as to remove from the metal surface mentioned any trace of the passive film thereon and so as to inhibit the subsequent formation of such passive film upon such metal surface incident to the subsequent contact thereof with an aqueous chemical nickel plating bath of the nickel cation-hydrophosphite anion type, and so as to activate such metal surface in order to bring about immediate initiation of the chemical nickel plating thereof upon subsequent contact thereof with the aqueous plating bath of the nickel cation-hypophosphite anion type.

Further features of the invention pertain to the particular arrangement of the steps of the process, 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 from the foregoing and following description.

In accordance with the process of the present invention, the workpiece to which the chemical nickel coating is to be applied to the outer surface thereof is formed of a metal that is characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water; which metal is selected from the group consisting of titanium, zirconium, hafnium, and their alloys, nickel-copper alloys, nickel-chrome alloys, nickel steels, chrome steels and high-alloy steels that are stabilized with an element selected from the class consisting of molybdenum, tungsten, vanadium and columbium.

More particularly, this group includes a wide variety of titanium alloys normally containing by weight, titanium in the general range 90 to 95% and other alloying elements in the range 5% to 10%.

A typical example of such a titanium alloy contains by weight the following principal components:

	Percent
Al	4
Mg	4
Ti	Remainder

Another typical titanium alloy of this type contains by weight the following principal components:

	Percent
Al	3.18
Cr	4.68
Fe	0.22
Ti	Remainder

Still another typical titanium alloy of this type contains by weight the following principal components:

	Percent
Cr	2.84
Fe	1.43
Ti	Remainder

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

	Percent
Mn	7.8
Ti	Remainder

Also, this group includes a wide variety of nickel-copper alloys, such, for example, as the typical Monel alloy having the approximate composition by weight:

	Percent
Ni	60–65
Cu	24–27
Fe	1–3
Sn	9–11

Also, this group includes a wide variety of nickel-chrome alloys, such, for example, as the typical inconel alloy having the approximate composition by weight:

Ni	72% min.
Cr	14–17%
Mn	1% max.
Fe	6–10%

Also, this group includes a wide variety of stainless steels, such, for example as the typical types 309, 414, 440, 446, etc.

Specifically, stainless steel type 309 essentially comprises by weight:

	Percent
Cr	22–26
Ni	12–14
Fe	Balance

Specifically, stainless steel type 414 essentially comprises by weight:

	Percent
Cr	13
Ni	2
Fe	Balance

Specifically, stainless steel type 440 essentially comprises by weight:

	Percent
Cr	14–18
Fe	Balance

Specifically, stainless steel type 446 essentially comprises by weight:

	Percent
Cr	23–30
Fe	Balance

Further, this group includes a wide variety of high-alloy steels that contain an element selected from the class consisting of molybdenum, tungsten, vanadium and columbium.

A typical molybdenum steel essentially comprises by weight:

	Percent
Mo	0.15–0.40
C	0.10–0.45
Mn	0.6–1.3
Fe	Balance

A typical tungsten steel essentially comprises by weight:

	Percent
W	1.7–2.2
C	0.30–0.45
Fe	Balance

A typical vanadium steel essentially comprises by weight:

	Percent
V	0.1–14.0
C	0.1–1.3
Fe	Balance

A typical columbium steel essentially comprises by weight:

Cb	0.5–0.9%
C	0.08% max.
Mn	1.5% min.
Cr	17.5–19.5%
Ni	13% min.
Fe	Balance

In carrying out the present process a pickling bath is employed, as explained more fully hereinafter, that essentially comprises an aqueous solution of hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./liter. Preferably, this pickling bath has the composition:

Hydrofluoric acid	2.75 moles/liter
Sulfuric acid	4.70 moles/liter
Cupric ion	About 0.5 gm./liter

As a matter of preparation, the pickling bath may be composed utilizing about 10% v./v. HF (52–55% technical grade), 25% v./v. H_2SO_4 and 0.50 gm./liter cupric ion (as $CuSO_4.5H_2O$).

Also in carrying out the present process, an aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type is employed; and while any one of a wide variety of such chemical nickel plating baths are suitable, that disclosed in U.S. Patent No. 2,822,294, granted on February 4, 1958, to Gregoire Gutzeit, Paul Talmey and Warren G. Lee is specifically recommended. A typical plating bath of this type has the following composition:

Nickel ion (as nickel sulfate)	0.08 m.p.l.
Hypophosphite ion (as sodium hypophosphite)	0.225 m.p.l.
Lactic ion (as lactic acid)	0.30 m.p.l.
Propionic ion (as propionic acid)	0.03 m.p.l.
Lead ion (as a stabilizer)	About 2 p.p.m.
pH (adjusted with H_2SO_4 and NaOH)	4.7.

While the content of lead ion as a stabilizer in the plating bath is subject to the usual variation in the range 1 to 5 parts per million thereof by weight, depending upon the particular composition of the workpiece that is to be coated, the content normally centers about the average of 2 p.p.m., as noted above.

In accordance with the present process, the workpiece, essentially comprising a metal selected from the previously-described group and characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water, is first subjected to preliminary cleaning, including both a conventional vapor degreasing step in order to effect substantial and ordinary cleaning thereof, and then an alkaline cleaning step to remove therefrom buffing compounds, etc., that may have been employed in the machining or forming thereof. In this alkaline cleaning step, Enthone #160, or the equivalent, may be used; and ordinarily, this alkaline cleaning is effected by soaking the workpiece for a suitable time interval in a hot aqueous solution of the alkaline cleaner mentioned (about 30 minutes), the alkaline cleaning solution being at a temperature of about 205° F. Next, the workpiece is rinsed in warm water at a temperature of about 113° F. for a time interval of at least 2 minutes. Thereafter, the workpiece is subjected to a series of specific steps, as explained more fully below, generally depending upon the particular composition thereof.

For example, in the plating of a workpiece comprising a metal selected from the previously-described group, including nickel-copper alloys, nickel-chrome alloys, nickel steels and high-alloy steels containing an element selected from the group consisting of chromium, molybdenum, tungsten, vanadium and columbium (but excluding the amphoteric metals, titanium, zirconium and hafnium, and their alloys), the following specific steps are recommended:

1A1. Following the previously-described preliminary cleaning, the thus prepared workpiece of the composition noted above is immediately immersed in the previously-described pickling bath at room temperature for approxi-

mately 5 seconds; and then the workpiece is rinsed in warm water at a temperature of about 113° F. for a time interval of about 1 minute.

1A2. Step 1A1 is repeated.

1A3. Step 1A1 is repeated.

1B. Immediately the thus prepared workpiece is immersed in the previously-described chemical nickel plating bath, the plating bath having a temperature in the range 95° C. to 100° C., and no less than 95° C. The workpiece is retained in the chemical nickel plating bath throughout an appropriate time interval in order to produce the required thickness of the nickel coating upon the outer surface thereof that is desired. A chemical nickel plating bath of the character described has a normal plating rate of about 1 mil/hour; and ordinarily such a workpiece may be provided with a coating having a thickness of about 1 mil. Further, it is noted that the coating that is inherently produced by a plating bath of this type essentially comprises a nickel-phosphorus alloy containing by weight about 89% to 97% nickel and about 3% to 11% phosphorus. Following this plating step 1B, the workpiece is again rinsed in warm water at a temperature of about 113° F. for a time interval of at least 2 minutes.

1C1. Thereafter, the thus coated workpiece is subjected to heat-treatment in either air or an inert atmosphere at an elevated temperature throughout a suitable time interval so as to effect a diffusion reaction at the interface between the nickel coating and the metal surface. If employed, the inert atmosphere comprises argon, and the temperature mentioned is at about 400° F., and the minimum time interval mentioned is for about 1 hour.

In view of the foregoing, it will be understood that in accordance with the process of the present invention, the pretreatment of the workpiece, preceding the chemical nickel plating thereof, involves the preliminary conventional cleaning steps described followed by the cyclic pickling steps 1A1, 1A2 and 1A3, as set forth above.

While it is recommended that the pickling steps 1A1, 1A2 and 1A3 be repeated cyclically, as explained above, this procedure is not always essential. However, this procedure is normally employed in the preparation of workpieces formed of the previously-described metals (excluding the amphoteric metals, titanium, zirconium and hafnium, and their alloys), since these metals are particularly susceptible to surface oxidation or "film-forming"; and are particularly difficult to prepare for chemical nickel plating, as previously explained. In other words, the repeated or cyclic pickling steps 1A1, 1A2 and 1A3 are employed positively to insure the complete removal of these oxide surface films from these metals, without the reformation thereof, preceding the chemical nickel plating step 1B, as described above. Also, the repeated or cyclic pickling steps 1A1, 1A2 and 1A3 positively insure activation of the metal surface of the workpiece, so that the chemical nickel plating in the plating step 1B will be immediately initiated.

Again referring to the composition of the previously-described pickling bath, the same contains the hydrofluoric acid content in the range 2.20 to 3.30 moles/liter and the sulfuric acid content in the range 3.75 to 5.65 moles/liter, in order to obtain both the required low pH of the pickling bath, without oxidizing effects, and the controlled etching effect of hydrofluoric acid with respect to these "film-forming" surface oxides.

The content of cupric ion in the range 0.4 to 0.6 gm./liter in the pickling bath is employed for the purpose of rendering the surface of the workpiece formed of the metals mentioned catalytically active toward the chemical nickel plating bath that is subsequently utilized in the chemical nickel plating step 1B, as described. The exact mechanism of the cupric ion content is not fully understood, but it is postulated that the same is effective to obtain at least some formation of metallic copper upon the active catalytic centers of the freshly cleaned surface of the metal of the workpiece, thereby preventing or protecting the surface against subsequent reoxidation, and also activating these catalytic centers for subsequent catalytic chemical nickel plating, utilizing the chemical nickel plating bath in the plating step 1B, as described. In any case, the cupric ion content mentioned is critical in obtaining satisfactory activation of the surface of the workpieces formed of the metals mentioned so as to obtain immediate initiation of the chemical nickel plating in the plating step 1B, as described above. Further, it is mentioned that with this activation of the workpieces, special racking, with electrical non-conducting materials, of the workpieces in the chemical nickel plating bath is not necessary. Specifically, the previously prepared workpieces are merely racked upon iron or aluminum wire and then suspended in the chemical nickel plating bath in an entirely conventional manner.

Also, in the overall process, it is emphasized that the final heat-treating step 1C, as previously described, is essential in order to obtain intimate bonding of the nickel coating upon the metal surface of the workpiece formed of any one of the metals mentioned. This heat-treating step 1C may be carried out in air, without danger of surface oxidation of the nickel coating, by virtue of the relatively low temperature of about 400° F. that is employed; which step is carried out throughout the minimum time interval of about one hour in order positively to insure a diffusion reaction at the interface between the nickel coating and the metal surface of the workpiece, as well as the resulting heat-hardening of the nickel coating. This heat-treating step positively insures intimate bonding of the nickel coating upon the surface of the workpiece and positively prevents subsequent flaking-off of the nickel coating in the subsequent utilization of the workpiece for its intended purpose.

For example, in the plating of a workpiece comprising a metal selected from the previously-described group, including the amphoteric metals, titanium, zirconium and hafnium, and their alloys (but excluding nickel-copper alloys, nickel-chrome alloys, nickel steels and high-alloy steels containing an element selected from the group consisting of chromium, molybdenum, tungsten, vanadium and columbium), the following specific steps are recommended:

2A1. Following the previously-described preliminary cleaning, the thus prepared workpiece of the composition noted above is immediately immersed in the previously-described pickling bath at room temperature for approximately 5 seconds; and then the workpiece is rinsed in warm water at a temperature of about 113° F. for a time interval of above 1 minute.

2X1. Immediately the workpiece is immersed in concentrated nitric acid at room temperature for a time interval of about 30 seconds; and then the workpiece is rinsed in warm water at a temperature of about 113° F. for a time interval of about 1 minute.

2A2. Step 2A1 is repeated.

2X2. Step 2X1 is repeated.

2A3. Step 2A1 is repeated.

2B. Immediately the thus prepared workpiece is immersed in the previously-described chemical nickel plating bath, the plating bath having a temperature in the range 95° C. to 100° C., and no less than 95° C. The workpiece is retained in the chemical nickel plating bath throughout an appropriate time interval in order to produce the required thickness of the nickel coating upon the outer surface thereof that is desired. A chemical nickel plating bath of the character described has a normal plating rate of about 1 mil/hour; and ordinarily such a workpiece may be provided with a coating having a thickness of about 1 mil. Further, it is noted that the coating that is inherently produced by a plating bath of this type essentially comprises a nickel-phosphorus alloy containing by weight about 89% to 97% nickel and about

3% to 11% phosphorus. Following this plating step 2B, the workpiece is again rinsed in warm water at a temperature of about 113° F. for a time interval of at least 2 minutes.

2C. Thereafter, the thus coated workpiece is subjected to heat-treatment in an inert atmosphere at an elevated temperature throughout a suitable time interval so as to effect a diffusion reaction at the interface between the nickel coating and the metal surface. Preferably, the insert atmosphere comprises argon, so as positively to prevent surface oxidation of the nickel coating, and the temperature range extends from about 800° F. to about 900° F., and the minimum time interval mentioned is for about one hour.

In the foregoing procedure, it will be understood that in the pickling step 2A1, the oxide film upon the surface of the amphoteric metal of the workpiece is substantially completely removed; while in the intervening pickling step 2X1, a fresh oxide film is formed upon the surface of the amphoteric metal of the workpiece. However, in the pickling step 2A2, the freshly formed oxide film is again removed; and, of course, these two separate effects are repeated in the steps 2X2 and 2A3. However, the intervening oxidiizng of the surface of the amphoteric metal of the workpiece in the intervening pickling steps 2X1 and 2X2 are useful in the overall cleaning, pickling and activating of the surface of the amphoteric metal of the workpiece, particularly since the freshly produced oxide films mentioned that are formed in the pickling steps 2X1 and 2X2 are readily removed in the respectively following pickling steps 2A2 and 2A3.

By way of recapitulation, it will, of course, be immediately appreciated that the steps 1A1, 1A2 and 1A3 of the first described procedure respectively correspond precisely to the steps 2A1, 2A2 and 2A3 of the second described procedure; while the steps 2X1 and 2X2 in the second described procedure have no counterpart in the first described procedure. This circumstance is explained in that the oxidizing films that are formed in the pickling steps 2X1 and 2X2 may be readily removed by the respectively following pickling steps 2A2 and 2A3 from the amphoteric metals, titanium, zirconium and hafnium, and their alloys, as previously noted. However, no corresponding steps are employed in the pretreatment of the metals mentioned selected from the group including nickel-copper alloys, nickel-chrome alloys, nickel steels and high-alloy steels containing an element selected from the group consisting of chromium, molybdenum, tungsten, vanadium and columbium, since this utilization of a concentrated nitric acid pickling bath would be productive of an oxide film upon the surface of these metals that would not be readily removed in the following pickling steps 2A2 and 2A3, as described.

Of course, the plating steps 1B and 2B in these two procedures are identical.

On the other hand, the heat-treating steps 1C and 2C only correspond to each other functionally; and specifically, a higher temperature range must be utilized in the heat-treatment step 2C than in the heat-treatment step 1C, so as to effect the previously-mentioned diffusion reaction at the interface between the nickel coating and the metal surface, as previously pointed out.

Further, it is pointed out that the second described procedure, including the principal pickling steps 2A1, 2A2 and 2A3 and also the intervening auxiliary pickling steps 2X1 and 2X2, constitutes a modification of the first described procedure that includes only the respectively corresponding principal pickling steps 1A1, 1A2 and 1A3. Moreover, it is noted that the first described procedure is also useful in the preparation for chemical nickel plating of the amphoteric metals, titanium, zirconium and hafnium, and their alloys; however, the second described procedure is even more advantageous, as previously explained; whereby the second described procedure is specifically recommended in the preparation of the workpieces formed of the amphoteric metals, titanium, zirconium, hafnium, and their alloys.

In view of the foregoing, it will be understood that in each of the procedures described, the workpiece essentially comprising a metal selected from the previously-described group and characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water, is first subjected to the previously-described preliminary cleaning. Then, the workpiece is subjected to the special pickling step, utilizing the pickling bath described; which pickling steps is ordinarily repeated in order positively to insure cleaning, removal of oxide film and surface activation. Thereafter, the thus prepared workpiece is subjected to chemical nickel plating; and ultimately, the workpiece is subjected to heat-treatment, so as positively to unite the nickel coating to the metal surface of the workpiece.

Utilizing the present process, a wide variety of the metals of the previously described group have been successfully coated with these chemical nickel-phosphorus alloy compositions, as previously explained; and the overall process of the present invention is very advantageous by virtue of the fact that substantially the same procedure may be thus employed in conjunction with the successful coating of the whole group of "film-forming" metals described. Furthermore, the coatings thus produced are smooth, continuous and tenaciously bonded to the base metal workpieces. Finally, it is pointed out that these coatings are heat-hardened in the overall process, having a hardness in the general range 1000 V.P.N. to 575 V.P.N., as disclosed in U.S. Patent No. 2,908,419, granted on October 13, 1959, to Paul Talmey and William J. Crehan.

In view of the foregoing, it is apparent that there has been provided an improved process of chemical nickel plating, utilizing an aqueous chemical nickel plating bath of the nickel cation-hypophosphite anion type, that is generally applicable to the total group of "film-forming" metals; whereby substantially the same procedural steps may be carried out in the preparation of such metals, preceding the chemical nickel plating step, regardless of the exact specification of such metal that is characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water.

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 surface of a metal workpiece, wherein said metal is characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water; said process comprising cleaning said metal surface 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 hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./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 workpiece to an elevated temperature throughout a time interval 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 surface of a metal workpiece, wherein said metal surface essentially comprises a titanium alloy; said process comprising cleaning said metal surface 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 hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./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 nickel plating upon said metal surface, and then heating said workpiece in an inert atmosphere to a temperature in the approximate range 800° F. to 900° F. throughout a minimum time interval of about one hour 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 surface of a metal workpiece, wherein said metal surface essentially comprises a titanium alloy; said process comprising cleaning said metal surface 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 hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./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 nickel plating upon said metal surface, and then heating said workpiece in an atmosphere or argon to a temperature in the approximate range 800° F. to 900° F. throughout a minimum time interval of about one hour 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 surface of a metal workpiece, wherein said metal surface essentially comprises a chrome-steel; said process comprising cleaning said metal surface 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 hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./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 workpiece to a temperature of about 400° F. throughout a minimum time interval of about one hour so as to effect a diffusion reaction at the interface between said nickel plating and said metal surface.

5. The process of plating with nickel the surface of a metal workpiece, wherein said metal surface essentially comprises a chrome-steel; said process comprising cleaning said metal surface 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 hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./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 workpiece in an atmosphere of argon to a temperature of about 400° F. throughout a minimum time interval of about one hour so as to effect a diffusion reaction at the interface between said nickel plating and said metal surface.

6. The process of preparing the metal surface of a workpiece for plating thereon by a chemical plating bath of the nickel cation-hypophosphite anion type, wherein said metal is characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water; said process comprising cleaning said metal surface 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 hydrofluoric acid in the range 2.20 to 3.30 moles/liter and sulfuric acid in the range 3.75 to 5.65 moles/liter and cupric ion in the range 0.4 to 0.6 gm./liter.

7. The process set forth in claim 6, wherein said metal is selected from the group consisting of titanium, zirconium, nickel-copper alloys, nickel-steels, and high alloy steels containing an element selected from the class consisting of chromium, molybdenum, tungsten, vanadium and columbium.

8. The process set forth in claim 6, wherein said metal is selected from the group consisting of titanium and its alloys.

9. The process set forth in claim 6, wherein said metal is selected from the group consisting of chrome-steels.

10. The process of preparing the metal surface of a workpiece for plating thereon by a chemical plating bath of the nickel-hypophosphite anion type, wherein said metal is characterized by the rapid formation of a passive film upon the surface thereof upon contact with air and water; said process comprising cleaning said metal surface 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 about 2.75 moles/liter of hydrofluoric acid and about 4.70 moles/liter of sulfuric acid and about 0.5 gm./liter of cupric ion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,928,757 Lee et al. ---------- Mar. 15, 1960

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

atent No. 3,029,158 April 10, 1962

Warren G. Lee et al.

It is hereby certified that error appears in the above numbered patnt requiring correction and that the said Letters Patent should read as orrected below.

Column 10, line 39, for "nickel-hypophosphite anion ype" read -- nickel cation-hypophosphite anion type --.

Signed and sealed this 31st day of July 1962.

SEAL)
:st:

EST W. SWIDER
:sting Officer

DAVID L. LADD
Commissioner of Patents