

1

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PROCESSES OF TREATING NICKEL-PHOSPHORUS ALLOY COATINGS AND THE RESULTING MODIFIED COATINGS

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The present invention relates to processes of treating nickel-phosphorus alloy coatings carried by workpieces, and applied thereto by chemical plating from aqueous plating baths of the nickel cation-hypophosphite anion type, so as to improve the appearance of such coatings as plated and so as to enhance the performance characteristics of such coatings as plated.

It is a general object of the invention to provide a process of treating a nickel-phosphorus alloy coating after it has been applied to a workpiece by chemical plating from an aqueous plating bath of the nickel cation-hypophosphite anion type, whereby the surface brightness of the coating as plated is significantly enhanced and surface stains on the coating are removed and the corrosion resistance of the coating as plated is materially increased.

Another object of the invention is to provide a process of the character described which may be carried out in a simple and economical manner and that is independent of both the composition of the workpiece and the composition of the chemical nickel plating bath that is employed in the plating of the alloy coating upon the workpiece.

A further object of the invention is to provide a process of the character described that is active specifically with respect to such nickel-phosphorus alloy coatings due to the phosphorus content thereof.

A further object of the invention is to provide a process of the character described that essentially comprises the single step of immersing the coated workpiece during a suitable time interval in a treatment bath that contains chromate ions.

A still further object of the invention is to provide as an article of manufacture, a workpiece carrying a nickel-phosphorus alloy coating, wherein the outer skin of the coating is formed of the reaction product of the nickel-phosphorus alloy and chromate ions and is produced by soaking the coating in a treatment bath containing chromate ions.

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 as the following specification proceeds.

In accordance with the present invention, there is provided a workpiece or article of manufacture having an outer surface that is to carry the desired coating. First, the workpiece is subjected to chemical nickel plating in a conventional chemical nickel plating bath of the nickel cation-hypophosphite anion type throughout a suitable time interval in order to produce the required thickness of the desired coating. Then the workpiece, carrying the coating that is inherently produced in the chemical nickel plating step and essentially comprising a nickel-phosphorus alloy, is rinsed in water and then soaked for a suitable time interval in a treatment solution containing chromate ions, whereby the outer skin of the coating is reacted upon by the chromate ions. Thereafter, the workpiece may be subjected to a heat-treatment step in

2

order to render the composite coating thus produced intimately bonded thereto and of finished character.

While the present process is independent of the composition of the workpiece, ordinarily the workpiece is formed of an industrial metal, such, for example, as steel or aluminium, although the workpiece may be formed of a non-metallic material. In the last mentioned instance, the workpiece is first subjected to pretreatment in order to activate the surface thereof so that it may subsequently receive the nickel-phosphorus alloy coating that is inherently produced in the chemical nickel plating step; such, for example as disclosed in U.S. Patent No. 2,690,401, granted on September 28, 1954, to Gregoire Gutzzeit, William J. Crehan and Abraham Krieg, and in U.S. Patent No. 2,690,402, granted on September 28, 1954, to William J. Crehan.

The present process is independent of the particular composition of the chemical nickel plating bath of the nickel cation-hypophosphite anion type that is employed in the chemical nickel plating step; whereby a wide variety of these conventional chemical nickel plating baths both in the acid range and in the alkaline range may be employed; which plating baths inherently produce platings or coatings essentially comprising by weight about 85% to 97% nickel and 3% to 15% phosphorus.

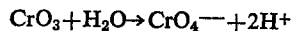
The plating bath disclosed in U.S. Patent No. 2,822,294 granted on February 4, 1958, to Gregoire Gutzzeit, Paul Talmey and Warren G. Lee is particularly recommended due to its simplicity and economy. More particularly, this plating bath is of the nickel cation-hypophosphite anion type, also containing lactic anion and propionic anion, and having a pH in the acid range 4.0 to 6.0. A typical example of this chemical nickel plating bath has the following composition:

NiSO ₄ ·6H ₂ O	-----m.p.l.	0.08
NaH ₂ PO ₂	-----m.p.l.	0.23
Lactic anion	-----m.p.l.	0.30
Propionic anion	-----m.p.l.	0.03
Pb ⁺⁺	-----p.p.m.	1
pH	-----	4.6

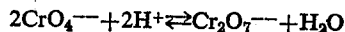
The chemical nickel plating step, utilizing the chemical nickel plating bath described above, is ordinarily carried out at a relatively high temperature in the general range 93° C. to 98° C.; and the chemical plating proceeds at a rate of about 1.0 mil/hour. The plating or coating that is inherently produced by the particular plating bath essentially comprises by weight about 88% to 94% nickel and about 6% to 12% phosphorus.

The treatment solution essentially comprises water containing by weight chromate ions in the range ½% to 5%; and preferably, the same essentially comprises by weight about 1% of chromate ions and may be readily prepared by simply dissolving in water an appropriate weight of a water-soluble compound of hexavalent chromium selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate. More particularly, the utilization of chromic acid anhydride (CrO₃) is preferred as a matter of simplicity, although the alkali metal chromates (Na₂CrO₄ and K₂CrO₄) and the alkali metal dichromates (Na₂Cr₂O₇ and K₂Cr₂O₇) are quite satisfactory.

The formation of the aqueous treatment solution mentioned utilizing chromic acid anhydride is represented by the equation:



Also, it is mentioned that in such an aqueous solution, there is inherently an equilibrium between chromate ions and dichromate ions in accordance with the equation:



In strong acid solutions, the ionic species is largely $\text{Cr}_2\text{O}_7^{--}$, while in basic solutions, the ionic species is largely CrO_4^{--} . Moreover, the equilibrium between the two ionic species mentioned is independent of the source of the chromate ions, whereby it is immaterial whether the same are derived from CrO_3 , Na_2CrO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$, etc.

After the nickel-phosphorus alloy coating of desired thickness has been produced upon the workpiece in the chemical nickel plating bath mentioned, the workpiece is rinsed in water and then transferred to the aqueous treatment solution described.

More particularly, the aqueous treatment solution preferably contains by weight about 1% chromate ions and is maintained at a hot bath having a temperature of about 50°C .; and specifically the coated workpiece is soaked in the hot aqueous treatment solution described for a time interval of at least about 15 minutes, but preferably for a time interval of about one hour. During the soaking of the coated workpiece in the hot aqueous treatment solution, the outer skin of the nickel-phosphorus alloy coating is reacted upon by the chromate ions to produce a reaction product. Presumably this reaction product comprises either nickel chromate or nickel oxyphosphate, or both; in any case, this outer reacted layer or skin of the nickel-phosphorus alloy coating carried by the workpiece comprises a film of substantially molecular thickness that is fundamentally different from the nickel-phosphorus alloy coating as plated, as explained more fully below.

In this treatment, neither the soaking time interval of the coated workpiece, nor the temperature of the aqueous treatment solution described is critical; whereby the usual relationship maintains that as the soaking time interval of the coated workpiece is increased, the temperature of the aqueous treatment solution may be reduced to produce identical effects upon the nickel-phosphorus coatings, and that as the soaking time interval of the coated workpiece is decreased, the temperature of the aqueous treatment solution may be increased to produce identical effects upon the nickel-phosphorus coatings.

Moreover, it is pointed out that this treatment of the coated workpiece in the treatment solution, as described above, materially enhances the general appearance of the coating with respect to the removal of surface stains therefrom and with respect to surface brightness, as well as imparts thereto a significant increase with respect to corrosion resistance.

Ordinarily, following the soaking of the coated workpiece in the treatment solution, as described above, the workpiece is rinsed with water and then subjected to a heat-treatment step. More particularly, the workpiece is heated to a temperature of about 400°F ., for a time interval of about one hour; which heat-treatment effects intimate bonding between the chemically deposited coating and the surface of the workpiece so that an adherent, smooth, continuous, bright and uniform coating is produced thereon.

The above described heat-treatment step is carried out in order to unify the nickel-phosphorus alloy coating with the workpiece; whereby this heat-treatment step may be carried out following the soaking of the coated workpiece in the treatment solution, as described above, or this heat-treatment step may be carried out preceding the soaking of the coated workpiece in the treatment solution.

In order to establish the increase in the corrosion resistance that is imparted to the nickel-phosphorus alloy coating of a workpiece by the chromation step of the present invention, a series of standard salt spray tests were conducted involving various coated workpieces, as described more fully below.

In a first series of these tests, eighteen workpieces in the form of panels of polished 1010 steel were uniformly coated to a thickness of one mil utilizing the aqueous chemical nickel plating bath as previously described. Six of these coated panels were then directly subjected to the

standard salt spray test; and it was established that the average time to failure of the one mil nickel-phosphorus alloy coatings (as plated) carried thereby was 216 hours. Twelve other of these coated panels were first subjected to the previously described chromation treatment, utilizing the aqueous treatment solution containing 1% by weight of CrO_3 during a time interval of 60 minutes, at a temperature of 50°C ., and then were subjected to the standard salt spray test; and it was established that the average time to failure of the one mil nickel-phosphorus alloy coatings (as chromate modified) carried thereby was 472 hours. The foregoing tests dramatically established that the corrosion resistance of the nickel-phosphorus alloy coatings of one mil thickness as plated carried by these workpieces was increased by more than 100% by the chromation step of the present invention.

In a second series of these tests, twelve workpieces in the form of panels of 61S aluminum were uniformly coated to a thickness of one mil, utilizing the aqueous chemical nickel plating bath as previously described. Six of these coated panels were then directly subjected to the standard salt spray test; and it was established that the average time to failure of the one mil nickel-phosphorus alloy coatings (as plated) carried thereby was 88 hours. Six other of these coated panels were first subjected to the previously described chromation treatment, utilizing the aqueous treatment solution containing 1% by weight of CrO_3 during a time interval of 60 minutes at a temperature of 50°C ., and then were subjected to the standard salt spray test; and it was established that the average time to failure of the one mil nickel-phosphorus alloy coatings (as chromate modified) carried thereby was 392 hours. The foregoing tests dramatically established that the corrosion resistance of the nickel-phosphorus alloy coatings of one mil thickness as plated carried by these workpieces were increased by more than 400% by the chromation step of the present invention.

In order to establish that the increase in the corrosion resistance of these coatings produced on workpieces by chemical nickel plating is peculiar to such coatings because of the nickel-phosphorus alloy composition thereof, a third of these standard salt spray tests were conducted involving steel workpieces provided with nickel coatings that were electrodeposited thereupon. More particularly, twenty-four workpieces in the form of polished cold rolled steel panels were uniformly coated to a thickness of $\frac{1}{2}$ mil utilizing a standard electroplating step. Twelve of these coated panels were then directly subjected to the standard salt spray test; and it was established that the average time to failure of the one-half mil nickel coatings (as electrodeposited) and carried thereby was 47.8 hours. Twelve other of these coated panels were first subjected to the previously described chromation treatment, utilizing the aqueous treatment solution containing 1% by weight of CrO_3 during a time interval of 60 minutes at a temperature of 50°C ., and then were subjected to the standard salt spray test; and it was established that the average time to failure of the one-half mil nickel coatings (as chromate modified) carried thereby was 64 hours. The foregoing tests definitely established that the chromation step is of little utility with respect to increasing the corrosion resistance of electrodeposited nickel coatings carried by steel workpieces.

By comparison of the foregoing results of these salt spray tests, it is readily apparent that the substantial increase in corrosion resistance that is produced by the chromation step of the present invention is peculiar to coatings of the nickel-phosphorus alloy type that are inherently produced in the chemical nickel plating process, and it is surmised that this peculiarity is predicated upon the phosphorus content of the chemically plated or deposited coatings. In other words, the outer layer or skin of the nickel-phosphorus alloy coating is reacted in some way by the chromate ions; which reaction is definitely

5

peculiar to this nickel-phosphorus alloy as distinguished from a nickel coating as produced by electrodeposition.

In view of the foregoing, it is apparent that there has been provided an improved process of producing improved nickel-phosphorus alloy coatings carried by a wide variety of workpieces; which coatings are smooth, bright, uniform, continuous and intimately bonded to the workpieces. Moreover, the process of the present invention fundamentally involves only the simple post-treatment described of the coatings that are inherently produced upon workpieces in the chemical nickel plating process; whereby the chemically deposited or plated coatings carried by the workpieces are substantially improved with respect to general appearance and are substantially improved with respect to the corrosion-resistance characteristic thereof.

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 increasing the corrosion resistance of a nickel-phosphorus coating carried by a metal workpiece and applied thereto by chemical plating from an aqueous plating bath of the nickel cation-hypophosphite anion type, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus; said process comprising immersing said coated workpiece during a suitable time interval in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath containing by weight at least about $\frac{1}{2}$ % chromate ions.

2. The process of increasing the corrosion resistance of a nickel-phosphorus coating carried by a metal workpiece and applied thereto by chemical plating from an aqueous plating bath of the nickel cation-hypophosphite anion type, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus; said process comprising immersing said coated workpiece during a time interval of at least about 15 minutes in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath having an elevated temperature and containing by weight at least about $\frac{1}{2}$ % chromate ions.

3. The process of increasing the corrosion resistance of a nickel-phosphorus coating carried by a metal workpiece and applied thereto by chemical plating from an aqueous plating bath of the nickel cation-hypophosphite anion type, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus; said process comprising immersing said coated workpiece during a time interval from about 15 minutes to about 1 hour in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath having a temperature of at least about 50° C. and containing by weight chromate ions in the range $\frac{1}{2}$ % to 5%.

4. The process comprising immersing a metal workpiece in a hot aqueous plating bath of the nickel cation-hypophosphite anion type, continuing said immersion during a time interval sufficiently long to obtain a nickel-phosphorus coating upon said workpiece having a thickness of at least about $\frac{1}{2}$ mil, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus, rinsing said coated workpiece with water after removal thereof from said plating bath, and then immersing said coated workpiece during a suitable

6

time interval in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath containing by weight at least about $\frac{1}{2}$ % chromate ions, whereby the surface brightness of said coating as plated is significantly enhanced and surface stains on said coating as plated are removed therefrom and the corrosion resistance of said coating as plated is materially increased.

5. The process comprising immersing a metal workpiece in a hot aqueous plating bath of the nickel cation-hypophosphite anion type, continuing said immersion during a time interval sufficiently long to obtain a nickel-phosphorus coating upon said workpiece having a thickness of at least about $\frac{1}{2}$ mil, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus, rinsing said coated workpiece with water after removal thereof from said plating bath, immersing said coated workpiece during a suitable time interval in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath containing by weight at least about $\frac{1}{2}$ % chromate ions, whereby the surface brightness of said coating as plated is significantly enhanced and surface stains on said coating as plated are removed therefrom and the corrosion resistance of said coating as plated is materially increased, rinsing said treated coating with water after removal thereof from said treatment bath, and then subjecting said thus treated coated workpiece to heat treatment at a temperature of about 400° F. for a time interval of about 1 hour, whereby said treated coating is unified upon said workpiece.

6. The process of increasing the corrosion resistance of a nickel-phosphorus coating carried by a metal workpiece and applied thereto by chemical plating from an aqueous plating bath of the nickel cation-hypophosphite anion type, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus; said process comprising immersing said coated workpiece during a time interval of about 1 hour in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath having a temperature of about 50° C. and containing by weight about 1% chromate ions.

7. An article of manufacture comprising a workpiece, a coating carried by said workpiece and formed of a nickel-phosphorus alloy, said alloy comprising by weight about 85% to 97% nickel and about 3% to 15% phosphorus, and an outer skin carried by said coating and formed of the reaction product of said alloy and chromate ions and produced by soaking said coating in an aqueous treatment bath containing chromate ions.

8. The article set forth in claim 7, wherein said coating has a thickness of at least about 1 mil, and said outer skin constitutes a film of substantially molecular thickness.

9. An article of manufacture comprising a layer of nickel-phosphorus alloy carrying a corrosion-resistant outer skin, said alloy comprising by weight about 85% to 97% nickel and about 3% to 15% phosphorus, said outer skin comprising the reaction product of said alloy and chromate ions and produced by soaking said layer in an aqueous treatment bath containing chromate ions.

10. The process comprising immersing a metal workpiece in a hot aqueous plating bath of the nickel cation-hypophosphite anion type, continuing said immersion during a time interval sufficiently long to obtain a nickel-phosphorus coating upon said workpiece having a thickness of at least about $\frac{1}{2}$ mil, wherein said coating comprises by weight about 85% to 97% nickel and about 3% to 15% phosphorus, rinsing said coated workpiece with water after

removal thereof from said plating bath, subjecting said coated workpiece to heat-treatment at a temperature of about 400° F. for a time interval of about one hour, then immersing said thus treated coated workpiece during a suitable time interval in a treatment bath, said treatment bath essentially comprising an aqueous solution of a water soluble compound selected from the class consisting of chromic acid anhydride, alkali metal chromate and alkali metal dichromate, said treatment bath containing by weight at least about ½% chromate ions, and rinsing said thus treated coating with water after removal thereof from said treatment bath, whereby the surface brightness of said coating as plated is significantly enhanced and

surface stains on said coating as plated are removed therefrom and the corrosion-resistance of said coating as plated is materially increased.

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