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NICKEL PLATING

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The present invention relates to a process for producing electro-deposits of nickel and more particularly, to a process for producing thick, ductile and adherent electro-deposits of nickel without streaks on foundation metals, especially on zinc-base compositions, such as zinc and zinc alloys.

Heretofore, the most commonly used processes for direct nickeling of zinc and zinc alloys were the so-called high-sulfate nickel bath and the type of bath disclosed in the Tuttle U. S. Patent No. 2,069,566 assigned to the Zialite Corporation. The high-sulfate bath comprises nickel sulfate, a chloride such as ammonium chloride or sodium chloride, boric acid and large quantities of sodium sulfate. The sodium sulfate permits deposition of nickel directly on zinc without the formation of black streaks on moderately low current density areas. The deposit, however, tends to be brittle and sometimes it is necessary to deposit a more ductile nickel coating over the thin high-sulfate nickel bath coating. However, in such cases, a good bond between the two nickel coatings is not always obtained. Furthermore, the useful current density range between burning and black streaking in the deposit from the high-sulfate nickel bath is too narrow for many complicated shapes; the applicable range for the high-sulfate nickel bath for depositing nickel directly on zinc being about 12 amperes to about 20 amperes per square foot. As the bond between the two nickel coatings is not always good, and as the useful current density range of the high-sulfate bath is narrow, copper coatings have largely taken the place of the high-sulfate nickel bath coating, particularly when bright nickel is used as a second coat. Generally speaking, the high-sulfate nickel bath is used only to obtain thin nickel coatings.

The Zialite bath is also used for direct electro-nickeling of foundation metals, particularly on zinc and zinc alloys. This bath, which has unusual ability to cover recesses without streaking, contains nickel in the form of complex pyrophosphates and citrates, and also contains sodium and ammonium sulfates, chlorides and free ammonia. The Zialite bath is normally operated at current densities of between 2 and 20 amperes per square foot. Even though the Zialite bath has good throwing power and a tolerance for zinc three or four times as great as prior art baths for direct electro-nickeling of zinc and zinc alloys, nevertheless, the useful current density range of the Zialite bath is considered to be

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narrow and the nickel deposits obtained therefrom on zinc and zinc alloys tend to be brittle.

As the aforementioned high-sulfate and Zialite baths, when used for direct electro-nickeling of zinc and zinc alloys, deposit nickel coatings that tend to be brittle, and as the useful current density range for these baths is narrow, there is a definite and well recognized need in the art for a process of depositing thick, ductile and adherent nickel plating without streaks on foundation metals such as zinc and zinc alloys over a wide range of current density between burning and streaking, and without use of intermediate ductile coatings such as copper.

We have discovered a process for electro-depositing nickel directly on foundation metals, particularly zinc base metal compositions, i. e. zinc and zinc alloys, whereby a thick, ductile and adherent nickel plating substantially without streaks is obtained over a wide range of current density without burning and streaking of the deposit and without necessity for using intermediate ductile coatings such as copper. In our novel and improved process, an easily controllable electro-plating bath having a simple composition is employed under plating conditions, including hydrogen ion concentration and current density, which are properly correlated with the bath composition.

It is an object of the present invention to provide a process for producing a thick, ductile and adherent electro-deposit of nickel substantially without streaks directly on metal foundations.

It is another object of the present invention to provide a process for producing thick, ductile and adherent electro-deposits of nickel substantially free from streaks directly on metal foundations, particularly zinc-base compositions i. e. zinc and zinc alloys.

Still another object of the present invention is to provide a process for producing a thick, ductile and adherent electro-deposit of nickel without streaks directly on metal foundations, particularly zinc-base compositions, by employing a novel electro-plating bath having a simple composition.

A further object of the present invention is to provide a process for producing thick, ductile and adherent electro-deposits of nickel substantially without streaks directly on metal foundations, particularly zinc-base compositions, by use of an electro-plating bath of simple composition that can be operated with desired results over a wide range of current density.

It is within the purview of the present inven-

tion to provide a process for producing a thick, ductile and adherent electro-deposit of nickel substantially without streaks directly on foundation metals particularly zinc-base compositions, without the necessity of employing an intermediate ductile coating such as copper.

It is still a further object of the present invention to provide an electro-plating bath for the electro-deposition of a thick, ductile and adherent nickel plating without streaks directly on metal foundations, particularly zinc-base compositions, over a wide range of current density and under plating conditions, including hydrogen ion concentration, properly correlated with the bath composition.

Various other objects, advantages and features of the present invention will become apparent from the following description.

Generally speaking, the process embodying the present invention contemplates the electro-deposition over a wide range of current density of a thick, ductile and adherent deposit of nickel substantially without streaks directly on suitable foundation metals, particularly zinc-base metal compositions such as zinc and zinc alloys, by use of a novel aqueous plating bath prepared from nickel chloride, tartaric acid and ammonium hydroxide. The invention also contemplates the operation of the novel bath embodied in the present invention under plating conditions, including hydrogen ion concentration and current density, properly correlated with the bath composition. The present invention further contemplates the electro-deposition of a thick, ductile deposit of nickel without streaks directly on foundation metals, especially zinc-base compositions such as zinc and zinc alloys, and including zinc-base die castings, whereby the thick, ductile nickel coating obtained has good adhesion to the foundation metal and has no tendency to peel off. Moreover the novel bath employed by the present invention is extremely simple in composition and can be readily controlled over a wide range of current density to obtain a nickel deposit that is thick, ductile, adherent and substantially free from streaks.

The nickel plating bath, employed by the present invention, as recited hereinbefore, contains tartaric acid and nickel chloride in an aqueous solution regulated to a desired pH value by addition of concentrated ammonium hydroxide. It is not necessary to add any other ingredients to the novel plating bath of the present invention to obtain therefrom electro-deposits of nickel directly on metal foundations, especially zinc-base compositions, that are thick, ductile, and adherent and substantially free from streaks when the novel bath is operated over a wide range of current density.

The aqueous plating bath employed by the present invention is generally controlled within the following ranges of composition and plating conditions:

Tartaric acid, about 20 to about 150 grams per liter

Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), about 15 to about 100 grams per liter

pH, about 5.0 to about 7.2

Current density, about 10 to about 90 amperes per sq. ft.

While the bath compositions and plating conditions given hereinbefore have been found satisfactory, in carrying the present invention into

practice, we prefer to employ compositions and plating conditions within the following ranges:

Tartaric acid, about 30 to about 60 grams per liter

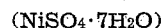
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), about 20 to about 40 grams per liter

pH, about 5.3 to about 6.2

Current density, about 15 to about 90 amperes per sq. ft.

In the compositions given hereinbefore for the novel tartaric acid-nickel chloride plating bath, the pH is regulated to the desired value by addition of concentrated ammonium hydroxide.

While it is stated herein that the aqueous plating bath provided by the present invention is principally a bath made by adding nickel chloride and tartaric acid to water and then regulating the pH to the desired value by an addition of ammonium hydroxide, it is to be understood that small amounts of minor constituents, impurities and incidental elements and/or compounds may be present, although not essential for obtaining the desired results; e. g. the bath may contain small amounts of zinc, oxalates, phosphates, sulfates, iron, copper, lead, cobalt, and alkali metals generally introduced as minor constituents and/or impurities of the principal ingredients, i. e. tartaric acid, nickel chloride and ammonium hydroxide of the plating bath. While small amounts of ingredients other than tartaric acid, nickel chloride and ammonium hydroxide may not detrimentally affect the nickel electro-deposit, we have found that the presence of sulfate ion, if present in substantial quantity in the plating bath, detrimentally affects the results obtained as compared to those obtained from an all-tartaric acid-nickel chloride-ammonium hydroxide bath. For example, when nickel sulfate is used to replace a substantial portion of the nickel chloride content of the bath composition employed by the present invention, inferior results are obtained as either no deposit or streaky deposits are produced when the bath containing a substantial amount of sulfate ion is operated within the ranges of pH and current density employed in the present invention. Thus it is preferable to maintain the plating bath of the present invention as substantially free of sulfate ion as is practically possible, although a small amount may be present. Generally, it is preferable that the sulfate ion content of the novel tartaric acid-nickel chloride bath be less than about 1.7 grams per liter of sulfate ion; e. g. the equivalent of about 5 grams per liter of nickel sulfate



The acidic limits for the novel tartaric acid-nickel chloride bath employed by the present invention are critical and must be maintained within about pH 5.0 to about pH 7.2 to obtain the desired results in electro-depositing thick, ductile and adherent nickel substantially free from streaks over a wide range of current density directly on metal foundations especially zinc-base compositions i. e. zinc and zinc alloys. Although satisfactory results are obtained when the novel electro-plating bath of the present invention is operated within a pH range of 5.0 to 7.2, we prefer to operate the bath within a pH range of 5.3 to 6.2, as we have found that when the pH of the novel electro-plating bath exceeds 6.3 there is a tendency for formation of an insoluble film at the anode. When the pH of the novel electro-plating bath is more alkaline than about

pH 7.2 conditions are such that there is a tendency for formation of colloidal nickel hydroxide. When the novel electro-plating bath of the present invention is operated at a pH more acid than pH 5.0, conditions are such that a zinc cathode surface is deleteriously attacked by the electro-plating bath.

As has been recited hereinbefore, the current density range generally employed by the present invention is generally controlled within about 10 amperes per square foot to about 90 amperes per square foot. Although thick, ductile and adherent nickel platings substantially free from streaks can be obtained on metal foundations, especially zinc-base compositions, when current densities down to about 10 amperes per square foot are employed, we have found that at current densities of about 15 amperes per square foot or lower the current efficiency is poor. An increase in the nickel concentration of the novel electro-plating bath tends to offset this effect of a decrease in current efficiency so that with the baths having a high concentration of nickel, it is feasible to operate the bath at about 10 amperes per square foot with desired results. As hereinbefore stated, the current density of about 90 amperes per square foot is generally employed as the upper limit of the current density range. This upper limit of current density is determined by voltage requirements, as for the anode to cathode spacing generally used in commercial practice, a current density of about 90 amperes per square foot requires the full voltage of an ordinary plating generator.

In order that those skilled in the art may have a better understanding of the present invention the following illustrative examples are given:

Example I

An aqueous plating bath was prepared having about 30 grams per liter of tartaric acid, about 20 grams per liter of nickel chloride, and regulated to a pH of about 5.3 by addition of concentrated ammonium hydroxide. At current densities of about 25 to about 90 amperes per square foot, at a temperature of 100° F. and employing nickel anodes, thick, ductile and adherent electro-deposits of nickel substantially free of streaks were obtained when electro-plated directly on zinc surfaces.

Example II

An aqueous bath was prepared having about 120 grams per liter of tartaric acid, about 80 grams per liter of nickel chloride and regulated to a pH of about 6.2 by addition of concentrated ammonium hydroxide. At a current density of about 45 amperes per square foot, at a temperature of about 100° F. and employing nickel anodes, thick ductile and adherent electro-deposits of nickel substantially free of streaks were obtained when electro-plated directly on zinc.

Example III

An aqueous plating bath was prepared having about 30 grams per liter of tartaric acid, about 40 grams per liter of nickel chloride, and adjusted to a pH of about 5.3 by addition of concentrated ammonium hydroxide. At a current density of about 10 to about 20 amperes per square foot, at a temperature of about 100° F. and employing nickel anodes, a thick, ductile and adherent electro-deposit of nickel without streaks was obtained when electro-plated directly on a zinc surface.

Example IV

An aqueous plating bath was prepared having 30 grams per liter of tartaric acid, about 20 grams per liter of nickel chloride, and regulated to a pH of about 5.3 by addition of concentrated ammonium hydroxide. At a current density of about 20 amperes per square foot, and employing nickel anodes, a thick, ductile, and adherent electro-deposit of nickel without streaks was obtained when electro-plated directly on a steel surface.

In the art of nickel electro-plating, a nickel electro-deposit of about 0.0002 inch or less is generally considered to be a thin deposit. By employing the process of the present invention, ductile electro-deposits of nickel substantially free from streaks can be obtained having a thickness of more than 0.0002 inch, e. g., more than about 0.0005 inch. Moreover, by employing the process embodying the present invention, ductile nickel electro-deposits exceeding 0.001 inch can be obtained directly on suitable foundation metals particularly zinc-base compositions.

Although the present invention has been described with particular emphasis on zinc-base compositions, such as zinc and zinc alloys, including zinc-base die castings, the novel tartaric acid-nickel chloride bath embodied in the present invention may be employed to obtain thick, ductile, and adherent nickel electro-deposits substantially free from streaks on other metal foundations, including aluminum-base compositions, such as aluminum and aluminum alloys, copper base compositions, such as copper alloys, and steel.

It will be apparent from the foregoing that the present invention provides a practical and satisfactory process for producing thick, ductile and adherent nickel electro-deposits without streaks directly on metal foundations, especially zinc-base compositions. The novel bath embodied in the present invention is simple in composition, easy to prepare and has good stability. When employing the novel tartaric acid-nickel chloride bath, the plating conditions that may be employed are such that desired results are obtainable over a wide range of current density as nickel electro-deposits that are not objectionable from the viewpoint of streaking can be produced. The nickel electro-deposits that are obtained are thick and ductile, as determined by bend tests, and adhere well without tendency to peel when electro-plated on metal foundations, particularly zinc-base compositions such as zinc and zinc alloys.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will understand that variations and modifications thereof can be made. Such variations and modifications are to be considered to be within the purview of the specification and the scope of the appended claims.

We claim:

1. A process for electrodepositing nickel directly on zinc-base metal compositions which comprises establishing a bath having a temperature of about 100° F. and a pH within the range of about 5.3 to about 6.2, and containing tartrate ions in an amount equivalent to a tartaric acid concentration of about 30 to about 60 grams per liter, nickel ions and chloride ions in amounts equivalent to a nickel chloride concentration of about 20 to about 40 grams per liter, ammonium ions equivalent to the amount of ammo-

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nium hydroxide required to regulate the pH of said bath within said range, and the balance of the bath being essentially water, said bath being substantially devoid of sulfate ion, and electrodepositing nickel from said bath at a current density of about 10 to about 90 amperes per square foot upon a zinc-base metal composition, whereby a thick, ductile and adherent nickel plating substantially free from streaks is obtained.

2. A process for electrodepositing nickel directly on zinc-base metal cathodes which comprises establishing a bath having a temperature of about 100° F. and a pH of about 5.3, and containing tartrate ions in an amount equivalent to a tartaric acid concentration of about 30 grams per liter, nickel ions and chloride ions in amounts equivalent to a nickel chloride concentration of about 20 grams per liter, ammonium ions equivalent to the amount of ammonium hydroxide required to regulate the pH of said bath to about pH 5.3, and the balance of the bath being essentially water, said bath being devoid of sulfate ion, and electrodepositing nickel from said bath at a current density of about 10 to about 90 amperes per square foot upon a zinc-base metal cathode, whereby a thick, ductile and adherent nickel plating substantially free from streaks is obtained.

3. An electroplating bath adapted for direct nickel plating on zinc-base metallic mate-

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rials which comprises a water solution containing about 30 to about 60 grams per liter of tartaric acid and about 20 to about 40 grams per liter of nickel chloride to which has been added ammonium hydroxide sufficient to regulate the pH of said bath within the range of about 5.3 to 6.2, the balance of the bath being essentially water, said bath being substantially devoid of sulfate ion.

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