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(54) SEMI-BRIGHT NICKEL PLATING BATH AND METHOD OF USING SAME

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(57) ABSTRACT

A nickel plating bath for plating a semi-bright nickel deposit on a substrate comprising a) nickel sulfateions; b) a soluble salt of chloroacefic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid; and c) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing. The semi-bright nickel plating bath described herein produces sulfur-free semi-bright deposits over a very wide current density range. The plating bath described herein is at least substantially free of coumarin and produces desirable leveling characteristics. The bath also requires no aldehydes to achieve simultaneous thickness and electrolytic potential (STEP) and has extremely low stress and excellent ductility.

SEMI-BRIGHT NICKEL PLATING BATH AND METHOD OF USING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation-in-part of U.S. application Ser. No. 12/620,746, filed on Nov. 18, 2009, the subject matter of which is herein incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates generally to semi-bright nickel plating baths that provide good properties with respect to leveling, ductility and stress and that are virtually sulfur-free.

BACKGROUND OF THE INVENTION

[0003] Bright nickel plating baths are used in the automotive, electrical, appliance, hardware and other industries. The most important functions of bright nickel plating are as an undercoating for chromium plating, helping finishers achieve a smooth bright finish and providing a significant amount of corrosion protection.

[0004] For decorative plated parts that need a high level of basis metal corrosion protection, semi-bright nickel deposits are almost always used in conjunction with subsequent deposits of bright nickel and chromium. The semi-bright nickel deposit is typically between about 60 and 70 percent of the total nickel deposited on the part, which offers the highest level of basis metal corrosion protection with the lowest total nickel thickness and the best appearance.

[0005] The most common nickel plating bath is a sulfate bath known as a Watts bath. A typical Watts bath contains about 20-40 oz/gal nickel sulfate, 3-12 oz/gal nickel chloride, and 4-6 oz/gal boric acid and operates at a pH in the range of about 2.0-5.2, a temperature in the range of 90-160° F. and a current density in the range of about 10-60 ASF. The large amount of nickel sulfate provides the necessary concentration of nickel ions, nickel chloride improves anode corrosion and increases conductivity, and boric acid is used as a weak buffer to maintain pH. In addition, in order to achieve bright and lustrous appearance of the nickel plating deposit, organic and inorganic agents (brighteners) are often added to the electrolyte. The types of added brighteners and their concentrations determine the appearance of the nickel deposit, i.e., brilliant, bright, semi-bright, satin, etc.

[0006] Traditionally, coumarin has been used to obtain a high-leveling, ductile, semi-bright and sulfur-free nickel deposit from a Watts nickel bath. However, coumarin-free solutions are now available. A semi-bright nickel finish is semi-lustrous, as the name implies, but it was specifically developed for its ease of polishing and buffing. In the alternative, if subsequently bright nickel is plated, buffing can be eliminated. Brightness and smoothness are dependent on operating conditions.

[0007] One of the reasons that semi-bright nickel finishes are so easily buffed and/or polished is that the structure of the deposit is columnar, whereas the structure of a bright nickel finish is plate-like (lamellar). However, the structure of the deposit can be changed with various additives, a change in pH, current density or an increase in solution agitation, which is not a problem unless it affects properties of the deposit such as internal stress.

[0008] Internal stress of the plated nickel deposit can be compressive or tensile. Compressive stress is where the deposit expands to relieve the stress. In contrast, tensile stress is where the deposit contracts. Highly compressed deposits can result in blisters, warping or cause the deposit to separate from the substrate, while deposits with high tensile stress can also cause warping in addition to cracking and reduction in fatigue strength.

[0009] The use of coumarin as an additive in nickel electroplating baths, especially semi-bright nickel processes, to produce ductile, lustrous deposits with excellent leveling is well known. It is also known that the degree of leveling obtained is generally proportional to the concentration of coumarin in the plating bath. A full coumarin bath typically contains about 150 to about 200 mg/L of coumarin and about 30 mg/L of formaldehyde. Thus, it can be seen that a high concentration of coumarin in the bath gives the best leveling.

[0010] However, such characteristics are short-lived, because such high coumarin concentrations also result in a high rate of formation of detrimental breakdown or degradation products. These degradation products are objectionable in that they can cause uneven, dull gray areas that are not easily brightened by a subsequent bright nickel deposit, they can reduce the leveling obtained from a given concentration of coumarin in the plating bath, and they can reduce the beneficial physical properties of the nickel deposits.

[0011] Because it is well known that coumarin breaks down or degrades under many conditions, it is imperative to monitor the degradation of a plating bath containing coumarin so that plating is not adversely affected. It has also been suggested to reduce the concentration of coumarin in the bath in order to reduce degradation products and thus increase bath life, but such reduction in coumarin concentration is often accompanied by a loss of leveling and also makes the bath more sensitive to degradant build-up. The use of various additives, such as formaldehyde and chloral hydrate has also been suggested to help overcome the undesirable effects of the coumarin degradation products. However, the use of such additives has certain limitations because even moderate concentrations of these materials not only increase the tensile stress of the nickel electrodeposits, but also significantly reduces the leveling action of the coumarin.

[0012] It has also been suggested to use an aqueous acidic nickel electroplating bath comprising a coumarin compound and an aryl hydroxyl carboxylic acid compound in a combined amount, as described for example in U.S. Pat. No. 4,441,969 to Tremmel, the subject matter of which is herein incorporated by reference in its entirety. However, the bath described in Tremmel still requires a relatively high concentration of coumarin to provide good leveling characteristics. While the bath required less frequent batch carbon treatments, the need for said treatments was not eliminated. Another problem with coumarin is odor. The amount of coumarin required for a plating bath produces an offensive odor that can irritate eyes and mucous membranes.

[0013] Because of the noted deficiencies of coumarin-based baths, researchers have been trying for a long time to develop a semi-bright nickel plating bath that is capable of providing the leveling achieved by a coumarin-based bath, which is considered to be the standard in the plating industry. Leveling refers to the ability of the deposit to fill in and smooth out surface defects such as scratches or polish lines. It is also important to provide these highly leveled deposits without sacrificing deposit ductility and stress. It is further preferable that the nickel deposit contain less than 0.004% sulfur.

[0014] Since the late 1970's plating suppliers have proposed many bath formulations which claim to level as well as a coumarin bath. However, to date, none of these baths formulations have met all of the necessary criteria. It is believed that the best baths developed to date can only achieve about 65% of the leveling of a coumarin-based deposit at equal deposit thickness.

[0015] As explained above, while the leveling of coumarin is exceptional, coumarin has a disagreeable odor, breaks down and forms harmful degradation products, and these degradation products can only be removed by batch carbon treatments of the plating bath. These treatments are expensive and time consuming and normally must be done at least monthly and in some cases, even weekly. Therefore, there is a need in the art to provide a nickel plating bath that is coumarin-free but that provides similar leveling characteristics.

[0016] Current semi-bright nickel solutions use hexyne diol and/or butyne diol, in combination with aldehydes such as chloral hydrate, formaldehyde and piperonal in further combination with salicylic acid or benzoic acid. The internal stress of these baths is relatively high, ranging from about 8,000 psi tensile to about 15,000 psi tensile. In addition, none of these baths level nearly as well as a full coumarin system.

[0017] Thus it would be desirable to provide a coumarin-free semi-bright nickel plating bath that approaches the leveling characteristics of a coumarin bath, is virtually sulfur-free, and meets the automotive requirements for stress and ductility.

SUMMARY OF THE INVENTION

[0018] It is an object of the present invention to provide a highly leveled semi-bright nickel deposit with excellent ductility and very low stress.

[0019] It is another object of the present invention to provide a coumarin-free semi-bright nickel plating bath that approaches or even equals the leveling characteristics of a coumarin bath and is virtually sulfur free.

[0020] It is another object of the present invention to provide a semi-bright nickel plating bath that does not require aldehydes to provide acceptable simultaneous thickness and electrolytic potential (STEP) results.

[0021] It is still another object of the present invention to provide a semi-bright nickel plating bath that provides good stability over the life of the bath.

[0022] To that end, the present invention relates generally to a nickel plating bath for plating a semi-bright nickel deposit on a substrate, the nickel plating bath comprising:

[0023] a) a source of nickel ions;

[0024] b) a halide substituted acetic acid, proprionic acid or salts of the foregoing; and

[0025] c) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing

[0026] wherein the nickel plating bath is preferably substantially free of coumarin, and preferably substantially free of aldehydes.

[0027] In another preferred embodiment, the present invention relates generally to a nickel plating bath for plating a semi-bright nickel deposit on a substrate, the nickel plating bath comprising:

[0028] a) nickel ions such as from a mixture of nickel sulfate and nickel chloride;

[0029] b) a soluble salt of chloroacetic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid; and

[0030] c) at least one diol selected from the group consisting of hexyne diol, butyric diol and combinations of the foregoing,

[0031] wherein the nickel plating bath is preferably substantially free of coumarin and preferably substantially free of aldehydes.

[0032] In another embodiment, the present invention relates generally to a method of plating a substrate to produce a sulfur-free semi-bright nickel deposit thereon comprising the steps of:

[0033] a) providing a nickel plating bath comprising:

[0034] i) nickel ions, such as from a mixture of nickel sulfate and nickel chloride;

[0035] ii) a halide substituted (i) acetic acid, (ii) proprionic acid, or (iii) salts of any of the foregoing, or a soluble salt of chloroacetic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid; and

[0036] iii) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing; and

[0037] b) contacting with the substrate with the nickel plating bath and applying current to provide a semi-bright nickel deposit on the substrate,

[0038] wherein the nickel plating bath is preferably substantially free of coumarin and preferably substantially free of aldehydes.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0039] The present invention relates generally to a nickel plating bath that includes a halide substituted (i) acetic acid, (ii) proprionic acid, or (iii) salts of any of the foregoing, or a soluble salt of chloroacetic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid in combination with hexyne diol and/or butyne diol and that is able to provide good leveling characteristics without the addition of coumarin.

[0040] More particularly, the present invention relates generally to a coumarin-free nickel plating bath which provides the leveling characteristics that are achievable with a coumarin-containing nickel plating bath.

[0041] To that end, the present invention relates generally to a nickel plating bath for plating a semi-bright nickel deposit on a substrate, the nickel plating bath comprising:

[0042] a) a source of nickel ions;

[0043] b) a halide substituted (i)acetic acid, (ii)proprionic acid or (iii)salts of the foregoing; and

[0044] c) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing.

[0045] wherein the nickel plating bath is preferably substantially free of coumarin and preferably substantially free of aldehydes.

[0046] In a preferred embodiment, the nickel plating bath contains nickel sulfate and nickel chloride. In addition, boric acid is typically added to control the pH of the solution.

[0047] In this embodiment, the plating bath contains a halide substituted (i) acetic acid, (ii) proprionic acid or (iii) salts thereof. Monochloroacetic acid is preferred, however dichloroacetic acid or trichloroacetic acid are also suitable. The aforementioned acids are generally added as sodium, potassium, lithium, magnesium and nickel salts because the addition of the acids tends to make the pH of the bath too low. The concentration of the soluble salt, such as sodium mono chloroacetate, is preferably between about 2.0 to 4.0 g/l but can range from as little as 0.5 g/l to as much as 20 g/l.

[0048] The hexyne diol concentration should preferably be between 100 to 200 mg/l, but can range from 50 mg/l to 500 mg/l. The preferred range for the butyne diol is 60 to 120 g/l but can range from 30 to 300 mg/l. Preferably both hexyne diol and butyne diol are used together, however, the inclusion of one of the two will work well. Even higher concentrations of these compounds can be used if they are used alone. If both diols are used the aggregate concentration can range from 50 mg/l to 600 mg/l. Supplementary additives include ethoxylated (or propoxylated) butyne diol, ethoxylated (or propoxylated) hexyne diol, ethoxylated (or propoxylated) acetylenic alcohols, and/or acetylenic alcohols.

[0049] In another preferred embodiment, the present invention relates generally to a nickel plating bath comprising:

[0050] a) a source of nickel ions;

[0051] b) a soluble salt of chloroacetic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid; and

[0052] c) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing,

[0053] wherein the nickel plating bath is preferably substantially free of coumarin and preferably substantially free of aldehydes.

[0054] In this embodiment, soluble salts of salicylic acid are preferred, such as sodium salicylate. The soluble salts of acetic acid, chloroacetic acid, glycolic acid, proprionic acid, benzoic acid and chlorobenzoic acid are also usable in the practice of the invention. The aforementioned acids are generally added as sodium, potassium, lithium, magnesium and nickel salts because the addition of the acids would make the pH of the bath too low.

[0055] The concentration of the soluble salt, such as sodium salicylate, is preferably between about 1.0 to 2.0 g/l but can range from as little as 0.3 g/l to as much as 20 g/l.

[0056] As described herein, the semi-bright nickel plating bath is preferably substantially free of coumarin and is most preferably free of coumarin. What is meant by substantially free is that the bath contains no functional amounts of coumarin. Free of coumarin means that no detectible amounts of coumarin have been added to the bath.

[0057] One important aspect of the present invention is that aldehydes are not required in the nickel plating bath to provide acceptable STEP results. "STEP" is an acronym for "simultaneous thickness and electrolytic potential" and is measured with a special device called a STEP tester, which measures not only the thickness of the given deposits but also the electrical potential difference between the bright and semi-bright nickel layers. This difference is very important because it relates to the corrosion protection of these duplex nickel layers. A STEP of at least 100 mv is required and 120 mv or higher is desirable. Normally, the addition of aldehydes is used to accomplish this end. However, the use of aldehydes is not desirable because these compounds increase the internal stress and may also decrease the ductility and the leveling of the semi-bright coatings. Thus the plating bath described herein is preferably substantially free of aldehydes, and most preferably is free of aldehydes. What is meant by substantially free is that the bath contains no functional amounts of aldehydes. Free of aldehydes means that no detectible amounts of aldehydes have been added to the bath.

[0058] The results obtained with the combination of the listed acid compounds with hexyne diol and butyne diol are quite surprising. STEP results of deposits prepared using plating baths with the foregoing additives range from 80 to 145 mv. In order to obtain the higher STEP results and better leveling, the pH should preferably be above 4.0, preferably higher than 4.3. This higher pH is desirable because it also improves the leveling of the deposit. The pH of the proposed bath is preferably from 4.1 to 5.0, more preferably from 4.4 to 4,8, most preferably 4.4 to 4.6. The fact that the stress of the deposit remains very low and the ductility very high is surprising. Normally, as one raises the pH of a semi-bright nickel bath or any nickel plating bath for that matter, the internal stress of the deposit goes up and the ductility is poorer.

[0059] The semi-bright nickel plating bath described herein also provides a nickel deposit that exhibits perfect ductility of 0.5 according to the Chrysler ductility method and exceptionally low internal stress ranging from about 1,000 compressive to about 4,000 tensile.

[0060] Furthermore, the leveling of deposits plated from the plating bath of the invention are comparable to a freshly made coumarin/formaldehyde bath. To date, while many claims have been made to the leveling characteristics of various processes, there have been no coumarin-free plating processes that have come close to the leveling of a fresh coumarin bath.

[0061] The STEP results achieved by the plating bath of this invention are completely unexpected. Until now, only the addition of aldehydes, such as chloral hydrate or formaldehyde, would increase the STEP to the required levels. Furthermore, previously the addition of other acids, such as salicylic acid and benzoic acid, was shown to reduce STEP. However, as seen from the examples set forth below, the addition of a soluble salt of an acid such as salicylic acid or benzoic acid can also be shown to provide desirable

[0062] STEP results. In addition, increasing the pH of the bath to increase STEP without the use of aldehydes is also completely unexpected.

[0063] Stress of the deposit is measured using various methods and is typically desired to be within the range of 15,000 psi tensile or less. The lower the internal stress, the better.

[0064] Ductility is normally measured using the Chrysler ductility method. The Chrysler ductility method involves plating a foil 0.001 inch thick. The foil is then cut into a strip the width of a micrometer jaw and folded over to make a "U" shape in the jaw of the micrometer. The micrometer is turned down until the foil breaks and ductility is equal to T/2R where T is the thickness of a plated foil and 2R is the measurement of deflection at which the foil breaks when it is bent over itself. For example, if the nickel thickness is 0.001" and the foil breaks at 0.005 diameter the ductility would be: D=0.001/0.005=0.2. Perfect ductility is 0.5 and most automotive companies require a number that is at least 0.4.

[0065] The present invention will now be discussed with reference to the following non-limiting examples:

EXAMPLE 1

[0066] A stock semi-bright nickel bath was prepared having 40 oz/gal nickel sulfate hexahydrate, 4.5 oz/gal nickel chloride hexahydrate and 5.5 oz/gal of boric acid. The solution was carbon and peroxide treated and filtered and the pH adjusted to 3.8 to 4.0. Thereafter, 0.3% v/v of a solution of 6% by weight di-hexylsulfosuccinate was added to prevent pitting in the subsequent deposits.

[0067] 330 cm^3 of this solution was added to a hull cell equipped with air agitation and heated to 135° F. 2 g/l of sodium acetate was added to the bath and a brass panel was plated at 2 amps for 15 minutes. The resulting deposit was overall gray with lustrous recesses. 0.1% of a 70/30 mixture of hexyne diol and butyne diol was added such that the aggregate concentration was 0.15 g/l. The resulting deposit was lustrous to semi-bright from about 0 to 40 ASF and dull above 40 ASF and very dull near the high current density (HCD) edge.

[0068] Another 0.1% of the mixture of hexyne diol and butyne diol was added and the panel was repeated using a scratched hull cell panel for the test. A scratched hull cell panel is one where the bottom 0.75 inch of the panel has been polished with a 200 grit belt. This leaves polishing lines and allows the researcher to evaluate leveling across a wide current density range.

[0069] The overall deposit was over-lustrous semi-bright from about 0 to 50 ASF and slightly dull above 50 ASF and very dull along the HCD edge.

[0070] This panel was then plated in a bright nickel bath directly across from the anode (not a hull cell) at 25 ASF for 5 minutes. The bright nickel under these conditions did not provide much leveling but made the deposit bright enough to evaluate leveling of the initial nickel deposit. The leveling of the deposit was about 65% of a commercial coumarin bath. It should be noted that the HCD area of the panel was still cloudy because the semi-bright deposit was dull.

EXAMPLE 2

[0071] A fresh semi-bright stock solution was added to the air agitated hull cell. Thereafter, 2.0 g/l of sodium mono chloroacetate was added to the bath and 0.2% of the mixture of hexyne diol and butyne diol was added such that the aggregate concentration was 0.30 g/l. A scratched brass panel was plated at 2 amps for 15 minutes. The resulting deposit was overall lustrous semi-bright with some slight dullness in the extreme HCD edge of the panel. The panel was over-plated with 5 minutes of bright as described above in Example 1 and the leveling was about 65% of a commercial coumarin bath.

EXAMPLE 3

[0072] Example 2 was repeated but the bath pH was increased to 4.6. The resulting deposit was a little brighter than that in Example 2. It was over-plated with bright nickel as above and leveling evaluated. The leveling of the deposit was almost equal to one plated from a full coumarin bath. The concentration of the mixture of hexyne diol and butyne diol was increased such that the aggregate concentration was 0.45 The leveling of the deposit was now equal to one plated from a commercial coumarin bath.

EXAMPLE 4

[0073] The tests in Examples 2 and 3 were repeated using 4 of sodium mono chloroacetate and the results were the same.

EXAMPLE 5

[0074] Example 1 was repeated at a bath pH of 4.6, and the results were the same.

EXAMPLE 6

[0075] A one liter solution of the bath of Example 3 was placed in a beaker equipped with air agitation. A foil was plated from this bath which had a thickness of about 1.0 mil. This was done by plating the deposit on a stainless steel panel at an average current density of 40 ASF. Because the substrate is passive, the deposit is readily removed by cutting the edges of the panel which releases the deposit. This allows the plater to cut strips of foil and measure the ductility. The ductility (T/2R value) of this deposit was 0.5.

EXAMPLE 7

[0076] A one liter solution of he bath in Example 3 was again placed in an air agitation beaker. This time, stress was measured using the strip method. This is done by measuring the deflection of a beryllium-copper strip before and after plating and plugging the data into a formula which uses deposit thickness, deflection and a constant to determine stress in units of pounds per square inch (psi). The stress of the deposit was determined to be 1560 psi tensile. As mentioned above, the lower the stress, the better, and most semi-bright nickel deposits have stress values of about 8,000 to about 15,000 psi tensile.

EXAMPLE 8

[0077] Example 1 was repeated using 2 g/l of sodium formate in place of the sodium acetate. The resulting deposit with the diols was overall lustrous over the entire current density range but the deposit had fair to poor leveling. While increasing the pH improved leveling, leveling was still less than 50% of a commercial coumarin bath.

EXAMPLE 9

[0078] A stock semi-bright nickel bath was prepared having 40 oz/gal nickel sulfate hexahydrate, 4.5 oz/gal nickel chloride hexahydrate and 5.5 oz/gal of boric acid. The solution was carbon and peroxide treated and filtered and the pH adjusted to 3.8 to 4.0. Thereafter, 0.3% v/v of a solution of 6% by weight di-hexylsulfosuccinate was added to prevent pitting in the subsequent deposits.

[0079] 330 cm^3 of this solution was added to a hull cell equipped with air agitation and heated to 135° F. 2 g/l of sodium salicylate was added to the bath and a brass panel was plated at 2 amps for 15 minutes. The resulting deposit was overall gray with lustrous recesses. 0.1% of a 70/30 mixture of hexyne dial and butyne diol was added such that the aggregate concentration was 0.15 g/l. The resulting deposit was lustrous to semi bright from about 0 to 60 ASF and slightly dull above 60 ASF and very dull near the high current density (HCD) edge.

[0080] Another 0.1% of the mixture of hexyne diol and butyne diol was added and the panel was repeated using a scratched hull cell panel for the test. A scratched hull cell panel is one where the bottom 0.75 inch of the panel has been polished with a 200 grit belt. This leaves polishing lines and allows the researcher to evaluate leveling across a wide current density range.

[0081] The overall deposit was over-lustrous semi-bright from about 0 to 80 ASF and dull above 80 ASF and somewhat dull along the HCD edge.

[0082] This panel was then plated in a bright nickel bath directly across from the anode (not a hull cell) at 25 ASF for 5 minutes. The bright nickel under these conditions did not provide much leveling but made the deposit bright enough to evaluate leveling of the initial nickel deposit. The leveling of the deposit was about 65% of a commercial coumarin bath.

EXAMPLE 10

[0083] A fresh semi-bright stock solution was added to the air agitated hull cell. Thereafter, 2.0 g/l of sodium salicylate was added to the bath and 0.2% of the mixture of hexyne diol and butyne diol was added such that the aggregate concentration was 0.35 g/l. A scratched brass panel was plated at 2 amps for 15 minutes. The resulting deposit was overall lustrous semi-bright with some slight dullness in the extreme HCD edge of the panel. The panel was over-plated with 5 minutes of bright as described above in Example 9 and the leveling was about 75% of a commercial coumarin bath.

EXAMPLE 11

[0084] Example 10 was repeated but the bath pH was increased to 4.6. The resulting deposit was a little brighter than that in Example 10. It was over-plated with bright nickel as above and leveling evaluated. The leveling of the deposit was equal to one plated from a commercial coumarin bath.

EXAMPLE 12

[0085] The tests in Examples 10 and 11 were repeated using 4 g/l of sodium salicylate and the results were the same.

EXAMPLE 13

[0086] A one liter solution of the bath of Example 11 was placed in a beaker equipped with air agitation. A foil was plated from this bath which had a thickness of about 1.0 mil. This was done by plating the deposit on a stainless steel panel at an average current density of 40 ASF. Because the substrate is passive, the deposit is readily removed by cutting the edges of the panel which releases the deposit. This allows the plater to cut strips of foil and measure the ductility. The ductility (T/2R value) of this deposit was 0.5.

EXAMPLE 14

[0087] A one liter solution of the bath in Example 11 was again placed in an air agitation beaker. This time, stress was measured using the strip method. This is done by measuring the deflection of the strip before and after plating and plugging the data into a formula which uses deposit thickness, deflection and a constant to determine stress in units of pounds per square inch (psi). The stress of the deposit was determined to be 1920 psi tensile. As mentioned above, the lower the stress, the better, and most semi-bright nickel deposits have stress values of about 8,000 to about 15,000 psi tensile.

EXAMPLE 15

[0088] Example 3 was repeated using 1.5 g/l of sodium benzoate in place of sodium acetate. The resulting deposit was overall semi-bright to lustrous over the entire current density range. The leveling of the deposit was comparable to deposits from a commercial coumarin bath.

EXAMPLE 16

[0089] Example 3 was repeated using 1.5 g/l of sodium chlorobenzoate in place of sodium acetate. The resulting deposit was overall lustrous over the entire current density range. The leveling of the deposit was comparable to deposits from a commercial coumarin bath.

EXAMPLE 17

[0090] The panels from the above examples as well as other similar test panels which were plated with both semi-bright and bright nickel were evaluated for STEP. Generally, the results indicated that the deposits which were plated at lower pH values, e.g., 3.6 to 4.0 had STEP values around 50 to 80 mv. Those deposits plated at a pH of 4.4 to 4.6 had values of 110 to 145 mv.

[0091] Thus, it is seen that the semi-bright nickel plating baths described herein produce sulfur-free semi-bright deposits over a very wide current density range. The nickel plating baths described herein are the only non-coumarin semi-bright baths known to produce leveling equal to a full commercial coumarin bath. The baths also require no aldehydes to achieve STEP and, as a result, the deposit has extremely low stress and excellent ductility.

What is claimed is:

1. A nickel plating bath for plating a semi-bright nickel deposit on a substrate, the nickel plating bath comprising:

a) nickel ions;

b) a soluble salt of chloroacetic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid, and

c) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing,

wherein the nickel plating bath is substantially free of coumarin, substantially free of aldehydes and has a pH from 4.1 to 5.0.

2. The nickel plating bath as claimed in claim **1**, wherein the soluble salt is a sodium, potassium, lithium, magnesium or nickel salt of salicylic acid.

3. The nickel plating bath as claimed in claim **2**, wherein the soluble salt is sodium salicylate.

4. The nickel plating bath as claimed in claim **1**, wherein the concentration of the soluble salt in the nickel plating bath is between about 0.5 and about 20.0 g/l.

5. The nickel plating bath as claimed in claim **1**, wherein the plating bath also comprises an additive selected from the group consisting of ethoxylated (or propoxylated) butyne diol, ethoxylated (or propoxylated) hexyne diol, acetylenic alcohols, and ethoxylated (or propoxylated) acetylenic alcohols.

6. The nickel plating bath as claimed in claim **1**, wherein the at least one diol comprises both hexyne diol and butyne dial.

7. The nickel plating bath as claimed in claim **6**, wherein the concentration of hexyne diol in the nickel plating bath is in the range of 50 mg/L to 500 mg/L and the concentration of butyne diol is from 30 g/l to 300 mg/L.

8. The nickel plating bath as claimed in claim **7**, wherein the concentration of hexyne diol in the nickel plating bath is in the range of 100 mg/L to 200 mg/L and the concentration of butyne diol is from 60 mg/L to 120 mg/L.

9. The nickel plating bath according to claim **1**, wherein the plating bath has a pH between about 4.4 and about 4.6.

10. The nickel plating bath according to claim **1**, wherein the plating bath does not include coumarin or an aldehyde.

11. A method of plating a substrate to produce a sulfur-free semi-bright nickel deposit thereon, the method comprising the steps of:

a) providing a nickel plating bath comprising:
  i) nickel ions;
  ii) a soluble salt of chloroacetic acid, acetic acid, glycolic acid, proprionic acid, benzoic acid, salicylic acid or chlorobenzoic acid; and
  iii) at least one diol selected from the group consisting of hexyne diol, butyne diol and combinations of the foregoing; and
b) contacting the substrate with the nickel plating bath and applying electrical current to provide a semi-bright nickel deposit on the substrate,

wherein the nickel plating bath is substantially free of coumarin, substantially free of aldehydes, and has a pH from 4.1 to 5.0.

12. The method according to claim **11**, comprising the step of plating a bright nickel layer over the semi-bright nickel deposit.

13. The method according to claim **12**, wherein a simultaneous thickness and electrolytic potential (STEP) of the plated deposits is at least about 100 mv.

14. The method according to claim **13**, wherein the STEP of the plated deposits is between about 110 and about 145 mv.

15. The method according to claim **13**, wherein the STEP of the plated deposits is at least about 120 mv.

16. The method according to claim **11**, wherein the plating bath has a pH between about 4.4 and about 4.6.

17. The method according to claim **11**, wherein the plating bath does not include coumarin or an aldehyde.

18. The method according to claim **11**, wherein the stress of the deposit is less than about 15,000 psi tensile.

19. The method according to claim **18**, wherein the stress of the deposit is less than about 4,000 psi tensile.

20. The method according to claim **11**, wherein the ductility of the deposit, measured in accordance with the Chrysler ductility method, is at least about 0.4.

21. The method according to claim **20**, wherein the ductility of the deposit, measured in accordance with the Chrysler ductility method, is about 0.5.

22. The method according to claim **11**, wherein the soluble salt in the nickel plating bath is a sodium, potassium, lithium, magnesium or nickel salt of salicylic acid.

23. The method according to claim **22**, wherein the soluble salt is sodium salicylate.

24. The method according to claim **11**, wherein the concentration of the soluble salt in the nickel plating bath is between about 0.5 and about 20.0 g/L.

25. The method according to claim **11**, wherein the plating bath also comprises an additive selected from the group consisting of ethoxylated (or propoxylated) butyne diol, ethoxylated (or propoxylated) hexyne diol, acetylenic alcohols, and ethoxylated (or propoxylated) acetylenic alcohols.

26. The method according to claim **11**, wherein the at least one diol comprises both hexyne diol and butyne diol.

27. The method according to claim **26**, wherein the concentration of hexyne diol in the nickel plating bath is in the range of 50 mg/L to 500 mg/L and the concentration of butyne diol is from 30 g/l to 300 mg/L.

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