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(54) **Electroplating of low-stress nickel**

(57) Nickel and nickel alloys can be electroplated from an aqueous acidic solution containing nickel al-

kane sulfonic acid and a stress-reducing additive that imparts compressive stress to an electrodeposit. The electroplating bath is acidic with a pH of 0 to 5.

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Description**BACKGROUND**

The field of the invention relates to a bath for electroplating low-stress nickel to conductive substrates and processes utilizing such baths.

Many industries provide corrosion resistance, decorative finishes and electroformed coatings to conductive substrates by continuous or batch plating the substrates with nickel in an electroplating coating bath.

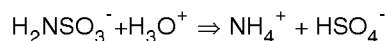
Nickel sulfamate baths are generally used when a low stress nickel coating is required, such as in electroforming applications, or where the nickel deposit will be subjected to external stress. Nickel sulfamate solutions are preferred over nickel sulfate solutions because (a) the mechanical properties of the sulfamate produced coating are superior to those formed from sulfate solutions, (b) high rates of deposition are possible from the sulfamate solution, and (c) the deposit quality is less affected by variations in pH and current density. However, several issues need to be addressed when a nickel sulfamate bath is used.

A typical nickel sulfamate solution contains nickel sulfamate (400 - 650 g/l), nickel chloride (5 - 20 g/l) and boric acid (30 - 40 g/l). The operating pH is between 3.5 - 4.5 and the temperature may vary from 35 - 50°C. Soluble nickel anodes are used to replenish the nickel which is plated on the cathode during electrolysis. Current density varies from 0.5 - 30 A/dm².

One of the issues with the use of a nickel sulfamate bath is stability of the sulfamate ion.

The sulfamate ion is stable in neutral or slightly alkaline solution even at elevated temperature. However, because of nickel hydroxide precipitation, these solutions are not used at a pH greater than 5.

Hydrolysis of the sulfamate ion may be a problem. The hydrolysis of sulfamate is generally characterized by the formation of ammonium ions and a bisulfate or sulfate anion:



The sulfamate hydrolysis reaction has been investigated and has been found to be at an increased rate at greater hydrogen ion concentrations (e.g., lower pHs). These investigators also found the sulfamate hydrolysis reaction increases with an increase in temperature of the electrolyte; thus nickel sulfamate solutions are commonly operated at lower temperatures than Watts type nickel plating solution.

The sulfamate ion also decomposes at the anode, for example, at insoluble anodes such as platinum and at passive nickel oxide electrodes. The decomposition of sulfamate appears to produce several intermediates such as sulfite, dithionate, azodisulfonate and another unknown species which may effect the quality of the electrodeposited coating.

It would be desirable to have baths other than nickel sulfamate from which to electrodeposit nickel.

When choosing a nickel solution from which to deposit a layer of nickel it is important to consider the resultant internal stress of the nickel coating. Stresses in nickel deposits range from -15,000 PSI (compressive) to about +100,000 PSI (tensile). A high tensile stress may lead to cracking of the nickel deposit particularly if the nickel is subjected to mechanical deformation (stresses and strains) or elevated temperatures. Nickel electroforms such as those produced from nickel sulfamate solutions may have warpage or change dimensions when the substrate is removed if the nickel is in a state of tensile stress. High tensile stresses may also lead to lower fatigue life of steels and aluminum alloys. Investigators have shown a twenty-two percent reduction in the fatigue life of high strength steels if the nickel is deposited in a compressive state but a fifty-nine percent reduction in fatigue life if the nickel is tensile stressed. Similarly, aluminum alloys plated with a nickel in a tensile stress exhibited a fifty-five percent reduction in fatigue life but only a ten percent reduction if the nickel was compressively stressed.

Organic additives are commonly added to nickel solutions to reduce the tensile stress of the deposits. The composition and concentration of the stress reducers is dependent upon the nature of the nickel electrolyte (e.g., nickel sulfate or nickel sulfamate). The effects of organic stress reducers on the internal stress of nickel deposits from a nickel sulfate solution has been examined. Additives which contain sulfur such as saccharin, naphthalene-1,5-disulfonic acid and naphthalene trisulfonic acid are effective stress reducers. Sulfur containing compounds and their influence on the internal stress in nickel coatings has also been studied. Sodium benzene sulfonate, benzene sulfonamide and sulfanilic acid reduce the internal stress but only benzene sulfonamide imparts a compressive stress. However, p-amino benzene sulfonamide causes the stress to become very tensile in nickel deposits plated from sulfate solutions.

An article by Kudryavtsev et al. entitled Nickel Electrodeposition from Methanesulfonic Acid-Based Bath, Proceedings of American Electroplaters, Surface Finishing, pages 837-841 (1996), compares electroplating nickel from a Ni (CH₃SO₃)₂, also designated, NiMSA, to electroplating from a nickel sulfamate bath.

Kudryavtsev et al. disclose that disadvantages of the sulfamate bath include (1) the sulfamate bath being chemically unstable (2) sulfamate starting to decompose at 60°C but the baths run at 45 to 60°C, and (3) the bath being very

sensitive to impurities of other metal ions, thus to prevent deterioration in coating quality, reduction in ductility and cathode current efficiency, the maximum Fe which can be present in the bath is 20 mg/L, maximum Cu is 10 mg/L, maximum Zn is 10 mg/L, maximum Pb is 2 mg/L and maximum Cr is 2 mg/L.

Kudryavtsev et al. disclose that the compositions they tested were comprised of $\text{Ni}(\text{CH}_3\text{SO}_3)_2$, 100 to 400 g/l; H_3BO_3 , 17 to 40 g/l; saccharin, .01 to 1.8 g/l; and sodium lauryl sulfate, .02 to 0.5 g; and that the electroplating process was at a pH of 0.8 to 2.0; temperature of 30 to 60°C; and a current density (CD) of 0.5 to 39 A/dm². However, there are problems with electroplating using the Kudryavtsev et al. disclosed composition. First, since sodium saccharin is extremely soluble in water but saccharic acid is not, saccharic acid begins to crystallize when the processing pH is <2 and particles of saccharic acid will be deposited with the electrodeposited nickel producing an unacceptable coating. Second, Kudryavtsev et al. disclose that the $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ composition tested resulted in a positive (tensile) internal stress and not the desired negative (compression) internal stress.

The general aim herein is to provide new and useful compositions and methods for electrodepositing nickel coatings; preferred aims include the reduction or elimination of one or more of the limitations and disadvantages of the known processes as discussed above. In particular a preferred aim is to avoid tensile stress in the coating.

As embodied and broadly described, the invention comprises a composition of matter which allows the use of nickel alkane sulfonic acid in an electrodepositing process to produce low-stress nickel coatings having compressive stress.

One embodiment of the invention is a composition of matter for producing low stress electrodepositing nickel coatings. The composition is an acidic aqueous electroplating bath comprising a nickel alkane sulfonic acid and a stress-reducing additive that imparts compressive stress to the coating.

Another embodiment of the present invention is a process for producing electrodeposited coatings by electroplating a cathodic conductive substrate in a coating bath having an anode inserted therein, the bath consists essentially of a nickel alkane sulfonic acid and a stress-reducing additive that imparts a compressive stress to the coating, maintaining the coating bath at a pH from about 0 to about 5; and maintaining the current density on the substrate at from about 1 to about 100 A/dm².

Another embodiment of the invention is a composition of matter for replenishing a spent electroplating bath for producing low stress electrodeposited nickel coatings, the spent bath initially containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (or other nickel alkane sulfonate) and a stress-reducing additive that imparts a compressive stress to the coating, the composition being a slurry comprising nickel carbonate and further said stress-reducing additive, e.g. an aromatic sulfonic acid.

We have found that processes and compositions as described herein can provide excellent nickel coatings on conductive substrates.

The description which follows sets forth additional features and advantages which may be used/achieved in the present procedures. The skilled artisan will realize the objectives and other advantages obtainable with the process and composition of matter particularly pointed out herein.

Preferred proportions, independently or combined, are as follows.

From about 50 to about 600 grams/liter, more preferably from about 150 to 450 grams/liter, of nickel alkane sulfonic acid.

From about 0.5 to 15 grams/liter, more preferably 5 to 10 grams/liter, of a stress reducing additive to impart a compressive stress to the electrodeposited coating.

From 0 to about 100 grams/liter, more preferably 20 to 40 grams/liter, of optional nickel halogen.

From 0 to about 60 grams/liter of optional buffer.

Nickel Alkane Sulfonic Acids

The nickel alkane sulfonic acids include sulfonic acids of the formula $(\text{R})(\text{SO}_3)_x$, where R and x are defined hereinafter.

The nickel alkane sulfonate comprises a water soluble compound by which it is meant that the compound is soluble in water at about room temperature (about 20°C) or lower (about 10°C to about 20°C), and preferably from these temperatures up to or slightly below the operating temperature of the bath, and preferably has the formula:



where

x has a value from 1 to about 3; and

y has a value from 1 to 2 so that y may be 1 when x is greater than 1.

R is an alkyl group having from 1 to about 15 carbon atoms and especially 1 to about 7 carbon atoms including the straight chain and branch chain isomers thereof such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, isobutyl, pentyl, isopentyl, and the like. Hydroxy substituted alkyls, as alkyl is defined herein, are also included. Specific nickel salts in this regard comprise nickel methane sulfonates, nickel ethane sulfonates, nickel propane sulfonates, nickel isopropane sulfonates, nickel butane sulfonates, nickel isobutane sulfonates, nickel t-butane sulfonates, nickel pentane sulfonates, nickel isopentane sulfonates, and the like, as well as the hydroxy substituted compounds thereof. R also includes cyclic, and heterocyclic hydrocarbon substituents such as cycloaliphatic, unsaturated cycloaliphatic, and aromatic groups having from 4 to about 16 carbon atoms and especially from about 6 to about 14 carbon atoms including cyclobutyl, cyclobutenyl, cyclohexyl, cyclohexenyl, cyclohexadienyl, cyclooctanyl, cyclooctadienyl.

The compound is present in sufficient quantity so that the concentration of Ni^{++} is preferably 25 to 135 g/l, more preferably 50 to 100 g/l, most preferably about 80 g/l.

Preferred for use in the bath of the present invention is nickel methane sulfonic acid - $\text{Ni}(\text{CH}_3\text{SO}_3)_2$.

Alloys of Nickel

The invention also includes depositing alloys of nickel as the nickel coating of the present invention, e.g. by employing alkane sulfonate salts of the alloying metals and nickel alkanesulfonates, where in formula (A), the alloying metal will be substituted for "Ni", "y" has a value of 1 up to the valence of the alloying metal, and "x" has the values given above.

Alloys of nickel may also be deposited employing alloying additives to the coating bath in lieu of or in addition to the sulfonate alloying compounds described herein. Any of the other Group IB, IIB, IIIA, IVA, IVB, VA, VB, VIB, VIIB or VIIIB metals may be used as alloying metals. Mixtures of alloying metals from Group VIII and/or Group IIB or Cr or Mn may also be prepared, especially the two component or three component alloys where the alloying metal is present in the coating in an amount anywhere from about 0.1 to about 20 percent by weight and especially from about 5 to about 15 percent by weight. Examples include NiZn, NiCr, NiFe, NiP, NiMn, NiSn and NiW.

The alloys are prepared by inserting the alloy metal into the coating baths either as an anode in a manner well known in the art or by adding a salt of the alloying metal to the coating bath.

Stress-Reducing Additive that Imparts Compressive Stress in Coating

A stress reducing additive that imparts a compressive stress to the electrodeposited coating is in the bath, usually at a concentration of 0.5 to 15 g/l, preferably 2 to 15 g/l, more preferably 5 to 10 g/l, and most preferably about 8 g/l. Usually the concentration of the additive will range from 5 to 20 % of the concentration of the nickel ion present in the bath.

Useful additives include those known as being useful in Watts and Sulfamate baths. Included are aromatic sulfonic acids e.g. in which the aromatic group of compound may be any six membered ring or polynuclear ring having from about 10 to about 14 carbon atoms, all of which are well known in the art. Anywhere from one to about three sulfonate groups can be substituted on the aromatic ring. Examples include aminobenzene sulfonic acid, benzene sulfonic acid, benzene disulfonic acid, naphthylamine disulfonic acid, naphthalene monosulfonic acid, naphthalene disulfonic acid, naphthalene trisulfonic acid, naphthol monosulfonic acid and p-toluene sulfonic acid.

Other useful stress reducing additives include benzene sulfamide, cysteine hydrochloride, saccharin (useful when the bath will be maintained at a $\text{pH} > 2$), p-toluene sulfonamide, thioacetamide, thiosemicarbazide and thiourea.

Preferred is naphthalene trisulfonic acid, especially 1,3,6-naphthalene trisulfonic acid.

Nickel Halogen

When soluble nickel anodes are used in the process, the bath preferably contains a nickel halogen, such as, for example, NiCl_2 or NiBr_2 . The nickel halogen aids in the dissolution of the soluble anode. The amount of nickel halogen is usually up to about 100 g/l, preferably 20 to 40 g/l.

Other Additives to the Bath

It is also within the scope of the invention to adjust the bath by the addition of other components known to those skilled in the art. Such other additives include, for example, 0 to about 60 g/l, preferably 35 to 45 g/l of buffers, such as boric acid and/or 0 to about 2 ml/l, preferably about 1 ml/l of a surfactant, for example, sodium lauryl sulfate, to reduce surface tension and prevent bubbling of hydrogen gas.

pH

Electrodeposition according to the process takes place at a pH from about 0 to about 5, preferably about 0.5 to about 4.5, and most preferably about pH 1 to 4.

Current Density

The composition and process typically operate at current densities from about 1 Amps/dm² to about 200 Amps/dm² and preferably from about 2 Amps/dm² to about 30 Amps/dm². In high speed plating such as on steel strip, the preferred current density is about 50 Amps/dm² to about 100 Amps/dm².

Temperature

The process usually proceeds at temperatures from about room temperature (20°C) to about 80°C, and preferably from about 30°C to about 70°C, and most preferably from about 40°C to about 60°C.

Agitation

In order to prevent "burning" of high current density areas and provide for more even temperature control of the solution, solution agitation may be employed. Air agitation, mechanical stirring, pumping, cathode rod and other means of solution agitation are all satisfactory. Additionally, the solutions may be operated without agitation.

In high speed plating such as on steel strip, the agitation of the bath preferably produces a flow rate of about 0.5 to 5 meters/sec.

Replenishing Composition

When the process utilizes an insoluble anode, eventually the bath solution will need to be replenished in order to have sufficient nickel present in the bath to enable the electrodeposition of low-stress nickel. A suitable composition for the replenishing the spent nickel alkane sulfonic acid and stress-reducing additive containing electroplating bath is a slurry comprising (a) nickel carbonate which replenishes the nickel and increases the pH of the bath, and (b) the stress reducing additive of the initial bath used to impart compressive stress to the electrodeposit.

The slurry usually will contain 0.5 to 10 g/l, preferably 1.5 to 5 g/l, of the stress reducing additive for every 1000 g/l of the nickel carbonate present in the slurry. However, the amount of the stress reducing additive will be dependent on the particular stress-reducing additive used in the slurry. For example, if 1,3,6-naphthalene trisulfonic acid is the stress reducing agent the amount will preferably be about 1 to 6 g/l, most preferably about 3 g/l per 1000 g/l of nickel carbonate.

The amount of slurry added to the bath will be based on the Amp hours to which the spend bath has been exposed and will be sufficient to maintain the amount of nickel in the bath at the concentration desired by the electroplater.

Anodes

The anodes useful in the process of the present invention include soluble anodes, such as, for example, nickel foil, and insoluble anodes, such as, for example, platinum and precious metal oxides.

The insoluble (inert) anodes used in this invention are insoluble (inert) in the electrolyte solution and consist of either a solid anodic metal or metal compound e.g., oxide, where the metals are of the Group IVB, VB, VIB, VIIB, VIIIB, and IB of the periodic table, or the anodes comprise the above-described metals or their alloys mounted on support materials including, for example, cheaper base metals from the Group IVB, VB, VIB, VIIB, and VIIIB metals and their alloys, e.g., stainless steels. A preferred anode metal compound is iridium dioxide (IrO₂). Alloy metals of IrO₂ are preferably the metals of Group VIB and VIIB, e.g, chromium, molybdenum, and nickel.

Insoluble anodes can be used to deposit any galvanic metal, in addition to nickel. The metals that can be deposited are known to those skilled in the art and include zinc, copper, lead, chromium, magnesium, tin, molybdenum and alloys thereof.

Substrate (cathode)

Electroplating proceeds in the manner described herein by electrolytically coating a conductive substrate with the composition of the invention, where the substrate (cathode) comprises any electrically conductive substrate or polymer substrate, or insulating substrate (e.g., a polymeric material, such as a synthetic polymeric substrate, or a ceramic

substrate) coated with a conductive material such as a metal or any art known conductive substrates such as a carbon substrate.

Although the examples describe the electroplating process as one that is conducted on a steel substrate, any conductive substrate may be employed whether a polymer, plastic, pure metal, a metal alloy, and includes other iron-alloy substrates or metals or alloys based on Groups IB, IIB, IIIA, IVA, IVB, VA, VB, VIB, VIIB or VIIIB metals and elements, the alloys comprising combinations of two or more of these metals and elements, especially the two or three or four component combinations of metals and elements.

Process

Coating proceeds by passing a current between the anode in the electrocoating bath to the cathode substrate in the bath for a period of time sufficient to deposit the desired nickel coating on the cathode.

The various numerical ranges describing the invention as set forth throughout the specification also include any combination of the lower end of the range with the higher end of the range set forth herein including, inter alia, ranges of concentrations of compounds, ratios of these compounds to one another, molecular weights, pH, current densities, temperatures, and the like, as well as all whole number and/or fractional number values and ranges encompassed within these ranges.

Example 1.

A bath was prepared containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (300 g/l) and 1,3,6-naphthalene trisulfonic acid (7.5 g/l). No nickel halogen or buffer was added.

The bath was employed to deposit a nickel coating on a steel plate using a 1 liter plating vessel with mild air agitation at 50°C. The anode was a piece of nickel foil. The average current density was about 4 amp per sq. dm. The pH of the bath at the start of plating was 3.5 and at the end of plating 2.1.

The deposition is carried out for 15 minutes to provide a coating 7 to 10 μm thick. The coating was smooth and semi-bright. The stress in the coating was -6000 PSI (compressive).

Example 2.

A bath was prepared containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (300 g/l); 1,3,6-naphthalene trisulfonic acid (7.5 g/l), NiCl_2 (40 g/l), and H_3BO_3 (45 g/l).

The bath was employed to deposit a nickel coating on a steel plate using a 1 liter plating vessel with mild air agitation at 50°C. The anode was a piece of nickel foil. The average current density was about 4 amp per sq. dm. The pH of the bath at the start of plating was 3.5 and at the end of plating 3.4.

The deposition was carried out for 15 minutes to provide a coating 9 to 12 μm thick. The coating was smooth and semi-bright. The stress was -5200 PSI (compressive).

Example 3.

A bath was prepared containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (300 g/l), sodium saccharin (1 g/l), NiCl_2 (40 g/l), and H_3BO_3 (45 g/l).

The bath was employed to deposit a nickel coating on a steel plate using a 1 liter plating vessel with mild air agitation at 50°C. The anode was a piece of nickel foil. The average current density was about 4 amp per sq. dm. The pH of the bath at the start of plating was 3.3 and at the end of plating 3.4.

The deposition was carried out for 30 minutes to provide a coating 19 to 23 μm thick. The coating was smooth and semi-bright. The stress was -2000 PSI compressive.

Example 4

A bath was prepared containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (300 g/l) and 1,3,6-naphthalene trisulfonic acid (7.5 g/l). The bath was employed to deposit a nickel coating on a steel plate using a 1 liter plating vessel with mild air agitation at 50°C. The anode was a piece of iridium oxide coated titanium. The average current density was about 4 amp per sq. dm. The pH of the bath at the start of plating was 1.8 and at the end of plating 1.7.

The deposition was carried out for 60 minutes to provide a coating 40 to 45 μm thick. The coating was smooth and semi-bright. The stress was -3200 PSI (compressive).

Example 5

A bath was prepared containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (300 g/l) and 1,3,6-naphthalene trisulfonic acid (7.5 g/l). The bath was employed to deposit a nickel coating on a steel plate using a 1 liter plating vessel with mild air agitation at 55°C. Two anodes were used, a soluble nickel foil and a piece of iridium oxide coated titanium. The average current density was about 5 amp per sq. dm. The pH of the bath at the start of plating was 2.0 and at the end of plating 1.8.

The deposition was carried out for 30 minutes to provide a coating 18 to 22 μm thick. The coating was smooth and semi-bright. The stress was -1500 PSI (compressive).

Example 6

A nickel methanesulfonate solution was prepared by dissolving 150 g/l NiCO_3 into 70% MSA. After complete dissolution of the nickel carbonate, this solution was filtered to remove any residual particulate matter. To this was added 30 g/l boric acid, 5 g/l naphthalenetrisulfonic acid. This solution was heated to 60°C to dissolve the boric acid. Upon cooling to room temperature, the pH was adjusted to 2.0 with 70% MSA.

A. A steel coupon was anodically cleaned in 50 g/l NaOH followed by water rinses. This was activated in 5% HCL, room temperature for five seconds. The steel was plated at 4 A/dm² for 15 minutes. The panel was bright and smooth. Cathode current efficiency was 89.3%.

B. To this solution was added 10 g/l Al_2O_3 (150 mesh), mixed. A second panel was pretreated as above and plated for 15 minutes. The panel was bright and semi-smooth. The cathode efficiency was 90.2%. Scanning electron microscopy showed co-deposition of the aluminum oxide particles in the nickel matrix.

Example 7

A nickel methanesulfonate solution was prepared by dissolving 150 g/l NiCO_3 into 70% MSA. After complete dissolution of the nickel carbonate, this solution was filtered to remove any residual particulate matter. To this was added 15 g/l nickel chloride, 30 g/l boric acid, 3 g/l naphthalene trisulfonic acid. This solution was heated to 60°C to dissolve the boric acid. Upon cooling to room temperature, the pH was adjusted to 3.2 with 70% MSA.

A. A steel panel was pretreated as above and plated in the solution. The panel was bright and smooth. Cathode current efficiency was 96%.

B. To this solution was added 2 g/l MoS_2 , molybdenum disulfide. This mixed for 10 minutes. A steel panel was pretreated as above and plated. The cathode efficiency was 94%. SEM analysis showed the presence of MoS_2 particles.

C. To a new nickel solution was added 2 g/l MoSi_2 . These particles were allowed to mix in the nickel solution for 10 minutes. A steel panel was cleaned as above and plated in this solution. SEM analysis confirmed the presence of MoSi_2 in the nickel coating.

Example 8

A 5% aqueous solution of sulfamic acid was prepared and the pH was adjusted to 3.0. A three electrode electrochemical setup was used to study the oxidation of the sulfamic acid. The counter-electrode was a IrO_2 grid. The reference electrode was silver/silver chloride. The working electrode was iridium-coated titanium. The potential of this system was scanned, starting from -0.2 V, in the anodic direction. A large oxidation peak was seen at +0.3 V.

A 5% MSA solution was prepared and the pH adjusted to 3.0 with sodium bicarbonate. The same three-electrode system was used in this study. No oxidation peak was observed at +0.3 V in this MSA solution.

Therefore, one can use insoluble anodes in the nickel methanesulfonate electrolyte and experience no degradation by-products. The use of insoluble anodes in the sulfamic acid solution will lead to breakdown products at the anode.

Comparative Example 1

A bath was prepared containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ (300 g/l) and sodium saccharin (1 g/l). No nickel halogen was used. The bath was employed to deposit a nickel coating on a steel plate using a 1 liter plating vessel with mild air agitation at 50°C. The anode was a piece of nickel foil. The average current density was about 4 amp per sq. dm. The pH of the bath at the start of plating was 3.3 and at the end of plating 1.7. A white precipitate was seen in the plating solution at the end plating. This is saccharic acid which precipitated due to the drop in pH.

The deposition was carried out for 30 minutes to provide a coating 17 to 23 μm thick. The coating was slightly rough and semi-bright. The stress was +4200 PSI tensile.

Comparative Examples 2 to 5

Five coatings of nickel electroplated from baths containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ were compared. Effects of H_3BO_3 , NiCl_2 , pH, CD and NTS (1,3,6-naphthalene trisulfonic acid) on stress are studied. All processes are operated at 60°C.

Summary of the Results

In absence of NTS, stress in all deposits were tensile. NTS is necessary to ensure compressive stress.

	Comparative Bath 2	Comparative Bath 3	Comparative Bath 4	Comparative bath of present invention 5	Comparative bath of present invention 6
$\text{Ni}(\text{CH}_3\text{SO}_3)_2$	300 g/l	300 g/l	300 g/l	300 g/l	300 g/l
NTS	no	no	no	7.5 g/l	7.5 g/l
NiCl_2	45 g/l	45 g/l	45 g/l	45 g/l	no
H_3BO_3	no	no	30 g/l	30 g/l	no
pH	4.5	1.2	1.47	1.47	1.21
<u>CD during process</u>	<u>Stress of coating</u>	<u>Stress of coating</u>	<u>Stress of coating</u>	<u>Stress of coating</u>	<u>Stress of coating</u>
4 Amp/dm ²	+17,344	+17,759	+20,115	-7,963	-7,543
8 Amp/dm ²	+37,890	+16,947	+20,529.	-7,445	-8,229
12 Amp/dm ²	+30,282	+21,298	+19,996	-7,824	-8,465
20 Amp/dm ²	+22,568	+25,078	+18,400	-9,335	-6,936
50 Amp/dm ²	+19,263	+16,272	burn	burn	+380 slight burn

Throughout the specification, the inventors refer to various materials used in their invention as based on certain components, and intend that they contain substantially these components, or that these components comprise at least the base components in these materials.

It will be apparent to those skilled in the art that various modifications and variations can be made to the composition and process of the invention without departing from the spirit or scope of the invention. It is intended that these modifications and variations of this invention are to be included as part of the invention.

Claims

1. A composition of matter for producing low stress electrodeposited nickel coatings, the composition being an acidic aqueous electroplating bath comprising

- a - a nickel alkane sulfonic acid,
- b- a stress-reducing additive that imparts compressive stress to the coating,
- c- optionally, a nickel halogen, and
- d- optionally, a buffer.

2. The composition of claim 1 wherein said nickel alkane sulfonic acid is present in a concentration from about 50 to about 600 gms/liter, said a stress-reducing additive is present in an amount from about 0.5 to about 15 gms/liter, said nickel halogen is present in an amount from 0 to about 100 gms/liter and said buffer is present in an amount from 0 to about 60 g/liter.

3. The composition of claim 1 wherein said nickel alkane sulfonic acid is present in a concentration from about 150 to about 300 gms/liter, said a stress-reducing additive is present in an amount from about 5 to about 10 gms/liter, said nickel halogen is present in an amount from 20 to about 40 gms/liter and said buffer is present in an amount from 35 to about 45 g/liter.

4. The composition of claim 1 wherein the stress-reducing additive is an aromatic sulfonic acid.
5. The composition of claim 1 wherein the nickel alkane sulfonic acid is nickel methane sulfonic acid and the stress-reducing additive is naphthalene trisulfonic acid.
6. The composition of claim 1, further comprising nickel halogen.
7. The composition of claim 6, wherein the nickel halogen is NiCl_2 .
8. A process for producing low-stress electrodeposited nickel coatings comprising:
electroplating a cathodic conductive substrate in a coating bath having an anode therein, the composition of said bath consisting essentially of:
 - a) a nickel alkane sulfonic acid;
 - b) a stress-reducing additive that imparts a compressive stress to the coating,
 - c) optionally, nickel halogen, and
 - d) optionally, a buffer;maintaining said coating composition at a pH from about 0 to about 5; and maintaining the current density on said substrate at from about 1 to about 200 A/dm^2 .
9. The process of claim 8 wherein said bath further comprises nickel halogen.
10. The process of claim 8 wherein the pH is maintained at from about 0.5 to about 2.0.
11. The process of claim 8 wherein said substrate comprises steel conduit.
12. The process of claim 8 wherein said substrate comprises steel wire.
13. The process of claim 8 wherein said substrate comprises flat steel.
14. The process of claim 8 wherein said nickel alkane sulfonic acid is present in a concentration from about 50 to about 600 gms/liter, said a stress-reducing additive is present in an amount from about 0.5 to about 15 gms/liter, said nickel halogen is present in an amount from 0 to about 100 gms/liter and said buffer is present in an amount from 0 to about 60 g/liter.
15. The process of claim 8 wherein said nickel alkane sulfonic acid is present in a concentration from about 150 to about 300 gms/liter, said a stress-reducing additive is present in an amount from about 5 to about 10 gms/liter, said nickel halogen is present in an amount from 20 to about 40 gms/liter and said buffer is present in an amount from 35 to about 45 g/liter.
16. The process of claim 8 wherein the nickel alkane sulfonic acid is nickel methane sulfonic acid and the stress-reducing additive is naphthalene trisulfonic acid.
17. The process of claim 8 wherein the nickel alkane sulfonic acid is nickel methane sulfonic acid and the stress-reducing additive is sodium saccharin and said composition is maintained at a pH above 2 to about 5.
18. A composition of matter for replenishing a spent electroplating bath containing $\text{Ni}(\text{CH}_3\text{SO}_3)_2$ and stress-reducing additive, the bath having been used for producing low-stress electrodeposited nickel coatings, the composition being a slurry comprising nickel carbonate and the stress reducing additive of the initial bath.
19. The composition of claim 18, wherein the slurry is comprised of 0.5 to 10 g/l of the stress reducing additive for every 1000 g/l of the nickel carbonate
20. The composition of claim 18, wherein the stress-reducing agent is an aromatic sulfonic acid.
21. A process for electrodeposition of a galvanic metal coating on to a conductive substrate in the presence of an

insoluble anode comprising immersing said anode and said substrate in an aqueous solution of a soluble alkanesulfonic acid or aromatic sulfonic acid salt of said galvanic metal, and passing an electrical current through said solution at a sufficient current density to deposit said galvanic metal on said substrate.

5 **22.** The process of claim 21 wherein said alkanesulfonic acid is methanesulfonic acid.

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