

Troubleshooting Electroplating Installations: Nickel Sulfamate Plating Systems

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The properties and behavior of nickel electrodeposits plated from a sulfamate solution are determined by many variables, including operating conditions, impurities in plating solutions composition, additives and others. Changes in operating variables such as solution temperature, current density, agitation or current form can change hardness, internal stress and crystalline structure. Changes in process chemistry such as nickel concentration, boric acid, chlorides and brightener system can produce minor or remarkable changes in the deposit; others have little influence. Characteristics of electrodeposits from nickel-sulfamate plating solutions resulting from these changes are discussed here. The mechanism of anodic reactions resulting in the decomposition of sulfamate ions is detailed. Testing and troubleshooting information is also provided, along with an up-to-date bibliography.

Introduction

In the last 50 years, nickel sulfamate solutions have been used extensively in electroforming and in electroplating for engineering applications. The properties of the deposits or the operating factors that make those baths attractive are low residual stress, high deposition rates and good ductility. In these respects, sulfamate baths are generally regarded as being superior to the conventional Watts bath. For decorative deposits, however, both bright and dull, the Watts bath has continued to be favored, because of the enormous background of practical operating experience with it.

The characteristics and properties of sulfamate nickel deposits that are influenced by plating conditions and impurities are numerous. They include ductility, hardness, tensile strength, intrinsic stress, deposit structure, porosity, smoothness, density, specific heat, coefficient of expansion, thermal conductivity, specific resistivity and modulus of elasticity.

Nuts & Bolts: What This Paper Means to You

This paper covers sulfamate nickel plating from top to bottom and offers a troubleshooting guide to operating the process. The information here is indispensable to those performing electroforming or heavy nickel plating.

High-speed nickel electroforming in general, and sulfamate baths in particular, have become popular as micro-electroforming techniques for the manufacture of micro-systems technologies. A knowledge of the effects of impurities, and alloying metals such as cobalt, are important to the successful use of nickel sulfamate plating solutions.

Solution Composition & Operating Conditions

Addition agents and impurities have a profound effect on deposit characteristics as is to be expected. Changes in solution composition, operating temperature, current density, solution agitation, can also alter the deposit characteristics. Table 1 presents a typical solution composition and operating conditions while Table 2 gives the mechanical properties of sulfamate nickel deposits from various common bath formulations.¹

It should be noted that the compositions shown in Table 2 are used for special purposes. In the concentrated sulfamate solution, extremely high rates of deposition are possible with current densities up to 40 A/dm² (372 A/ft²) without high agitation. For a given plating rate in this bath, the internal stress decreases rapidly with increasing temperature.

It has been reported that when operating above 40 A/dm² (372 A/ft²), 300 g/L (40 oz/gal) baths can produce brittle deposits.² To avoid this, a more concentrated bath (675 g/L; 90 oz/gal) is used, with a higher temperature of 71°C (160°F) and an increased anode area to minimize anode sludge formation.

Function of Bath Ingredients

Nickel. Nickel sulfamate is the source of the nickel metal. Concentrations of 90 to 135 g/L (12 to 18 oz/gal) of nickel metal are used in most cases for high-speed plating, when coupled with very high solution agitation. Current densities of 43 to 430 A/dm² (400 to 4000 A/ft²) have been used. High metal content is also used to improve throwing power at very low current densities of 0.1 to 0.4 A/dm² (0.9 to 3.7 A/ft²). High metal content does not appreciably change the characteristics or properties of the deposit. Low metal content coupled with moderate to high current densities will cause deposition of basic nickel salts (i.e., "burning").

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Table 1
Typical Solution Composition & Operating Conditions

Nickel, as metal.....	75 g/L (10 oz/gal)
Boric acid.....	45 g/L (6 oz/gal)
Chloride.....	2.2 g/L (0.3 oz/gal)
Wetting agent.....	0.1 - 0.3 vol%
Brightener / stress reducer.....	Optional
Temperature.....	49°C (120°F)
Cathode current density.....	0.5 - 21.0 A/dm ² (4.6 - 195.0 A/ft ²)
Cathode current efficiency.....	99.0 - 99.9% (for S-depolarized anodes)
Specific gravity.....	1.23 - 1.28
pH.....	4.0

Boric acid. Its concentration should vary with operating temperature from 30 g/L (4.0 oz/gal) at ambient temperature to over 45 g/L (6.0 oz/gal) at 52°C (125°F). Low boric acid can cause “orange peel” type of pitting. High boric acid will tend to salt-out of solution at lower temperatures. Once crystallized (salted out), it is difficult to redissolve. About 30 g/L (4.0 oz/gal) boric acid will remain in solution at 20°C (68°F). The lowest practical operating temperature for current densities over 16 A/dm² (149 A/ft²) is 32°C (90°F).

High current densities and/or low temperatures can cause familiar “burning.” Lower nickel contents (below 75 g/L; 10 oz/gal) require higher amounts of boric acid.

Chlorides/bromides. Chlorides or bromides are used in small amounts and are useful in promoting optimum anode corrosion. Poor anode corrosion results in compressive stress, brightness, loss of ductility, increased hardness and increased porosity. The addition of small amounts of chlorides to the plating solution slightly increases the tensile stress of the deposit, a trade-off that serves the purpose. For most applications, the increased stress is too small to cause any problem such as distortion of an electroformed product. Others have found that for low or moderate current densities, chloride is not necessary if sulfur-depolarized anodes are used with sufficient anode area.

Traditionally, electroplaters and electroformers prefer faster deposition rates and higher cathode current densities of at least 4 A/dm² (37 A/ft²). Since the anode/cathode ratio is seldom larger than one-to-one, in order to plate fast, the chloride concentration is raised to 8 to 10 g/L (1.0 to 1.3 oz/gal) to avoid anode polarization, the precursor of sulfamate decomposition. In turn, one needs to add stress reducers to counter the influence of the higher chlorides. True high-speed plating achievable at the levels obtained with a Watts bath is often impractical with sulfamate solutions.

Influence of Processing Variables

pH. The acidity of the bath can also affect deposit stress. A solution with 76.5 g/L (10.2 oz/gal) of nickel yields the lowest stress at pH 3.8 to 4.8.

A solution with 107 g/L (14.3 oz/gal) of nickel yields its lowest stress at pH 2.9 to 3.8. The stress increases rapidly at pH values above 5.0 because of the codeposition of basic nickel salts.

Hardness is affected by pH as with other nickel plating solutions. As pH rises, it is fairly constant up to a critical value of about 5.0, above which it rises sharply. A pH below 3.5 reduces the cathode efficiency, slows the plating rate slightly, but does not change the deposit hardness.

For rack plating, the standard pH is 4.0. At this value, iron contaminants cannot remain in solution. Iron precipitates as ferric hydroxide and is picked up in the filter. Deposit characteristics such as ductility remain good. Above pH 5.0, hardness increases and ductility decreases through codeposition of small amounts of basic nickel salts. For low current density purification (dumming), a low pH (3.0 to 3.5) favors the removal of metallic impurities.

Barrel plating must be done at a pH between 3.2 and 3.5 to prevent laminated deposits arising from the making-and-breaking of electrical contact as the barrel rotates. Low pH also results in faster accumulation of impurities.

Temperature. The influence of temperature on hardness is a parabolic function. As it is increased or decreased from 39°C (102°F), the hardness of the deposit is increased, the increase

Table 2
Mechanical Properties of 127 µm (5 mil) or Thicker Sulfamate Nickel Deposits¹

Type of Bath	Tensile Strength	Hardness Vickers	Elongation (% in 2 in.)	Internal Stress
Electroforming 43°C (110°F), pH 4	483 MPa (70,000 lb/in. ²)	200	20	27.6 MPa (4,000 lb/in.)
Sulfamate (conventional) 60°C (140°F), pH 4 5.4 A/dm ² (50 A/ft ²)	621 MPa (90,000 lb/in. ²)	200	25	27.6 MPa (4,000 lb/in. ²)
Sulfamate (concentrated) 60°C (140°F), pH 4 22 A/dm ² (200 A/ft ²)	483 MPa (70,000 lb/in. ²)	170	25	27.6 MPa (4,000 lb/in. ²)
Sulfamate (hard) 54°C (130°F), pH 5 6.4 A/dm ² (60 A/ft ²)	896 MPa (130,000 lb/in. ²)	470	10	-34.5 MPa (-5,000 lb/in. ²) (compressive)

being more rapid at lower temperatures.^{3,4} Hardness is not appreciably affected between 35 and 50°C (95 and 126°F). Stress has a pronounced minimum at 50°C (126°F) with a value of about 13.8 MPa (2000 lb/in²), in tensile,³ increasing uniformly above and below 50°C (126°F).

Current density. Within normal operating limits, current density and temperature have little effect on the hardness and the structure of the deposits. On the other hand, current density has varying effects on stress. It may fluctuate from compressive to tensile, and the properties and characteristics of the deposit are also affected by current density.⁵ Increasing current density causes a minor increase in tensile stress in chloride free baths. Ductility decreases rapidly with increasing temperature. In sulfate/chloride baths, as the current density is increased, stress increases at an even rate. As the nickel sulfamate concentration is raised from 300 to 700 g/L (40 to 93 oz/gal), the maximum plating rate, without burning, passes through a maximum and the deposit stress passes through a minimum.⁶

Impurities

Impurities in all plating solutions can cause changes in the deposit characteristics. Some can have a dramatic effect. The nickel-sulfamate formulations have found favor in electroforming where their ability to control internal stresses is particularly useful. Since stress is so critically important in these applications, the effects of various impurities on stress will be discussed next. Limiting concentrations of impurities are summarized in Table 3.⁷⁻¹⁰

Metallic Impurities

Chromium. Chromium is a very harmful impurity in either hexavalent or trivalent form. As little as 3 ppm of hexavalent or 8 ppm of trivalent chromium can cause tensile stress so high as to cause cracking, dark deposits, peeling and low cathode current efficiency. Trivalent chromium can cause pitting. Chromium can be removed using a high pH treatment.¹¹

Copper. Copper has little effect on stress or ductility, but it can give an unsatisfactory appearance. Adhesion can be affected with as little as 8 ppm of copper when there is a delay in starting the current. Copper as high as 40 ppm has been tolerated when the parts are introduced into solution with live entry. Copper causes dark deposits in low current density areas. It is introduced from the dissolution of buss bars, contacts and racking material or from impure salts and anodes. Copper is removed by low current density dummyming at 0.5 A/dm² (4.6 A/ft²).

Iron. Iron concentrations of 5 to 10 ppm reduce the ductility of the deposit. It usually comes from dissolved basis metal, improper rinsing or drag-in. Iron can cause roughness, pitting and dark deposits. It can be removed using a high pH treatment.¹¹ Nickel-sulfamate solutions, which operate at pH values above 4.0, will not sustain iron in the solution. As iron is oxidized at the anodes, ferric hydroxide will precipitate and is removed by filtration. For that reason among others, continuous filtration is necessary.

Lead. The presence of lead in the deposit increases tensile stress but not nearly as much as some other impurities. However,

Table 3
Limiting Concentrations of Impurities
in Nickel-Sulfamate Solutions

Impurity	Concentrations (ppm)				
	Literature Source	Schneck ⁷	Marty ⁸	Lowenheim ⁹	Safranek ¹⁰
Aluminum		6	---	---	---
Ammonium		500	500	N. I.*	---
Cadmium		---	---	---	1000
Calcium		1000	1000	---	4000
Chromium (III)		8	1	N. I.	10
Chromium (VI)		2	1	3	80
Cobalt		125	125	---	7000
Copper		200	200	5	1000
Iron		200	300	N. I.	900
Lead		10	10	---	600
Magnesium		100	100	---	5000
Manganese		200	200	---	700
Nitrates		5	5	N. I.	500
Organics		N. I.	---	N. I.	---
Phosphates		5	5	N. I.	500
Potassium		400	400	---	---
Sodium		3000	3000	---	1000
Solids		N. I.	---	---	---
Silver		N. I.	N. I.	---	---
Sulfates		1000	1000	---	---
Sulfur		5	5	---	---
Tin		2	2	N. I.	---
Zinc		150	150	20	---

* "N. I." (Not Indicated) is used to show that the impurity is mentioned for its harmful effects, but no quantitative levels have been published in the literature.

lead causes dark deposits in low current density areas. Since lead deposits preferentially at 0.26 to 0.32 A/dm² (2.0 to 3.0 A/ft²), it is easily removed by dummyming at low current density (0.2 A/dm²; 1.8 A/ft²).

Magnesium. Magnesium may be introduced into a nickel-sulfamate solution from nickel salts, anodes, water and other chemical additions. In some cases, it is added intentionally. Recent studies¹² have shown that up to about 2.5 g/L (0.33 oz/gal) of magnesium has very little effect on the internal stress or ductility of the nickel deposit. For the range studied an increase in the tensile stress of about 7 MPa (1020 lb/in.²) was observed. These recent studies show that the influence of magnesium is in close agreement with the other alkaline earth and alkali metals. These ions have very little effect on the hardness of the nickel deposit. Sodium has the greatest effect on hardness with only a slight decrease.

Sodium. In relatively large amounts, sodium will affect the deposit. The limit is 30 g/L (4.0 oz/gal) and when in excess sodium can cause brittleness. It arises from water, impure anodes, plating salts or the use of caustic soda to raise pH. The latter should be avoided. There is no known removal method.

Tin. Stannous tin, (Sn⁺²), has little effect in low concentrations. Stannic tin, (Sn⁺⁴) can cause high tensile stress.

Zinc. When zinc is present in the deposit it increases tensile stress slightly (less than lead). Zinc in small amounts (50-150 ppm) is not harmful.¹³ In higher concentrations it causes burning, peeling and dark streaked deposits, which are brittle. Zinc also lowers

Table 4
Troubleshooting Guide for Sulfamate Nickel Plating

Problem	Cause	Remedy
Roughness	<ol style="list-style-type: none"> 1. Suspended matter or filter aid, anode sludge, etc. 2. Iron hydrate. 	<ol style="list-style-type: none"> 1. Improve filtration; check for torn anode bags. 2. High pH & H₂O₂ treatment; filter and lower pH.
Pitting	<ol style="list-style-type: none"> 1. Organic contamination. 2. High pH. 3. Iron present. 4. Low boric acid. 5. Other metal contamination. 6. Dissolved air in the bath. 	<ol style="list-style-type: none"> 1. Carbon treat and filter. 2. Lower pH with sulfamic acid. 3. High pH & H₂O₂ treatment; filter and lower pH. 4. Add boric acid. 5. Low CD electrolysis (“dummying”). 6. Check system for leaks.
Burning	<ol style="list-style-type: none"> 1. Low boric acid. 2. Insufficient agitation. 3. Low metal content. 4. Current density too high. 5. Iron present. 	<ol style="list-style-type: none"> 1. Add boric acid. 2. Increase agitation rate; raise temperature. 3. Add Sulfamate nickel concentrate. 4. Decrease current. 5. High pH & H₂O₂ treatment; filter and lower pH.
Dark Plate	<ol style="list-style-type: none"> 1. Cu, Zn, Pb, etc. 2. Iron present. 3. Low pH or boric acid 	<ol style="list-style-type: none"> 1. LCD dummy. 2. High pH & H₂O₂ treatment; filter and lower pH. 3. Raise pH with NiCO₃; and/or add boric acid.
Poor Adhesion	<ol style="list-style-type: none"> 1. Poor cleaning. 2. Chromium present. 	<ol style="list-style-type: none"> 1. Improve cleaning cycle 2. High pH & H₂O₂ treatment; filter and lower pH.
Low Anode Current Efficiency	<ol style="list-style-type: none"> 1. Wrong type of anodes. 2. Poor anode-to-cathode area ratio. 3. Polarized anodes. 	<ol style="list-style-type: none"> 1. Use SD anodes or increase chloride / bromide content. 2. Maintain adequate anode area. 3. Lower CD, increase A:C area ratio and add chloride / bromide.
Low Cathode Current Efficiency	<ol style="list-style-type: none"> 1. Low pH. 2. Chromium contamination 3. Metallic contamination. 4. High hydroxide peroxide. 5. Nitrates present. 	<ol style="list-style-type: none"> 1. Raise pH with NiCO₃. 2. High pH & H₂O₂ treatment; filter and lower pH. 3. LCD dummy; heat to 150°F (66°C) until removed. 4. No practical remedy available. 5. No practical remedy available.
Brittleness	<ol style="list-style-type: none"> 1. Organic contaminations 2. Metallic contamination. 3. High pH. 4. Low boric acid. 	<ol style="list-style-type: none"> 1. Carbon treatment. 2. LCD dummy. 3. Lower pH with sulfamic acid. 4. Add boric acid.
Poor Throwing Power	<ol style="list-style-type: none"> 1. Low pH. 2. Low temperature. 3. Low boric acid. 4. Low nickel metal content. 5. Metallic contamination. 6. Poor electrical contacts. 	<ol style="list-style-type: none"> 1. Raise pH with NiCO₃. 2. Raise temperature. 3. Add boric acid. 4. Add Sulfamate nickel concentrate. 5. LCD dummy. 6. Check connections, clean and secure.
High Tensile Stress	<ol style="list-style-type: none"> 1. Inorganic contamination. 	<ol style="list-style-type: none"> 1. LCD electrolyze at 0.3 to 0.5 A/dm² (~3 to 5 A/ft²) on large corrugated dummy cathode.
Compressive Stress	<ol style="list-style-type: none"> 1. Sulfur contamination; anode phenomenon. 	<ol style="list-style-type: none"> 1. Electrolyze at 8 to 32 A/dm² (75 to 100 A/ft²) using A:C area ratio of about 15:1 at pH 2.4

cathode efficiency. It can be removed by electrolytic purification at 0.26 to 0.32 A/dm² (2.0 to 3.0 A/ft²). Its upper limit is about 0.15 g/L. Zinc generally originates from impure plating materials and basis metal.

Manganese. When manganese is present in small amounts, it decreases the stress to a small extent. It originates from impure salts or anodes or from residues remaining from potassium permanganate treatments. It is removed by low current density dummyming.

Despite of difficulties of depositing manganese in appreciable amounts, it can be codeposited in small amounts of less than 1% from simple acid baths, such as Watts or nickel-sulfamate plating solutions.¹⁴⁻¹⁷ The sulfur present in organic stress reducing agents such as saccharin can be incorporated into unalloyed nickel deposits and will cause embrittlement upon exposure to temperatures higher than 200°C (392°F). Manganese, which can preferentially combine with sulfur during heat treatment, can prevent the diffusion of sulfur into grain boundaries. Nickel-sulfide can thus form and improve the high-temperature ductility of the electrodeposited nickel.

Cobalt. Cobalt is added to control tensile strength and hardness. In significant quantities however, it will increase tensile stress at a rapidly increasing linear rate.¹⁸ Trace amounts of cobalt have little effect. The limit is about 0.1 g/L. Noticeable changes start to occur at about 1% of the nickel concentration, typically at about 7 g/L. There is potential merit in using cobalt as a hardening agent rather than conventional sulfur-bearing organic compounds. The nickel-cobalt alloy deposits, unlike nickel deposits containing incorporated sulfur, do not embrittle on heating. Heat treatment at 204°C (400°F) increase the strength and ductility of the nickel-cobalt alloy, possibly via the reduction of internal stresses around grain boundaries.¹⁹

The effects of temperature, pH, current density and boric acid on nickel-cobalt alloys were reported by Barrett.²⁰ Of primary interest was the effect of current densities in the range from 25 to 75 A/dm² (2.7 to 8.1 A/ft²) on alloy composition and the effect of cobalt concentration on tensile properties. Current density influences nickel-cobalt alloys with higher cobalt content and agitation, which in turn are influenced by the concentration polarization of Co⁺² ions.^{21,26} The alloy content is also influenced by agitation and the relative concentrations of nickel and cobalt.

Impurities may preferentially deposit at different current densities. Consequently, the effect will be different at different current densities. Impurities such as lead, that codeposit at very low current densities may have little or no effect at high current densities.²⁶ Smith, et al.²³ verify the importance of assuring the quality of sulfamate salts.

Non-metallic Impurities

Ammonium. Ammonium ions can increase the tensile stress and lower the ductility of the deposit.²⁴ Ammonia is present in even the best grades of sulfamic acid used to manufacture sulfamate nickel plating solutions. In addition, if the temperature is too high or the pH is too low during manufacture, more ammonia can be generated. Ammonia is generated in a plating solution at high temperatures, (above 63°C; 145°F) and at low pH, less than 2.2, by hydrolysis of sulfamic acid. Increased ammonia increases the affected current density range and tendency for pitting.²⁵ At concentrations below 500 ppm, ammonia seems to have little effect. At or above 500 ppm, a dark area is noted that begins to form at a current density of 2.2 A/dm² (24 A/ft²). Ductility is mostly affected in a narrow range of current densities around 2.2 A/dm² (24 A/ft²). However, at higher or lower current densities, the loss of ductility is very small if at all. At 2500 ppm of ammonia and 3.2 A/dm² (30 A/ft²),

there is only a small loss of ductility. At mixed current densities, as would be found in barrel plating, the effect is minimal. At high current densities, such as in wire plating, high ammonium can cause a more porous and brittle deposit.

Halogens. All halogens will increase tensile stress. Bromides and chlorides act the least, with fluorides next. Iodides are the most harmful in this regard. Precipitation with silver sulfate might be successful, but is expensive. Silver halogens can be reclaimed by regeneration to silver sulfate with sulfuric acid.

Nitrates. Nitrates cause a drastic increase in stress. The limit is 0.3 g/L. They should be avoided entirely, since there is no known method of removal.

Sulfur. The presence of sulfur in the deposit causes compressive stress and an increase in brightness. Divalent sulfur causes the most dramatic effects. High compressive stresses, brittle deposits and loss of ductility are all the result of even a small amount of sulfur (24 ppm) in the deposits.

Only with sulfur in its higher oxidation state, as sulfate, does it have no effect on stress. Organic sulfur-bearing compounds, where sulfur is lower than the S⁺⁶ state, (e.g., saccharin) are added deliberately to change the stress from tensile to compressive. Compressively stressed deposits increase the fatigue life of the basis metal. Heating the deposit to 316°C (600°F) reverts the stress to tensile.

However, monitoring the sulfate in the plating solution gives an idea of the amount of hydrolysis which may have taken place over time, or either through low pH or high temperature. Monitoring sulfate is meaningful only when there is no drag-in of sulfate such as from a sulfuric acid or sulfate containing pre-plate solutions.

Organic addition agents. Organics can alter the deposit characteristics profoundly. Examples include a long list of proprietary brighteners designed to be used in bright nickel plating solutions.²⁶ Primary brighteners can cause compressive stress, loss of ductility and loss of heat resistance. Secondary brighteners cause tensile stress and loss of ductility. It is possible to balance the two types of brighteners to achieve virtually zero stress. However, the result will be a more brittle deposit much like that from bright Watts solutions. The advantages they bring are grain refinement and smoother deposits.

Saccharin and similar compounds act like primary brighteners. Brighteners considerably harden the deposit. Proprietary products containing similar compounds also contain other organic compounds that impart hardness. The breakdown products are more easily handled and stabilized. Removal is accomplished by a series of carbon/hydrogen peroxide treatments.¹¹

Surfactants. Surfactants are often used in sulfamate nickel solutions. Careful selection with a very low level of impurities is essential for best results. Appropriate surfactants have virtually no effect on the deposit properties, if used in the proper ranges.

Anodes & Anodic Reactions

For any soluble plating anode to perform adequately it should meet, among others, the following characteristics:

- It should dissolve (corrode) uniformly with high current efficiency,
- It should have low polarization, and
- It should not introduce into solution any new compound that will adversely effect the deposits.

The anodes used in sulfamate baths typically consist of nickel to which has been added a low amount of sulfur (e.g., 0.02 %) to promote dissolution. However, in the absence of chlorides, nickel anodes tend to form resistive passive films on their surfaces.^{27,28} Highly positive anodic potentials generally associated with high

speed nickel plating tend to increase this passivity, resulting in increased applied bath voltage, power costs,²⁹ and decreased nickel metal concentration. In addition, unwanted changes in the pH can induce possible decomposition of sulfamate ion.

To minimize these problems, halide ions are usually added to the plating bath to promote anode dissolution by destabilizing the passive film on its surface. However, stress can be effected. Tsuru, et al.³⁰ recently discussed the effects of chlorides, bromides and iodides on stress. Chloride or bromide ions tend to decrease the deposit tensile stress slightly.^{18,24} Conversely, iodide ion at the same concentration tends somewhat to increase it.³¹ When adding halides, one must take into account not only the reduction of anode passivity, but also the tensile stress in the deposits. In nickel-sulfamate plating, anodes should be the sulfur-depolarized type.²⁶ Using the wrong anode, exhibiting a higher oxidation potential, could lead to decomposition of the sulfamate. In turn, this would lead to the formation of a divalent sulfur product which could codeposit causing an increase in brittleness. Compressive stress could result with a concomitant increase in hardness. High chloride (25 g/L; 3.3 oz/gal) will minimize this effect.

Anodes should be contained in titanium baskets,^{11,32,33} which should be double bagged using polypropylene bags. Bags should be removed and cleaned periodically to assure free solution flow through them. Particulate materials are retained in the bags and prevented from entering the plating solution where they would cause roughness. Symptoms of poor anode corrosion are increased brightness, loss of ductility, increased hardness, compressive stress and increased porosity.

In some operations where insoluble anodes must be used, an anode phenomenon may occur whereby sulfur is produced and codeposited on cathode, thereby increasing brightness and yielding harder more highly stressed deposits. The deposit will become brittle, and deteriorate further on heating to 240°C (394°F).

Anodic decomposition products of sulfamate ions have been known to exert significant effects on the quality of electroformed nickel deposits. Compared with Watts nickel plating solutions, the anodic behavior of sulfamate based solutions is more complex. Klingenmaier³⁴ reported that an oxidation product, which decreased tensile stress and increased the sulfur content, was formed during anodic polarization. Marti⁸ noticed a similar phenomenon in a nickel sulfamate bath with passive or insoluble anodes and suspected that it was the effect of sulfite, produced during anodic decomposition. Greene³⁵ detected the product of the anodic reactions as an azodisulfonate ($\text{SO}_3\text{N}=\text{NSO}_3$), which affects the deposit in a manner similar to other sulfur-containing additives, i.e., decreasing the stress and increasing the sulfur content. The effect of sulfur is also influenced by the usual variables, pH, current density and agitation. This explanation has been well accepted.^{9,26} Kendrick³⁶ and Kendrick and Watson³⁷ claimed that the decomposition reaction was different at a passivated nickel anode than that at the platinum electrode. Although the tensile stress of the deposit was decreased in both cases, the sulfur content was only increased with the platinum anode.

L. Jiazhu, et al³⁸ detected hydrazine-disulfonate and dithionate in the anodic decomposition products. In later work, Zhang and Park³⁹ separated decomposition products and they identified the unknown substance as diimide S-sulfonate ($\text{H}_2\text{N}=\text{N-S-O}_3$).

Table 5
Variables Affecting Mechanical Properties of Sulfamate Nickel Deposits

Property	Operating Conditions	Solution Conditions
Tensile strength	<ul style="list-style-type: none"> •Decreases with increasing temperature to 49°C (120°F), then increases slowly with further temperature increases •Increases with increasing pH and decreasing CD. 	<ul style="list-style-type: none"> •Decreases slightly with increasing nickel content. •Increases slightly with increasing chloride content.
Elongation	<ul style="list-style-type: none"> •Decreases as temperature varies in either direction from 43°C (110°F) •Decreases with increasing pH. •Increases moderately with increasing cathode current density. 	<ul style="list-style-type: none"> •Increases slightly with increasing nickel concentration.
Hardness	<ul style="list-style-type: none"> •Increases with increasing solution temperature within suggested operating range. •Increases with increasing pH. •Reaches a minimum at about 13 A/dm² (120 A/ft²). 	<ul style="list-style-type: none"> •Decreases slightly with increasing nickel concentration. •Increases slightly with increasing chloride content.
Internal stress	<ul style="list-style-type: none"> •Decreases with increasing solution temperature. •Reaches a minimum at pH 4.0-4.2. •Increases with increasing cathode current density. 	<ul style="list-style-type: none"> •Relatively independent of nickel content within suggested range. •Increases significantly with increasing chloride content.

The sulfamate ions can hydrolyze under certain conditions introducing detrimental ammonium bisulfate.⁴⁰ The rate of hydrolysis is a function of concentration, temperature and pH. Hydrolysis takes place very slowly in the plating solution when operated normally. However, local overheating, and very high and localized anode current densities, with an accompanying drop in pH can set the stage for runaway hydrolysis.

Stress & Stress Control

Residual stress is a term used to describe the inherent force present in an electrodeposited layer of metal that is free of external force or temperature gradient. Platers are usually concerned with tensile stress, as the compressive stress is more often than not beneficial except under some extremely critical conditions.

If a highly stressed deposit is plated on a rigid object and it is unable to relieve stress by distorting the basis metal, poor adhesion or blisters may result, or cracks may form in the deposit. The nickel-sulfamate solution has found favor in electroforming where the ability to control internal stresses is particularly useful. Two other electroforming processes, iron and copper, can have limitations which a nickel electroform can often overcome.

Internal stress-reducers that contain sulfur may be divided into two groups, according to their chemical behavior in the nickel plating solutions. First, there are compounds capable of providing traces of sulfur in electrodeposited nickel without causing a detectable accumulation of the corresponding decomposition products. Examples are 1,3,6-naphthalenetrisulfonic acid (NTSA) and paratoluene sulfonamide (TSA). Sulfur deposition by NTSA and TSA generates, respectively, naphthalene and toluene as byproducts of the cathodic reaction.⁴¹

In the second group is saccharin (benzoic acid sulfimide). The cathode reaction has been recognized as having several alternate paths. Each of these reaction paths results in detectable levels of organic compounds delivered to the plating solution. According to a comprehensive study,⁴¹ saccharin is one of the most effective and universal stress-reducing agents. Not only is it capable of influencing internal stress at levels much lower than NTSA and TSA, but it exceeds these compounds in versatility as well. At higher current densities in certain baths (e.g., nickel-cobalt), saccharin is the only known internal stress-reducing agent available. High-Performance Liquid Chromatography (HPLC) can be used to monitor both saccharin and its decomposition products.

At the low current densities (0.8 to 1.6 A/dm²; 7.4 to 14.8 A/ft²) used to obtain adequate throwing power in electroforming, zero or even slightly compressive stresses can sometimes be obtained from nickel sulfamate baths without organic stress reducers. However, this is only in the absence or near absence of chlorides. Such baths will have far from optimum plating speed and will not adequately dissolve the anodes. Unlike properly functioning wetting agents, which are subject to drag-out losses only, stress reducers enter the deposit, possibly after partial decomposition and recombination. Brighteners and levelers enter the deposit in a similar manner. Most stress reducers are minor or secondary brighteners and refine the grain of the nickel. Saccharin also has the advantage of not only hardening but also of improving the ductility of the deposit under most conditions.

Stress reducers act in proportion to quantity; a small addition will decrease stress. The optimum amount reduces stress to zero, while an excess induces compressive stress in the deposit. Stress tends to go from tensile to compressive as the temperature goes up, with approximately zero stress at 54°C (130°F). The tensile stress reaches a minimum between pH 3.5 and 4.5. The pH should never be allowed to go below 3.0, and the nickel-sulfamate bath is best operated at pH 4.0.

Clear understandings of the stress profile of the bath are needed together with the operable process window.

Too high a temperature can cause sulfamate decomposition with consequent increase in the stress. A temperature of 71°C (160°F) must not be exceeded. If immersion heaters are used, circulation of the solution must be sufficient to prevent overheating near the heaters. The best temperature range is from 54 to 60°C (130 to 140°F).

From an operational standpoint, the number of the ways of controlling stress is as wide-ranging as the number of variables that affect it. Among them are stress reducing agents, current density adjustment, temperature adjustments and agitation control. It is vital however to keep all processing variables, except the controlled one, constant. Control variables should only be changed in response to stress changes in the deposit. By constantly monitoring stress, adjustments can be made to maintain stress within the specified range.

A methodical approach,⁴² coupled with vigilant process control and good housekeeping makes stress control entirely possible.⁴³ Steady stress monitoring will also help detect increased contaminants or other process deviations that can result in abrupt stress changes.

Stress Measurement Methods

Since stress is emphasized in the use of nickel-sulfamate processes, stress measurement methods should be briefly discussed here. Stress measurements can be done in several ways, but two basic methods are most widely used, the spiral contractometer and rigid strip methods.^{44,45}

When performing an internal stress test, it important to establish the solution parameters and the test procedure because any deviations will effect the internal stress. The solution concentration, pH and temperature can all effect the internal stress. Active sulfur-depolarized anodes must be used to avoid any anode phenomena which may effect the internal stress while performing the test.

Rigid strip method. This method is simple, yet sensitive enough for most industrial applications. The intricacy involved with accurately measuring the radius of curvature of a single strip may have contributed to the fact that this simple, sensitive and clear-cut method has been often forgotten in favor of the spiral contractometer that has become the more popular of the two techniques. An improved apparatus^{46,47} uses disposable two-legged brass strips whose opposite sides are plated. The resulting leg deflection (curvature) caused by deposit stress can be measured on a simple scale and from the simple formula residual stress can be calculated. Since tests can be performed directly in the plating tank, it should not alter established electrochemical and hydrodynamic patterns in the tank.

Brenner-Senderhoff spiral contractometer. The spiral contractometer is a reliable method for determining intrinsic stress in sulfamate nickel deposits. This technique detects small changes in stress. Such small changes can be observed because the movement of the helix is magnified through gears. Such sensitivity is especially important when the plating solution is operated at or near zero internal stress.

The test procedure must also be established. Such items as helix calibration, helix preparation, cleaning cycle, plating current density and deposit thickness must all be specified to minimize any external effect on the stress readings. This method is based on plating the outside of a stainless steel helix, which has been masked on the inside. The procedure is detailed in the literature.¹¹

Analytical Control & Maintenance

Control and maintenance have been reduced to a minimum in the nickel-sulfamate plating bath. Because of the simplicity of the bath composition, routine analysis need be no more complicated than

taking a hydrometer reading. Boric acid control is not critical and a monthly analysis is sufficient. The pH should be checked periodically, preferably daily. In normal operation, pH tends to rise slowly with use and may be adjusted quickly with small additions of sulfamic acid. Methods are published for determining ammonia and TSA.⁴⁸ High-performance liquid chromatography is suitable for monitoring organic additives and their decomposition or reaction products.³⁹

Since ductility is sensitive to metallic impurities and to variations in internal stress, monitoring it will help to maintain best performances of the bath and plated deposit. The ductility tests can be as simple as vise test, or the more precise ball micrometer method,⁴⁹ More sophistication is available with a displacement transducer and microprocessor control.⁵⁰

The nickel-sulfamate bath has a relatively low sensitivity to contaminants. However, in many instances they can tolerate higher amounts of metallic and organic impurities than other conventional nickel plating baths. Good engineering practice provides for solution circulation with continuous low current density electrolytic purification either in compartmented tanks or in separate cells. In this way, periodic dummaging can be performed during shutdown.

In applications involving extra heavy deposits, continuous filtration is advised. Activated carbon should not be used, as it will remove the organic wetting agent or stress reducer(s). Severe cases of organic contamination can be removed by the usual activated carbon treatment along with subsequent replenishment of the addition agents thus removed. In more severe cases of organic contamination, permanganate treatment is required.

Sulfamate nickel plating solutions can be used with any equipment normally used with high chloride Watts solutions, providing that lead be excluded from contact with the solution. Lead sulfamate is very soluble, and lead must never be used for heating coils and thermostat control bulbs.

Despite best efforts in analysis and control, trouble can develop and quality can stray. Table 4 provides a troubleshooting guide for sulfamate nickel on those occasions when problems do arise. Also, Table 5 summarizes how the mechanical properties are affected by operating and solution conditions. This only serves to emphasize the need for close analysis and control.

Hull Cell Control

Although analytical methods can be used for the additives, the use of the time-honored Hull Cell⁵¹ provides a quick, practical method of control. Hull cell tests are typically operated without agitation under the following conditions:

- Time, 24 min
- Current, 1.0 A
- Temperature, 38°C (100°F)
- Panel, polished brass

A common practice is to determine any required additions with the Hull cell tests and add about half the amount at one time to the plating tank. These conditions can be varied, if desired, to simulate tank conditions more closely. With experience, Hull cell testing can be a rapid method of additive control as well as a troubleshooting tool. If the plated panel shows dark low current density areas, impurities such as lead, copper, zinc and/or certain organic contaminants are present. Other organic contaminants may be seen in middle and high current density areas on the panel. Carbon treating the solution would be suggested followed by another test to verify organic contamination. Chromium contamination sometimes causes a dark low current density area and can cause blisters on a properly cleaned panel.

Summary & Conclusions

Sulfamate nickel plating solutions best fill the requirements for engineering applications because of the low residual deposit stress, high deposition rates and good ductility obtained. It is important to start with the purest possible sulfamate nickel plating solution, free from metallic contaminants and particulate particles including colloidal matter.

Parameters and impurities that can change the deposit characteristics are numerous. Characteristics of the deposit can be altered deliberately to achieve desired results by changing operating conditions, or additives can be used to produce specific changes. Sulfamate nickel is widely used, but not widely understood. We hope this paper has provided some better understanding of the process.

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