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## Guest Editorial -For Plateworld.com



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### Introduction Sulfamate Nickel Plating

Ductility, hardness, tensile strength, intrinsic stress, deposit structure, porosity, smoothness (degree of roughness) density, (specific gravity), specific heat, coefficient of expansion, thermal conductivity, specific resistivity, modulus of elasticity in tension and other characteristics and properties of electroplated deposits from nickel solutions based on the sulfamate anion are influenced by plating conditions and impurities.

### Solution Composition

Addition agents and impurities have a profound effect on deposit characteristics as is to be expected. These will be discussed in detail. However, changes in solution composition, operating temperature, current density, solution agitation, can also alter the deposit characteristics.

### Typical Solution Composition

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 .....0.3% By Volume  
pH .....4.0  
Temperature .....49 degrees C. (120 F.)

### Solution Composition range

Nickel as metal .....75-90 g/L  
(10-12 oz/gal.)  
Boric acid .....37-45 g/L (4-6 oz/gal.)  
Chloride .....0.2-22.5 g/L (0.3-3 oz/gal.)  
Wetting agent .....0.3% By Volume  
pH .....3.2-4.6  
Temperature .....Ambient to 60 C.  
Specific gravity .....1.25-1.28  
Current Density .....0.54 to 21.5  
A/dm<sup>2</sup> (5-200 amps/sq.ft., also called "ASF")

Cathode efficiency .....95-99.9% for "Sulfur depolarized" anodes Note, variations in composition are used for special purposes.

Nickel concentration of 90 to 135 g/L is sometimes used for high speed plating, when coupled with very high solution agitation. Current densities of 400 to 4000 amperes per square foot have been used.

High metal content is also used to improve throwing power coupled with very low current density, (1-4 ASF) High metal content does not change the characteristics or properties of the deposit. Low metal content coupled with moderate to high current density will cause deposition of basic nickel salts. This is known as "burning".

Boric acid content should vary with operating temperature from 4 oz/gal at ambient temperature to over 6 oz/gal at 125 degrees 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 re-dissolve. 30 g/L boric acid will remain in solution at 20 C. The lowest practical operating temperature for current densities over 16 A/dm<sup>2</sup> is 32 C. (90 F.) High current density and low temperature could cause "burning". Lower nickel content (below 75 g/L) requires higher boric acid.

The pH of the sulfamate nickel plating solution is important in controlling the deposit characteristics. A low pH, below pH 3.5 reduces the cathode efficiency, slows plating rate slightly, but does not change the deposit. Barrel plating must be done at a pH of 3.2 to 3.5 in order to prevent laminated deposits due to make and break of electrical connection as the barrel rotates. Low pH results in faster accumulation of impurities. For rack plating the normal pH is 4.0. At this pH iron contamination cannot remain in the solution. It precipitates as ferric hydroxide and is picked up in the filter. Deposit characteristics such as ductility remain good. At pH 5 or above, hardness increases and ductility decreases due to the co-deposition of nickel oxides in very small amounts. For electrolytic purification (dummy plating) a low pH (3-3.5) favors removal of metallic impurities.

Chloride is useful in small amounts to promote the best dissolving of the nickel anodes. The addition of chlorides to the plating solution slightly increases the tensile stress of the deposit. 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 density plating chloride is not necessary if sulfur depolarized anodes are used with sufficient anode area. Poor anode corrosion results in compressive stress, brightness, loss of ductility, increased hardness and increased porosity.

Anodes for sulfamate nickel plating should be sulfur depolarized type. Rolled depolarized anodes have been used, but require much higher chloride content (or bromide is occasionally used). These anodes are less active than the sulfur depolarized type. Thus the oxidation potential at the anode would be higher and could lead to decomposition of the sulfamate resulting in the production of a di-valent sulfur compound which will co-deposit causing some brittleness. It could cause compressive stress in the deposit. Hardness is increased also. High chloride (25 g/L) will minimize this effect. Electrolytic anodes or "nickel 200" anodes are the least active. These anode materials are not recommended for use in sulfamate nickel plating solutions. Use of these anodes will produce higher amounts of sulfur causing greater effects than for rolled depolarized anodes.

Anodes should be contained in titanium baskets which are double bagged using polypropylene bags in combination with polypropylene felt 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 rough deposits.

Symptoms of poor anode corrosion are increased brightness, loss of ductility, increased hardness, compressive stress and increased porosity.

pH also has an effect on stress in the deposit. A solution with 76.5 g/L has the lowest stress between pH 3.8 and 4.8. A solution with 107 g/L nickel has the lowest stress between pH 2.9 and 3.8. The stress increases rapidly above pH 5 due to the co-deposition of basic nickel salts. Hardness is effected by pH.

Current density effects stress. Increase in current density causes an increase in tensile stress.

Impurities in the plating solution can cause changes in the deposit characteristics. Some of which can have a dramatic effect. Chromium in as little as 3 ppm as hexavalent or 8 ppm as trivalent chromium can cause tensile (intrinsic) stress so high as to cause the cracking, dark deposits peeling and low cathode efficiency. Trivalent chromium can cause pitting. Chromium can be removed using a "high pH treatment", where the pH is first lowered to pH 3-3.5, 1 lb/1000 gallons sodium bisulfite is added, stir for 1 hr. add 3 gal/1000 gal. hydrogen peroxide, stir then raise the pH to between 5 and 5.2 using nickel carbonate packed onto a filter and the solution re-circulated through the filter pack., changing or adding additional nickel carbonate as required. Add 2 lbs/100 gallons of filter aid, settle for 6-8 hours and filter into plating tank. Adjust chemistry to correct values. Hydrogen peroxide plays a part if iron contamination is present by oxidizing any iron which helps reduce chromium to trivalent. It is difficult to reduce chromium if iron is not present.

Copper has little effect on stress or ductility, but adhesion can be effected with as little as 8 ppm 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 the solution with the current on at plating voltages. Copper causes dark deposits in low current density areas. Copper is removed by low current density dummy plating (5 ASF).

Ammonium ions can cause an increase in tensile stress and loss of ductility in the deposit. (1.) Ammonia is present in even the best 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. The process of generating ammonium ions is called hydrolysis. Ammonia is generated in a plating solution at very high temperatures, above 145 degrees F. and at low pH, below pH 2.2. At concentrations below 500 ppm, ammonia seems to have little effect. At or above 500 ppm, a dark area is noted at 20 amps/sq.ft in a Hull Cell. Ductility is lessened at that current density. However, at higher or lower current densities, the loss of ductility is very small if at all. At 2500 ppm and 30 amps per sq. ft., there is only a small loss of ductility. But at 10-20 ASF, there is a significant loss of ductility. At mixed current densities, as would be found in barrel plating, the effect is minimal. At high current density high ammonium can cause a more porous and brittle deposit as in wire plating.

Cobalt is often added to increase tensile strength and hardness. However cobalt in significant quantities will increase tensile stress. Trace amounts of cobalt have little effect. Noticeable changes start to occur at about 1% of the nickel concentration, typically about 7 g/L. Note that almost always an increase in stress (in either direction) and results in an increase in hardness and a decrease in ductility.

Sulfur in the deposit causes compressive stress and increase in brightness. Sources of divalent sulfur cause the most dramatic effects. High compressive stress, brittle deposits, loss of ductility are all the result of even a small amount of sulfur (20 ppm) in the deposits. Sulfate has no effect on stress. However, monitoring the sulfate in the plating solution gives an idea of the amount of hydrolysis which may have taken place over time or due to 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 solution.

Lead in the deposit increases tensile stress but not nearly as much as some other impurities. However, lead causes dark deposits in low current density areas, brittle and streaked deposits. Since lead deposits preferentially at 2-3 ASF. It is easily removed from the plating solution by "dummy" (electric purification) at low CD. (2 ASF)

Tin as stannous tin, valence +2, has little effect in low concentrations. Stannic tin, valence +4, can cause high tensile stress.

Zinc in the deposit also causes tensile stress (less than lead). Zinc causes "burning", peeling and dark streaked deposits which are brittle. Zinc also lowers cathode efficiency. Zinc can be removed by electrolytic purification at 2-3 ASF.

Iron contamination in concentrations of 5-10 ppm reduces the ductility of the deposit. Iron can cause roughness, pitting and dark deposits.

Iron can be removed using a "high pH treatment". Iron can be oxidized to the ferric state by adding hydrogen peroxide, raising the pH to about 4.5-5 and filtering the solution.

Remember to re adjust the pH to normal operating value. Sulfamate nickel solutions which operate at pH 4 or higher will not retain iron in the solution. As iron is oxidized at the anodes, ferric hydroxide will precipitate and is removed by filtration. For that reason (and others) continuous filtration is necessary.

Magnesium (Mg) 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 studies have shown that up to about 2.5 g/L 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 mega Pascal (MPa) or 1000 pounds per square inch (psi) was observed. These results are not in agreement with previous reported results which indicate a much greater influence on the internal stress of the nickel deposit. A previous study indicated stress caused by magnesium. We believe that impurities in the magnesium salt used for the tests caused the increase in tensile stress. Pure Mg salts are now available commercially. These recent studies show that magnesium is in close agreement with the other alkaline earth's 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 reduction.

Hydrolysis takes place very slowly in the plating solution when operated normally. The products of hydrolysis are sulfate and ammonia.

Impurities may deposit at different current densities. As a result, the effect will be different at different current densities. Impurities such as lead which co-deposit at very low current densities may have only a small effect (or none) at high current densities. Impurities which plate out at high current densities may have little effect in low current densities.

Stress measurements can be done in several ways. But there are two basic types of instruments for measuring internal stress of plated deposits. 1. Spiral Contractometer method. 2. Rigid strip method

#### Advantages of the spiral contractometer method:

1. ASTM B636 is a Standard Method
2. Operation of the spiral contractometer is well studied.
3. stress can be measured at operation temperatures.
4. Provide better resolution, especially at lower stress levels.

#### Advantages of the rigid strip method:

1. Simple to set up and run.
2. Can be used in tank
3. Can be heat treated.
4. More economical apparatus

The spiral contractometer stress measurement is recommended for a reliable method to determine intrinsic stress in sulfamate nickel deposits.

When conducting a stress measurement with a Brenner-Senderoff spiral contractometer, small changes in stress can be detected. These small changes can be observed because the movement of the helix is magnified through gears. These small changes are especially important when the plating solution is operated at or near zero internal stress.

When performing an internal stress test, it is very important to establish the solution parameters and the test procedure because any deviations will effect the resultant internal stress to the deposit. The solution concentration, pH and temperature can all effect the internal stress. Active anodes, sulfur depolarized, must be used to avoid and "anode phenomena" which may effect the internal stress while performing the test. 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 effect on the stress readings. Good scientific practice must be followed to provide consistent and reproducible results.

This method is based on plating the outside of a stainless steel helix which has been masked on the inside. A pre- masked helix may be used. The free end of the helix is attached to an indicating needle through gears that magnify the movement of the helix. The other end is fixed to the instrument As the helix is plated, the stress causes the helix to wind or unwind depending on the type of stress (Tensile-wind, or compressive, unwind). From the amount of deflection of the needle when plated to a specific thickness and at a specific current density the stress is calculated. Intrinsic is defined as the net stress free from external forces.

**The procedure for using the spiral contractometer is as follows:** *Follow the manufacturers directions for calibration.*

1. Pre-clean the helix and hydrochloric acid dip and rinse the helix.
2. Woods nickel strike, or low pH sulfamate nickel strike at 5 amps for 1 minute. In come cases, if the helix is allowed to soak in the nickel bath and come to temperature a strike may be omitted
3. Rinse with water, final rinse DI.
4. Dry with acetone, dry and weigh accurately. (Quickly)

5. Carefully mount the Helix on the contractometer and center it at Zero degrees on the dial.
6. Immerse the assembled instrument helix into DI water which is at the same temperature as the plating solution (Usually 120 degrees F.). Level the instrument. Allow a few minutes for the temperature to stabilize. Record the dial reading.
7. Transfer the instrument to the plating solution which in a 4 liter beaker with a titanium basket that surround the helix, filled with sulfur depolarized anodes, preferably bagged (to prevent rough deposits). Level the instrument. Take a reading on the dial. It should be the same as when in the DI water at the same temperature.
8. Connect the leads and plate at exactly 25 ASF to a thickness of exactly 0.0006 inches. This is important if your readings are to be compared with others, literature, etc., and to meet the ASTM standard.
9. Take the dial reading while the helix is in the solution, and at the same temperature. Slightly tap the dial to make sure the needle is free.

**Factors affecting accuracy are :** The solution must be adjusted to standard operation concentration each time the test is performed, i.e., the solution composition must be the same each time. The pH, time, temperature, and current density must be the same, and according to ASTM specifications in order to achieve results comparable to others.

Organic addition agents can alter the deposit characteristics profoundly. Examples of this type of organic agents are a long list of proprietary "brighteners" designed to be used in bright nickel plating solutions. Primary brighteners 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 brittle deposit much like bright Watts nickel solutions.

Saccharine and similar compounds act in a similar way to primary brighteners. They add considerable hardness to the deposit. So that they are used for that purpose. Proprietary products containing similar compounds also contain other organic compounds which impart higher hardness using lower quantities than when saccharine is used. The breakdown products are more easily handled and are stabilized. Removal is accomplished by a series of carbon/hydrogen peroxide treatments, using 7-10 g/L activated carbon and 0.2% by vol. hydrogen peroxide (30%). Heat to 49-54 degrees C. (120-130oF). Stir for 1 hour. Repeat two or three times for complete removal.

Wetting agents are often used in sulfamate nickel solutions. Careful selection of just the right type and with very low impurities is essential for best results. These wetting agents (also called anti-pit agents) have virtually no effect on the deposit properties if used in the normal concentration ranges. Since some wetting agents have a negative effect on deposit characteristics and on adhesion, it is best to select proprietary products specifically designed for use in sulfamate nickel plating solutions.

## Summary

Factors which change the deposit characteristics from sulfamate nickel solutions are many. It is important to start with the purest possible sulfamate nickel plating solution. Colloidal matter and other insolubles should not be present. It is important to keep impurities out of the solution by careful attention to keeping the pre-rinse water clean and free from contaminants. Characteristics can be altered deliberately to achieve desired results by changing operating conditions or adding chemicals designed to produce specific changes. For example, Cobalt or certain organic compounds to harden or strengthen the deposit.

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## References

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