Nickel Plating, Past, Present and Future.

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Significant changes have occurred over the last 100 years of nickel plating. These changes relate mainly to the additives used and not in basic nickel plating electrolytes. This paper discusses the different types of nickel electrodeposits; semi-bright nickel, bright nickel and special types of nickel electrodeposits and their usage. Control and purification of nickel electroplating solutions is also discussed.

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Nickel Plating- The Past

Nickel metal was discovered over 250 years ago and since then many uses have been found for this metal. The most significant event in nickel plating was O. P. Watts' development of his fast nickel plating electrolyte in 1916. This solution is still the major nickel plating electrolyte in use today. The introduction of the Watt's nickel electrolyte can be seen as the beginning of modern nickel electroplating.

The Watt's nickel electrolyte consists of nickel sulfate, nickel chloride and boric acid. The $NiSO_4$ is used as the primary source of nickel ions and the $NiCl_2$ is used as a source of halogen ions to help corrode the anode and operate at a higher current density. Boric acid buffers the cathode film, which in turn, allows higher current densities without burning the electrodeposit.

All decorative bright and semi-bright nickel electroplating is performed in a Watt's type electrolyte with some modification depending on the application. For example, a bright nickel solution typically consists of about 300 g/L of $NiSO_4$ and 100 g/L of $NiCl_2$, whereas a semi-bright nickel solution would have 340 g/L of $NiSO_4$ and 45 g/L of $NiCl_2$. Reasons for these differences are discussed later.

Besides nickel sulfate and nickel chloride, the most commonly used salt for electroplating is nickel sulfamate. Nickel sulfamate is used primarily for electroforming and accounts for about 10% of the total nickel plating market. The sulfate and chloride salts account for the rest. There are other nickels salts, such as nickel fluoroborate, but these enjoy very limited use.

In addition to bright and semi-bright nickel processes, some nickel solutions were formulated for special applications, such as direct plating of nickel onto zinc diecast[1]. Another example of a specialty nickel solution would be the Wood's nickel strike that is formulated for plating onto passive surfaces such as stainless steels and other high nickel alloys. The high chloride and low efficiency of this electrolyte helps remove the natural oxide present on these surfaces. There are other specialty nickel solutions that have been developed for high hardness. However, these vary only slightly from the basic nickel electrolytes already mentioned.

Bright Nickel Plating – The Present

The most common type of bright nickel plating is performed with organic additives to impart desired properties in the coating. The additives serve three functions: brightening, leveling and stress reduction. Brighteners, as their name implies, enhance the brightness (or specular reflection) of the plated deposit. Leveling additives usually do not produce lustrous coatings, but increase the surface smoothing of the deposit, by minimizing (or eliminating) the transmission of substrate recesses or protrusions to the plated surface. Thus, a good leveling bath plates thicker deposits in the recesses and thinner deposits on the substrate peaks. Some additives impart both brightness and leveling (e.g. unsaturated alcohols).[2,3]

Stress reducers, again as the name implies, reduce the tensile stress in the electrodeposit. Sometimes they can even shift the stress of the nickel deposit to a compressive stress. This is usually done by the codeposition of sulfur into the deposit. Stress reducers are often needed because many brighteners significantly increase the tensile stress of the plated nickel. Thus, stress reducers are usually added to counteract this effect of the brighteners.

The requirements of a modern brightener system are:

1. A wide operating window.
2. It must not embrittle the deposit more than the stress reducer can offset.
3. It should have good chromability, and not make the nickel deposit passive.
4. The brightener must not form decomposition products that cause faults in the electrodeposit. The decomposition products should be removable with activated carbon.

5. The brightener should be able to be determined by analysis.
6. The brightener should be economical.

Semi-Bright Nickel Plating – The Present

The properties of semi-bright nickel are usually higher than that of bright nickel. For example, the ductility of semi-bright nickel coatings is usually 0.4-0.5 based on ASTM B-490 method. Some bright nickels have this high ductility but they typically lack good leveling which limits their use.

Semi-bright nickel deposits usually have higher tensile stress than bright nickel deposits because sulfur-bearing additives are not used to control the stress. The maximum amount of sulfur in semi-bight nickel is usually specified at 0.005% by wt.

The main purpose of a semi-bright nickel deposit is to prevent base metal corrosion. This is accomplished by being more noble than the bright nickel. When a corrosion site forms in the bright nickel and penetrates to the semi-bright nickel deposit, the corrosion is retarded at the semi-bright nickel layer and proceeds to move laterally in the bright or high sulfur layers. Figure 1 shows a cross section of the various nickel deposits.

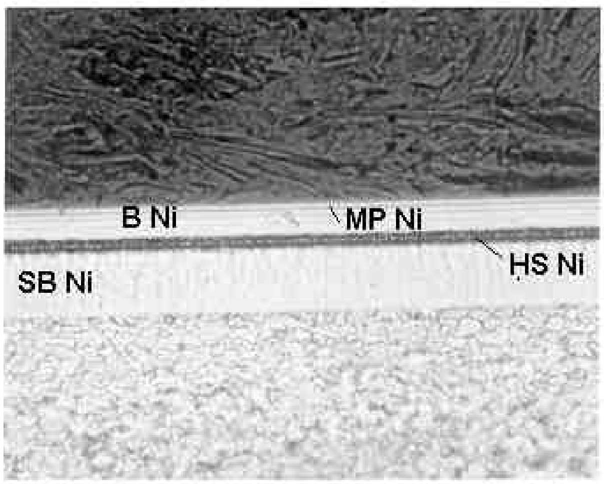

Figure 1. Cross section of various Nickel electrodeposits. 1000X. SB – Semibright Ni, HS- High Sulfur Ni, BN- Bright Ni, MP- Particle Ni

Electrochemical examination of a decorative nickel system often gives one a better understanding of how the different components contribute to the overall performance. Figure 2 provides such as picture by illustrating the result of a S.T.E.P test[4] on a nickel system. This test basically indicates the electrochemical activity of the various nickel layers.

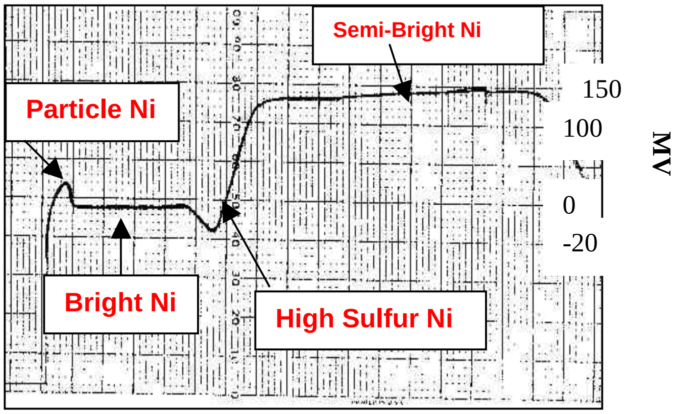

Figure 2. S.T.E.P. test a multi-layered Nickel Electrodeposit.

From the diagram, the thin microporous nickel is more noble than the underlying bright nickel. Microporous nickel is sometimes applied above bright nickel. It has non-conductive inclusions evenly dispersed across the surface and its purpose is to cause discontinuities in the top chromium layer, such that corrosion or aging proceeds uniformly and more slowly across the chromium surface.

A triplex nickel usually refers to a system consisting of bright nickel and semi-bright nickel with an active high sulfur nickel intermediate layer. One purpose of the high sulfur nickel is to keep the bright nickel brighter longer and another is to retard base metal corrosion. This is accomplished by the high sulfur nickel corroding away laterally between the bright and semibright nickel. This layer is also noted in Figure 2.

With the duplex system, corrosion starts in the bright nickel and proceeds laterally once the semi-bright nickel is reached. Here, some brightness is lost due to surface pitting, but significantly, more time occurs before base metal attack occurs in service. This is due to the potential differences between the bright and semi-bright nickel electrodeposits.

The semi-bright nickel plays a significant role in the duplex system and extreme care is given in its operation. Since bright nickel electrodeposits contain sulfur to control stress, the nickel electrolyte is formulated differently from a semi-bright nickel solution. A typical bright nickel solution would contain about 350 g/L of $NiSO_4 \cdot 6H_2O$, 75 g/L of $NiCl_2 \cdot 6H_2O$ and 45 g/L of H_3BO_3. A typical semi-bright nickel solution would have a similar amount of $NiSO_4 \cdot 6H_2O$ and H_3BO_3 but should have a maximum of 45 g/L of $NiCl_2 \cdot 6H_2O$.

The main reason for lower chloride in semi-bright nickel is to limit the stress of the deposit and to a lesser extent the leveling of the deposit. As mentioned earlier, semi-bright nickel deposits do not use sulfur additives to lower the stress therefore the deposit is always stressed tensile and this stress is kept in check by proper bath chemistry and appropriate additives. Figure 3 shows the effect of stress additive and brightener on stress in a semi-bright nickel electrolyte.

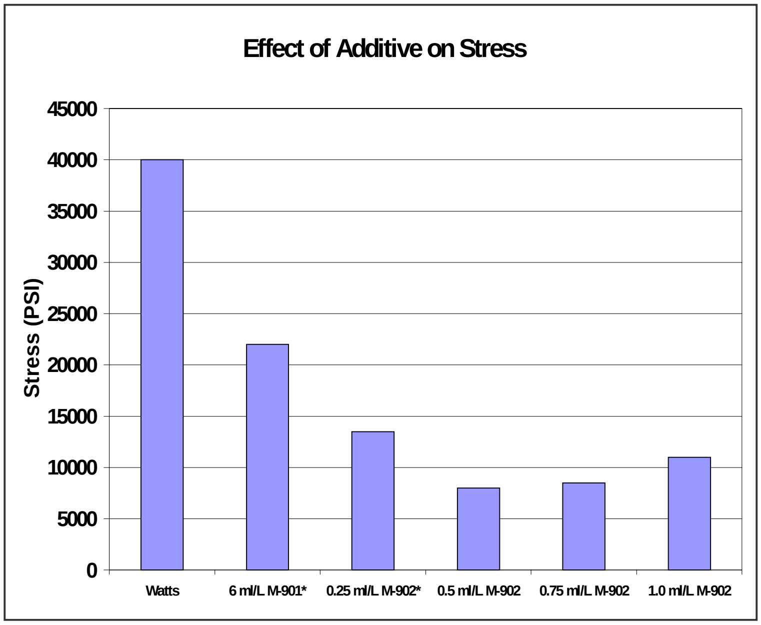

Figure 3. Stress of Semi-bright Nickel

The stress was measured with a spiral contractometer at 40 ASF for 30 minutes. There is a synergistic effect between the brightener (M-902) and stress reducer (M-901) in lowering the stress of the deposit. The initial Watts solution has a stress of 40,000 psi tensile and the solution composition is 340 g/L of $NiSO_4 \cdot 6\ H_2O$ and 45 g/L of $NiCl_2 \cdot 6H_2O$ and 45 g/L of H_3BO_3. The temperature is 60°C and the pH was maintained between 3.7-4.0.

Leveling is also effected by the amount of $NiCl_2$ in the semi-bright electrolyte. Figure 4 shows the results. Using the same concentration of $NiSO_4$ and Boric Acid as figure 7.

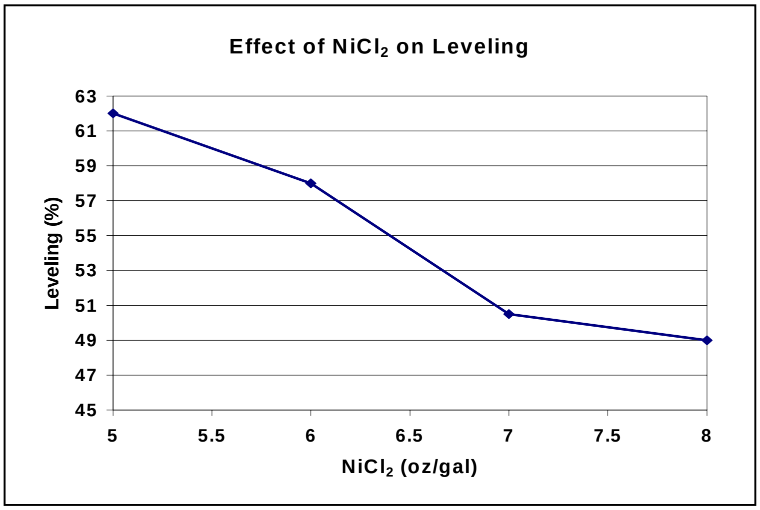

Figure 4. Effect of $NiCl_2$ on Leveling.

The higher the chloride the lower the leveling and the higher the stress in the electrodeposit. This is why lower levels of chloride are usually used in a semi-bright nickel electrolyte.

Other significant properties of the semi-bright nickel are its potential difference between the bright nickel and sulfur content in the deposit. Table 1 and 2 show these results.

Table 1. Effect of Additive on S.T.E.P

Semi-Bright Brightener (mls/L)	S.T.E.P. (mv)
0.25	120
0.50	135
0.75	140
1.00	135

Table 2. Amount of Sulfur in Deposit.

Nickel Deposit	Mass % S
Watts	<0.001
Semi-Bright	<0.001
Bright	0.013

Nickel Plating- Future

There are a number of different nickel electrolytes proposed in the literature for electro/electroless nickel plating. Most of them are based on nickel sulfate, nickel chloride or mixtures of these salts. In addition, nickel sulfamate is the third most used nickel salt for electroplating. There has been little work on nickel methane sulfonate reported unlike the other methane sulfonate metal salts, e.g. tin, lead or copper.

Over the last 20 years, there has been considerable amount of work with tin and lead methane sulfonate electroplating. These sulfonate salts are currently being used to replace fluorborate-based tin and lead salts for numerous reasons and have achieved commercial success.

Copper methane sulfonate electroplating was evaluated in 1947 and is characterized by a high solubility of the copper salt and high limiting current density.[5] Similarly methane sulfonic acid has high solubility for many electroplating metals.[6]

With all this work with methane sulfonic acid (MSA) in electroplating a logical progression of evaluating the various metal salts has occurred. Since MSA is more expensive then say sulfuric or hydrochloric acid, one looking to replace these metal salts would have to see a significant improvement in properties to justify the cost.

Note that sulfamate nickel deposits typically have lower internal stress than a sulfate, chloride or mixed sulfate/chloride electrolyte. The internal stress of nickel coatings decreases with the molecular weight of the cation, Table 3 lists the order of stress of the various nickel plating salts.[7]

Table 3 Stress
Lowest to Highest Stress

Sulfamate
Methane Sulfonic Acid
Bromide
Fluorborate
Sulfate
Chloride

From this table the higher the molecular weight of the anion the lower the stress of the electrodeposited nickel.

Electrodeposited Nickel from MSA Electrolyte

Nickel Sulfonate has a solubility of 660 g/L at 25°C that is slightly higher than Nickel Sulfate and less than Nickel sulfamate. In addition, the molecular weight of Nickel Sulfonate, $Ni(CH_3SO_3)_2$, is 248.8 and Nickel Sulfamate, $Ni(NH_2SO_3)_2$ is 250.8. From above, the higher the molecular weight of the anion the lower the stress. Table 4 shows the stress results of an electrodeposited nickel from a methane sulfonate electrolyte compared to the other anions.

Table 4 Stress values of Various Ni Salts.

Salt	Tensile Stress (PSI)
Sulfamate	0-8000
Methane Sulfonate	500-5000
Sulfate	20-40,000
Chloride	50-80,000

From these results, the $Ni(CH_3SO_3)_2$ without any additives produces stress values that are significantly lower than the value of $NiSO_4$ and are in the range of $Ni(NH_2SO_3)_2$.

Nickel Sulfate has a tensile stress of 125 to 370 Mpa (20,000 to 40,000 psi) and Nickel Sulfamate has a tensile stress of 0 to 55 Mpa (0- 8000 psi).[8]

The amount of codeposited sulfur from the methane sulfonate electrolyte is very low;

similar to a sulfamate and Watts electrolyte. Table 5 lists the results.

Table 5. Mass % Sulfur in Deposit.

Solution	Mass %S
Watts	< 0.001
Sulfamate	< 0.001
Methane Sulfonate	< 0.001

Plating rate of the $Ni(CH_3SO_3)_2$ is similar for both the sulfamate and Watts solution. When the pH of the MSA electrolyte is lowered to 2.0, the efficiency is decreased in both the high and low current density areas, Figure 5 shows the results. The plating rate was measured on Hull cell panels plated at 2 amps for 15 minutes.

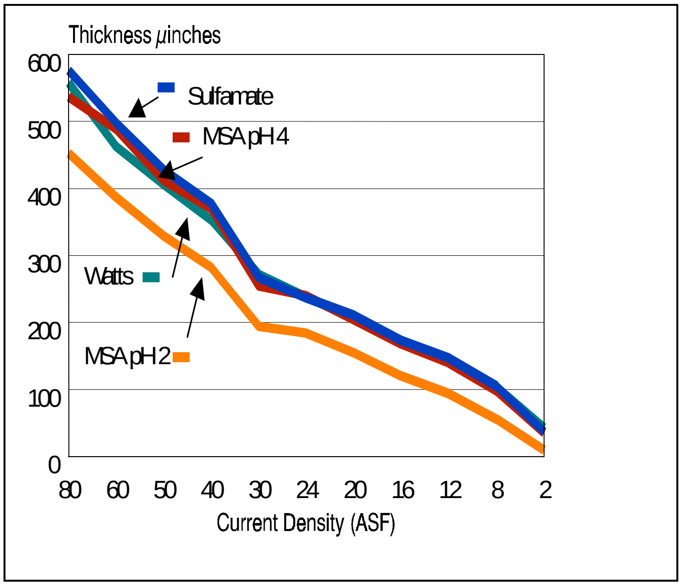

Figure 5. Plating rate of MSA, Watts and Sulfamate Nickel Electrolyte.

Anode corrosion is another property that was evaluated. Halogen salts are added to help in the dissolution of the anode but halogens can increase stress in the deposit, Figure 6 shows voltammograms of sulfamate and methane sulfonate electrolyte with a carbon depolarized nickel anode. From this graph, neither electrolyte dissolves the anode uniformly.

Adjusting the pH of the methane sulfonate electrolyte to 2.0, the anode is active until about 1.2 V and then becomes passive. Comparing the sulfamate electrolyte to the methane sulfonate electrolyte with the addition of $NiBr_2$, significantly less Br^- is needed to keep the anode active, Figure 6 shows the results. From this voltammagram, the Br^- is four times more active in the MSA electrolyte than the sulfamate electrolyte. A Watts nickel solution was run as a comparison to see how the other electrolytes compared in dissolving the anode.

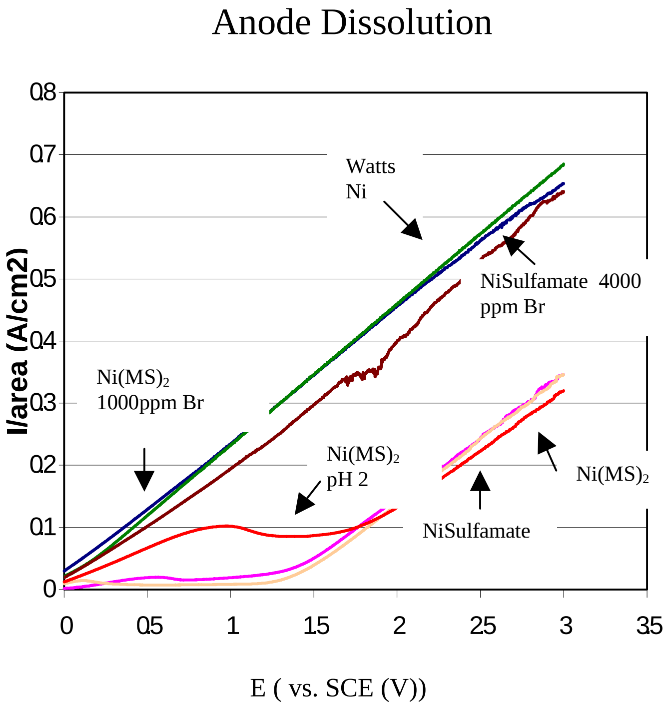

Figure 6. Voltammagram of $Ni(MSA)_2$ and NiSulfamate.

Additives that are used in sulfamate plating can also be used in the methane sulfonate electrolyte. Sodium saccharin, for instance, can be used as a stress reducer.[9] The results obtained from this electrolyte were 4 – 60 MPa (500 – 9000 psi). This number is similar to the additive free deposit mentioned above. With the addition of SN-1* the stress nickel electrodeposit from the MSA electrolyte is compressively stressed at 34-55 MPa (5000-8000 psi).

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Semi-bright nickels are typically tensile stressed depending on the type of chemistry, coumarin or non-coumarin. The internal stress of a semi-bright nickel is usually tensile, 35 – 150 MPa, (5000 – 22,000 psi). Substituting $Ni(CH_3SO_3)_2$ for $NiSO_4$ and using the typical amount of $NiCl_2$ for a semi-bright nickel 37.5 g/L(5 oz/gal), stress values are listed in Table 6.

Table 6 Stress Values of MSA based Semi-Bright Nickel with additives.

Current Density (ASF)	Tensile Stress(psi)
60	1000
40	800
20	1200
10	2000

Significantly lower stress values can be obtained in the methane sulfonate electrolyte than the Watts electrolyte. The methane sulfonate anion is more stable than the sulfamate anion and does not break down to ammonium and sulfate. Therefore, the use of insoluble anodes should be much more trouble free. Also, since there is usually no rinse between the semi-bright and bright nickel the drag in of methane sulfonate would not degrade and cause problems in the bright nickel electrolyte based on the Watt's formula.

Sulfamate nickel would initially lower the stress values to similar values but the sulfamate would eventually break down into ammonium and sulfate in the bright nickel electrolyte. Ammonium would cause the bright nickel deposit to become brittle and make the deposit cloudy.

Trouble shooting and Waste Minimization

As with any process, a thorough understanding of the operating parameters is essential to its maintenance. In addition to understanding the process, analytical methods for analyzing every component and their break down products is also essential in trouble shooting the process. With modern analytical techniques like ion chromatography (IC), high performance liquid chromatography (HPLC) and atomic absorption (AA) available to the plater, the plating solution can be monitored for contamination and the appropriate treatments can be implemented before rejects are produced.

The need for purification is inversely proportional to the degree of housekeeping used to maintain the entire process. With this said, maintaining just your nickel tanks will not solve your problems. But, maintaining the whole line will minimize your problems. When problems do arise solving them is easier with proper documentation on each individual process tank. Seeing which ones have changed will make troubleshooting easier.

One way to minimize out of balance process solutions is to maintain them in their optimum condition. To maintain the nickel processes in their optimum condition, filtration is critical to removing unwanted material from the tank. In addition, some carbon should be continuously packed onto the filter to remove oils and organic breakdown products from the solution.

There are a number of papers which deal with the purification of nickel solution The following reference is an excellent start in understanding how to purify nickel plating solutions.[10] Since the time of that article, there are newer technologies available for purifying nickel plating solutions. One process uses a special polymer that adsorbs organic material, Nickotect Adsorber System.*

Previously, the only way to remove these contaminating materials was dilution, dummy plating, or carbon treatment followed by filtration. In addition, the electroplating solutions are sometimes treated with oxidizing agents such as hydrogen peroxide or potassium permanganate to polymerize some of the shorter chain molecules for ease of removal. This polymer adsorber system allows continuous removal of virtually all harmful organic material without the use of batch

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carbon, hydrogen peroxide and potassium permanganate treatment.

The organic contamination is adsorbed on a polymeric resin in a system. The harmful materials can be easily eluted when the resin is fully loaded by simple regeneration with acid, alkali and hydrogen peroxide. The bright nickel deposits from this system are maintained in their optimum state so that brightness, ductility, leveling and chromium receptivity are maintained like an optimum operating solution.

Conclusion

Environmental and regulatory concerns over the practice of nickel electroplating have caused some to question its future. However, with proper handling, waste treatment procedures and implementation of new technologies to treat and purify the baths, nickel waste can be greatly minimized, allowing nickel plating to be around for years to come.

Nickel plating has undergone a significant amount of development over the years. As a result, platers use a variety of nickel deposits, often in combination, to achieve functional and aesthetic demands of the applications. Given all of the current efforts to further improve the performance of nickel electroplated coatings, the future looks “bright”.

Reference:

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