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Nickel sulphamate solutions

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NiDI Technical Series N° 10 052

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1. INTRODUCTION

Nickel-plating solutions based upon nickel sulphamate are used mainly for electroforming purposes because the internal stress in the nickel deposits is lower than in deposits from Watts-type solutions. Also, higher deposition rates can be achieved. Some engineering nickel plating is done in sulphamate solutions and they have been used for decorative plating. However, these applications usually use Watts-type formulations which, for the same nickel content, are about half the price of the sulphamate solutions.

Conventional sulphamate nickel baths contain about 300 g/l of nickel sulphamate, together with nickel chloride and boric acid, *Table 1*:

Table 1
Conventional sulphamate nickel solutions

Nickel sulphamate	$\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$	300 g/l
Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30 g/l
Boric acid	H_3BO_3	30 g/l

Deposit internal stress increases with increasing nickel chloride content and so some solution formulations contain only a few grams per litre of nickel chloride. The solutions are usually used agitated at a temperature of 25° to 60°C with 55°C being used most frequently, pH 3.5 to 4.5. Current densities of about 2 to 15 A/dm² are used, giving a deposition rate of 25 to 180µm per hour.

More concentrated nickel sulphamate plating solutions are also used, for example 450 grams per litre in the United States.⁽¹⁾ In Europe a great deal of work has been carried out with the 600-grams-per-litre solution of the Ni-Speed process.⁽²⁾

2. CONVENTIONAL SULPHAMATE SOLUTION

Nickel deposited from the conventional sulphamate solutions is about 10 HV units harder than Watts nickel deposited under the same plating conditions and is less ductile with an elongation of ca. 18-20%. Reported values of internal tensile stress are typically 3 MN/m² (450 psi) for a solution containing no chloride ions, rising to 53 MN/m² (7950 psi) with 30 g/l nickel chloride present. In a given solution, stress increases as current density is raised or solution temperature is lowered. Stress is also affected by the electrochemical activity of the anode material used. The tensile strength of the deposits is similar to that of Watts deposits, ca. 460 MN/m² (69000 psi). Throwing power of the solution is marginally better than that of the Watts solution.

Sulphamate nickel solutions are more sensitive to the effects of impurities than Watts-type solutions and must be carefully purified and then maintained in a pure state. The effects of some impurities on the deposits and suggested maximum tolerable limits⁽³⁾ are shown in Table 2.

Table 2
Effects of impurities in conventional sulphamate nickel solutions

Impurity	Typical maximum tolerable limit, ppm	Effects	Typical level in a pure bath
Iron	200	Increased stress and hardness, reduced ductility.	< 10
Copper	10	Reduced ductility and cathode efficiency, Dark color.	0.1
Zinc	10	Reduced ductility and cathode efficiency. Streaky deposits.	< 0.1
Lead	2	Reduced hardness. Reduced ductility of nickel after heating.	< 0.1
Aluminium	6	Burned deposits.	Nil
Chromium, tri-or hexa-valent	2	Reduced ductility and cathode efficiency.	Nil

These impurities and others also affect deposit internal stress. Their concentrations, in parts per million, that alter the deposit stress by approximately 7 MN/m², (1050 psi) together with likely sources of the impurities, are shown in Table 3.⁽⁴⁾

Table 3
Concentrations of common impurities that change stress by ca. 7 MN/m² (1050 psi)

Impurity	Limit	Method of introduction
Chromium	1ppm	Airborne, drag-in, impure anodes and salts.
Tin	2ppm	Low-melting alloy mandrel material, impure anodes and salts.
Sulphur	5ppm	Dissolution of sulphurized rubber salts, wetting agents and stress reducers, anodic effects.
Phosphate	5ppm	Impure salts, drag-in from cleaning solutions, impure activated carbon.
Nitrate	5ppm	Drag-in, impure salts, improper addition of nitric acid.
Lead	10ppm	Dissolution of improperly engineered equipment, low-melting alloy mandrel material, and solder; salt and anode impurities.
Magnesium	100ppm	Impure anodes and salts, water.
Manganese	100ppm*	Permanganate purification treatment. Impure anodes and salts.
Copper	100ppm*	Dissolution of bus bars, contacts and racking material, drag-in, salt and anode impurities.
Iron	150ppm	Environment, dissolution of equipment, dissolution of basis metal improper cleaning, hard water, drag-in, salt and anode impurities.
Zinc	150ppm	Impure anodes and salts.
Ammonium	500ppm	Hydrolysis, impure salts, erroneous addition of ammonium hydroxide
Sulphate	1000ppm	Hydrolysis, impure salts, improper addition of sulphuric acid, drag-in.
Sodium	3000ppm	Water, impure anodes and salts, drag-in, use of sodium hydroxide to raise PH.

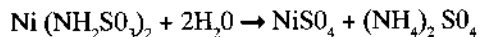
*Copper and manganese do not affect internal stress as impurities up to 100 ppm.

Hydrolysis of sulphamate ions to form sulphate and ammonium ions occurs if the solution is made too hot or too acidic, see Table 4.⁽²⁾

Table 4
Effect of pH and concentration on hydrolysis of nickel-sulphamate solution

Nickel sulphamate concentration	Temperature °C	pH	Increase in ammonium-ion concentration g/l, per 336 hrs.
300	70	2.0	9.7
		4.0	0.95
		5.5	0.1
450	70	2.0	—
		4.0	0.33
		5.5	0.1
600	70	2.0	8.5
		4.0	8.18
		5.5	0.1
600	65	4.0	0.035

As shown in *Table 3*, these ions cause the stress to move in the tensile direction and ammonium ions have twice the effect of an equivalent amount of sulphate ions. As the ammonium ion concentration is increased, stress rises to a value of ca. 37 MN/m², as shown in *Figure 1*.⁽⁴⁾ The hydrolysis reaction shown below is irreversible:



Sulphate ions can be removed by treatment with barium sulphamate but there is no way of removing the ammonium ions. Therefore, although hydrolysis is not a problem when operating sulphamate nickel solutions at 60-65°C and pH 4.0, care must be taken not to overheat the solution or allow pH to fall, especially when the solution is hot. This means that it is important not to overshoot when correcting pH by additions of sulphamic acid.

A comprehensive account of conventional sulphamate nickel solutions is included in the literature review made in 1971 by Hammond.⁽⁵⁾

3. CONCENTRATED SULPHAMATE SOLUTION

As the concentration of nickel sulphamate in a sulphamate plating solution is increased from the conventional 300 g/l to 700 g/l, maximum plating rate without burning passes through a maximum, and deposit stress passes through a minimum, as shown in *Figure 2*. The concentration giving optimum results is 600 g/l and that is the concentration used in the solution employed in the operation of the Ni-Speed process. The solution employed was disclosed by Kendrick⁽³⁾ in 1964 and an explanation of the stress control that can be achieved using the Ni-Speed process was put forward in 1966⁽⁶⁾.

Table 5 shows the optimum, and the normally acceptable, range of composition for the solution:

The Ni-Speed process is used principally by electroformers and offers them four major advantages:

- (i) Maximum plating rate is much higher than a Watts or conventional sulphamate solution.

Table 5
Ni-Speed composition

Composition	Optimum concentration g/l	Normal acceptable range g/l
Nickel sulphamate Ni(NH ₂ SO ₃) ₂ ·4H ₂ O	600	500-650
Nickel chloride NiCl ₂ ·6H ₂ O	10	5-15
Boric acid H ₃ B ₃ O ₃	40	30-40

- (ii) Deposits stress can be varied at will between wide limits without the use of addition agents, simply by varying the solution temperature and the cathodic current density. Since no addition agents are required, the solution is easy to control and can be easily maintained.
- (iii) Since the deposits do not contain sulphur incorporated from organic stress-reducing agents, they do not suffer embrittlement on heating. This is most important to their application as moulds and dies and in some aerospace applications.
- (iv) The Ni-Speed solution has superior throwing power compared with conventional sulphamate and Watts-type solutions. This allows the current density over complex shapes to be some two or three times greater than with these other electroforming solutions, and therefore allows a shorter plating time and greater production rate.

The concentrated sulphamate nickel solution, when operated according to the Ni-Speed process and giving deposits of controlled stress, is said to be *conditioned*.

A diagrammatic representation of a Ni-Speed installation is shown in *Figure 3*.

Control of the deposit stress in the Ni-Speed process is achieved via the conditioning treatment carried out in a small tank separate from the main tank but connected to it by the solution circulation system. The main electroforming tank is preferably fitted with titanium baskets containing fully-activated nickel to ensure proper dissolution of the nickel, even at current densities up to 50 A/dm². The anodes in the conditioning tank must, however, be of nonactivated nickel which dissolves at a higher potential than do the activated forms of nickel.

The cathode in the conditioning tank can conveniently be a corrugated sheet so that plating out of any metallic impurities on the cathode takes place at the same time as the solution conditioning at the cathode.

3.1 Mechanism of stress control in the Ni-Speed process

Within a range of current density of about 0.5 to 1.0 A/dm² on the anode in the conditioning tank, a stress-reducing substance is produced that controls the stress in the nickel electrodeposited in the main tank. Since it is consumed in the exercise of its stress-controlling function, it must be generated continuously in the conditioning tank. Experience has shown that stable conditions are maintained when the solution is circulated through the system between two and five times an hour, and the current used for conditioning is not less than 3% of the current passing through the main tank. Conveniently, the capacity of the conditioning tank is then 10 to 20% of the capacity of the main tank.

Figure 4 illustrates the relationship between the conditioning current density range and the anode-potential region over which the Ni-Speed stress-reducing substance is formed.

At fully-activated nickel anodes the steady dissolution potential, ca. -0.3 volts vs S. C. E., is too negative to influence sulphamate ions.

When nonactivated nickel anodes are dissolving within a current density range 0.5 to 1.0 A/dm² in the 600 g/l nickel sulphamate solution of the Ni-Speed process, the potential reached is positive with respect to S. C. E. but is below the steady dissolution potential, approximately 0.2 volts vs. S. C. E., that is maintained over a wide range of higher current densities up to the limiting current density at which the nickel becomes passive. Holding the nickel at that lower potential leads to the production of the substance that controls deposit stress in the Ni-Speed process. Unlike azo-disulphonate ions (SO₃·N=N·SO₃)⁻ that are produced at insoluble anodes in sulphamate solutions, the Ni-Speed substance is not destroyed on heating to 65°C, nor by hydrogen peroxide or potassium permanganate. Its use does not cause incorporation of sulphur in the nickel deposit, unlike use of azo-disulphonate ions as a stress-reducer.

Early in the development of the Ni-Speed process it was established that the stress-reducer was produced at the anode, by electrolyzing a fresh solution in two beakers joined by a U-tube filled with the solution and plugged with glass wool to

prevent bulk circulation; the anolyte subsequently gave compressively-stressed deposits while the catholyte did not.

Since stress-reducer is produced by anodic action only in sulphamate solutions its structure is presumably derived from the sulphamate ion, (SO₃·NH₂)⁻. Possibly its structure resembles the sulphonamide group of para-toluene sulphonamide, a well-known organic stress reducer. Research at the Wuhan Research Institute has investigated anodic reaction products in sulphamate solutions using differential pulse polarography but does not seem to have identified the Ni-Speed special substance.⁽⁷⁾ If it could be isolated, it could perhaps be added to the cheaper Watts solution and produce low-stress sulphur-free deposits.

Full conditioning of the Ni-Speed solution is indicated by a satisfactory value for the stress in the deposit. A fully-conditioned solution gives deposits having a compressive stress of 48 MN/m² ± 14 MN/m² (7200 ± 2100 psi) determined under standardized conditions: these conditions are a cathodic current density of 4.3 A/dm², solution temperature 60°C, and pH 4.0. When the solution is fully conditioned, the deposit is ductile and lustrous in appearance. By contrast, deposits from the unconditioned solution as made up are dull.

3.2 Changing the stress in the Ni-Speed deposits at will

With the conditioned solution, deposit stress is affected both by cathodic current density and by solution temperature.

Figure 5 shows the relationship between stress and current density; the line moves bodily as the solution temperature is raised so that zero-stressed deposits are obtainable at higher and higher current densities.

Since stress moves in the tensile direction with increasing current density, and in the compressive direction with increasing solution temperature, it is possible to choose pairs of values that give deposits with zero internal stress. These values are shown in *Table 6*.

Table 6
Zero-stress conditions for the Ni-Speed process

Temperature °C	35	40	45	50	55	60	65	70
Current density A/dm ²	1.1	2.7	4.3	8.1	13.5	17.8	21.6	32
Plating rate (approximate) μm/h	12	31	50	94	156	206	250	375

It is also possible to use lower current densities or higher solution temperatures than these paired values to give deposits that are compressively stressed and are thereby able to accommodate the tensile-stress-inducing effects of additives with valuable properties. For example, cobalt can be added to give a harder, sulphur-free alloy with low or zero stress. Alternatively, butyne 1:4 diol can be added to give a smoother and still sulphur-free nickel deposit.

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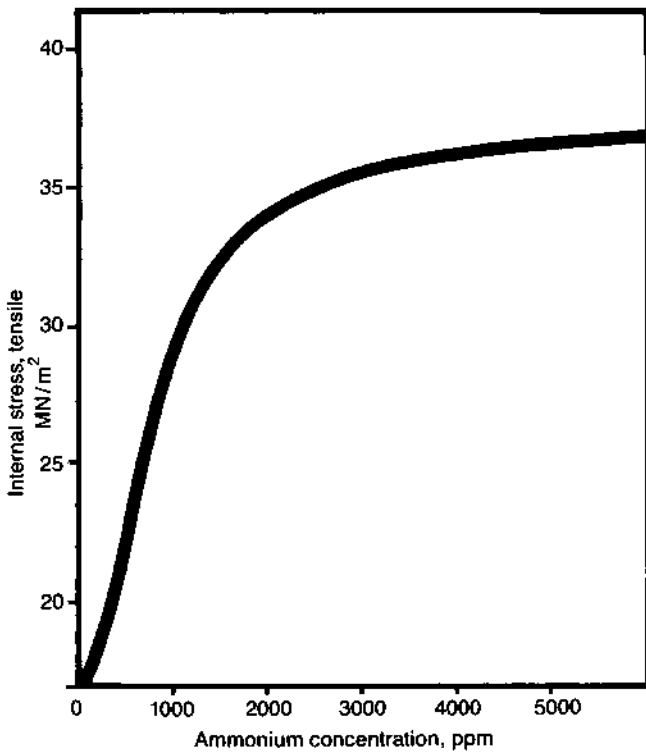


Figure 1 Effect of ammonium ion on internal stress in nickel sulphamate deposits.

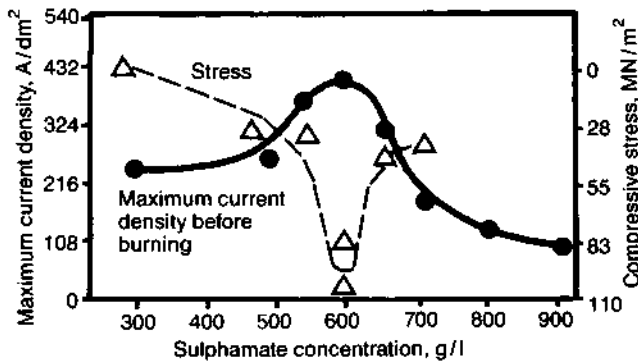


Figure 2 Effect of concentration of nickel sulphamate on maximum current density and stress in deposits 25µm thick obtained at 5.4 Adm², 60°C

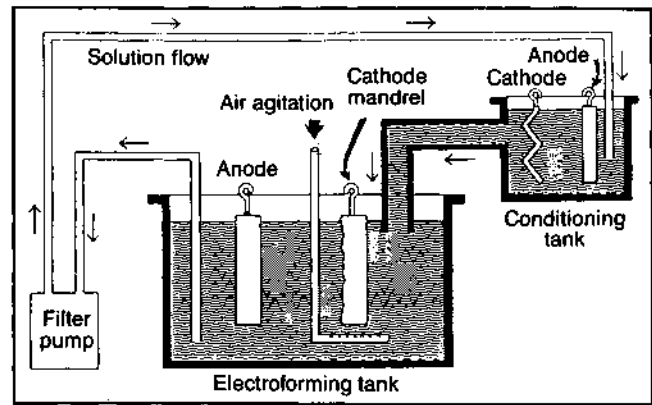


Figure 3 Ni-speed installation.

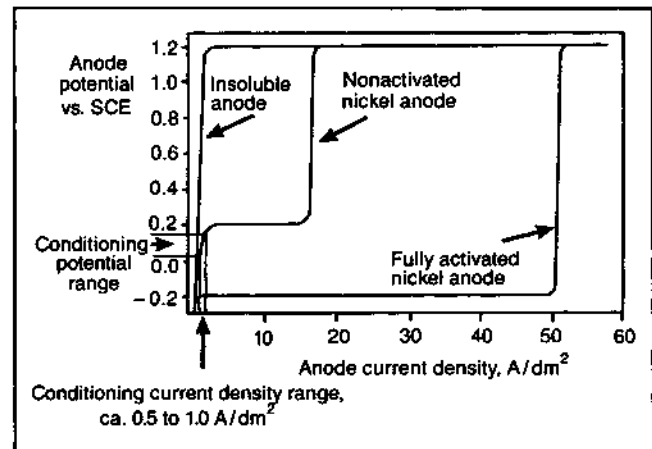


Figure 4 Relationship between conditioning current density range and anode-potential region over which Ni-Speed stress reducing substance is formed.

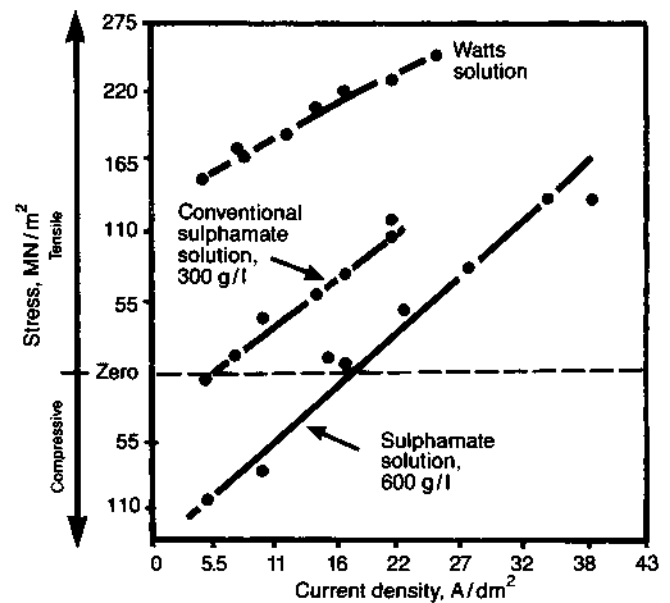


Figure 5 Variation of mean stress in 25µm thick deposits with current density at 60°C

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