# A Novel Brightener System for Decorative Nickel Plating

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Nickel brighteners are divided into two classes. Class I brighteners are aromatic or unsaturated aliphatic sulfonic acids, sulfonamides, sulfonimides, and sulfimides. Class I brighteners incorporate sulfur into the deposit, which reduces the internal tensile stress of the deposit. Class II brighteners are derived from acetylinic or ethylenic alcohols and pyridine compounds. Class I and II brighteners are combined to obtain maximum brightness or ductility for a given rate of leveling. Class II brighteners cause brittleness and increase internal stress in a deposit, and cannot be used alone. A new brightener system for nickel plating baths has been developed that provides an extremely ductile, leveled, and highly bright deposit over a wide range of current densities without the need for alkyl sulfonate and pyridine-based brightening and leveling agents.

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## Introduction

Nickel is one of the most important electrodeposited metals due to its excellent decorative and corrosion-resistance properties. Most nickel electrolyte systems are based on the Watts plating bath, which contains nickel sulfate, nickel chloride, and boric acid. Electroplating baths have been developed to produce ductile, low-stress, high leveling, semi-bright and bright nickel deposits. A multilayered nickel deposit, containing a sulfur-free semi-bright nickel layer with a sulfur-containing bright nickel layer, significantly improves corrosion protection.

A variety of organic compounds are used as brighteners in nickel baths to provide a bright, level, and ductile nickel deposit. Nickel brighteners are generally divided into two classes.<sup>1</sup> Class I, or primary, nickel brighteners include compounds such as aromatic or unsaturated aliphatic sulfonic acids, sulfonamides, sulfonimides, and sulfimides. Class I brighteners are used in relatively high concentrations and produce a hazy or cloudy deposit on the metal substrate. Decomposition of Class I brighteners during the electroplating process causes sulfur to be incorporated into the deposit, which reduces the tensile stress of the deposit.

Class II, or secondary, nickel brighteners are used in combination with Class I brighteners to produce a fully bright and leveled nickel deposit. Class II brighteners are generally unsaturated organic compounds. A variety of organic compounds containing unsaturated functional groups such as aldehydic, olefinic, acetylinic, nitrile, and pyridine groups have been used as Class II brighteners. Typically, Class II brighteners are derived from acetylinic or ethylenic alcohols, ethoxylated acetylenic alcohols, coumarins and pyridine based compounds. Mixtures of such unsaturated compounds with mixtures of Class I brighteners are combined to obtain maximum brightness or ductility for a given rate of leveling. Class II brighteners, however, cause brittleness and increase internal stress in a deposit, and, therefore, cannot be used alone.

A variety of amine compounds have been reported as brightening or leveling agents. Acyclic amines have been used as Class II brighteners that require the use of other Class I and Class II brighteners. Popescu<sup>2</sup> describes the derivatization of unsaturated amines to form quaternized olefinic or acetylenic sulfobetaines and carboxybetaines. Acetylenic amines<sup>3, 4</sup> have been used in combination with acetylenic compounds to improve leveling and low current density coverage. Preiss, *et al.*<sup>5</sup> describes the synthesis of N-alkyl-substituted aminoalkynes, which could potentially be used as a brightener in nickel baths.

Other patents disclose the use of single or multi-ring nitrogen containing heterocyclic amines as Class II brighteners for bright nickel electroplating systems. Gündel and Wennnemar<sup>6</sup> describe brightness and leveling improvements to electodeposited nickel with internal salts of alkyl-sulfonic acids of pyridine and C-substituted pyridines. Rosenberg and Saas<sup>7</sup> discuss the synergistic effects of pyridine sulfobetaines with acetylenic alcohols and their derivatives. Patsch and coworkers<sup>8</sup> expanded on the pyridine-based brighteners to include mononuclear and polynuclear aromatic heterocyclic nitrogen bases. Burkhart, Oftring, *et al.*<sup>9-12</sup> described the use of N-allyl or N-vinyl based derivatives of nitrogen containing heterocycles as brighteners for nickel electroplating systems. The N-heterocyclic compounds were based on pyridine, quinoline, or isoquinoline which can be further derivatized with one or two C<sub>1</sub>-C<sub>4</sub> alkyl substituents.

The above mentioned brightener systems, however, may exhibit one or more of the following limitations: poor ductility; limited low-current density coverage; poor leveling at low-current densities; burning at high current densities; or decreased receptivity to subsequent chromium

deposits. Therefore, a brightener system for an acidic nickel-plating bath that will produce an extremely ductile, leveled and highly bright deposit over a wide range of current densities is desirable.

# **Experimental**

The nickel-plating baths used in these studies were Watts-type plating baths having the following general formula: 225-375 g/l nickel sulfate (NiSO<sub>4</sub>.6H<sub>2</sub>O); 60-120 g/l nickel chloride (NiCl<sub>2</sub>.6H<sub>2</sub>O); and 35-50 g/l boric acid (H<sub>3</sub>BO<sub>3</sub>). A wetting agent was added to the plating bath to eliminate pitting. Plating evaluations were conducted in a 267 ml heated Hull cell. Plating was conducted using a nickel anode and brass or steel cathodes. Prior to plating, the brass Hull cell panels used as the cathode were anodically cleaned in an alkaline electrolyte. The steel Hull cell panels were pickled in 40% hydrochloric acid prior to plating. The panels were plated at two amperes for ten minutes with air agitation. The pH of the bath was adjusted to 4.0 using sulfuric acid. All plating was performed at 55-65°C.

# **Results and Discussion**

A new and improved brightener system for acidic nickel or nickel-alloy plating baths was developed to provide an extremely ductile, leveled and highly bright nickel deposit over a wide range of current densities without the need for alkyl sulfonates and pyridine-based brightening and leveling agents. This novel brightener system is based on the use of n-allyl substituted amines and their salts.<sup>13</sup> This brightener can be used in conjunction with other Class I and II brighteners, such as, sodium saccharin and acetylenic alcohols.

The N-allyl substituted amines and their salts act as Class II brighteners. Thus, N-allyl substituted amines are preferably used in combination with at least one Class I brightener. Additionally, the deposit can be enhanced with the inclusion of one or more secondary brighteners. Examples of Class II brighteners suitable for use with N-allyl substituted amines include allyl alcohols, propargyl alcohols, butenediols or butynediols. The specific composition of the Watts nickel-plating bath with the specific Class II brighteners used to evaluate the various substituted amines is given in Table 1.

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Bath Component	Concentration		
NiSO <sub>4</sub> .6H <sub>2</sub> O	300 g/l		
NiCl <sub>2</sub> .6H <sub>2</sub> O	90 g/l		
$H_3BO_3$	45 g/l		
1,2-benzisothizolin-3-one-1,1-dioxide, Na salt	5 g/l		
propargyl alcohol ethoxylate	3 mg/l		
2-butyne-1,4-diol	10 mg/l		
butynediol ethoxylate	5 mg/l		

Table 1 Basic composition of the nickel-plating bath

The brightening and leveling capabilities of nickel baths containing N-allyl substituted amines or their salts were evaluated based on plating tests under the above conditions. The results of the use of N-allyl substituted amines as brightening agents are given in the following Table 2.

Table 2. Ferformance comparison of N-substituted annues.			
Brightener	<b>Concentration</b> (mg/l)	<b>Appearance</b> (brightness)	Leveling
None		Cloudy	Poor
N-Allylaniline	20	Cloudy	Poor
	40	Cloudy	Poor
	80	Cloudy	Poor
	160	Cloudy	Poor
N-Allylpyridine	6	Bright	Excellent
1-Allylimidizole	20	Cloudy	Fair
	40	Cloudy	Fair
1-Diethylamino-2-propyne	12.5	Cloudy	Poor
Diallylamine	20	Bright	Excellent
Triallylamine	20	Bright	Good
	40	Bright	Excellent
Diallyldimethyl	20	Slightly cloudy	Fair
Ammonium	40	Bright	Good
Chloride	80	Bright	Excellent

Table 2. Performance comparison of N-substituted amines.

As can be seen from Table 2, simple and relatively inexpensive amines can perform comparably to traditional pyridine-based brightening agents. Di-substituted alkenyl amines were the most effective.

## Conclusions

This study has demonstrated a process for producing an extremely leveled and highly bright nickel or nickel-alloy deposit over a wide range of current densities without the need for alkyl sulfonates and pyridine-based brightening and leveling agents. Simple secondary alkenyl amines are effective Class II brighteners.

An additional advantage of using N-allyl substituted amines as the primary brightening and leveling agent as compared to commonly used pyridine derivatives, for example pyridine sulfobetaine, is improved ductility. The improved ductility can be attributed to the reduced levels of sulfur in bright nickel deposit.

The primary brightening and leveling agent of this system has the general formula:

 $\begin{array}{l} H_2C=CHCH_2NR_1R_2\\ or\\ [H_2C=CHCH_2N^+R_1R_2R_3]_nX^{n-}\end{array}$ 

where  $R_1$ ,  $R_2$  and  $R_3$  are selected from the functional groups consisting or hydrogen, methyl, ethyl, propyl, allyl, propyn, propanediol and combinations thereof; and  $X^{n-}$  is an n-valent inorganic or organic anion. The N-allyl substituted amine or their salts are preferably present in a nickel-plating bath at a concentration of from about 5 mg/l to approximately 100 mg/l.

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88

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