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**EVALUATION OF
META-BENZENEDISULFONIC ACID AS
A STRESS-REDUCING ADDITIVE IN A
WATTS NICKEL ELECTROPLATING BATH**

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Greenbelt, Md.



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ABSTRACT

This paper describes the determination of the internal stress level and deposit hardness of nickel electrodeposited from a Watts-type bath containing controlled quantities of meta-benzenedisulfonic acid. The internal stress level was found to be highly sensitive to current density at low concentrations of the additive. As the additive concentration was increased, the stress level increased substantially, passed through a maximum, and then decreased at high concentrations. Deposit hardness was found to be more sensitive to current density than to stress level; no predictable relationship between stress and deposit hardness was observed.

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INTRODUCTION

Electrodeposited nickel is used widely for coating metals and electroforming parts. However, during the electrodeposition of metals, particularly of hard metals such as nickel, iron, and chromium, large internal stresses can occur. Internal stress can be particularly objectionable in electroforming because the electroformed part may warp or fracture when it is removed from the mandrel.

Watts-type nickel baths are used widely because they provide a high rate of metal deposition. However, the stress in deposits from unpurified solutions can be as high as 35 kg/mm^2 (50,000 psi). Stress can be reduced to approximately 10 kg/mm^2 (14,000 psi) through careful preparation of the bath and operation under controlled conditions. Although this usually is not objectionable, it may not be suitable for critical applications, and the stress level may be reduced further by adding certain organic substances to the bath.

Many proprietary brightening agents that reduce the internal tensile stress of the deposit are available. These brighteners are composed chiefly of those compounds having a ($=\text{C}-\text{SO}_2-$) group in the molecule, including meta-benzenedisulfonic acid, other sulfonic acids, sulfonides, sulfonimides, sulfinic acids, and sulfones. The sulfonic acids most frequently used have double-bonded carbon atoms furnished by the aryl ring. Meta-benzenedisulfonic acid has double-bonded carbon atoms supplied by the benzene ring.

Meta-benzenedisulfonic acid has been reported successful in reducing stress and producing harder printing plates from sulfamate baths (Reference 1). In addition, deposits produced over a wide current-density range have been more uniform in hardness. Watts nickel baths have also been used for printing plates (Reference 1), and some success has been reported in the use of disodium meta-benzenedisulfonate as a hardener and stress-reducer (Reference 2).

TEST PROCEDURE

The test program was designed to provide information on the residual stress and hardness of nickel electrodeposited at various current densities from a Watts-type bath containing various quantities of meta-benzenedisulfonic acid. The plating bath was prepared from technical-grade salts in the following composition.

<u>Constituent</u>	<u>Concentration (gm/liter)</u>
Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	300
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	37.5
Boric acid (H_3BO_3)	45
SNAP antipit wetting agent (Allied Chemical Corporation)	0.37
Nickel carbonate to increase pH to 4.5	

The commercial-purity meta-benzenedisulfonic acid was analyzed by means of atomic absorption spectrophotometry to determine the presence of contaminants (iron, zinc, and copper) that could increase tensile stress in the nickel platings. Iron and zinc concentrations were found to be less than 0.002 percent, and copper less than 0.001 percent.

Before the bath was used, the solution was filtered for several hours through a filter aid and then electrolyzed, using corrugated cathodes for several days at low current-density to remove harmful impurities introduced with the reagent salts. Dummy cathodes "worked" or "aged" the bath at normal current density for a week before the test samples were plated.

Test samples used were 18-gauge (0.0478-in.), cold-rolled steel strips 19 by 115 mm (3/4 in. by 4-1/2 in.). The strips were vapor-degreased in trichloroethylene, ultrasonically cleaned in hot detergent, and then acid-cleaned before plating. A motor-driven mixer agitated the bath, and bath temperature was maintained at 54°C by an immersion heater. Meta-benzenedisulfonic acid was added after completion of each specimen group by dissolving the weighed powder in 1 liter of the bath and returning the solution to the bath. The pH (electrometric) was maintained between 4.0 and 4.5 through periodic additions of nickel carbonate.

The following measurements were made on the plated samples.

1. Residual stress measurement by means of X-ray diffraction—Samples having thin deposits (approximately 5 microns) yielded diffraction patterns that were too diffuse for stress analysis. Stress data were not collected for these samples.

2. Hardness by use of a Wilson Tukon tester with a Knoop diamond indenter—Samples were edge-mounted in plastic, then ground and polished by standard metallographic techniques.

3. Deposit thickness using a metallurgical microscope fitted with a calibrated filar eyepiece—Three or more readings were made on each section.

RESULTS AND DISCUSSION

Figure 1 shows internal stress plotted against concentration of additive for four current densities. At additive concentrations ranging from 0.2 to 0.4 gram per liter, residual stress increases significantly. At least 7 grams per liter are required before the additive becomes effective, and approximately 28 grams per liter would be required to reduce the stress to zero. Hinton, Schwartz, and Cohen (Reference 3) reported similar results in studies of the effects of potassium ethyl xanthate on the structure of electrodeposited silver.

The initial increase in residual stress seen in Figure 1 seems to be caused by a "mechanism-sensitive" effect rather than by the presence of meta-benzenedisulfonic acid. The effect is more pronounced at low current-densities. This factor seems to indicate the presence of impurity ions in the bath since these are usually plated out on low current density areas. However, the presence of contaminants should show additional effect at higher additive concentrations, whereas larger additions actually reduce stress. The metallic ions of iron, zinc, and copper contribute less than 0.1 part per million to the bath at the concentration at which maximum stress occurs.

Table 1 shows the deposition rate at each current density level. The effect of current density in the range of 1 to 10.8 amp/sq dm on the internal stress may be assessed from the data presented in Figure 1. With no additive in the bath, there is little difference in the stress level. The effect of the additive is much more pronounced at 1 amp/sq dm than at higher current densities. At high additive concentrations, the stress level is relatively insensitive to current density.

An attempt was made to correlate Knoop hardness with internal stress level; no obvious correlation was apparent. However, it was noted that the hardest coatings were deposited at low current density where the stress levels are generally highest.

Little agreement has been reached among investigators regarding the mechanisms by which organic compounds reduce internal stress. Proposed theories include "blocking," "electron-pair," and "adsorption-cleavage-reduction-inclusion" mechanisms. Regardless of the mechanism,

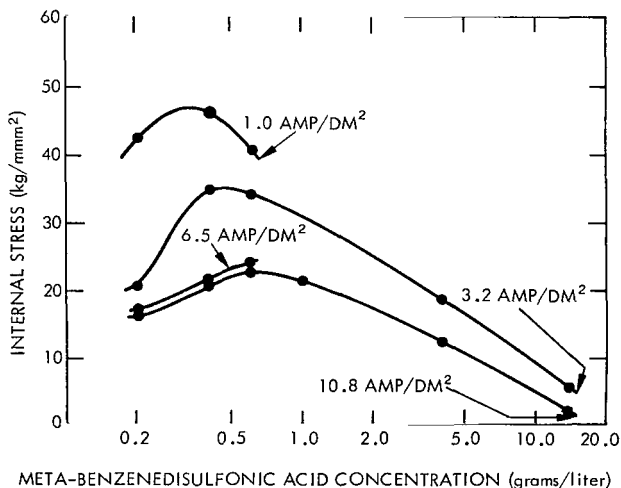


Figure 1—Effect of additive concentration on residual stress at various current densities.

Table 1

Deposition Rates at Various Current Density Levels.

Current density (amp/sq dm)	Deposition rate (mm/min $\times 10^{-4}$)
1.0	1.93
3.2	5.0
6.5	9.5
10.8	17.1

localized compressive microstresses must be generated for effective overall stress reduction. These compressive stresses must nullify the effects of tensile stress inherent in the deposit.

The blocking theory (Reference 4) requires that an organic molecule with at least one polar group attach itself to a high current density area on the cathode. When attached to a geometric peak, or other high current density area, it would repel the approach of other cations to the region it "blocks," and therefore would prevent large grains from preferentially capturing approaching cations. This action would promote leveling and fine grain size and would hinder the formation of a preferred orientation. Stress reduction is effective only at high concentrations of meta-benzenedisulfonic acid and most effective at high current density. Under the blocking theory, the polar organic molecule must not be adsorbed onto the deposit when the concentration and current density are both low. The driving force for attracting the organic molecules is low at low current density. If the organic molecule is not adsorbed onto the cathodic surface, the larger grains of the surface will capture the attracted nickel cations preferentially, yielding very large grains with preferred orientation, no leveling action, and high internal tensile stress.

The electron-pair theory, described by Roth and Leidhesiser (Reference 5), is based on experimental results that indicate an increase in cathode potential during the deposition of nickel in the presence of organic compounds. Higher voltage was necessary to maintain a predetermined current density after the addition of certain organic compounds. Experimental evidence pointed to the adsorption of the organic compound on the nickel surface, causing more difficulty in the deposition of nickel ions as metallic nickel.

Several investigators (References 4 through 9) have shown that certain organic additives codeposit with the nickel and that the additives can interfere either with electron transfer at the nickel surface or with the crystal growth. These results led Roth and Leidheiser (Reference 5) to describe their concept of available electron-pairs, defined as those electrons capable of being shared with other atoms, through association or chemical reaction, without completely severing the original bonds. If the electron-pair theory is accepted, then the sensitivity of internal stress to current density must be explained either through the inability of the organic molecule to be attracted to the surface and adsorbed at low current density, or through the lack of potential required to cause interaction of the available electron-pairs with the surface of the deposit. Studies of leveling mechanisms by Beacom and Riley (Reference 9), using radioactive sodium allyl sulfonate, indicate that both carbon and sulfur occur in the deposit throughout the current density range of 1 to 6 amp/sq dm. Since similar behavior is expected of the meta-benzenedisulfonic acid, the blocking theory is invalidated because the sensitivity of stress level to current density can be explained only by the failure of adsorption to occur.

Beacom and Riley (References 8 and 9) revealed that cleavage of organic additives occurs. A stepwise sequence of adsorption, cleavage, and reduction was shown to occur in sodium allyl sulfonate, and a cleavage mechanism has been supported by other investigators who have measured the sulfur content supplied to the deposit by sulfonated additives. It is believed that the organic molecule is adsorbed at the cathode, and the carbon-sulfur bond cleaved. The sulfur is then reduced and included in the deposit. The hydrogen evolution and the fresh nickel surface at the

cathode provide ideal conditions for the necessary reduction processes. If cleavage of the carbon-sulfur bond is required for sulfonated additives to be effective as stress reducers, the electron-pair theory must be refuted because it does not provide for a cleavage mechanism.

Of the theories available, only the adsorption-cleavage-reduction-inclusion theory can provide a mechanism to describe the sensitivity of internal stress to current density. It is postulated that the sensitivity results from failure of reduction or cleavage of the carbon-sulfur bond to occur at low current density. The organic molecule may be adsorbed onto the nickel surface and mechanically trapped by approaching cations. The effect of a large organic molecule on the properties of the deposit would be expected to be far different from that of a cleaved and reduced molecule.

Vacant sites and small impurity atoms in nickel atom sites cause lattice disturbances that result in tensile microstresses. These tensile microstresses cause the residual tensile microstress found in deposits from baths containing no effective additive. The inclusion of a large atom or molecule in a nickel site, or the inclusion of any atom in an interstitial site causes lattice disturbances that create compressive microstresses. The function of the additive is to supply interstitial or substitutional atoms to provide sufficient compressive microstress to balance the tensile microstress produced by the vacant sites. Although the additive increases total lattice strain, as evidenced by X-ray diffraction line broadening, the net microstress is reduced.

CONCLUSIONS

1. Experimental evidence supports the adsorption-cleavage-reduction-inclusion theory as the prevalent mechanism for stress reduction. The sensitivity of internal stress to current density is thought to be caused by failure of cleavage or reduction to occur at low current density.

2. A high concentration of meta-benzenedisulfonic acid is required to produce low-stress deposits from the Watts-type bath.

3. The hardness test cannot be used to measure the effectiveness of the additive in reducing residual stress levels. A stress test using one of several techniques (References 10 and 11) would be more appropriate.

4. For applications such as heavy electroforming, where low-stress deposits are required, it would be advisable to use current densities of at least 6.5 amp/sq dm.

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