Effect of Bath Stabilizers
On Electroless Nickel Deposition on Ferrous Substrates

By L. Das and D.-T. Chin

A study has been made of electroless nickel (EN) deposition on ferrous substrates in the presence of four bath stabilizers—lead ion, iodate ion, mercaptobenzothiazole and maleic acid. Deposit morphology and spreading of EN to carbon inclusions in carbon steel and gray cast iron were examined by SEM/EDS analysis. The porosity of EN coatings was measured as a function of bath stabilizer concentrations. It was found that the stabilizers retarded the rate of EN deposition on carbon inclusions and increased the porosity of EN coatings. Maleic acid decreased the phosphorus content of EN coatings. Sulfur and lead codeposited in the presence of mercaptobenzothiazole and lead ion, respectively. This paper summarizes the results of these investigations.

Electroless nickel (EN) plating baths can operate satisfactorily for a long period of time; however, they may decompose unexpectedly at any moment. This auto-decomposition process is usually controlled by the addition of trace amounts of catalytic inhibitors, called stabilizers, to the EN bath. Stabilizers, although added in very small amounts, can have important consequences for the EN plating process.

It is generally observed that addition of stabilizers decreases the EN deposition rate and, beyond certain critical concentrations, they may completely inhibit the plating process. Some stabilizers, such as thiourea, can increase the deposition rate when added in small quantities.[1] Stabilizers also affect the properties of the EN deposit. Some stabilizers, especially those containing heavy metal and sulfur compounds,

tend to codeposit, along with nickel and phosphorus and lower the corrosion resistance of EN deposit.[2,3] This study was performed to investigate the effect of four commonly used bath stabilizers: Lead ion, iodate ion, maleic acid and mercaptobenzothiazole, on the deposition rate and porosity of EN coatings on ferrous substrates.

Stabilizers most frequently used in commercial EN plating baths are divided into four classes:[4] (i) heavy metal cations: Sn^{+2}, Pb^{+2}; (ii) oxygen-containing anions: AsO_2^-, IO_3^-; (iii) unsaturated organic acids: maleic, itaconic; and (iv) compounds containing sulfur: thiourea, thiocyanate. In this study, one stabilizer was chosen from each class; this includes lead ions from group (i); iodate ions from group (ii); maleic acid from group (iii); and mercaptobenzothiazole (MBT), a sulfur-containing stabilizer, from group (iv). The following concentration ranges were used: Lead ions, 0-3 ppm; iodate ions, 0-600 ppm; maleic acid, 0-5000 ppm; MBT, 0-8 ppm. Lead ions were added in the form of lead acetate, while iodate ions were added in the form of potassium iodate.

Experimental Procedure
EN Bath and Plating Procedures

Electroless nickel deposition was carried out with a generic bath containing 44 g/L of nickel sulfate hexahydrate, 10 g/L of sodium hypophosphite hydrate, 42 g/L of amino acetic acid and 10 g/L acetic acid. The pH of the bath was adjusted to 4.5 and the bath temperature was maintained at 88-90 °C. Lead, iodate and maleic acid stabilizers were added to the EN bath in adequate quantities to provide the required concentration. MBT is insoluble in aqueous solution; a solution was prepared by dissolving 0.1 g of MBT in 100 mL of absolute ethanol. This solution was then added to the EN bath in adequate quantities to provide MBT concentration of 0-8 ppm.

AISI 1010 carbon steel and graphite coupons were used as substrates. The graphite coupon was activated for EN deposition by galvanic coupling to an AISI 1010 steel coupon with a conducting wire outside the EN bath; a piece of Teflon™ sheet of 1.6 mm thickness was placed between them to maintain the steel and graphite at a constant distance inside the bath. Prior to EN plating, the steel coupons were mechanically polished to a 120 grit finish,

Table 1
Structure of EN Deposit as a Function of Bath Stabilizer Concentration

| Stabilizer	Conc. ppm	Structure*	Nodule Size, μm Steel	Graphite
None	–	Spherical nodular	5-12	3-5
Pb^{+2}	0.5	Spherical nodular	3-10	2.2-2.5
	1	Spherical nodular	3-8	2.2-2.5
IO$_3^-$	20	Spherical nodular	3-6	2.5-3
	40	Spherical nodular	3-6	2.5-3
Maleic acid	40	Spherical nodular	3-6	2-2.5
	100	Long flake	2.5 x 9	1.1 x 2
	3000	Spherical nodular	4.5-6	1.8-2.5
Mercapto-benzothiazole	0.5	Spherical nodular	16-18	5.5-8.5
	1	Long flake	1.5 x 5	1.1 x 1.7

* Size of spherical nodules is expressed as diameter.
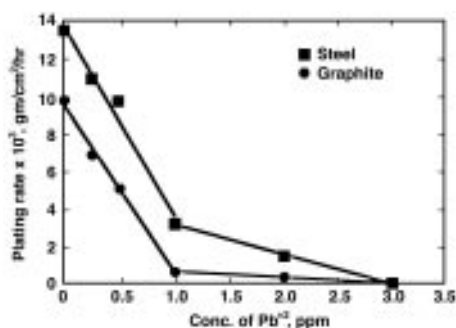
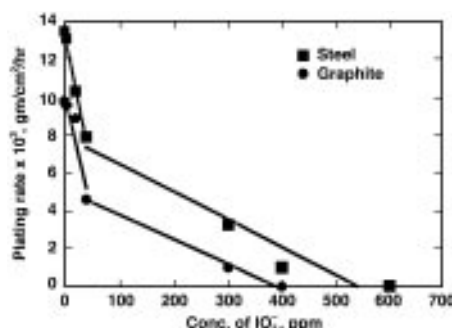Fig. 1—Effect of Pb+2 concentration on EN deposition rate; 90 °C, pH 4.5.

Fig. 2—Effect of IO3- concentration on EN deposition rate; 90 °C, pH 4.5.

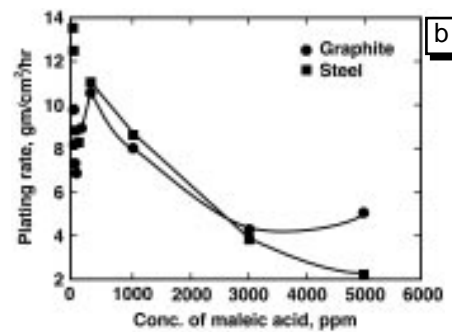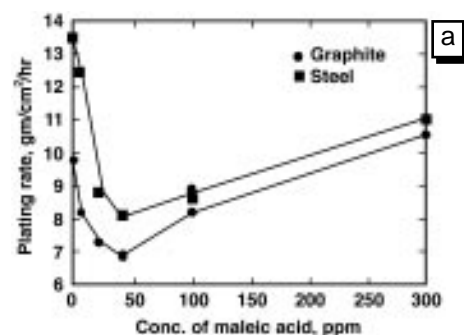
Fig. 3—Effect of maleic acid concentration on EN deposition rate; 90 °C, pH 4.5: (a) conc. range 0-300 ppm; (b) conc. range 0-5000 ppm.

Porosity Measurement

To evaluate the effect of a stabilizer on the porosity of EN coatings on ferrous substrates, experiments were performed to determine coating porosity as a function of stabilizer concentration. AISI 1010 carbon steel coupons were used as the substrate. The coupons were polished to a 120 grit finish, anodically electrocleaned in 1 M NaOH solution and activated by dipping in 37-percent HCl prior to plating. They were then immersed in EN baths containing a known amount of a stabilizer. The thickness of the coating on each coupon was controlled at 14 ±0.7 μm by adjusting the time of immersion. The EN-plated coupon was then immersed in a solution containing 3 wt percent of HCl and 1.5 wt percent of H_2O_2 and its corrosion potential with respect to a reference electrode was measured with an electrometer.

anodically electrocleaned in 1 M NaOH at 6 A/dm² and activated by dipping in 37-percent HCl. The graphite coupons were rinsed in acetone and water prior to EN plating. The substrates were immersed in the EN plating bath containing a known concentration of a particular stabilizer, and plated for a period of two hr. The plating rate on steel and graphite coupons was measured from their mass gain.

SEM/EDS Analysis

A scanning electron microscope (SEM) was used to examine the surface characteristics of the deposit. X-ray spectra were used to identify the elements present in the deposit and energy dispersive X-ray spectroscopy (EDS) was used to determine nickel and phosphorus content of the deposit.

A set of SEM/EDS element mapping experiments was performed to examine the effect of stabilizers in the plating bath on the spreading of EN deposits to the graphite part of the gray cast-iron microstructure. Gray cast-iron coupons were polished with 1-μm alumina powder, anodically electrocleaned in 1 M NaOH solution at 6 A/dm² for 2 to 3 min, and etched for 60 sec in a solution containing 95 mL of methanol, 5 mL of water and 3 mL of 70-percent HNO_3. The coupons were marked with a reference scratch line and a particular spot was observed under the SEM to identify the locations of the graphite flakes on the substrate microstructure. The coupons were then washed in acetone and coated with EN in a bath containing a known amount of a stabilizer, for a period of 10 min. The EN-coated samples were then re-examined at the same spot under the SEM, and an X-ray map for the distribution of Fe, C, Ni and P was obtained with the EDS analysis. A comparison of these maps with the uncoated substrate provided information on how the stabilizer affected the spreading of EN on the graphite inclusions of gray cast iron.

Electrochemical Polarization Measurement

Electrochemical polarization measurements were carried out to examine the effect of bath stabilizers on EN deposition reactions. The effect of the stabilizers on the anodic and cathodic half-cell reactions were studied separately, using half-EN baths. The cathodic half-bath contained nickel ion and complexing agents (amino acetic and acetic acids), but no hypophosphite ion, while the anodic half-bath contained hypophosphite ion and complexing agents, but no nickel ion. The solution pH for the half-baths was adjusted to 4.5 and the temperature maintained at 88 °C. To determine the effect of a stabilizer on the partial reactions, a known quantity of the stabilizer was added to each half-bath. The polarization

Table 2
Effect of Maleic Acid Conc.
On Phosphorus Content of EN Deposit

Maleic acid conc. ppm	Percent P	
	On steel	On Graphite
0	9.9	9.9
40	8.1	8
100	7.5	7
300	7.5	7.1
1000	7.0	7.5
3000	9.8	9.5

studies were carried out in a three-compartment cell. A nickel rotating disk, coated with EN, was used as the working electrode. A platinum gauze was the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The anodic and cathodic polarization curves were measured with a computer-interfaced potentiostat at a potential scan rate of 10 mV/sec. The mixed potential and current density were determined from the intersection of the anodic and cathodic polarization curves.

Fig. 4—Effect of mercaptobenzothiazole concentration on EN deposition rate; 90 °C, pH 4.5.

Results and Discussion
Rate of EN Deposition vs. Stabilizer Concentration

The effect of bath stabilizer concentration on the EN deposition rate on AISI 1010 steel and graphite is shown in Figs. 1-4 for lead ion, iodate ion, maleic acid and mercaptobenzothiazole (MBT), respectively.

With lead and iodate ions, the plating rate on both steel and graphite substrates decreased steadily with increasing concentration of stabilizer in the bath. The EN plating rate was completely inhibited on steel at the lead concentrations greater than 3 ppm, and on graphite at the lead ion concentrations greater than 2 ppm. With the iodate ion, the concentration necessary to completely stop the EN deposition on steel and graphite substrates were 600 ppm and 400 ppm respectively.

Maleic acid had a rather unusual effect on the deposition rates on both steel and graphite substrates. The EN deposition rates first decreased with increase in stabilizer concentration till the concentration of maleic acid reached about 40 ppm. Further increase in maleic acid concentration caused an increase in the EN plating rate, which reached a maximum at about 300 ppm of maleic acid in the bath. Afterward, further increase in the maleic acid concentration resulted in a decrease
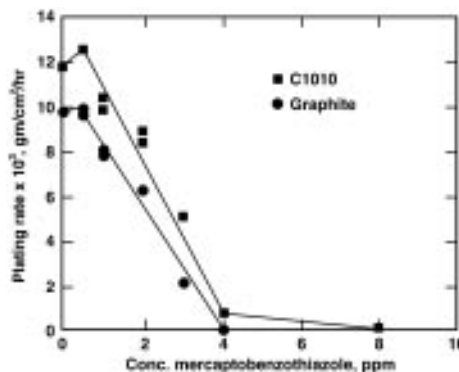
in the plating rate. The plating rate decreased more rapidly on the steel substrate than on the graphite, resulting in a higher plating rate on the graphite for maleic acid concentrations greater than 3000 ppm. This phenomenon was confirmed by visual observation of hydrogen gas evolution on the substrate surface. When the maleic acid concentration in the bath was 300 ppm, the rate of hydrogen bubble evolution from the substrate surface was higher than when the maleic acid concentration was 100 ppm. When the maleic acid concentration reached 5000 ppm, there was considerable delay in hydrogen evolution from both graphite and steel surfaces; once EN deposition was induced on the graphite surface, there was nearly twice as much hydrogen evolution from the graphite surface as on the steel surface.

The EN deposition rate was increased by the addition of MBT to the bath, when the MBT concentration was less than 0.5 ppm. When the concentration was increased beyond 0.5 ppm, the EN deposition rate began to decrease on both steel and graphite substrates. The EN plating rate on steel and graphite was totally inhibited when the MBT concentration exceeded 8 ppm for steel and 4 ppm for graphite. The maximum on the plot of EN deposition rate vs. MBT concentration was also observed in the study by Altura[2] and De Minjer and Brenner[1] for the sulfur-containing stabilizers, such as thiourea and thiocyanate.

Morphology of EN Deposits

Figure 5a is a SEM photomicrograph of a steel substrate coated with 27 μm of EN from a bath without any stabilizers. The photomicrograph of an EN deposit (21 μm thick) on a graphite substrate without use of bath stabilizers is shown in Fig. 6a. The inset on each photomicrograph is the X-ray spectrum showing the elements present on the sample surface.
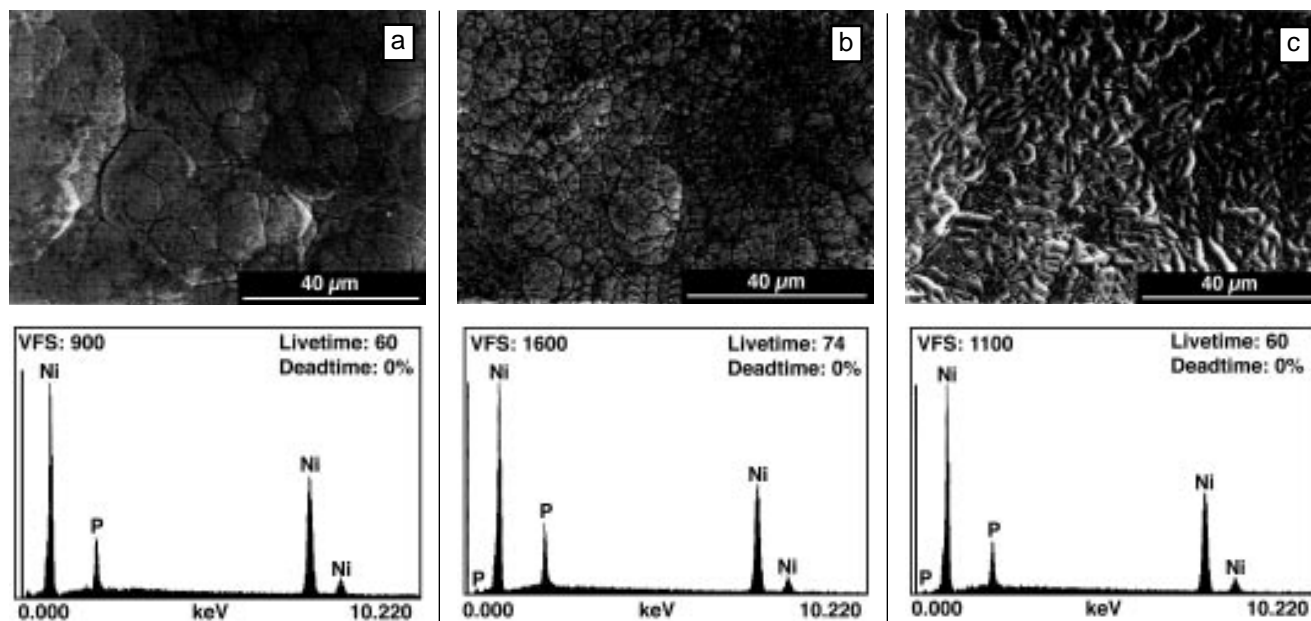

Fig. 5—SEM photomicrograph of EN on steel substrate from a bath: (a) without stabilizer (avg. coating thickness, 27 μm); (b) with 20 ppm IO_3^- (avg. coating thickness, 20 μm); (c) with 100 ppm maleic acid (avg. coating thickness, 17.5 μm).
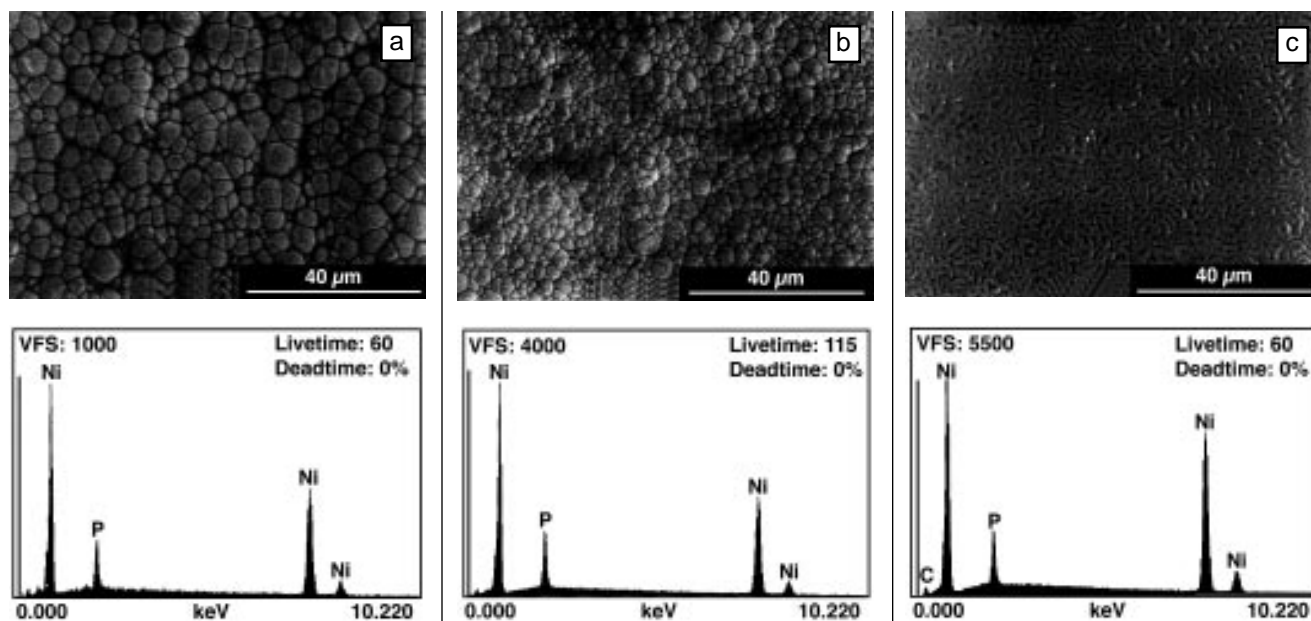
Fig. 6—SEM photomicrograph of EN on graphite substrate from a bath: (a) without stabilizer (avg. coating thickness, 21 μm); (b) with 20 ppm IO₃⁻ (avg. coating thickness, 14 μm); (c) with 100 ppm maleic acid (avg. coating thickness, 15.8 μm).

The deposit on both substrates had a spherical nodular structure. The deposits obtained from the baths containing lead and iodate ions also had a nodular structure of a similar nature, although the nodule size decreased in the presence of lead or iodate ions. Figures 5b and 6b are the SEM photomicrographs of EN deposits obtained from a bath containing 20 ppm of iodate ion on steel (20 μm thick) and graphite substrates (14 μm thick), respectively. They are

Fig. 7—EDS spectrum of EN on steel substrate obtained from a bath: (a) with 2 ppm Pb⁺² (avg. coating thickness 4 μm); (b) with 4 ppm MBT (avg. coating thickness 2.2 μm).

representative of the deposit structure obtained from the baths containing lead and iodate stabilizers.

When maleic acid was added to the EN plating bath, spherical nodular structure similar to those shown in Figs. 5b and 6b was observed for all EN deposits except those obtained in the maleic acid concentration range of 100 to 300 ppm. Those deposits had a completely different structure, showing long, flaky formations on both steel and graphite surfaces, as shown in Figs. 5c and 6c, and had a bright appearance. It may be noted that in this concentration range, the EN deposition rate increased with increase in maleic acid concentration, and peaked at 300 ppm. Baths containing MBT produced deposits with spherical-nodular structure similar to that shown in Figs. 5b and 6b when the MBT concentration was below 1 ppm. Deposits obtained from the baths containing 1-2 ppm of MBT had a flake-like structure similar to that shown in Figs. 5c and 6c. Table 1 summarizes the structure of EN deposits obtained with different stabilizers at various concentrations.

Energy dispersive spectroscopy (EDS) of the EN deposits revealed that lead was codeposited along with nickel and phosphorus on the substrate surface when the plating baths contained more than 1 ppm of lead ions. Figure 7a is an X-ray spectrum of an EN deposit (4 μm thick) obtained from a bath
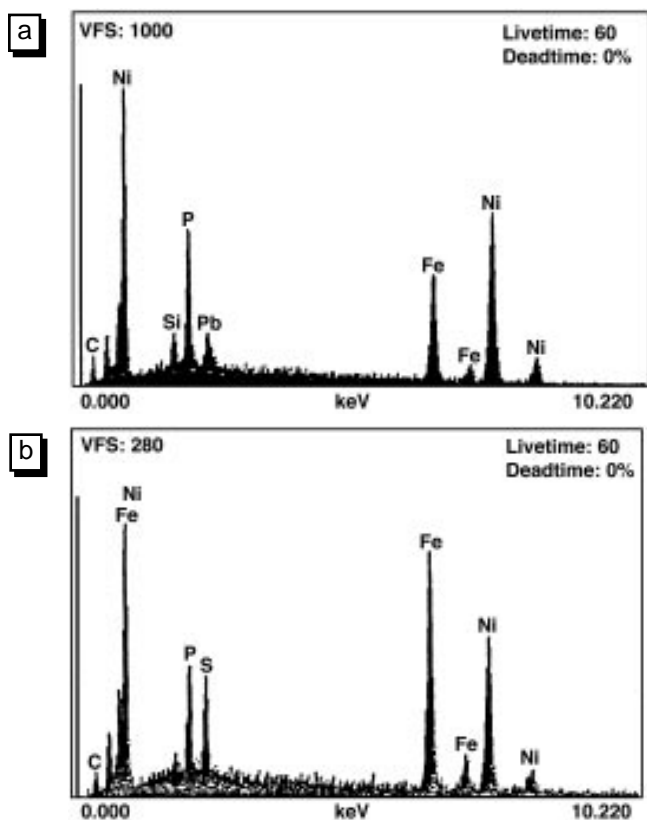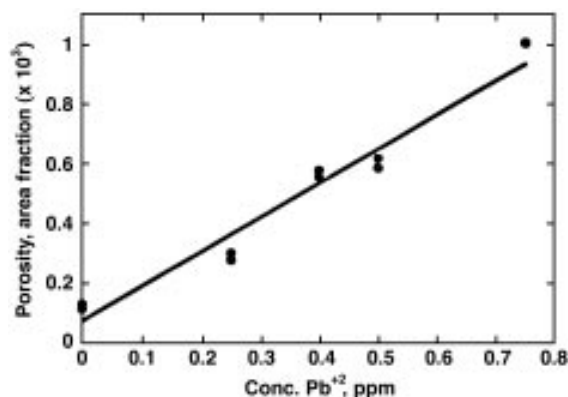

Fig. 8—Effect of Pb⁺² concentration on porosity of EN deposit on AISI 1010 carbon steel. Coating thickness 14 ±0.7 μm.

containing 2 ppm of lead ion. A strong lead peak indicated that lead was present in the deposit. Plating in the MBT-stabilized bath led to codeposition of sulfur, as indicated by the sulfur peak in the X-ray spectrum, Fig. 7b. Electroless nickel plating in the maleic-acid-stabilized bath decreased the phosphorus content of the deposit, as shown in Table 2. The EDS analysis revealed that phosphorus content in the EN deposit decreased from 10 to 7 percent when the maleic acid concentration increased from 0 to 300 ppm. The phosphorus content returned to 10 percent when the maleic acid concentration was 3000 ppm (Table 2).

Fig. 9—Effect of IO_3^- concentration on porosity of EN deposit on AISI 1010 carbon steel. Coating thickness 14 ± 0.7 μm.

ppm of MBT, with coating thicknesses of 2, 1.7 and 0.2 μm, respectively. With no MBT, the EN deposit covered the substrate completely. With 1 ppm of MBT, a small portion of the graphite was left uncoated; there was no Ni-P deposit on some of the locations where graphite was initially present. When the MBT concentration was increased to 5 ppm, most of the graphite flakes on the substrate surface were left uncoated after 10 min plating time. The amount of sulfur on the deposit was greater at 5 ppm of MBT, compared to the sample obtained from a bath containing only 1 ppm. These results demonstrate that increasing the concentration of MBT in the bath reduced the rate of EN deposition on the graphite inclusions of the ferrous alloys and caused sulfur to codeposit. Sulfur inhibits the catalytic reaction of EN deposition and enhances the possibility of pore formation in EN deposits.

Element Mapping Analysis

A set of element mapping experiments, using the SEM/EDS analysis, was performed to determine how the spreading of EN deposits to the graphite part of the gray cast microstructure was affected by the addition of different types of stabilizers to the bath. The experiments were carried out with lead, iodate, maleic acid and MBT stabilizers. The effect of MBT may be taken as a typical example: Three gray cast iron coupons were plated with EN in baths containing 0, 1 and 5

The SEM/EDS mapping analysis of EN samples obtained from the baths containing lead ions, iodate ions and maleic acid also showed that increasing the concentrations of these stabilizers in a plating bath reduced the rate of spreading of EN deposits to the graphite inclusions on the microstructure of ferrous alloys. When 100 ppm of maleic acid was added to
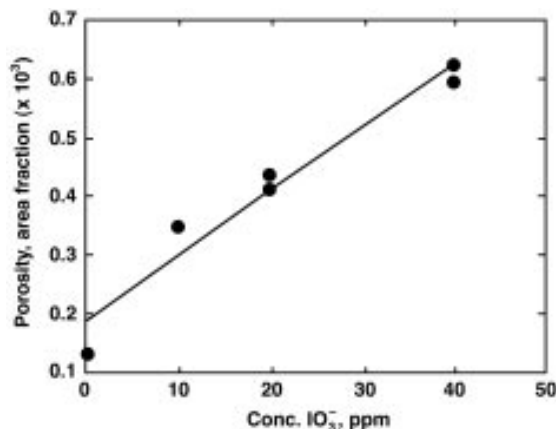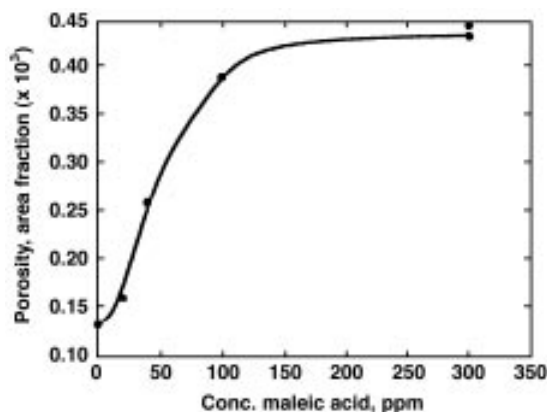

Fig. 10—Effect of maleic acid concentration on porosity of EN deposit on AISI 1010 carbon steel. Coating thickness 14 ± 0.7 μm.

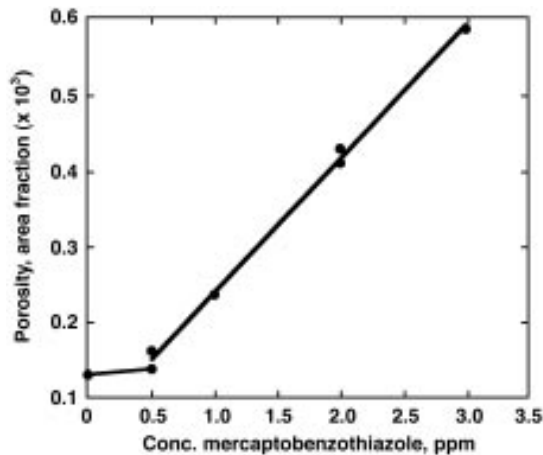*Fig. 11—Effect of mercaptobenzothiazole concentration on porosity of EN deposit on AISI 1010 carbon steel. Coating thickness 14 ± 0.7 μm.*
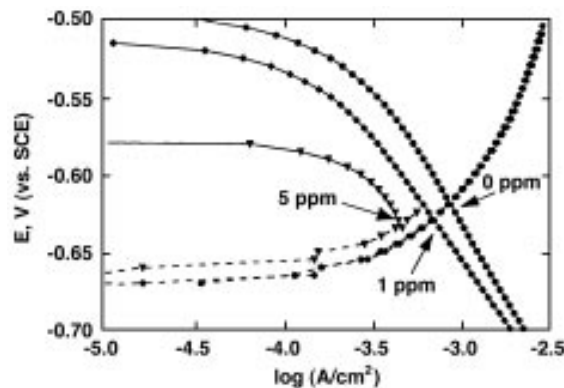

Fig. 12—Effect of Pb^{+2} stabilizer on the mixed potential for EN deposition on electroless nickel electrode.
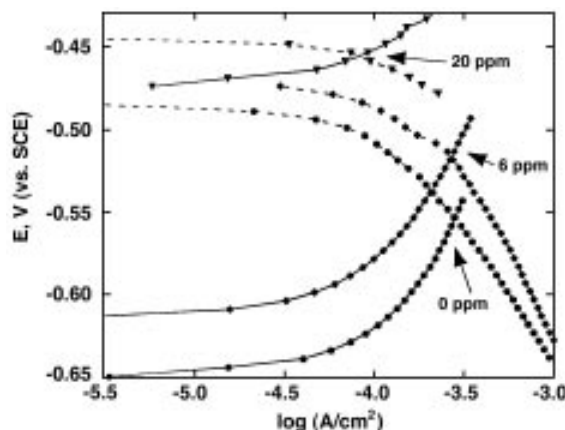

Fig. 13—Effect of IO_3^- stabilizer on the mixed potential for EN deposition on electroless nickel electrode.

a bath, the EN deposit was so thin that some graphite flakes were still visible after 10 min.

Porosity of EN Deposit

To evaluate quantitatively the effect of stabilizers on the porosity of EN coatings on ferrous substrates, a set of non-destructive electrochemical porosity measurements was performed to determine the coating porosity as a function of stabilizer concentration. AISI 1010 carbon steel substrates were coated with 14 ±0.7 μm thick EN from baths containing a known amount of stabilizer. Figures 8-11 show the porosity of EN deposits vs. the concentration of stabilizer in the bath for lead ion, iodate ion, maleic acid and MBT, respectively. The coating porosity increased linearly with increasing lead concentration (Fig. 11). The addition of iodate ions also resulted in an increase in the porosity of EN deposits (Fig. 9). The results for maleic acid indicate (Fig. 10) that in the concentration range of 0-100 ppm, the coating porosity increased with increase in concentration. In the range of 100-300 ppm, EN porosity leveled off to a constant value of 0.0004 (area fraction of pores on coating surface). This was probably a result of the flaky structure of EN deposits obtained from the bath containing 100-300 ppm of maleic acid (Fig. 5c). Electroless nickel deposits obtained from baths containing 0-0.5 ppm of MBT had the same porosity. When MBT concentration exceeded 0.5 ppm, porosity increased linearly with increase in concentration of MBT, as shown in Fig. 11.

Electrochemical Polarization Study

The effect of stabilizers on the anodic and cathodic half-cell reactions were studied separately, using EN half-baths. The cathodic half-bath had no hypophosphite, while the anodic half-bath did not contain any nickel ions. These half-cell reactions were first studied in the absence of stabilizers. To determine the effect of a stabilizer on a half-cell reaction, the stabilizers were added to the half-bath.

The anodic polarization and the cathodic polarization curves in the presence of lead ions are presented as an Evans diagram in Fig. 12. The anodic polarization curve was not affected by the addition of lead ions; increasing lead ion concentration caused a shift of the cathodic polarization curve toward the negative potential. This indicates that lead ions stabilize the bath by inhibiting the reduction reaction of nickel ions. For each lead ion concentration (Fig. 12), the anodic and cathodic polarization curves intersected at a mixed potential, as shown by a small arrow in the figure. The point of intersection also gave the mixed-current density, which represented the rate of EN deposition reaction at a given lead ion concentration. The mixed-current density decreased with increasing lead ion concentration. This trend agreed with the result of actual EN plating rate measurement.

The effect of iodate (IO_3^-) ions on the anodic and cathodic half-reactions is shown in Fig. 13. Both anodic and cathodic polarization curves shifted toward the positive potential with increasing iodate concentration. The open-circuit potential of the anodic polarization curve was -650 mV vs. SCE with no iodate ion, and was shifted to -360 mV vs. SCE when 100 ppm of iodate was added to the solution. This was probably caused by the adsorption of iodate ions on the surface of the working electrode, which reduced the number of catalytic sites available for oxidation of hypophosphite ions. Feldstein and Amadio[5] also observed this effect, attributing it to a reaction between adsorbed iodate ions and hypophosphite
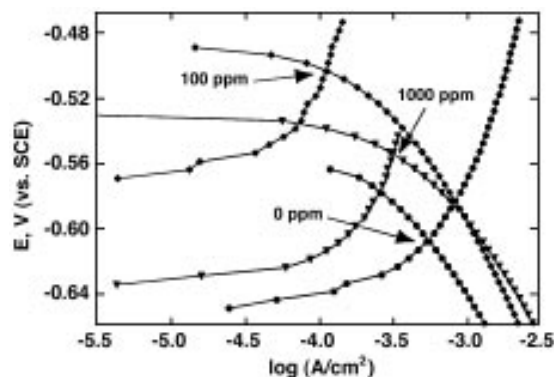

Fig. 14—Effect of maleic acid stabilizer on the mixed potential for EN deposition on electroless nickel electrode.
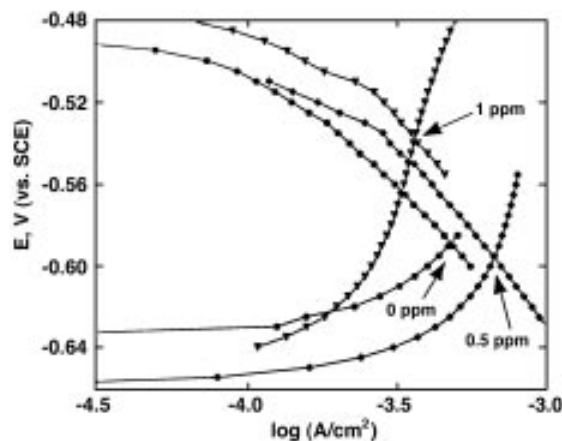

Fig. 15—Effect of mercaptobenzothiazole stabilizer on the mixed potential for EN deposition on electroless nickel electrode.

ion. The mixed-current density decreased with an increase in iodate concentration.

The anodic and cathodic polarization curves in the presence of maleic acid are shown in Fig. 14. The anodic polarization curves show a shift in the open circuit potential in the positive direction when the maleic acid concentration was increased from 0 to 100 ppm. When the concentration was 1000 ppm, the open circuit potential of the anode was shifted back in the negative direction. A similar phenomenon was observed for the cathodic polarization curves. The mixed potential for the EN deposition reaction was shifted in the positive direction in the maleic acid concentration region of 0-100 ppm; the drop in the mixed-current density in this initial concentration region was probably caused by the absorption of maleic acid on the working electrode surface. Maleic acid is unsaturated; at a sufficiently high concentration (greater than 100 ppm), it could undergo hydrogenation to succinic acid on the working electrode surface. Once hydrogenated, it no longer functioned as a stabilizer, and the EN plating rate increased with further increase in concentration, as shown in Figs. 3a and 14.

The effect of MBT on the anodic and cathodic polarization curves of the EN deposition reaction is shown in Fig. 15. The effect of MBT on the shape of anodic polarization curves was small; however, MBT shifted the open-circuit potential of the cathodic polarization curve in the positive direction. The mixed-current density for EN deposition was increased by the addition of MBT in the concentration range of 0-0.5 ppm. This result agreed with the plating rate measurement that the EN deposition rate had a maximum at the MBT concentration of 0.5 ppm, then decreased with further increase of MBT concentration.

Summary

Addition of lead and iodate ions to the bath resulted in decrease of the plating rate on steel and graphite substrates. When maleic acid was used as the stabilizer, the EN plating rate initially decreased until the concentration reached about 40 ppm. Further increase in maleic acid concentration caused an increase in the plating rate and a maximum was observed at 300 ppm. Less than 0.5 ppm MBT increased the EN deposition rate, but reduced it when the concentration was higher than 0.5 ppm.

Lead and sulfur codeposited with nickel and phosphorus when EN plating was carried out in the baths containing lead ions and MBT, respectively, as the stabilizers. Addition of maleic acid to the bath decreased the phosphorus content of the EN deposit and changed the morphology from a spherical nodular structure to an elongated, flake-like structure.

Bath stabilizers decreased the rate of EN spreading on graphite inclusions in the microstructure of gray cast iron. This enhanced the possibility of pore formation at the locations where graphite was present on substrate surfaces. The porosity measurement for EN coatings on AISI 1010 carbon steel revealed that increasing stabilizer concentration resulted in an increase in the porosity of EN deposit.

The results of electrochemical polarization measurement indicates that lead ions and MBT affected the cathodic half-reaction, while iodate ions and maleic acid affected both anodic and cathodic half-reactions. The EN plating rate calculated from mixed-potential theory, as a function of the stabilizer concentration, showed similar trends as those observed in actual plating rate measurement.

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