

## CORROSION RESISTANCE OF ELECTROLESS NICKEL COATINGS

Replacement or repair of corrosion damaged equipment is the largest maintenance requirement for industry. In the United States alone, the cost of corrosion is estimated to be 70 billion dollars annually, or 4.2 percent of the gross national product. Probably 15 percent of this loss could be saved with better materials, procedures or designs through the use of presently available technology<sup>1</sup>. The direct cost of corrosion in other industrial countries has been found to be similar to those in the USA<sup>2</sup>.

One technique for reducing the corrosion of metals is to coat them with thin layers of less reactive metals or alloys. Various techniques, including electroplating, vapor deposition, metal spraying, and electroless deposition, have been used with varying success. Unfortunately, most metallic coatings are inherently porous and historically have been of little value as barriers against corrosion. Recently, with the development of Electroless Nickel, these problems have largely been overcome. Today, because of its superior corrosion resistance and because of the increased importance being given equipment cost and reliability, this coating is being considered for more and more uses.

### CORROSION RESISTANCE IS OUTSTANDING

Electroless Nickel is a barrier coating. It protects the underlying metal by sealing it off from the environment, rather than by galvanic or sacrificial action. Because of its amorphous nature and passivity, however, the corrosion resistance of Electroless Nickel is excellent and in most environments superior to that of pure nickel or chromium alloys. When properly applied, the coating is almost totally resistant to alkalies, to salt solutions and brines, to chemical and petroleum environments, and to all types of hydrocarbons and solvents.

deposits also have good resistance to ammonia solutions, to organic acids, and to reducing acids. They are only significantly attacked by strongly oxidizing media, such as strong nitric acid.

### ATMOSPHERIC CORROSION

Electroless Nickel is almost immune to attack in rural, industrial and marine atmospheres. In exposures at Kure Beach, N.C., Corpus Christi, Texas, and Washington, D.C., even very thin coatings were found to provide complete protection to properly prepared substrates for periods of 6 to 15 months<sup>3 4</sup>. These studies also showed 0.5 mil (12  $\mu$ m) thick Electroless Nickel coatings to provide better protection than 1 mil (25  $\mu$ m) thick coatings of electrolytic nickel.

An unique property of Electroless Nickel is its freedom from under-deposit or interfacial attack. Unlike electrolytic coatings, even if corrosion does begin through pin holes or damaged areas, there is no tendency for it to spread in either atmospheric or submerged water environments. Often as the affected area fills with rust, further attack of the substrate slows and may stop.

### SEAWATER

coatings can provide very effective protection against corrosion in seawater systems. Shipboard hardware, fittings and valves, as well as land based systems, are commonly protected with 3 mil (75  $\mu\text{m}$ ) thick deposits. In the Ghawar Field in Saudi Arabia, coated ball valves have been used in the seawater injection system for 5 years without any corrosion. One valve was removed and inspected after 4 years of operation and was found to be in perfect condition.

Laboratory investigations in aerated, synthetic seawater at temperatures up to 200°F (95°C) have shown the maximum loss of Electroless Nickel to be only 0.04 mpy (1  $\mu\text{m}/\text{y}$ ). Because of its high hardness, the deposit has excellent resistance to impingement and erosion/corrosion in seawater and is frequently used for pumps, valves and similar equipment. Vibratory cavitation tests have shown coatings to have resistance equal to stainless and high chromium alloys in both sea and fresh waters.

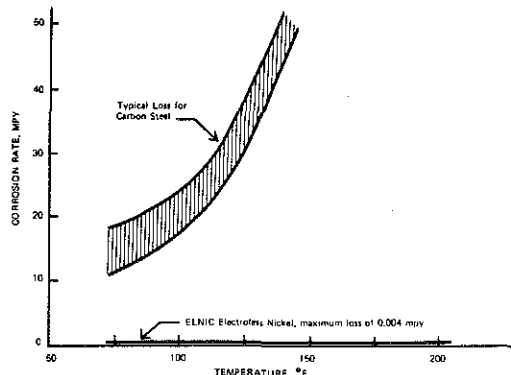
### NATURAL WATERS

Corrosion of Electroless Nickel in fresh and high purity waters is also slight. Tests in tap water have shown corrosion rates of only 0.01 to 0.03 mpy (0.3 to 0.8  $\mu\text{m}/\text{y}$ ) at ambient temperature. Corrosion in air saturated, deionized water is illustrated by Figure 1, which compares the coating to plain steel. Even at temperatures as high as 200°F (95°C), the maximum loss of the deposit is only 0.004 mpy (0.1  $\mu\text{m}/\text{y}$ ).

Similarly the resistance of coatings to corrosion in cooling water, boiler feed water, condensate and the like is superior. Even at temperatures of 650°F (350°C), its loss in deaerated, double distilled water is less than 0.008 mpy (0.2  $\mu\text{m}/\text{y}$ ).

FIGURE 1

Comparison of the corrosion of carbon steel and electroless nickel in oxygen saturated deionized water

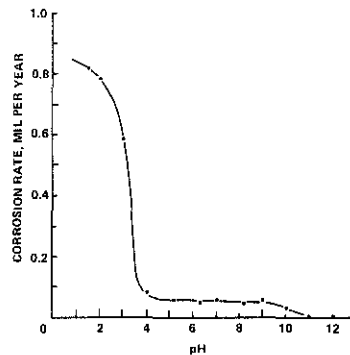


electroless nickel also has good resistance to condensing steam. Autoclave tests in which 360°F (180°C) steam, saturated with O<sub>2</sub> and CO<sub>2</sub>, was condensed on heat transfer panels showed the coating to be unattacked after 108 hours. Within this period commercial glass linings normally are severely etched.

Solution pH has a pronounced influence on the corrosion of most metals, including electroless nickel. The results of tests conducted to establish this effect are shown in Figure 2.

FIGURE 2

Effect of pH on the corrosion of Electroless Nickel



For these tests, 0.1 percent HCl in deionized water was neutralized with sodium hydroxide to produce solutions with pH values ranging from 1.4 to 12. Immersion tests at ambient temperature showed that above 3 pH corrosion of the deposit was uniformly less than 0.08 mpy (2  $\mu\text{m}/\text{y}$ ) and averaged only 0.04 mpy (1  $\mu\text{m}/\text{y}$ ). At lower pH values attack was increased, but did not exceed 0.8 mpy (20  $\mu\text{m}/\text{y}$ ).

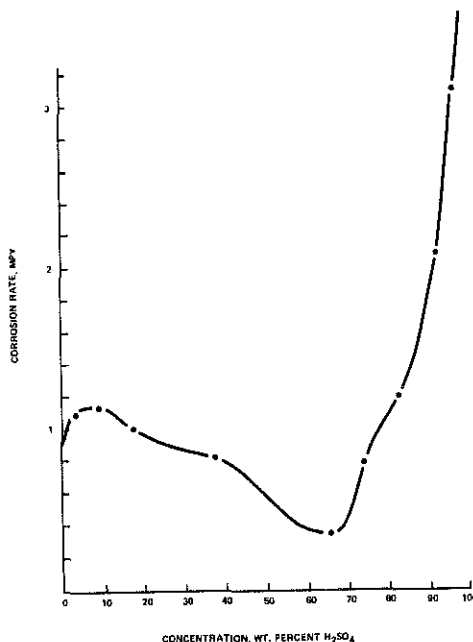
### INORGANIC ACIDS

electroless nickel has useful resistance to reducing acids. Typically the deposit's loss rate will range between about 0.3 and 1 mpy (8 and 25  $\mu\text{m}/\text{y}$ ). Accordingly, the coating is not commonly used for prolonged exposures, although it can be used safely for intermittent or short term services such as acid cleaning or back washing. Electroless nickel deposits generally have poor resistance to oxidizing acids. In these environments, losses can be quite high and electroless nickel is not normally used.

Sulfuric Acid. Sulfuric acid is the most widely used mineral acid. Its behavior, however, is unusual. At ambient temperature, with concentrations less than 85 percent, it is a reducing acid. At higher concentrations it becomes an oxidizing acid. The behavior of electroless nickel follows that of sulfuric acid. Below about 85 percent concentration, these coatings have good resistance at ambient temperature, with rates generally between 0.3 and 1.1 mpy (8 and 28  $\mu\text{m}/\text{y}$ ). Above 85 percent, corrosion of the deposit increases rapidly and in oleum may exceed 10 mpy (250  $\mu\text{m}/\text{y}$ ). The resistance of electroless nickel to sulfuric acid is summarized in Figure 3.

FIGURE 3

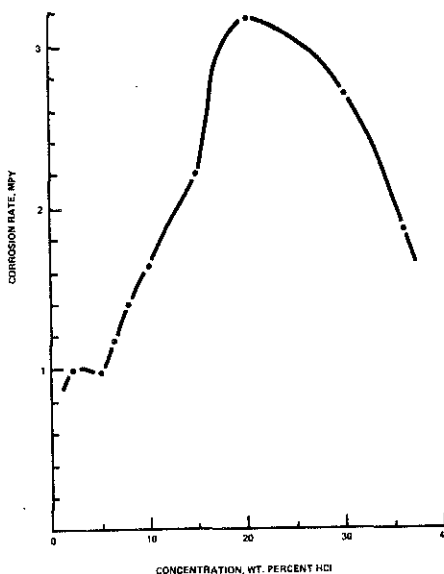
Corrosion of Electroless Nickel in sulfuric acid



Hydrochloric Acid. At ambient temperature deposits have useful resistance to hydrochloric acid only up to about 10 percent concentration. In these dilute solutions losses are generally about 1 mpy (25  $\mu\text{m}/\text{y}$ ). At higher concentrations corrosion is increased to between 2 and 3 mpy (50 and 75  $\mu\text{m}/\text{y}$ ). Attack is also increased by increased temperature or by the presence of oxidizing salts. The resistance of electroless nickel to hydrochloric acid is summarized in Figure 4.

FIGURE 4

Corrosion of Electroless Nickel in hydrochloric acid



Hydrofluoric Acid. Although chemically hydrofluoric is a weaker acid than hydrochloric or sulfuric, it is much more corrosive than either and very difficult to contain. Only gold, platinum and Teflon are completely resistant to attack. The resistance of commercial nickel base alloys, however, can be adequate for most applications. These alloys develop thin adherent protective fluoride films on their surfaces which retard continued attack.

The resistance of coatings to hydrofluoric acid solutions is useful for dilute solutions. Below 25 percent concentration, corrosion rates are generally about 1 mpy (25  $\mu\text{m}/\text{y}$ ). The behavior of electroless nickel in hydrofluoric acid solutions is summarized in Table 1.

TABLE 1

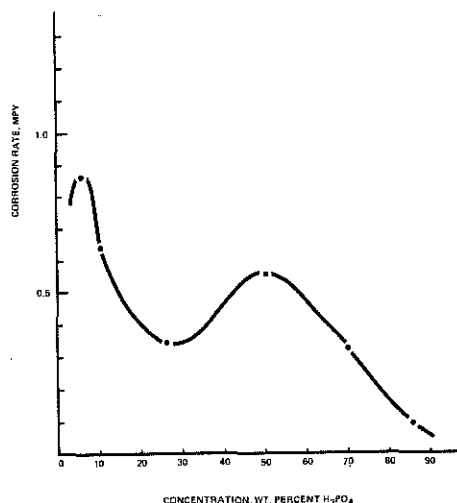
CORROSION OF ELECTROLESS NICKEL  
IN HYDROFLUORIC ACID SOLUTIONS  
AT AMBIENT TEMPERATURE

<u>CONCENTRATION,</u> <u>Wt. Percent</u>	<u>CORROSION RATE,</u> <u><math>\mu\text{m}/\text{y}</math></u>	<u>CORROSION RATE,</u> <u>mpy</u>
2	27	1.1
10	30	1.2
25	30	1.2
40	53	2.1
52	46	1.8

Phosphoric Acid. The resistance of electroless nickel to reagent phosphoric acid is good at ambient temperature with all concentrations. At 85 percent, its loss is only 0.1 mpy ( $2\frac{1}{2}$   $\mu\text{m}/\text{y}$ ). This is illustrated by Figure 5. With commercial acid containing ferric salts, however, accelerated attack may occur and the coating is not commonly used. Corrosion is also increased in fortified acids or by increased temperature.

FIGURE 5

Corrosion of Electroless Nickel in phosphoric acid



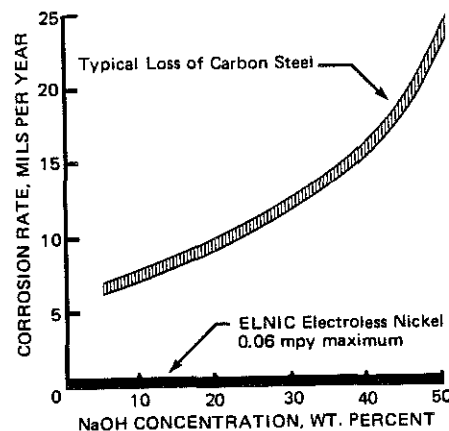
Nitric Acid. Nitric acid is a very strong oxidizing agent at all concentrations. Accordingly, the resistance of nickel alloys is very limited. electroless nickel can only be used for concentrations up to 10 percent at ambient temperature. In this range losses are generally between 0.5 and 1 mpy (12 and 25  $\mu\text{m}/\text{y}$ ). At higher concentrations, corrosion increases catastrophically and can exceed 1 inch per year (25 mm/y) in concentrated acid.

### CAUSTIC ALKALIS

coatings have outstanding resistance to caustic soda, caustic potash and most other alkalis, even at high concentrations and elevated temperatures. At concentrations below 50 percent, corrosion is negligible due to the formation of protective oxide films. A comparison of the performance of coatings with plain steel at 200°F (95°C) in up to 50 percent sodium hydroxide is shown in Figure 6. Even at concentrations as high as 72 percent with temperatures of about 230°F (110°C), electroless nickel coatings have useful resistance; in one field test the loss rate of the deposit was only 0.7 mpy (18  $\mu\text{m}/\text{y}$ ) compared to 0.5 mpy (13  $\mu\text{m}/\text{y}$ ) for wrought nickel and 41 mpy (1000  $\mu\text{m}/\text{y}$ ) for plain steel.

FIGURE 6

Comparison of the corrosion of carbon steel and electroless nickel in caustic soda at 200°F



Chlorates and some sulfur compounds increase the attack of nickel alloys in caustic soda and should be removed if possible. For example, the addition of 0.4 percent sodium chlorate will increase the corrosion of electroless nickel more than 10 times. The addition of sulfur compounds, such as sodium sulfite, may also increase attack of the coating. The presence of hydrogen sulfide, however, is not detrimental and may improve the resistance of coatings.

## AMMONIA SOLUTIONS

coatings have excellent resistance to ammonia and useful resistance to ammonium hydroxide solutions. In pure ammonia, the loss of coatings is generally less than 0.2 mpy (5  $\mu\text{m}/\text{y}$ ). When water is also present, however, ammonia begins to hydrolyze, forming nickel complexes and corrosion increases as illustrated by Table 2.

TABLE 2

CORROSION OF ELECTROLESS NICKEL  
IN AMMONIACAL SOLUTIONS  
AT AMBIENT TEMPERATURE

SOLUTION	CORROSION RATE	
	$\mu\text{m}/\text{y}$	mpy
2% $\text{NH}_3$	28	1.1
10% $\text{NH}_3$	23	0.9
28% $\text{NH}_3$	16	0.6
27% $\text{NH}_4\text{Cl}$	8	0.3
66% $\text{NH}_4\text{NO}_3$	10	0.4
25% $\text{NH}_4\text{H}_2\text{PO}_4$	5	0.2
43% $(\text{NH}_4)_2\text{SO}_4$	3	0.1

In ammonium salt solutions, electroless nickel also displays useful resistance. In ammonium chloride and nitrate its loss is about 0.4 mpy (10  $\mu\text{m}/\text{y}$ ), while in phosphate and sulphate solutions losses are only 0.2 mpy (5  $\mu\text{m}/\text{y}$ ). This is also summarized in Table 2.

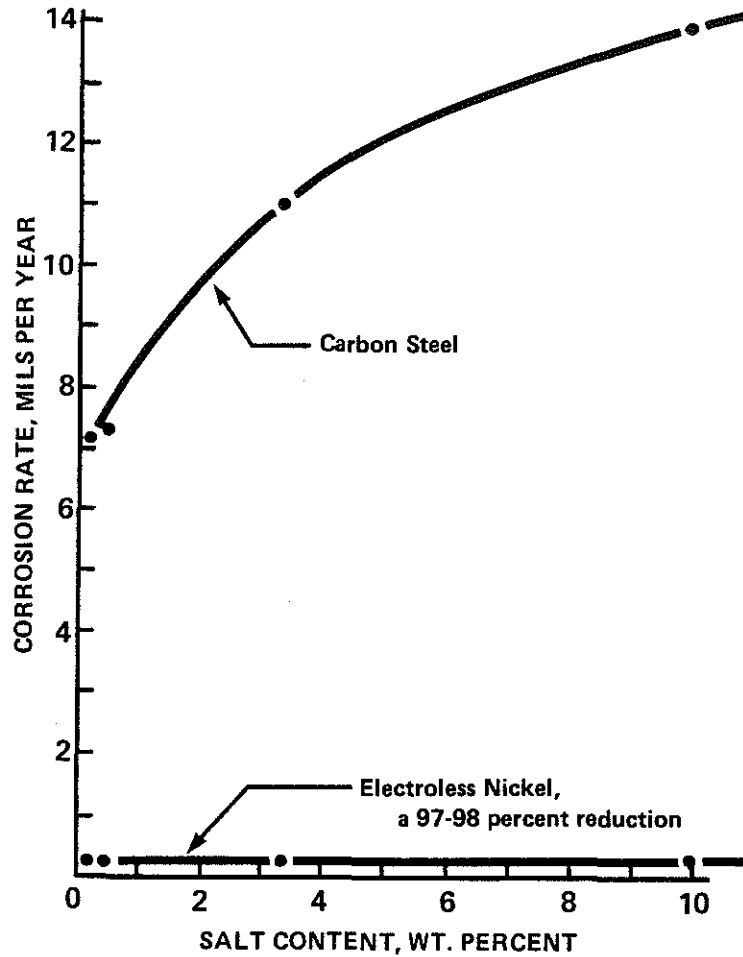
## PETROLEUM ENVIRONMENTS

Corrosion in petroleum production environments is usually complex, consisting of several corrosives, with the additive effect of temperature, pressure, velocity, and abrasives. The most common corrodents in the oil field are salt water, carbon dioxide and hydrogen sulfide, although oxygen, nitrogen and sulfur compounds, and organic and inorganic acids may also be present.

Electroless nickel coatings have long been used in the petroleum industry to mitigate corrosion and erosion. The results of a recent study to characterize the performance of electroless nickel in oil field environments are summarized in Figures 7 and 8. In these tests brine concentrations from 0 to 10 percent TDS, and various acid gas conditions, were studied at temperatures up to 350°F (180°C)<sup>6</sup>.

FIGURE 7

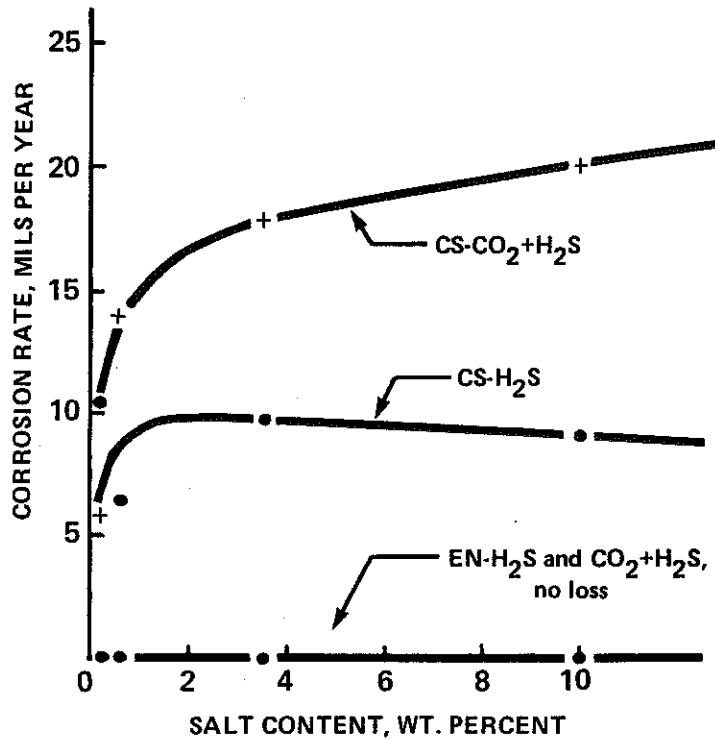
Comparison of the corrosion of carbon steel and electroless nickel in CO<sub>2</sub> saturated brines at 95°C



In CO<sub>2</sub> saturated brines at 200°F (95°C), the corrosion rate of electroless nickel is about 0.2 mpy (5 μm/y). This represents a 98 percent improvement over the loss of plain steel. In H<sub>2</sub>S saturated and mixed CO<sub>2</sub>/H<sub>2</sub>S saturated brines, electroless nickel does not corrode. When hydrogen sulfide is present, a tenacious sulfide film forms, increasing the passivity of the coating and preventing further attack. Other tests have showed that sulfide films will form with H<sub>2</sub>S concentrations as low as 4 ppm and at temperatures as high as 350°F (180°C)<sup>6</sup>.

FIGURE 8

Comparison of the corrosion  
of carbon steel and electroless  
nickel in H<sub>2</sub>S containing brines  
at 95°C



Since most production environments contain at least a trace of H<sub>2</sub>S, nickel coatings provide almost complete protection against oil field corrosion. In one sour gas system in the Middle East, nickel coated chokes and valves have been used for 8 to 10 years at 200°F (95°C) and velocities up to 50 fps (15 mps) without any measurable corrosion. Previously used steel components experienced losses of 80 to 120 mpy (2 to 3 mm/y)<sup>7</sup>.

## ORGANIC ACIDS

Typically organic acids are weak and non-oxidizing. They normally become weaker as their molecular weight increases and the carbon chain becomes longer. Like ammonia, most organic acids have good complexing ability with nickel ions and water; thus, the loss of electroless nickel is accelerated by increasing water content.

electroless nickel coatings have excellent resistance to all types of concentrated organic acids. In diluted solutions, however, attack is increased. Corrosion is also increased by aeration and elevated temperature. The results of tests with deposits in some aerated organic acids are shown in Table 3.

TABLE 3

CORROSION OF ELECTROLESS NICKEL  
IN ORGANIC ACIDS  
AT AMBIENT TEMPERATURE

ACID	CORROSION RATE	
	<u>µm/y</u>	<u>mpy</u>
Glacial Acetic	0.8	0.03
10% Acetic	25	1.0
0.25% Benzoic	10	0.4
90% Carbolic	0.2	0.01
5% Carbolic	5	0.2
5% Citric	2	0.07
Cresol	0.2	0.01
88% Formic	13	0.5
85% Lactic	1	0.05
Oleic	nil	nil
10% Oxalic	3	0.1

## HIGH TEMPERATURE ENVIRONMENTS

The melting point of electroless nickel is 1630°F (890°C). Accordingly, its usefulness at elevated temperatures is limited. Like other high nickel alloys, the deposit is very resistant to nitriding and is sometimes used as a maskant for commercial surface hardening treatments. In oxidizing flue gases, air or steam, electroless nickel coatings experience little attack at temperatures up to their melting point. In sulfur containing environments, however, such as reducing flue gases and some refinery process streams, sulfidation of the coating may occur at temperatures above about 525°F (275°C).

## SALTS

deposits have excellent resistance to neutral and alkaline salts, as well as most acid salts. Solutions of such compounds as sodium and potassium chlorides, sulfates, phosphates and carbonates have little effect on coatings. Accordingly, the deposit has been widely used in chemical environments and for food, pharmaceutical and medical applications. The loss of Electroless Nickel in some salt solutions is summarized in Table 4.

TABLE 4

CORROSION OF ELECTROLESS NICKEL  
IN SALT SOLUTIONS  
AT AMBIENT TEMPERATURE

<u>SALT</u>	<u>CORROSION RATE</u>	
	<u>μm/y</u>	<u>mpy</u>
27% Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5	0.2
26% BaCl <sub>2</sub>	0.2	0.01
42% CaCl <sub>2</sub>	0.2	0.01
5% CuCl <sub>2</sub>	25	1.0
5% CuSO <sub>4</sub>	18	0.7
1% FeCl <sub>3</sub>	200	8.0
25% KCl	nil	nil
28% K <sub>2</sub> CO <sub>3</sub>	0.2	0.01
35% MgCl <sub>2</sub>	2	0.1
26% NaCl	0.2	0.01
18% Na <sub>2</sub> CO <sub>3</sub>	1	0.05
47% NaNO <sub>3</sub>	nil	nil
46% NaH <sub>2</sub> PO <sub>4</sub>	3	0.1
14% Na <sub>2</sub> S	nil	nil
31% Na <sub>2</sub> SO <sub>4</sub>	0.8	0.03
36% Pb(NO <sub>3</sub> ) <sub>2</sub>	0.2	0.01
80% ZnCl <sub>2</sub>	7	0.3

Acid salts, such as magnesium chloride, zinc chloride and aluminum sulfate, cause increased attack of Electroless Nickel. The deposit, however, has useful resistance to these compounds and usually provides satisfactory service.

Oxidizing halide salts, such as cupric, mercuric, and particularly ferric chloride, cause severe attack of Electroless Nickel deposits and should be avoided. Oxidizing solutions containing chlorine, such as sodium hypochlorite, also cause rapid damage of the coating.

### STRESS CORROSION CRACKING

One intriguing property of Electroless Nickel coatings is their ability to retard stress corrosion cracking of the underlying substrate. They can prevent cracking of a metal in environments that would normally cause rapid failure. For instance, in one series of tests in boiling 42 percent magnesium chloride, samples of 18Cr-9Ni stainless steel coated with 0.4 mil (10  $\mu$ m) of heat treated, Electroless Nickel were found to be unaffected after 1900 hours of exposure, while uncoated specimens failed in 6 to 8 hours<sup>5</sup>.

coatings have also been found to be quite effective in preventing caustic cracking of plain and low alloy steel, particularly in steam and condensate environments. Some recent tests imply that these coatings may also be beneficial in reducing sulfide cracking of high strength steels in petroleum environments.

The effect of Electroless Nickel coatings on stress corrosion cracking appears to be due to two separate factors. First, the coating acts as a barrier between the part and the cracking environment. Second, and more important, the deposit apparently causes a shift in the corrosion potential of the substrate from the stress corrosion region into a potential range where cracking is not possible.

### EFFECT OF HEAT TREATMENT

One of the most important variables effecting the corrosion of Electroless Nickel is heat treatment. As deposits are heated to temperatures above about 500°F (260°C), structural changes begin to occur within the alloy. First coherent and then distinct particles of nickel phosphide ( $\text{Ni}_3\text{P}$ ) form throughout the coating. Then at temperatures above 650°F (340°C), Electroless Nickel begins to crystallize and to lose its amorphous character. At higher temperatures the particles conglomerate, forming a matrix of  $\text{Ni}_3\text{P}$ . Not only do these changes have a dramatic effect on the hardness of the coating, but they can also cause a severe reduction in corrosion resistance.

As the nickel phosphide particles form within the coating, they reduce the phosphorus content of the remaining material. This reduces its passivity and increases its corrosion. The particles also create small active/passive corrosion cells, further contributing to the deposit's destruction. A secondary effect of heat treating is that the deposit shrinks as it hardens, often resulting in cracks through the coating, which can expose the substrate to attack.

TABLE 5  
 THE EFFECT OF HEAT TREATMENTS  
 ON THE CORROSION OF ELECTROLESS NICKEL  
 IN 10% HCl

HEAT TREATMENT	DEPOSIT HARDNESS, VHN	CORROSION RATE	
		$\mu\text{m}/\text{y}$	mpy
None	480	15	0.6
375°F (190°C) for 1½ hours	500	20	0.8
550°F (290°C) for 6 hours	900	1900	74
550°F (290°C) for 10 hours	970	1400	56
650°F (340°C) for 4 hours	970	900	34
750°F (400°C) for 1 hour	1050	1200	49

The effect of these changes is illustrated by the test results in Table 5. For these tests, specimens of the deposit were heat treated to represent different commercial treatments and then exposed to 10 percent HCl at ambient temperature. Baking at 375°F (190°C), like that used for hydrogen embrittlement relief, caused no significant increase in corrosion. Hardening, however, caused the deposit's corrosion rate to increase from 0.6 mpy (15  $\mu\text{m}/\text{y}$ ) to more than 30 mpy (750  $\mu\text{m}/\text{y}$ ) or by 50 times. Tests in other environments showed a similar reduction in resistance after hardening. Where corrosion resistance is necessary, it is important that hardened coatings not be used<sup>6</sup>.

### CONCLUSION

Electroless Nickel is commonly used for a number of different, but often complimentary reasons. In different applications, this coating can reduce corrosion and erosion, reduce friction and wear and avoid stress cracking. This can reduce investment and maintenance costs and improve equipment reliability and life. Because of its unique combination of properties, Electroless Nickel has proved to be valuable for industry, and has been frequently used to replace more expensive alloys.