

CORROSION RESISTANCE OF HIGH PHOSPHORUS ELECTROLESS NICKEL COATINGS

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ABSTRACT

Experience has shown high phosphorus, electroless nickel coatings to have exceptional resistance to corrosion and erosion in many environments. The results of test programs to characterize the performance of these coatings in a broad range of industrial environments are reported, together with data on the effects of deposit composition and heat treatment.

INTRODUCTION

Corrosion is one of the most severe problems today faced by industry. Its effects range from simple loss of appearance, through loss of saleable products, to increased operating cost. Less obvious effects include the depletion of our natural resources and the safety hazards produced by equipment failures.

The economic impact of corrosion is significant and includes costs for equipment replacement, maintenance, excess capacity, increased inventories, corrosion control, technical support and increased investment. In one study, the annual cost of corrosion in the United States was estimated to be 70 billion dollars or 4.2 percent of the gross national product¹. The estimate is in good agreement with earlier investigations in the German Federal Republic and in the United Kingdom, which found corrosion losses to be 3 and 3.5 percent of their GNP². Each of the three investigations also found that much of these costs could be avoided through the use of presently available technology. These savings ranged from 15 percent in the USA to 25 percent in Germany.

Corrosion is the electrochemical reaction of a metal with its environment resulting in its loss of size or strength. One method for reducing corrosion of a metal is to coat it with a thin layer of a less reactive metal. Various techniques — including electrolytic and electroless plating, vapor deposition and metal spraying — have been used for this, but with varying success. Unfortunately, most metallic coatings are inherently porous and have been of little value as barriers against corrosion.

With the development of high purity, high phosphorus, electroless nickel coatings, this problem has been largely overcome. Because of their superior chemical resistance and freedom from porosity, these coatings provide greatly improved protection and are today being used for more and more applications.

AMBIENT TEMPERATURE AND REFRIGERATED TESTS

The ambient temperature and refrigerated corrosion tests were conducted in 500 or 1000ml, screw top polyethylene or glass bottles. For most tests, the caps on the bottles were left loose, to allow access of air to the solution. For the deaerated tests, the caps were tightly sealed and taped to prevent oxygen contamination.

For the ambient temperature tests, the bottles were stored in a laboratory cabinet whose temperature was $22^{\circ}\text{C} \pm 2^{\circ}\text{C}$. For the refrigerated tests, the containers were placed in a 400 dm³ capacity refrigerator, whose temperature was maintained at $2^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

The time period for each test was selected based upon the environment being evaluated and the estimated loss of the specimen. In general, the exposure period was selected in accordance with TM-01-69's guidelines that the duration should equal 50,000 divided by the expected corrosion rate in $\mu\text{m}/\text{y}$. For environments, such as solvents or alkalis, where little or no loss was expected, the test period was 3000 to 8000 hours. For solutions where losses of $25\mu\text{m}/\text{y}$ or less were likely, a period of 1000 to 3000 hours was used. For environments, such as nitric acid, where attack was thought to be severe, the test period was limited to a few hundred hours.

ELEVATED TEMPERATURE TESTS

Tests at 60° and 95°C were conducted in pressure resistant, 200ml capacity, glass bottles, sealed with neoprene gasketed, porcelain stoppers. The tests were maintained at temperature $\pm 1^{\circ}\text{C}$ by submerging the vessel in a 200 liter, ethylene glycol bath. The period for these tests was 72 to 550 hours depending upon the environment and the metal being tested.

For tests at higher temperatures, special 500ml capacity, Teflon lined, Type 316 stainless steel, DOT 3E1800 gas cylinders were used. The cylinders were heated in an electric convection oven with an accuracy of $\pm 3^{\circ}\text{C}$. Because of the expected high rate of attack, the period for these tests was limited to 24 hours.

ENVIRONMENTS

Except for tests in natural environments, all solutions were prepared using reagent grade chemicals and deionized water, whose resistivity exceeded $1\text{M}\Omega\text{-cm}$. Most solutions were neither intentionally aerated nor deaerated and contained only their normal atmospheric, equilibrium concentration of oxygen, approximately 8mg/l.

The solutions were not replenished during the test period. The amount of the solution was selected to provide a volume to coupon area ratio of at least $20\text{ml}/\text{cm}^2$ to avoid depleting the solution of corrosives. In most cases, the actual ratio was higher, generally between 40 and $60\text{ml}/\text{cm}^2$. Except for the movement caused by periodic examinations of tests, the solutions were not agitated. In general, duplicate tests were conducted for each condition, with separate specimens exposed in different vessels.

To study the effect of oxygen content on corrosion, some acids were deaerated with nitrogen. These were purged for at least 2 hours with commercial, high purity gas (99.8% N₂), prior to insertion of the test specimen. The deaerated solutions were also carefully blanketed with flowing nitrogen before and during sealing of the test vessel. In some tests, mixtures of reagent carbon dioxide and hydrogen sulfide gas were also added after deaeration.

Seawater. The synthetic seawater used in these tests was made using reagent grade salts in accordance with ASTM Standard D1141, Substitute Ocean Water, with heavy metal additions⁴.

Oil Field Brines. One series of tests was conducted to simulate the effects of petroleum production environments. The corrosion of both electroless nickel and mild steel specimens was measured in brines containing 0 to 10 percent total dissolved solids at 95°C. The salt solutions were saturated with carbon dioxide, hydrogen sulfide or a mixture of the two gases. The conditions of these tests, and the composition of the brines, are shown in Table 4, and are described in more detail in Reference 5.

Additional tests were conducted to establish the effects of higher temperatures and lower hydrogen sulfide concentrations on the corrosion of electroless nickel. These were run with 3½ percent TDS brine under conditions similar to those shown in Table 4.

Foods. Another series of tests was conducted to characterize the performance of electroless nickel in food products, and to compare its corrosion with that of other common materials of construction.

Standard packages of commercial foods and beverages, obtained from local retailers, were used for the test environments. Most tests were conducted at ambient temperature. Tests with dairy products, eggs, lard and margarine, however, were refrigerated to avoid degradation of the food. In addition, some elevated temperature tests were run with coffee, tea, soups, milk and grapefruit juice. These tests are described in more detail in Reference 6.

Synthetic Atmospheres. In addition, some tests were conducted in synthetic industrial⁷ and marine atmospheres. They were conducted in accordance with ASTM Standards, G87, Conducting Moist SO₂ Tests⁸, and B117, Salt Spray (Fog) Testing⁹, respectively. Standard polished specimens, whose edges were masked with tape were used. While these tests are more correctly a measurement of a coating's porosity, and not its corrosion resistance, they can provide useful information on the protection it offers its substrate.

RESULTS

The results of the corrosion tests with electroless nickel and other metals are summarized in Tables 1 through 15. The corrosion experienced in different waters and atmospheres is shown in Tables 1,2 and 3; that in oil field brines in Tables 4,5,6 and 7; and that in oils, solvents and hydrocarbons in Table 8. In Tables 9 and 10, the losses of electroless nickel in organic and inorganic acids, respectively, are listed. The corrosion found in ammonium, alkali metal and heavy metal salts are shown in Tables 11,12 and 13, respectively. Tables 14 and 15 describe the losses measured in foods and beverages. The compositions of the test solutions shown in these tables are in percentage values, by weight.

Except for some minor, under-deposit corrosion in a few strongly complexing environments, no evidence of localized attack — pitting, crevice corrosion, or corrosion cracking — was observed in any of the electroless nickel tests. Corrosion was uniform, resulting, at worst, in a minor etching of the coating. In some tests, the coating developed a grey to gold discoloration, due to the formation of a passivation film. This was most common in environments where little or no corrosion occurred, and was especially evident in those containing sulfur compounds.

In most environments, the corrosion of electroless nickel was low, generally less than 5um/y. Higher losses, however, were measured in complexing and strongly acidic media, and in some highly oxidizing solutions, like nitric acid, corrosion exceeded 100um/y.

DISCUSSION

Electroless nickel is a barrier coating. It protects the substrate by sealing it off from the environment, rather than by sacrificial action. Because of its superior chemical resistance and freedom from porosity, however, electroless nickel can provide more effective and more economic protection than any other coating in most environments.

These tests confirmed that the corrosion resistance of electroless nickel is excellent and in many environments is superior to that of pure nickel or chromium alloys. When properly applied, high phosphorus, electroless nickel is almost totally resistant to alkalis, to salt solutions and brines, to chemical and petroleum environments, and to all types of hydrocarbons and solvents. The coating also has good resistance to ammonia solutions, to organic acids, and to reducing inorganic acids. It is only significantly attacked by strongly oxidizing media.

WATERS

Corrosion of electroless nickel in waters is slight. Typically its loss in deionized water, tap water and sea water is less than 2um/y, even at temperatures up to 95°C. As shown in Table 1, this is a significant improvement over carbon steel. In fact, the protection provided by electroless nickel in most waters is equal to that of stainless steel. One set of vibratory cavitation erosion-corrosion tests confirmed this equality in fresh and salt water¹⁰.

A water's pH has a pronounced influence on corrosion. The results of tests conducted to establish this effect is shown in Table 2. Deionized water containing 1000mg/l HCl, was neutralized with sodium hydroxide to produce solutions ranging from 1.5 to 12 pH. These tests showed that above 3 to 4 pH, corrosion of electroless nickel was only 2um/y or less. At lower values, attack increased, reaching 21um/y at 1.5 pH.

This change in corrosion behavior between pH 3 and 4 was also evident in the tests shown in Table 1. For instance, mine water at 3.3 pH produced a loss of 7um/y, while in fountain solutions and tap waters at 3.6 to 8.8 pH, electroless nickel corroded at about 2um/y. This effect, although less distinct, was also apparent with solutions of non-complexing acids, salts and foods, as shown in later tables.

ATMOSPHERIC CORROSION

While not part of this study, previous investigations have shown electroless nickel coatings to be almost immune to attack in rural, industrial and marine atmospheres. In various outdoor exposures, even very thin deposits, were found to provide almost complete protection for many months^{11,12}.

Tests in synthetic atmospheres — summarized in Table 3 — showed that 12½µm/y thick coatings are capable of providing more than 1000 hours of neutral salt fog resistance⁷, or more than 2 cycles (48 hours) of Kesternich resistance⁸. This is significantly better than other commonly used coatings.

PETROLEUM ENVIRONMENTS

Corrosion in petroleum production environments consists of several corrosives, complicated by the effects of temperature, pressure and velocity. The most common corrodents are salt water, carbon dioxide and hydrogen sulfide, although oxygen and acids may also be present.

Electroless nickel coatings have long been used to mitigate corrosion in the oil field. The results of tests to characterize the performance of these coatings in these environments are described in Tables 4,5,6 and 7.

In CO₂ saturated brines at 95°C, the corrosion of electroless nickel is about 5µm/y. This represents a 98 percent improvement over the loss of plain steel. In H₂S and mixed CO₂/H₂S brines, the coating 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 shown that this film forms at temperature as high as 180°C (as shown in Table 6) and with H₂S concentrations as low as 4mg/l (as shown in Table 7)⁵.

Since most oil field environments contain at least a trace of sulfide, electroless nickel coatings, provide almost complete protection against corrosion. In one sour gas system, for instance, coated chokes and valves were used for 10 years, at high temperatures and pressures, without any measurable corrosion. Previously, used steel components experienced losses of 2 to 3µm/y¹³.

OILS, SOLVENTS AND HYDROCARBONS

The corrosion of electroless nickel in oils, solvents and hydrocarbons is very low. The worst attack measured in these tests was in formaldehyde, where corrosion was only 5µm/y. In most hydrocarbons, the loss of electroless nickel is almost zero. Because of its inertness, the coating is especially useful for preventing contamination or degradation of solvents or alcohols intended for pharmaceutical or cosmetic applications.

In ammoniacal salt solutions, electroless nickel also displays useful resistance. In ammonium chloride and nitrate, its loss is between 10 and 20um/y, while in phosphate and sulfate solutions losses are only about 5um/y.

CAUSTIC ALKALIES

Electroless nickel coatings have outstanding resistance to caustic soda, caustic potash and other alkalies, even at high concentration and elevated temperature. In caustic, at concentrations below 50 percent, corrosion is negligible, due to the formation of protective oxide films. As shown in Table 12, the maximum loss measured at 95°C was 1um/y, while that of mild steel was 550um/y.

Unlike other nickel alloys, the corrosion of high phosphorus deposits in caustic is not increased by the presence of sulfur compounds. The addition of even trace amounts of sulfur will increase the loss of wrought nickel by 10 times or more¹⁴. Corrosion of electroless nickel, however, is passivated by sulfides, and in sodium sulfide, is nil.

SALTS

Electroless nickel deposits have excellent resistance to neutral and alkaline salts, as well as most acid salts. Solutions of sodium and potassium chlorides, sulfates, phosphates and carbonates were found to have little effect on high phosphorus coatings. Accordingly, the deposit has been widely used in chemical, pharmaceutical and medical environments. The loss of electroless nickel in salt solutions is summarized in Tables 12 and 13.

Oxidizing halide salts such as cupric and particularly, ferric chloride, cause severe attack of electroless nickel deposits and should be avoided. In these solutions, corrosion rates in excess of 100um/y have been measured.

FOODS

Electroless nickel also has excellent resistance to foods and beverages. As illustrated by Tables 14 and 15, corrosion in most foods is less than 2um/y. In foods containing large quantities of organic acids, such as vinegar or coffee, corrosion may increase, but the coating can still provide adequate protection. For applications requiring prolonged exposure of the food to the deposit, corrosion may cause a minor amount of dissolved nickel in the product. This is, however, well below the toxicity limits for metallic nickel⁶.

The superior corrosion resistance of electroless nickel is due to its unique structure. In the as-deposited condition, high phosphorus coatings are completely amorphous. They have no crystal structure and contain no separate phases. They are metallic glasses.

It is the amorphous character of electroless nickel that improves its corrosion resistance. Glasses are generally more resistant than equivalent polycrystalline alloys, because of their freedom from phase boundaries, and because of the glassy films which form on and passivate their surfaces.

The phase boundaries, and resulting segregated impurities, in crystalline metals produce discontinuities in their surface films, which are preferred initiation sites for corrosion. Metallic glasses, however, are homogeneous and have neither separate phases nor boundaries. Thus, their surface films are continuous, providing little opportunity for attack.

In addition, alloys containing metalloids, such as electroless nickel, tend to form more passive and more protective surface films than other metals. Metalloids, like boron and phosphorus, promote the formation of glass like films and rapid passivation. Accordingly, thicker, more dense, and more resistant surface films are produced. The growth of a nickel-phosphorus-sulfur, glass tarnish on the surface of electroless nickel is probably mostly responsible for the high resistance of the coating in sulfide solutions.

EFFECT OF COMPOSITION

The corrosion resistance of electroless nickel is largely a function of its phosphorus content, with higher phosphorus levels providing more passive and more resistant deposits. The trace elements or contaminants present in the deposit, however, can also be important. Most coatings are applied from baths stabilized with lead, cadmium, or sulfides. Codeposition of these elements, in more than trace quantities, can cause a large reduction in the coating's corrosion resistance. Two additional sets of tests were conducted to establish the effects of phosphorus content and contaminant level on the performance of electroless nickel.

EXPERIMENTAL PROCEDURE

In addition to the previously tested deposit, specimens were prepared from several other, proprietary, plating solutions, representing the range of those commercially available. The solutions were made up as 3 liter baths, and 25um/y thick foils were plated from them. The foils were cut or broken into 10cm² coupons. Foils were used for these tests to avoid any error that might be introduced by substrate attack through pores or discontinuities.

In one set of tests, the baths were operated in accordance with their manufacturer's recommendations. This provided a cross-section of typical commercial deposits, and of phosphorus contents. In the other tests, the baths were operated at lower pH, in order to provide deposits with more constant and higher phosphorus contents. This was done to allow the effect of contaminants to be more easily judged.

Three environments were studied. In the first set of tests, specimens of nine deposits were exposed to 10 percent hydrochloric acid at ambient temperature. The test period was 53 hours. The results of these exposures are shown in Table 16.

In the second series, samples of six deposits were tested for 168 hours in CO₂ saturated, 3½ percent brine at 95°C, and in N₂ deaerated, 10 percent hydrochloric acid at 22°C. The brine had the same composition as that shown in Table 4. The results of these tests are summarized in Table 17. Except that foils were used for coupons, both sets of tests were conducted in the same manner as those previously discussed.

DISCUSSION

As shown in Table 16, the first set of tests revealed a strong effect of deposit phosphorus content on corrosion. Coatings containing more than 10.4 percent phosphorus, all had losses of about 50um/y. When the phosphorus content fell below this level, corrosion increased to 130 to 2090um/y. These results confirmed that baths which produce high phosphorus deposits, also produce those with the highest corrosion resistance.

The second set of tests also showed the influence of phosphorus content, but more importantly demonstrated the detrimental effect of heavy metal and sulfur additions. As shown in Table 17, in brine Deposits G and I had losses of 5 to 7um/y, while those of the other deposits were 120 to 480 percent higher. In HCl, their corrosion rates varied from 15um/y for Deposit G to 660um/y for Deposit D.

The primary difference between the coatings was not their phosphorus content, but rather their bath's stabilizing system. Deposits A,D,G and I all contained 10 or 11 percent phosphorus, but their corrosion rates varied by 15 to 45 times. Deposits G and I, which had the lowest losses, were applied from organically stabilized baths and contained only trace amounts of heavy metals. Baths A and D were stabilized with cadmium and lead, and contained 0.2 to 0.4 percent of these elements.

EFFECT OF HEAT TREATMENT

One of the most important factors affecting the corrosion resistance of electroless nickel is its heat treatment. Improper heat treatment can cause a severe loss of corrosion resistance in most environments. Earlier researchers reported that 750°C treatments improved the performance of electroless nickel in outdoor exposures¹¹. Unfortunately, these results have commonly been assumed to be correct for all heat treatments and for all environments. Most users have believed that hardened electroless nickel was more resistant to attack than the as-deposited coating. To evaluate the effect of heat treatments at different temperatures, several more tests were conducted.

EXPERIMENTAL PROCEDURE

In the first set of tests, as-deposited electroless nickel, coatings baked at 190°C (as for hydrogen embrittlement relief), and deposits hardened to approximately 1000 VHN₁₀₀ were evaluated. These tests were conducted along with our investigation of oil field environments, and so, many of the same solutions were used. These were CO₂ saturated, 3½ percent brine at 95°C; CO₂ saturated, 3½ percent brine containing approximately 90mg/l H₂S at 95°C; and N₂ deaerated, 10 percent hydrochloric acid at ambient temperature.

Two types of specimens were used. These were the plated steel coupons used for previous tests, and 10cm² sections of electroless nickel foil, like those used for the composition study. The samples were heat treated in an electric convection oven, whose temperature was controlled within ± 30°C. After heating, the specimens were removed from the oven and allowed to cool in still air.

The test period for the brine tests and for most of the HCl tests was 192 hours. For a few of the HCl tests, the period was reduced to 24 hours because of the high expected loss of the specimens. The tests were conducted in duplicate, using the same procedures as described for previous experiments. Their results are shown in Table 18.

In the second test series, a more complete range of heat treatment temperatures was studied. For these tests, only foil coupons were used, since it had already been shown that the shrinkage cracks resulting from hardening would allow substrate attack and added loss. In addition to the as-deposited coating, specimens with 16 different, one hour, heat treatments at temperatures between 100° and 650°C were tested in duplicate. These were also treated in a ± 30°C accuracy, electric oven.

The environment selected for these tests was non-deaerated, 10 percent HCl. Hydrochloric acid was selected for these tests, both because it is a more aggressive environment and shows up differences more rapidly, and because it is often used to clean oil field and process equipment. The duration of these exposures was limited to 53 hours, because of the severe attack expected with hardened coatings. The corrosion measured in this series is summarized in Table 19.

DISCUSSION

These tests confirmed that the corrosion resistance of electroless nickel is greatly reduced by heat treatment. In the first tests, corrosion in the CO₂ saturated brine was almost doubled by baking the specimens at 190°C. Hardening caused corrosion to increase by 4 to 7 times. In deaerated HCl, baking caused only a small change in corrosion resistance. Hardening, however, caused the corrosion rate of the foil to increase 60 to 90 times. The losses of the plated coupons were even higher, because of the shrinkage cracks through the coating produced by heating⁵.

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