The Effect of Solution Age on Corrosion Resistance Of Electroless Nickel Deposits

By R.N. Duncan

This paper* describes the results of tests, conducted to quantify how the age of the plating solution affects the corrosion resistance and other properties of a high phosphorus, electroless nickel deposit. Specifically, the composition, internal stress, ductility, corrosion protection and chemical resistance of the coating were investigated, along with the bath's plating and contaminant buildup rates. The paper also describes tests conducted to establish the effect of orthophosphite and sulfate accumulation and suggests possible causes for the changes observed.

The usage of an electroless nickel plating solution can have a significant effect upon the bath and upon the properties of its deposit. As the bath ages, sulfates, phosphites, and other salts accumulate, and begin to affect the deposition of nickel and phosphorus. Ultimately, these changes cause the deposit's internal stress and porosity to increase and its chemical resistance to decline.

Test Procedures

The specimens for this study were plated from a proprietary, non-heavy metal or sulfur stabilized, malate/citrate-based solution of the type used to obtain electroless nickel deposits containing 10 to 12percentphosphorus.Twodifferent batches of plating solution were used for the tests. Both batches were identical, except that two different sources of sodium hypophosphite were used for the manufacture of their makeup concentrates and hypophosphite replenishers. The solutions were made in production quantities at the same time, and from the same raw materials. The initial nickel and sodium hypophosphite concentrations of the plating solutions were 7.1 and 40 g/L respectively.

The baths were made up and operated in air-agitated, 50- L polypropylene tanks. The solutions were maintained at a temperature of 88 ± V: °C and a pH of 4.8 + 0.1 by paper. Their plating rates varied with age, but typically was 10 to 12 µm/ hr. With this formulation, the deposition of 7.3 g/L of nickel (or 8.2 g/L of Ni-1 IP) equals one cycle of operation, or one turnover.

The baths were operated for five cycles, while 38 g/L of nickel was plated from solution. Specimens for testing were obtained from the new bath and then at the end of each cycle of operation. The bath loading was approximately 0.25 dm^2/ L while the specimens were being plated. In between, the baths were aged, using steel panels as surface area, at a loading of approximately 1 dm^2/L. A 50-percent (by volume) solution of ammonium hydroxide was used to maintain solution pH within the desired range.

Composition

The concentration of nickel, hypophosphite and orthophosphite in the plating solutions was measured by conventional wet analysis.[1] A colorimetric titration with HOT A was used to establish nickel content, while hypo- and orthophosphite were analyzed by the iodine method.

To determine deposit composition, foils were plated to a thickness of about 25 µm on passivated titanium shim stock. After plating, the foils were mechanically removed from the shims and dissolved in nitric acid. Their phosphorus content was then analyzed colorimetrically, using the molybdatevanadate procedure described in ISO Standard 4527.[2]

Plating Rate

The deposition rate of the solutions was measured by before and after micrometer thickness measurements of commercial steel razor blades. Before plating, the blades (and all other steel substrates) were prepared by alkaline soak cleaning, periodic reverse electrocleaning, activation in 30-percent (by volume) hydrochloric acid, and periodic reverse electrocleaning, with intermediate cold water rinsing.

Internal Stress

The internal stress of each deposit was measured according to ASTM Standard B-636,[3] using a Brenner-Senderoff spiral contractometer with a stainless steel helix. Before plating, the helix was prepared by soak cleaning, periodic reverse electrocleaning, immersion in 30 percent (by volume) hydro-

Figure 1
Effect of Bath Age
On Hypophosphite Consumption

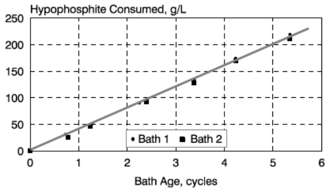


Figure 2
Effect of Bath Age
on Orthophosphite Production

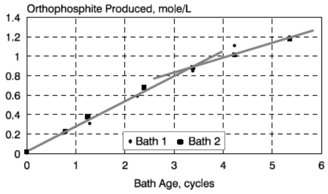


Figure 3
Effect of Bath Age on Plating Rate

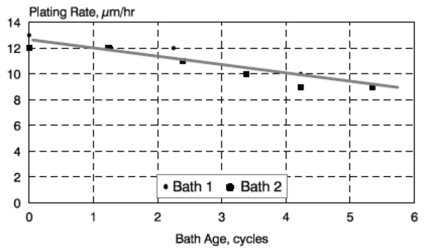
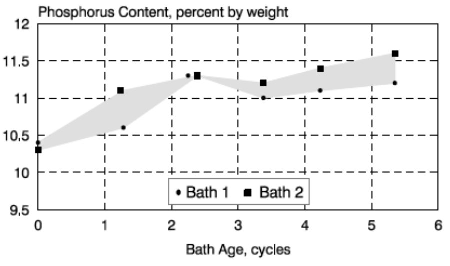


Figure 4
Effect of Bath Age
on Deposit Phosphorus Content



chloric acid, and electrolytic activation in a Wood’s strike solution (240 g/L $NiCl_2$-$6H_2O$ and 250 mL/L HC1) at a current density of 1 to 2 A/dm^2, with intermediate cold water rinsing. Plating on the helix was initiated with direct current for about 10 sec as it was placed into the electroless nickel solution to assure uniform deposition.

Ductility

The foils collected for composition analysis were also used to measure the ductility of the deposit. These tests were conducted using the procedure described by ASTM Standard B- 490.[4] The foils were cut into specimens, approximately 1 x 5 cm in size. The specimens were then bent into a “U” shape and placed between the jaws of a vernier caliper that was slowly tightened until the foil cracked. Ductility was then calculated from the minimum radius of the bend and the thickness of the deposit.

Ductility measured by this method is different from that measured by a more conventional pull or bulge test, because the foil is under both compressive and tensile stresses. The method is convenient to use with many metallic coatings, however, and provides a method of comparing them. This test might be more correctly described as bending ductility or flexibility.

Corrosion Resistance

Two types of corrosion tests were conducted. To establish the effect of age on the chemical resistance of electroless nickel, immersion-type tests were conducted according to ASTM Standard G-31[5] in hydrochloric and sulfuric acids. Moist SO_2, synthetic industrial atmosphere tests, according to ASTM Standard G-87[6] (also called the Kestemich test) were conducted to quantify the protection provided by the coating as it varied with solution age. This test is more correctly a porosity test, because it finds (and sometimes creates) holes through the coating to the substrate.

The acid immersion tests were also conducted using 1x5 cm foils as specimens. Foils were used to avoid any error that might be introduced by substrate attack through pores or discontinuities. After cleaning and drying, the specimens were weighed to the nearest 0.1 mg and immersed in either 20-percent (by weight) hydrochloric acid or concentrated 98- percent (by weight) sulfuric acid. These acids were selected because hydrochloric is strongly reducing, while concentrated sulfuric is oxidizing, so that two totally different environments were obtained.

Both solutions were at ambient temperature with a volume-to-specimen area ratio of 50 mL/cm^2. After 112 hr, the specimens were removed, cleaned and weighed a second time. The weight loss of the coatings during the exposure was then used to calculate their corrosion rate.

Polished steel rods, 3 cm in diameter and 20 cm long, were plated with 30 |im of electroless nickel for the moist SO_2 tests. Before exposure, the ends of the specimens were masked with tape. The rods were then suspended in a sealed 300-L test chamber, which was charged with 2 L of deionized water and 2 L of reagent-grade sulfur dioxide gas and heated to 40 ±2 °C. After 8 hr, the chamber’s heater was turned off and the specimens were allowed to cool to ambient temperature during the next 16 hr.

Following this exposure (which is one test cycle), the specimens were removed, cleaned with a soft brush under running tap water, and examined for evidence of corrosion. Failure was considered to be the presence of red rust after cleaning. This procedure was repeated until failure occurred. The number of 24-hr cycles for the specimen was then recorded as its rating.

Passivity

The nitric acid test was used to measure coating passivity. Passivation is the electrochemical process in which the chemically active surface of a metal becomes less reactive. This

Figure 5 Effect of Bath Age on Deposit Stress

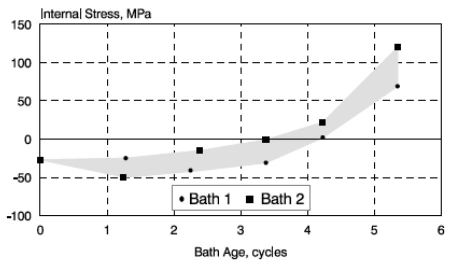
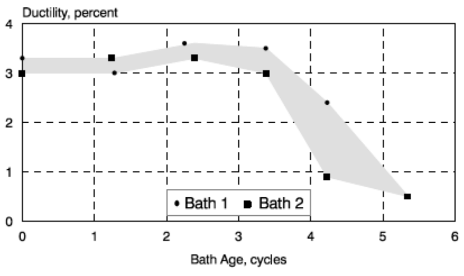


Figure 6 Effect of Bath Age on Deposit Ductility



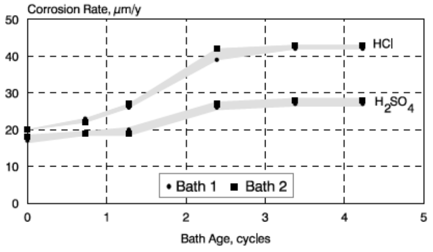


Figure 7
Effect of Bath Age on Corrosion

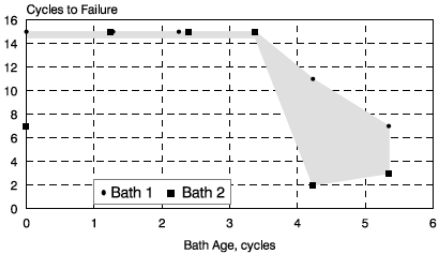


Figure 8
Effect of Bath Age
on Moist SO_2 Resistance

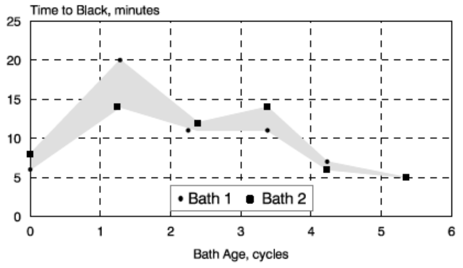


Figure 9
Effect of Bath Age
on Nitric Acid Resistance

process is usually the result of the formation of thin, protective films on the surface. Passivity is not the same as corrosion resistance, but is a related property. Generally, as passivity increases, resistance to chemical attack, especially localized attack, also increases.

Electroless nickel loses its passivity and then is attacked by nitric acid and other strongly oxidizing environments. Once passivity has been lost, the coating begins to dissolve freely, forming Ni^{+2} and $NiO_4^{‘2}$ ions. This etches the surface and causes it to turn black. This change, however, occurs slowly for high-phosphorus coatings. It takes time for the surface films to dissolve and for attack to begin. This is the basis of the nitric acid test. The time required for blackening to occur is used as a measure of passivity, and indirectly of corrosion resistance.

Commercial steel razor blades, 1x2 cm, plated to a thickness of 5 µm, were used as the specimens for these tests. After drying, the panels were immersed in concentrated nitric acid (70 percent by weight) at ambient temperature, and the appearance of their coatings observed. The amount of discoloration of the deposit after 1 min was recorded as one measureof passivity. A black or dark gray color in this period was total failure, while no discoloration was passing. A second measure of passivity was the period required for the coating to blacken.[7] The longer it takes a coating to blacken, the more passive it is.

Age Causes Degradation

The effect of age on the composition and plating rate of the two electroless nickel baths is summarized in Figs. 1-3, while the effect on deposit properties is shown in Figs. 4-9.

Solution Composition

These tests showed a linear consumption of hypophosphite and production of orthophosphite over bath life. During each cycle of operation, 40.5 g of sodium hypophosphite were used, as shown in Fig. 1. This is equivalent to 5.6 g of hypophosphite per gram of nickel reduced, or about 3 moles per mole. The average efficiency of the baths, consequently, was 33 percent (based upon conventionally accepted deposition reactions), which is typical for most acid electroless nickel formulations.

For the first three cycles of operation, the production of orthophosphite was linear at 0.26 mole per cycle. After that, however, the build-up rate declined and, between the fourth and fifth cycles, was only about 0.20 mole per cycle. This change is shown in Fig. 2. No other change in the bath chemistry was observed that would explain this reduction. The oxidation of hypophosphite did not slow, nor was there any evidence that the missing phosphite precipitated as an alkali or nickel salt. Although the rate of phosphorus deposition did increase during this period, the change was not large enough to account for all of the lower orthophosphite production.

To try to establish whether there was a fault with the analytical procedure such that it did not measure all of the orthophosphite in older samples, the total phosphorus content of four solutions was measured. This analysis was accomplished by oxidizing all of the phosphorus compounds present to P_2O_5 with perchloric and nitric acids, precipitating them with ammonium molybdate, redissolving them in NaOH, and measuring their concentration by titrating the excess caustic with nitric acid.

These results were then compared to the sum of the previous hypo- and orthophosphite tests. In each case, however, the two different procedures provided results within 1 or 2 percent of each other. Accordingly, it was concluded that the iodine procedure was accurate and was detecting all of the phosphite present in the samples. The decline in the rate of orthophosphite production could not be explained.

Plating Rate

As with most electroless nickel solutions, the plating rate of the baths declined as they were used. With the new baths, the plating rate was about 12 pin/hr. After the first cycle, however, the rate began to fall, and by 5 cycles it had settled to 9 µm/hr. This change is illustrated by Fig. 3. No attempt was made to maintain the rate at a higher level by increasing the pH or temperature, because this action might have also changed the properties of the deposits.

Deposit Phosphorus Content

The phosphorus content of the deposits from the baths increased with age, but not greatly. Over five cycles of operation, the phosphorus content of the coatings increased from about IOV2 percent to about 11V2 percent, as shown in Fig. 4. This increase is typical of the deposits from this bath formulation.

Figure 10
Effect of Salt Additions
on Plating Rate

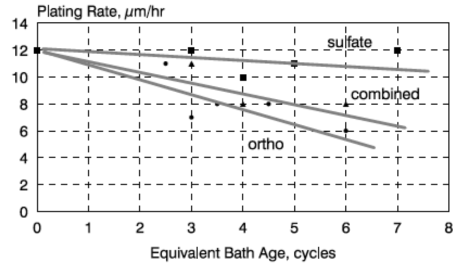
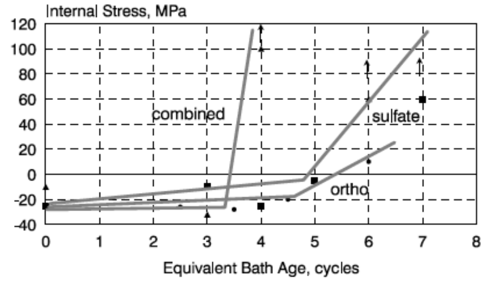


Figure 11
Effect of Salt Additions
on Deposit Stress



Internal Stress

The effect of bath age was readily apparent with the internal stress of the coatings. Initially, the stress of the deposits was compressive at 27 MPa. The coatings retained this level of stress through the first three cycles of bath operation, as shown in Fig. 5. Afterward, however, their stress became tensile, then increased rapidly.

Ductility

The relationship of ductility and age of the coatings is illustrated by Fig. 6. It was observed to be the reverse of that of stress. Through the first three cycles, the bending ductility of the deposits was constant at about 3 percent as elongation. It then began to decline, reaching values of less than 0.5 percent by the fifth cycle of age.

Corrosion Resistance

Chemical resistance and corrosion protection were found to be different properties, which are not directly related to each other. The chemical resistance of the coatings began to decline as soon as the baths were used and showed a distinct reduction between the first and second turnovers. During the latter part of bath life, the chemical corrosion of the deposits in both reducing and oxidizing acids appeared to stabilize. These changes are shown in Fig. 7.

Corrosion protection, on the other hand, followed the same transitional patterns as stress and ductility. During the first three turnovers, with one exception, the deposits consistently provided more than 15 cycles of Kestemich resistance, which is considered superior. As illustrated in Fig. 8, after the third turnover, the Kestemich resistance of the coatings began to decline, reaching values as low as 2 to 3 cycles. This pattern was also the reverse of that of the deposit stress.

Passivity

The passivity of the electroless nickel deposits was found to be similar to their chemical resistance. All of the test specimens passed a one-min nitric acid exposure, showing no discoloration. As shown in Fig. 9, however, the time required for the deposits to blacken showed a steady decline after the first cycle, similar to the increased corrosion that the coatings experienced in hydrochloric and sulfuric acids.

Effect of Salt Accumulation

The transition of the physical properties of the coatings from high to low values occurred at the same age that the orthophosphite concentration of the plating solutions reached 1 mol/L. Traditionally, it has been thought that there is a causal relationship between these two occurrences.

In addition to orthophosphite, other salts are accumulating. Primary among these is the sulfate from the nickel sulfate used to make up and replenish the bath. Also, sodium or ammonium hydroxides or potassium carbonate are continually being added to neutralize the hydrogen ions formed during deposition, and small amounts of organic acids are added to control the solubility of nickel.

To provide a better understanding of some of these changes, another experiment was conducted. A series of plating solutions from the same formulation previously tested were made up in 2-L beakers, heated on hot plates and agitated with magnetic stirrers. To these solutions, measured amounts of orthophosphite [as $H_2(HPO_3)$ neutralized with sodium hydroxide] and sodium sulfate were added. The plating rate of the solutions and the internal stress of their deposits were then measured. The concentrations of the salts added and the results of these tests are summarized in the table. Also shown in this table are the results of a similar experiment reported by Linka and Riedel using the same electroless nickel formulation.[8] The results of both tests are also shown in Figs. 10 and 11.

Both groups of experiments showed the same rapid shift from compressive to tensile stress observed with baths aged naturally. Tensile stresses were produced, but only after the equivalent of about six cycles of either orthophosphite or sulfate was added to the test solutions. Based upon this result, it appears likely that neither salt by itself is the cause of this phenomenon.

When a combination of the two salts was added to the solution, however, much smaller amounts were needed to cause the loss of compressive stress. The shift occurred at the equivalent of between 3 and 4 cycles of operation, which was similar to that observed with the naturally aged solution.

The fact that the addition of orthophosphite and sodium sulfate can make deposit stress become tensile at the same age as a natural bath implies that this is the chemical cause of coating transitional behavior. Other factors may also contribute, however. For instance, the viscosity or total salt content of the solution, including all of the acids and bases added, may establish the point at which this change occurs. Also, the degradation of the organic acids used as complexers and buffers, or the accumulation of stabilizers and brighteners may contribute.

Effect of Deposit Structure

The results of both sets of experiments confirmed that solution age and salt content have a pronounced effect upon deposit properties. Between 3 and 4 cycles of operation, there is a rapid shift in many properties of the coating. At this age, internal stress becomes tensile, ductility declines to a low level, and much of the corrosion protection is lost.

The transitional behavior of these properties resembles the response of an electroless nickel deposit to changes in its composition and structure.[9] This similarity suggests that after a bath has aged to a critical point, the amorphous character of a high-phosphorus deposit may be lost. Previous studies have shown that no crystal structure can be detected with X-rays in 6-cycle-old baths of this formulation.[8] This may only mean, however, that the quantity of crystalline phase formed in older baths is too small to be distinguished by X-rays. Alternatively, it is possible that instead of crystals, islands or phases of amorphous material form in older deposits, so that they are not continuous and that mismatched structure develops, promoting stress and porosity. Structures with obvious fault sites have been observed in some experiments and have been shown to result in increased corrosive attack.[1011]

Another alternative is that orthophosphite from older baths is codepositing with the coating, producing coherent particles that distort the matrix and degrade deposit properties. This suggests a partial explanation of the reduced orthophosphite build-up rate in baths after 3 or 4 cycles, and the slight increase in deposit phosphorus content.

The corrosion of the coatings in hydrochloric and sulfuric acids did not produce the same type of transitional behavior observed with other deposit properties. Instead, their chemical resistance declined proaressively as the baths aged.

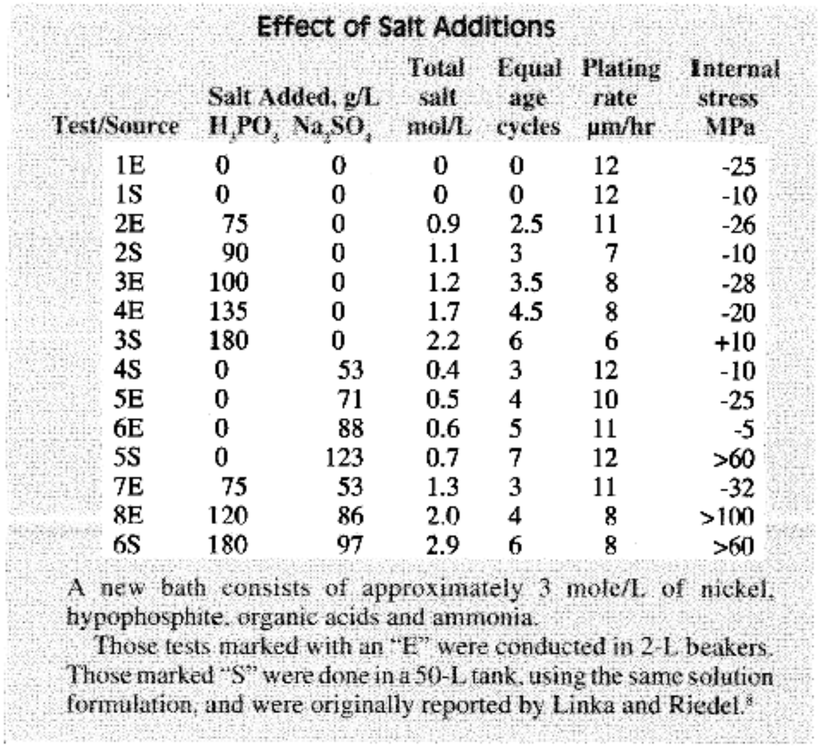
The formation of crystalline material or separate amorphous phases within the deposit, however, could result in increased corrosion through active/passive cell attack. [912]The precipitation of phosphites could also result in the same type of attack. To explain the increased chemical attack of the deposit by this theory, however, these phases would have to accumulate at a constant rate and not form after a critical concentration in the bath was reached.

Conclusion

Although the cause may not be completely understood, it is certain that the age of an electroless nickel bath has a pronounced and detrimental effect upon the corrosion resistance and other properties of deposits. This change in properties appears to result from the changing chemistry of the plating solution, and especially its salt content. The structure of the deposit may also be in transition, but the exact nature of this change is not yet known.

About the Author

Ronald N. Duncan is vice president of Palm International, Inc., 1289 Bridgestone Pkwy., Lavergne, TN37086, and is responsible for the company's technical and educational activities. Formerly, he was director of research for Elnic, Inc., where he was in charge of electroless nickel formulation and materials research. He holds a BS in mechanical and metallurgical engineering from Vanderbilt University and is a registered professional engineer, and is certified as a corrosion specialist by NACE. He is the principal author of the chapter on electroless nickel in Vol. 5 of the Metals Handbook.



Effect of Salt Additions

Test/Source	Salt Added, g/L H_3PO_3	Na_2SO_4	Total salt mol/L	Equal age cycles	Plating rate µm/hr	Internal stress MPa
1E	0	0	0	0	12	-25
1S	0	0	0	0	12	-10
2E	75	0	0.9	2.5	11	-26
2S	90	0	1.1	3	7	-10
3E	100	0	1.2	3.5	8	-28
4E	135	0	1.7	4.5	8	-20
3S	180	0	2.2	6	6	+10
4S	0	53	0.4	3	12	-10
5E	0	71	0.5	4	10	-25
6E	0	88	0.6	5	11	-5
5S	0	123	0.7	7	12	>60
7E	75	53	1.3	3	11	-32
8E	120	86	2.0	4	8	>100
6S	180	97	2.9	6	8	>60

A new bath consists of approximately 3 mole/L of nickel, hypophosphite, organic acids and ammonia.

Those tests marked with an "E" were conducted in 2-L beakers. Those marked "S" were done in a 50-L tank, using the same solution formulation, and were originally reported by Linka and Riedel.[8]

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Ronald N. Duncan

BIOGRAPHICAL SKETCH

In Memory of Ron Duncan

Ron Duncan served as Vice President of Palm International, Inc., where he led the company's technical and educational initiatives. Prior to joining Palm, he was Director of Research at Elnic, Inc., focusing on electroless nickel formulation and materials research.

Before entering the metal finishing industry, Ron spent 12 years in the oil sector with Exxon and Caltex Petroleum Corporations, tackling materials and corrosion challenges. His work took him across the globe—including the United States, Middle East, Europe, South America, and Africa—where he developed a reputation for his deep expertise and practical problem-solving.

Ron held a BE in Mechanical and Metallurgical Engineering from Vanderbilt University. He was a Registered Professional Engineer and a certified Corrosion Specialist through NACE. A leader in technical standards, he chaired NACE task groups T-1G-19 and T-6A-53, contributing to authoritative reports on electroless nickel and other metallic coatings. He also served on the AESF's Electroless Committee.

Throughout his distinguished career, Ron authored more than fifty technical papers on corrosion, coatings, and electroless nickel. His work appeared in Materials Performance, Plating and Surface Finishing, Metals Progress, Products Finishing, and Finishers Management, as well as in numerous industry conferences. He was the principal author of the electroless nickel chapter in Volume 5 of the Metals Handbook and was honored with the AESF Gold Medal in 1996 for the best paper published in Plating and Surface Finishing.

Ron also directed the Electroless Nickel School, a comprehensive four-day seminar presented by Palm, which educated professionals in all aspects of electroless nickel technology.

Ron Duncan passed away on December 15, 2006. He is deeply missed by his family, colleagues, and the broader surface finishing community. His legacy of innovation, mentorship, and integrity continues to inspire all who had the privilege of working with him.