“The Effect of the Substrate on Defects

In Electroless Nickel Coatings”

by

Ronald N. Duncan

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Introduction

Many different defects can occur with electroless nickel coatings. The most common and most obvious ones are:

- Pits and pores,
- Incomplete coverage,
- Roughness,
- Lack of adhesion, and
- Non-uniform appearance.

These defects can greatly degrade the coating's corrosion protection, wear resistance and performance.

Sometimes, even with the most conscientious pretreatment and with the best bath formulation and operation, defects will occur in a coating. Usually these defects are the result of a defect in or a characteristic of the substrate being plated. This paper explains how the substrate's alloy, forming, mechanical finishing, and handling can lead to defects in the applied coating. It will also suggest techniques that can be used to help avoid some defects and failures.

Substrate Defects

Substrate defects or characteristics that lead to defects and failures in the electroless nickel coatings can be loosely divided into six types.

- Voids resulting from forming,
- Surface separations resulting from forming,
- Deformation due to machining or grinding,
- Secondary phases inherent in the metal,
- Foreign phases transferred to the substrate during fabrication, and
- Dissimilar metal combinations.

These substrate defects are described in the following paragraphs, along with the coating defects that they can produce. These defects are also summarized in Table 1.

Voids Resulting From Forming

Voids or substrate porosity is one of the more common sources of defects in electroless nickel coatings and probably the one that causes the most problems. Pores can be present in castings, welds, and powdered metal parts. Voids are not normally present in forged or wrought metals.

In castings, voids are produced either by dissolved gas or by shrinkage. As a metal solidifies, the gasses dissolved in it are released and are often trapped in cavities. These defects are called *gas* or *blow holes* and are usually round or oval in shape. They can be found anywhere within a casting. Shrinkage of the metal during solidification can also tear voids in it. These *shrinkage cavities* are usually irregular in shape and are most prevalent toward the center of the casting. Blow holes and shrinkage cavities can be microscopic or large enough to be seen with the unaided eye.

Small gas pockets (sometimes called *worm holes* or *piping*) may also form during welding, usually when parts have not been properly cleaned or dried. Like blow holes, gas pockets form when water vapor or gas cannot get out before the metal freezes. Cracks may also occur in welds due to low melting contaminants or high residual stresses. Open cracks produce the same defects as other voids. Tightly closed cracks, usually do not affect subsequent plating.

Powder metallurgy (P/M) is frequently used to form parts because its near net-shape finish reduces subsequent machining. With powder metallurgy, one or more metal powders are pressed into the desired shape, and then sintered at high temperature to join the particles together. The structure of P/M parts is always porous, containing many voids between the particles. The porosity of most P/M parts is between 10 and 25 percent. Even copper infiltrated parts contain about 5 percent porosity.

Where voids are located within the casting, weld or P/M part, they are not a concern to the plater. However, when they are near the surface, they can produce many plating problems. They can cause coating porosity, skip plating, poor adhesion, patterned deposits, roughness, and stains.

Voids, even small ones, are preferential sites for pores to begin in electroless nickel coatings. They are discontinuities replicated through the deposit's thickness. Open cracks can also act as initiation sites for porosity.

Obviously, a pore with a five mil opening cannot be bridged by an electroless nickel coating one or two mils thick. In fact, such voids will rarely be closed by even a five mil coating. Hydrogen bubbles will mask the dimple formed at the pore and will keep it open through the coating's thickness. Figure 1 shows a typical shrinkage cavity in an aluminum casting and the pore that resulted in its electroless nickel coating.

However, the larger problem is not the pore, but the contaminants it contains. Any material that the metal has previously contacted may be, and probably is, in the pore. These contaminants may include machining and cutting oils, coolants, cleaning compounds, and rust preventatives.

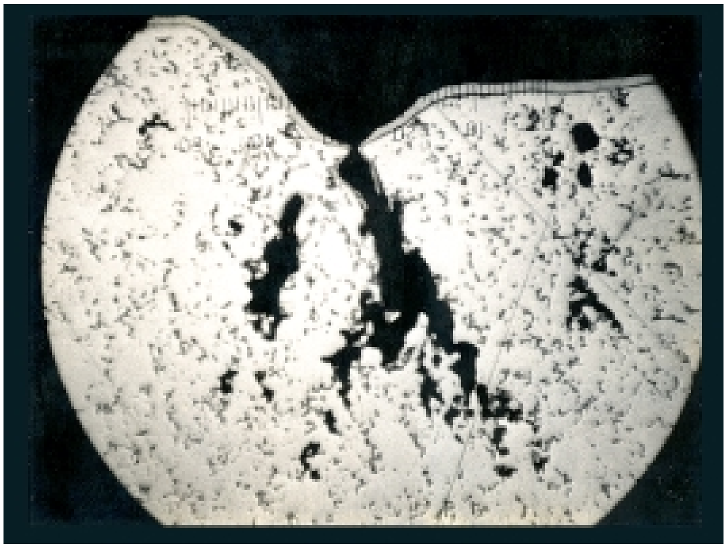

Figure 1
Shrinkage cavity in an aluminum casting and the pore through the coating that it produced. 50X magnification.

Pretreatment solutions cannot easily remove these contaminants. Pretreatment is even more difficult when the void has a small opening, like that in Figure 1. Even when the shape of the void is amenable to cleaning, its contents will only be replaced by the chemicals from the pretreatment tanks.

When the part is placed into the hot electroless nickel solution, the contaminants are forced out of the void and onto the part or into the plating solution. Oils exuding from a pore, help ensure that the coating cannot bridge the pore's opening. Oils dissolved in the bath may result in universal fine pitting (star dusting) of the deposit. Surfactants and inhibitors can act as stabilizers and can slow plating or result in edge pull back, skip plating and incomplete coverage. Sometimes the contaminants seeping from the void will mask the adjacent surface, allowing it to passivate and causing poor coating adhesion. The pull back pattern shown in Figure 2 resembles an oyster shell. It resulted from the bleed out of contaminants from a pore at its bottom.

Figure 2
Skip plating defect resembling an oyster shell due to contaminants bleeding from a pore at its bottom. 50X magnification.

Alkaline cleaners bleeding from a pore will often cause a mottled, cloudy pattern in the electroless nickel deposit around it. A rapid discharge of cleaner can also produce a localized area of high bath activity and can generate particles of nickel hydroxide or phosphite, producing roughness. Abrasives and metal chips from previous machining or cutting operations may also be present in a void. These can be spit into the bath, causing more roughness.

After releasing their contents, pores will fill with electroless nickel solution. This solution is just as difficult to remove from the void as the oil or chemical that previously filled it. After the part has been rinsed and dried, the bath will seep out, straining the coating around it.

Cleaning contaminants from pores is always difficult and sometimes nearly impossible. The shape of many pores is such that cleaners cannot penetrate to their interior. With difficult pores, alternating the part between the cleaner and a cold and a hot rinse is often beneficial. The difference in temperature will help to *pump* the contaminant out of the void and to replace it with water. The temperature of the hot rinse should be as least as hot as the electroless nickel bath. This rinsing technique was used to prepare the P/M part shown in Figure 3 and helped obtain deep penetration of the electroless nickel coating into the substrate.

Another way to remove organic contaminants, especially where other cleaning methods have failed, is to burn them out. The parts must be heated to a temperature greater than 300°C for 30 minutes to consume an oil completely. Afterwards, the parts should be abrasively cleaned to remove the carbonaceous char covering their surfaces.

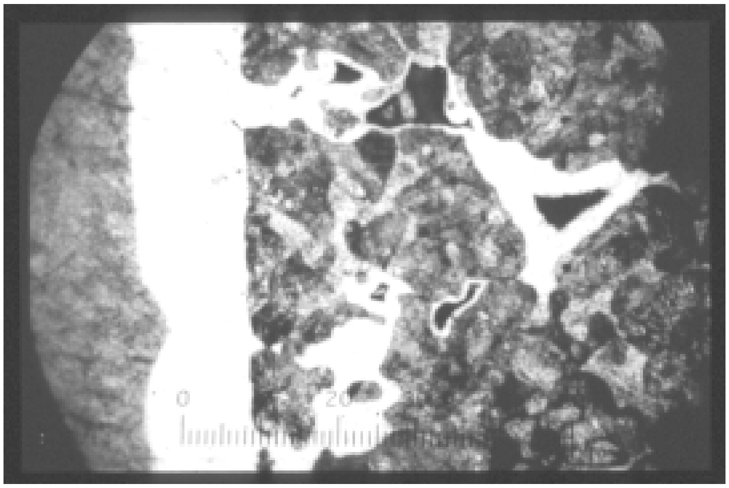

Figure 3
38 µm thick electroless nickel coating penetrating deeply into a powder iron-copper substrate. 400X magnification.

With parts that have not yet been exposed to contaminating solutions, pores may be filled with an anaerobic resin like Loctite®. Once sealed, the pores cannot carry contaminants along to the plating bath. This technique works best with powdered metals in the as-sintered condition.

Surface Separations Resulting From Forming

Rolled or forged metals usually do not contain voids or pores. However, they can contain areas where the metal is separated from itself, which can also produce defects in subsequent electroless nickel coatings. The most common defects in wrought metals are *laps*, *laminations*, *seams, slivers* and *scabs.*

Laps are small metal folds in the surface of a metal that resulting from rolled in protrusions. Minor laps consist only of a crack from the surface passing into the metal and are not usually detrimental to subsequent metal finishing. Major laps are like voids and can produce the same types of porosity problems.

Laminations and seams are due to inclusions or blow holes in the original metal ingot that were not welded together during rolling. Laminations are separations parallel to the surface and inside the metal. Seams are similar, but perpendicular to the surface. Unless they have been machined through, laminations do not affect subsequent coatings. Seams act like tightly closed cracks and have little effect on plating.

Slivers and scabs are similar defects. Slivers (also called *tongues*) are thin layers of metal rolled onto the surface and only loosely attached to it. Scabs are the same, except that the layer is made of non-metallic scale. These defects do not affect the structure of electroless nickel coatings. However, they can severely affect the coatings' adhesion. When slivers and scabs are placed under stress they can separate and lift subsequent coatings. These failures appear to be due to coating adhesion, while they are really due to a failure of the substrate. An example of a failure due the separation of a sliver from its substrate is shown in Figures 4 and 5. The substrate in this example was a 4130 adhesion test panel whose coating failed when it was bent.

If they are found, slivers and scabs can easily be removed by abrasive blasting or grinding. Unfortunately, both defects are difficult to identify and usually appear to only be fine cracks with a circular shape. Fortunately, these defects are not very common with parts that are to be electroless nickel plated.

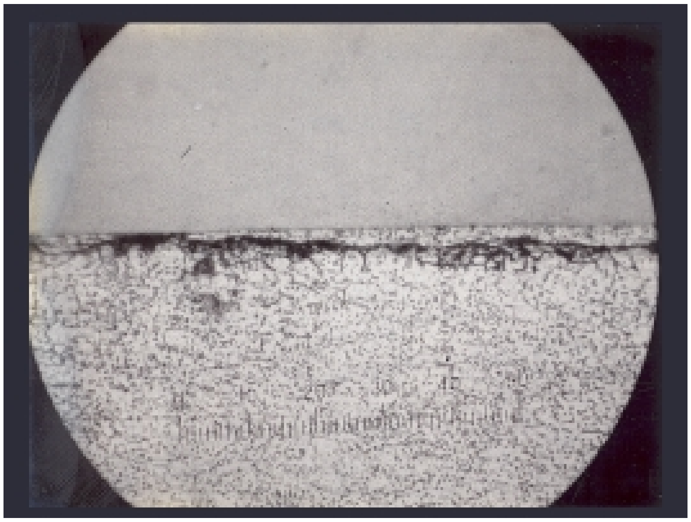

Figure 4
Sliver on the surface of a SAE 4130 substrate coated with 75 µm of electroless nickel. 400X magnification.

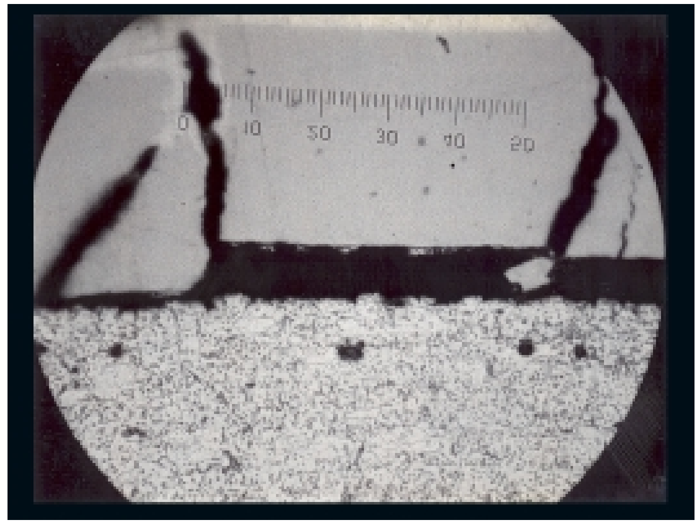

Figure 5
Loose electroless nickel coating with pieces of the sliver attached to its underside. 400X magnification.

Deformation Due to Machining or Grinding
Mechanical finishing operations also create defects in a substrate that can produce defects in its electroless nickel coating. M & T likened machining and grinding of a metal to the “action of a plow through soil.” Whether the plow is a single point cutting tool or a multi-grained abrasive wheel, it digs furrows through the metal and raises edges with splinters and burrs.[1] Machining also disturbs the metal beneath the cut groove, sometimes causing severe deformation and damage.

Porosity is the most common coating defect arising from machining damage. Pores usually grow from the crevice beneath burrs and splinters. These crevices are shielded from fresh solution flow and become blocked by hydrogen bubbles. These pores may be quite narrow or wide, but are always tunnels through which the substrate may be attached. Typical pores growing from burrs on a mild steel surface are shown in Figure 6.

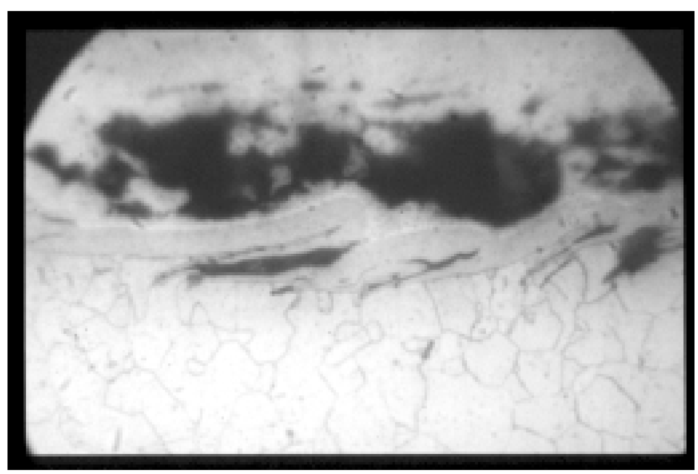

Figure 6
Pores growing from beneath burrs on the surface of mild steel plated with 12 µm of electroless nickel. 400X magnification.

Pores can also form from the disturbed metal beneath the machined area. If machining is so aggressive that the metal is work hardened or severely deformed, the surface can craze or crack. These cracks can also act as initiation sites for defects.

Mechanical finishing can also produce coating roughness. Substrate clips held on the surface by magnetism or soils will plate and form a bump in the coating. Metal hairs or thin splinters also will plate and form protrusions. Sometimes hairs will even stand up perpendicularly under the action of the electrical charge in the electrocleaner or nickel strike. A roughness protrusion resulting from a metal splinter is shown in Figures 7 and 8.

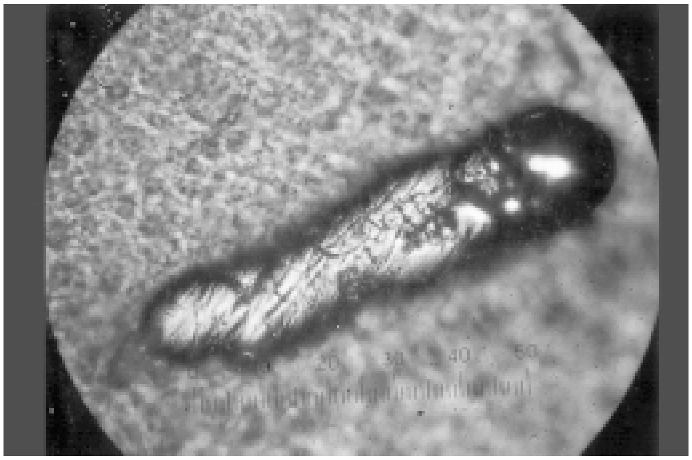

Figure 7
Roughness protrusion on the surface of an electroless nickel coating. 50X magnification.

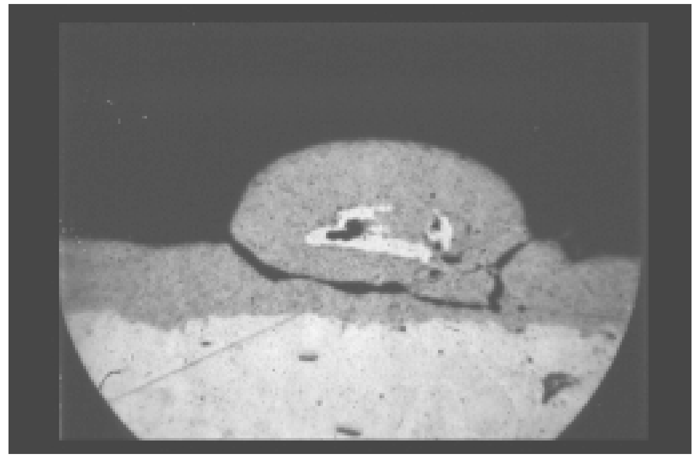

Figure 8
Aluminum chip inside the roughness protrusion shown in Figure 7. 100X magnification.

Finishing damage can also cause roughness if the chips are not held on the surface, but are released when the part is placed in the hot plating bath. The particles are then spread through the solution, causing shelf type roughness, not only on the machined part, but on all the parts in the tank.

Another effect of machining steel is the residual magnetism that can be produced. Magnetism will depend on the part’s shape, the type of steel, and the severity of cold work. It will attract most particles in the bath, including metal chips, iron oxides, and plated dust. When the particles plate, they make roughness. Often, this type of roughness will have a pattern that resembles a machined feature, like a drilled hole or a milled slot.

Detecting finishing damage can be difficult. Sometimes, splinters or burrs can be felt, or will catch fibers from a paper tissue dragged across the surface. Sometimes, they can be seen with a low power magnifier, or can be identified by profilometer measurements. However, usually their presence can only be assumed from the type of machining done on the part. Cracks can be confirmed by dye penetrant or magnetic particle inspection.

Mechanical finishing damage can only be removed by further finishing. Blasting with aluminum oxide or steel shot can be very effective in removing chips, splinters and hairs. It can also expose and open cracks or other defects hidden by metal smeared by grinding. Blasting can also sometimes seal very fine cracks by peening them together.

Residual magnetism in a machined steel part can be easily detected. Magnetic field indicators can measure up to 50 gauss of magnetism. These gauges cost less than 100 dollars and should be available in every plating shop. If residual magnetism is detected, the parts can be demagnetized (*degaussed*) using a rapidly alternating magnetic field.

Secondary Phases Inherent in the Alloy

The previous sources of coating defects have themselves been defects in the substrate. The next source is not a defect, but a normal part of the substrate's structure. These are the secondary phases present in many alloys.

When some metals (like copper and zinc or tin) are mixed, they produce a *solid solution* where only one phase is present in the alloy (brass and bronze). Other metals (like iron and carbon or aluminum and copper) do not form a single solid solution. Instead they consist of secondary phases mixed with the solid solution (steel and Alloy 2024 aluminum). Sometimes, elements (like manganese and sulfur or lead) are added to alloys to form separate phases to modify their properties (free machining steel or brass). Other phases can be minerals or glass (*inclusions*) left over from the casting or forming process. These secondary phases are another source of coating defects.

Inert phases like graphite and slag inclusions are not catalytic to electroless nickel deposition. They will not begin plating on their own, although deposits can grow over them from the metal plating beside them. Lead and manganese sulfide (MnS) are stabilizers and can poison an electroless nickel solution. Both types of phases can act as initiation sites for pores through the coating. Because the coating cannot plate, or is slow to plate, on these phases, a dimple or pit is formed as the coating grows beside them. This dimple will sometimes be bridged over. However, it usually stays open and produces either a gas pit or a pore through the coating. Like the pores formed from voids, evolving hydrogen bubbles mask the surface and keep the pore growing.

Separate phases can also result in etch pits in the substrate. These pits are common with active metals like aluminum, but can also occur with steel. With aluminum alloys, secondary phases are usually intermetallic compounds like $CuAl_2$ and $Al_{12}Fe_3Si$, that form along grain boundaries. Where these phases are exposed at the surface, they promote pitting during alkaline or acid cleaning. Either the phase itself is attacked or it causes the aluminum to dissolve preferentially. With either case, deep pits form, which cannot be covered by an electroless nickel coating and replicate as pores. Often, this kind of pit results from over aggressive cleaning of the aluminum or of stripping a previous coating. An etch pit and the pore that it produced is shown in

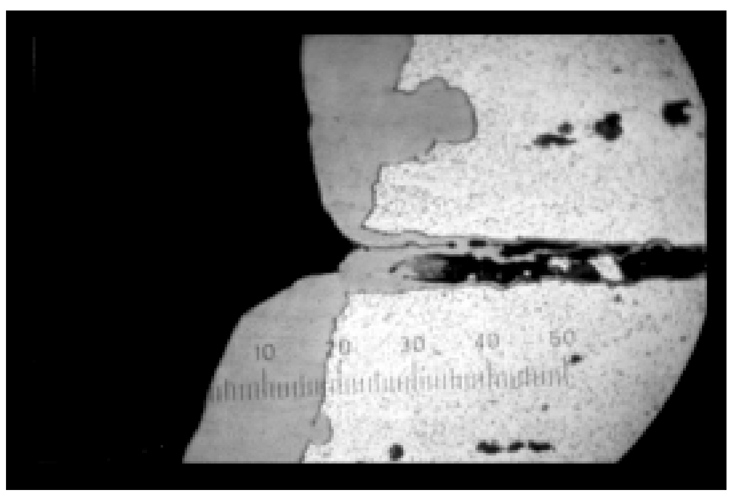

Figure 9
Pit formed in Alloy 2024 aluminum by over etching and the pore resulting from it. 400X magnification.

Figure 9.

With free machining steel, similar but less severe etching can occur. Resulfurized steels contain elongated MnS particles (called *stringers*) which ease machining by causing chips to break away from the part. Where these stringers are exposed at the surface, they can be preferentially removed (especially during electrocleaning) causing a pit. These pits are also locations for pores and gas pits to begin.

These defects are especially difficult to prevent since the phases that cause them are a normal part of the substrate metal. The only absolute preventive is to substitute another metal that does not contain secondary phases. However, usually such a change is not possible because of cost or production requirements. Sometimes, abrasive blasting followed by thorough cleaning can help remove inert phases like slag. With others, like aluminum alloys, providing only the minimum cleaning that will give adequate adhesion is best.

Foreign Phases Transferred to the Substrate During Fabrication
Another source of defects in electroless nickel coatings is particles transferred to the metal's surface from another process. These particles are usually produced by a previous abrasive blasting, grinding or honing operation. They are most commonly fragments of the abrasive, but may also include particles of metal or scale mixed with the abrasive. Abrasive particles are inert and will not initiate electroless nickel plating. Metal or scale particles will usually begin plating by themselves.

The most obvious defect that these particles produce is roughness. If the electroless nickel deposit grows over them, they will produce a bump in the coating. However, if the coating does not start plating on the particle and the particle's size is larger than the coating's thickness, the particle becomes a large pore, like that shown in Figure 10. Even if the particle's size is smaller than the coating, it still may serve as an initiation site from which a pore or gas pit may grow.

Figure 10
Alumina abrasive particle protruding through a 50 µm thick coating. 400X magnification.

The best way to avoid roughness and porosity associated with foreign particles is to keep them off the part. The correct sized abrasive for the job should be selected, and it should be kept clean of contaminants and broken media. Embedded abrasive particles can be very difficult to remove by normal cleaning processes. For these cases, further mechanical finishing may be the only way to remove them. Hand scrubbing with brushes or Scotchbrite pads, or power-washing with high pressure water, may be needed.

Dissimilar Metal Combinations
Coating defects can sometimes result from combining different metals in the same part. These problems usually occur because the designer or manufacturer of the part does not know that combinations can be disastrous to the plater. Typical examples are brazed or soldered connections, stainless steel repair welds in tool steels and cast iron, and lead or solder filled repairs in any metal. These are bad enough when the plater knows that they are present (like copper brazed steel). However, when they are hidden (like stainless steel in ground tool steel) they can be destructive and costly.

When a steel part contains an unknown stainless steel repair or insert, the stainless steel probably is not going to be properly activated. It probably will not start plating initially, and the coating on it will not be adherent. If the plater is lucky, these areas will blister when they are placed into the post plating rinse tank. If he is not, they will flake off after the part has gone into service. Similar adhesion failures are likely with many dissimilar metal combinations.

With lead or solder repairs, the failure may be more general. If the lead is hidden (as inside a mold's water passages) and unknowingly placed into a plating bath, it will not plate. Instead, it begins to dissolve into the plating solution. Within hours, the bath will contain enough lead to cause skip plating and perhaps enough to stop all plating.

Many dissimilar metal defects can be overcome by educating the part's manufacturer about the possible results. Usually, they will gladly provide the fabrication history of the part, detailing its manufacture and repair. Where dissimilar metal combinations cannot be designed out, plating the part with copper or nickel to cover up the two metals may be necessary. For combinations like a stainless steel repair in a tool steel part, preparing and activating the part like it was all stainless steel usually eliminates adhesion problems.

Conclusion

The quality of the substrate on which electroless nickel coatings are plated can severely affect their quality and performance. Different substrates can contain holes and voids, separated surfaces, burrs and deformed metal, secondary and foreign phases, and presence of other metals. These defects often replicate into the coating, affecting the deposit's porosity and corrosion protection, adhesion, wear resistance, and appearance.

Reference

1. H. Chessin, E. C. Knill and E. J. Seyb, Defects in Hard Chrome Deposits, SUR/FIN '81, American Electroplaters' Society, Boston, June 30, 1981.

Table 1
Defects in Electroless Nickel Coatings

Defect	**Possible Source**
Pits or Pores	Blow holes or shrinkage cavities in castings or welds Voids in powdered metal substrates Laps in forgings Burrs, splinters and cracks in machined surfaces Graphite or slag inclusions and lead or MnS phases in substrate surfaces Pits etched from intermetallic compounds Abrasive or scale particles on substrate surfaces
Star Dusting Universal Fine Pitting	Organic contaminant or solvent exuded from voids in castings or powdered metal substrates
Skip Plating and Edge Pull Back	Contaminants exuded from voids in castings or powdered metal substrates Lead or other poisonous metal hidden inside parts
Roughness	Cleaners or abrasives or metal chips exuded from voids in castings or powdered metal substrates Machining hairs, splinters or chips on substrate surfaces Residual magnetism in iron or nickel-based parts Abrasive or scale particles on substrate surfaces
Poor Adhesion	Contaminants exuded from voids in castings or powdered metal substrates Separation of slivers or scabs from substrates Combination of passive metal with non-passive substrates
Patterned Deposit	Cleaners or contaminants exuded from voids in castings or powdered metal substrates Residual magnetism and associated roughness
Stained Deposit	Plating solution exuded from voids in castings or powdered metal substrates

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.