

Troubleshooting Decorative Electroplating Installations—Part 3: Pores, Spotting-out, Pits, Peeling & Blistering

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The background, symptoms and causes for pores, pits, stains, blistering and “spotting-out” phenomena are analyzed from phenomenological and practical standpoints. Origins and tests for porosity are discussed, as well as detection methods. Corrective steps are included.

Rationale

Electroplating is the process of electrochemistry that produces a uniform, smooth and adherent metal deposit. Deposits start from a nucleation site. Fast lateral growth, compared to outward growth, results in continuous adherent deposits at the fastest possible rates. Still, deposits of definite thickness often have minute gaps exposing the substrate either as stress-related cracks, pits or as pores that will be the primary subject of discussion.

Much torment in the electroplating department is caused by the condition of the basis metal before the part enters the first electroplating solution. Some problems could not possibly be prevented by the best solutions and finest techniques known to the electroplating industry. These are inherited from the quality of the as-received basis metal, available technology in the polishing and buffing room, or the design of electroplating production lines. Nevertheless, it is important for the plater to be able to identify these problems correctly and in a timely manner. In some cases, the defects can be remedied by appropriate treatment if the plater knows the cause of the problem.

The main concern of the majority of electroplaters and metal finishers is *how* to overcome problems, so that rejects can be reduced to a reasonable number. It has been mainly through trial and error, and by taking note of the work of other practitioners, that a number of empirical techniques have been developed for solving some of the problems. Conversely, “sweating-out,” a.k.a. “spitting-out,” “bleeding-out” or, to use a more delicate term, “spotting-out,” or the more elegant European term, “blooming-out,” is one of the aggravating exceptions because, in this instance, we know *why* it happens, but as it happens, we do not really know *how* to overcome it completely. Unfortunately, spotting-out has been like the weather -- we can talk about it but can't do much more than that. Many avenues of approach for the solution of this problem have been contemplated over the years, with moderate success at best, and we will discuss them in detail.

Porosity & Pitting

Definition of Pores & Pits

In everyday electroplating jargon, and often in technical literature, different descriptions of these two unpleasant perennial electroplating symptoms can be found.

Figure 1 depicts different kinds of pores (a-f), and pits (g-l), as well as cracks (m, n), blisters (o), laminations (o-p), and inclusions (r, s). It is obviously wrong to make distinctions between a pore's being microscopic and a pit's being macroscopic. In general, it can be maintained that a pore is a slight interruption of the metal deposit that, more often than not, can

be seen with the naked eye. To be more particular, it can be defined as a discontinuity in a plated deposit in which a processing solution can be trapped, or when testing for porosity, a corrosive agent can penetrate to the basis metal, causing it to corrode.

Pores can also be defined as hollow spaces in the electroplated surface, conditioned by production circumstances. The pores are filled with air, electroplating solution or foreign bodies. The first distinction must be made between pass-through pores (Fig. 1a, b, c, d), and masked-off (sealed) pores (Fig. 1e, f). In actual practice, pores and their cousins, pits, are of a threefold nature:

1. Surface defects in the substrate material (*e.g.*, surface roughness, traces of previous mechanical preparations, porosity, slag lines, oxides, etc.).
2. Defects resulting from out-of-order electroplating conditions (*e.g.*, gas bubbles, grease and oil, graphite, carbon, grinding and polishing residues, loose metal particles, insoluble hydroxides or basic metal salts, anode slime, and other foreign particles, suspended in the bath).
3. Defects as a result of bath actions or subsequent effects (*e.g.*, partial covering (“missing”), stress-induced cracks (Fig. 1m, n), polished-off surfaces, and chemical action after deposition or corrosion (Fig. 1i), etc.). In Fig. 2, a comprehensive set of surface imperfections is shown.

A pit is a pore as well, although of different origin, because it is mostly formed during the electrodeposition process. It is formed, either by hydrogen gas bubbles clinging to the metal and interrupting the regular growth of the metal (“gas pitting”), or by “dirt pitting,” caused by impurities in the electroplating bath itself. The former exhibits a characteristic tail, while the latter shows dark color at the bottom of the pit and is often called surface inclusion.

Origin of Porosity

There are three kinds of porosity that the suspecting or unsuspecting electroplater must deal with: (A) intrinsic porosity, (B) the porosity present in the basis metal and (C) porosity induced by electroplating bath effects.

A. *Intrinsic porosity.* In some thin electrodeposits, it is always present and inevitable. It is a basic parameter predicated on the very nature of the electrodeposition mechanism. Thus, the type of bath, current density, agitation, and temperature and, probably, the host of other factors will influence the extent to which the deposit will be inherently porous. Chromium and gold are most familiar and common examples of this. Intrinsic pores can be troublesome in thin nickel deposits used for some special purpose, such as underplate for gold.

The pores in plated metal could allow chemicals to leak out by capillary action and stain the surface, inducing spotting-out. This is relatively uncommon, however, unless the basis metal (substrate) itself is porous.

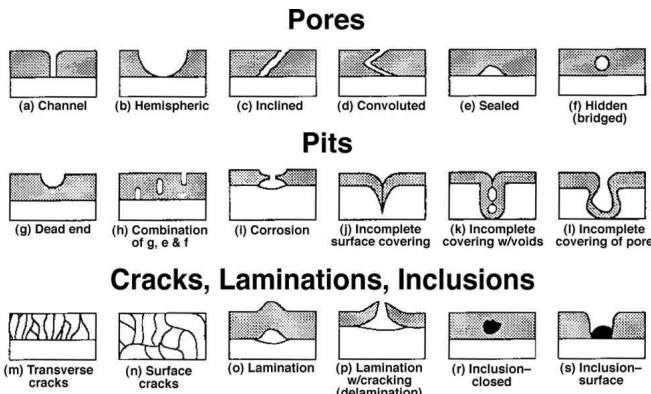


Fig. 1—Surface faults: (a-f) pores; (g-l) pits; (m-n) cracks; (o-p) laminations; (r-s) inclusions.

B. Porosity in the basis metal. This is quite common and often originates in the preparation of parts prior to electroplating. For example, if there is any sequence of solutions used in the particular electroplating process that can cause entrapment and/or precipitation of insoluble products in substrate metal pores, holes, lap seams, crevices and so forth, a condition is being set up that will cause problems later. The presence or absence of porosity, however, is rather a matter of definition. A metal part is declared to be sound if it passes a particular test for soundness.

Pores in the base material can be subdivided as follows: (a) pores already present in the unplated, base material and (b) inclusions in the base material having poor conductivity.

Although present but not apparent, porosity in most instances will not cause a problem, but occasionally spotting-out can occur. Taking place on most occasions after processing from cyanide baths (notorious for high alkalinity and difficulty of rinsing), the spots will mostly turn up at the parting lines where flash removal has exposed porous metal under the skin of castings. If the work consists of sand castings, it is likely that it will be inherent in die casting process. Porosity can be caused by shrinkage of the metal during freezing in low-cost casting processes. If the porosity is minute, dispersed through the metal, or consists of shallow holes that can be rinsed, it will not be apparent at the electroplating line.

Pores will also tend to appear at the edges of stampings where fine burrs form pockets, or on bends where the metal has been stretched. In addition, they can materialize on flat sheets where dirt has been rolled in on the surface during the steel mill rolling operations, and in the straight line along the die marks produced during extrusion and wire drawing. And to cause sleepless nights, they more often than not, do not show up immediately, but only days later when the components have been assembled. One obvious, but not popular or recommended solution to remedy this problem is to reject porous work outright.

For this variety of spotting-out to occur, the top surface layer of basis metal obviously must have pores, and there also must be a reservoir of chemicals or liquid beneath. This situation is commonly found on unplated zinc, aluminum or iron castings and powder metallurgy parts, or parts made of graphite. Alloys such as pot metal are often sufficiently porous to cause unsuccessful electroplating because of heterogeneous chemical attack on different alloy phases. Zinc die castings and cast iron may have a sound surface but may also have a porous interior that is exposed after some surface metal is removed by machin-

ing and finishing operations, or by acid activation, and/or chemical or electrochemical cleaning steps. It is often important not to over-clean or over-activate, as this can just make the majority of the pores larger.

Glass beading may sometimes close the pores, as can burnishing or buffing operations. A metal-cutting operation, such as machining, honing or belt polishing is more likely to open them. If the pores are shallow or partially open, they may not cause a problem. If they are deep or interconnected, however, they can result in enough trouble to cause parts to be rejected. In such a case, pores should be evident by close visual examination. Such deep pores cannot be rinsed free from the solution in the rinse tanks. Consequently, the process solution from a cleaner, acid dip, or strike-plating bath, can be carried to the next bath, which will cause spotty conditions at the final rinsing stage and, if sufficiently pronounced, may cause skips, pits, blisters and adhesion problems.¹

On the other hand, pores are often difficult to detect because they have been completely or partially closed at the surface by working the metal in mechanical preparation (*i.e.* buffing) operations. Any porosity that is prominent and readily apparent means that it is unlikely that the work can be salvaged. Porosity in the substrate can be confirmed by microscopic examination, by liquid-penetrant inspection of the work prior to electroplating, or by metallurgical cross sectioning.

Figure 3-3 depicts the condition that will cause the trouble. The pore has a small opening on the surface. Mechanical working of the surface, which can incompletely close the pore, can create such a condition. The bath solution replaces part of the air, but not all of it (Fig. 3-6). When the work is placed in a warm bath, air expands within the pore, causing push of the solution in front of the bubble. After the parts reach the cold rinse tank, the trapped air inside will contract, the solution will be siphoned in, while the air bubble is trapped within the pore. In consequence, the pore will be very sensitive to any temperature changes and the bubble will act as a mini-thermal pump to force the solution in and out in the various cold and warm electroplating steps; or worse, it will pump the solution in and out by contraction and expansion after the work is plated and in use.

C. Electroplating bath effects. Pores and pitted electroplating may occur even in the non-porous substrate. Once the deposition process begins, the substrate precursors can initiate a family of pores. Unless the bath is operated under unusual conditions, porosity always decreases with the increase of deposit thickness. For a given thickness, the number of pores often varies with the concentration of all the salts in the bath, the presence of addition agents, the accumulation of aging byproducts, the current density and the form of applied direct current, degree of agitation and bath temperature.

Pores, spots and pits can be the result of trouble in the bath, such as loss of bath control, dissolved gases, presence of oil or poor rinsing of the final plated part. If the spots are a result of bath troubles, they will be apparent as the work leaves the

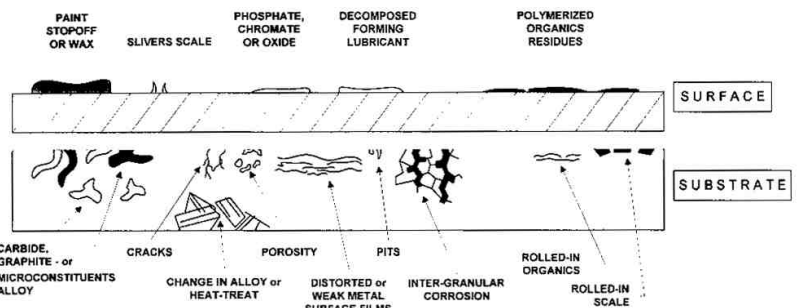


Fig. 2—Types of substrate and surface defects.

bath. On the other hand, if spots show on the work after the final rinse, or if they develop or worsen with time, they are generally a result of the previously mentioned basis metal porosity.

The deposit may also be pitted or blistered because of occlusion of the contaminants that are floating in a bath. Oil and soil from insufficient cleaning can cause voids and bare spots in the form of "skip" plating. This results in: (a) no metal being plated over the soil, but just around it, or (b) from electroplating over the soil, which then delaminates because of poor adhesion and/or high stress.

The rejects can often be stripped and reprocessed only if the plated deposit is porous and the substrate metal is not. Close inspection under magnification is needed, along with perhaps hand cleaning of parts to pinpoint and possibly eliminate the problem.

Spotted work, not being a result of pores or pits, can be tracked to insufficient rinsing, to the previous electroplating step and/or intermediate rinsing, or from final post-electroplating rinsing steps. For the former, the deposit may be thin, porous or non-adherent on contaminated areas. Small, often numerous, non-adherent areas may appear as blisters when the work is heated, sometimes in a drying oven. Aluminum alloys plated with tin-lead, for example, have shown blisters after heating to 1200 °C for half an hour. In the latter case, if the final rinse is inadequate, electroplating surface stains may be present. Irregularly shaped, these types of stains can be characterized as "hollow blemishes" caused by the concentration of the soluble salts from electroplating or final rinse tanks during drying of the rinsewater.^{2, 3} Stains, surface contamination and water spots, seen after rinsing and drying, are unacceptable defects for semiconductor and hybrid electronic parts. The structure of water film should be viewed as a series of layers of water molecules. Water is vaporized in layer-by-layer fashion, beginning with the uppermost layer, where relatively weak attractions exist. A strong molecular interaction exists between the lowest molecule and the metal substrate. As the upper layer is vaporized, the lower level stays in the liquid state where the soluble salts are concentrated to the solubility level where they begin to redeposit.

Porosity Testing

Microscopic and other more subtle forms of deposit porosity are often best detected by various corrosion tests.^{4,5} The time-

Deposit	Base Metal	Solution Composition g/L	Table Test Time, min	Procedure
Copper	Steel	K ₃ Fe(CN) ₆ - 10 NaCl - 2	20	Application of filter paper wetted with reagent
Nickel	Steel	Same	5	Same
Nickel	Steel, copper & brass	Same	10	Application of filter paper wetted with reagent, treat paper with K ₄ Fe(CN) ₆ solution
Chromium	Steel, copper & brass	K ₃ Fe(CN) ₆ - 10 NaCl - 6 NH ₄ Cl - 30	10	Same
Chromium	Nickel	Same	10	Application of filter paper wetted with reagent, treat paper with dimethylglyoxime solution
Tin	Steel	K ₃ Fe(CN) ₆ - 10 NaCl - 5	60	Application of filter paper wetted with reagent
Tin	Copper & brass	K ₃ Fe(CN) ₆ - 10 Na ₂ SO ₄ - 10	5	Anodic treatment at 0.5 to 0.6 A/dm ²
Zinc	Steel	K ₃ Fe(CN) ₆ - 40 Na ₂ SO ₄ - 2	5	Anodic treatment at 4 V
Lead	Steel	K ₄ Fe(CN) ₆ - 40 NaCl - 2	5	Anodic treatment at 6 V
Lead	Copper	K ₃ Fe(CN) ₆ - 10 K ₄ Fe(CN) ₆ - 10 Na ₂ SO ₄ - 10	1-2	Anodic treatment at 0.2 to 0.35 A/dm ²
Copper, Nickel & Chromium	Steel	K ₃ Fe(CN) ₆ - 10 NaCl - 1 Gelatin - 2	5	Place solution on surface of deposit
Gold	Copper & copper	K ₃ Fe(CN) ₆ - 10 NaCl - 6 NH ₄ Cl - 30	10-60	Application of filter paper wetted with reagent, treat paper with K ₄ Fe(CN) ₆ solution
Gold	Nickel	K ₃ Fe(CN) ₆ - 10 NaCl - 2	10-60	Application of filter paper wetted with reagent, treat paper with dimethylglyoxime solution

honored salt spray test (ASTM B 117), in particular, is used to detect the presence of pores in deposits of nickel, copper and chromium on steel. There are other porosity tests available (e.g., acetic acid accelerated salt spray (ASTM B 287), cyclic humidity tests (ASTM G 60), ferroxyl print tests, and a number of others. In many instances, porosity tests can be overaggressive and lead to formation of enlarged pores on the more active regions in the deposits. Discretion is needed, therefore, when interpreting the results.

Salt spray or salt fog tests, developed around 1914, are used primarily for quality evaluation and control, whereas electroplating line troubleshooting needs quicker tests, even if they are less accurate. Porous nickel on steel is simply and easily detected by immersion of the part in hot water. The part is immersed in hot water (180 °F) for 3-6 hr, at pH range 4.5-7, after which it is removed, dried and inspected for rust spots. This test is particularly useful for checking the gross porosity on areas where complete inspection is necessary.

The ferroxyl test (ASTM B 765-1993) is more versatile and dependable, albeit imperfect. It has been available since 1909.⁶ This test reveals discontinuities, such as pores in deposits of Sn, Ni, Cu, Co, Cr, iron and steel. It consists of a solution of sodium chloride, NaCl, (or hydrochloric acid) which opens any pores and helps dissolve the underlying metal, and potassium ferricyanide (K₃Fe(CN)₆), as both are oxidizers to accelerate the reaction. Ferrous chloride, formed by the action of chloride ions upon any exposed iron of the basis metal reacts with K₃Fe(CN)₆ to give a blue precipitate,

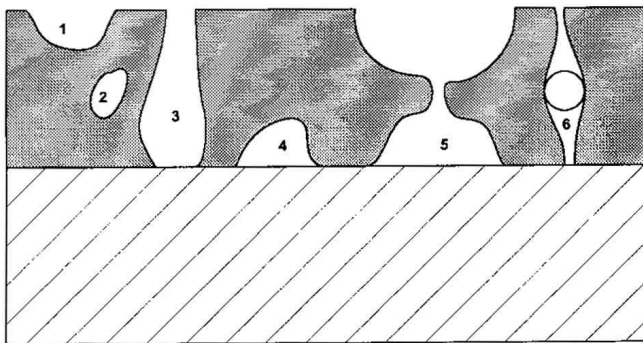


Fig. 3—Types of pores: (1) dead end; (2) void; (3) continuous; (4) bridged; (5) combination of (1) and (4), connected by a small channel; (6) continuous, with air bubble.

Turnbull's Blue: $\text{KFe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6$ or Prussian Blue: $\text{K}_3\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$. This solution with iron and silver ions produces blue; with copper, brown; and with nickel, a yellowish color.

Another simple test is a 10-min exposure to a 3-pct NaCl, 1.5-pct hydrogen peroxide solution, to develop rust spots on a porous deposit.⁷ The time varies from 30 min to four hr.

Accelerated test methods produce quicker results than the salt spray test, but they are less reliable in terms of reproducibility. The electroplater must be a bit hesitant about any test that relies on inducing corrosion as a means of detecting defects. The times must be closely monitored to ensure that minimally plated, but acceptable deposits are not incorrectly rejected. These tests can be useful, however, for troubleshooting on the electroplating line, and for developing acceptable electroplating cycles for lower priced and lower quality substrates.

The porosity of the top metal deposit is less critical when the deposit is sacrificial, or corrodes more easily, than the substrate. Zinc or cadmium on steel is a typical sacrificial deposit. Clearly, a porous substrate is also undesirable because it may be too porous to plate properly, allowing it to trap solution that may bleed out and spot-out the deposit. On the other hand, if spotting is not severe, it may be reduced by chromating the zinc or cadmium surface. It should be noted that lead, for example, present in traces in hot-dip zinc deposits, could give similar, spotted appearance defects, with poor chromating or paint adhesion on the lead spots.

It is much easier to detect porosity in a noble metal deposit over a sound basis metal. It requires the immersion of the plated part in a chemical solution that will selectively attack the substrate beneath the pore and not harm the top, final deposit. Electronic connectors that are gold-plated over nickel plus copper underplate are routinely tested for pore-free quality by this means. The connectors are immersed in dilute nitric acid and are observed for evidence of gassing because of attack of the nickel and/or copper beneath a pore in the deposit.⁸ In the nitric acid vapor test⁹ for copper alloy substrate, parts are immersed in the fumes of concentrated nitric acid in a closed vessel for one hr,^{10,11} two hr,¹² or several hr.⁹ Several chemicals have been used for specific testing that will selectively attack a substrate in this way. Pores are detected by observation of gassing, or by formation of a colored reaction product.

Galvanic cells of "base metal deposits" are formed at the location of the pores. The current of these cells, which for cathodic deposits is practically all that is necessary for dissolution of the basis metal, is proportional to the initial difference between the potentials of the basis metal and the deposit, and is inversely proportional to the anode and cathode polarization and to the ohmic resistance. The initial

difference between the potentials of the basis metal and the deposits is always slightly higher than the difference between the potentials of the electrodes of the acting galvanic element or cell, because in the latter, the potential of the cathode decreases, becoming more electronegative, while the potential of the anode increases, becoming more electropositive.

Electrochemical methods have been devised to make the substrate anodic and then to observe the corrosion current. An example is the ferroxyl print test,¹³ where the pore size and number of pores appearing are detected on a porous piece of paper, which can then be easily dried and saved for a record. Another example⁴ is a more recent technique based on charge under the anodic peaks during the reverse cathodic scan of cyclic voltammograms for various immersion times in a solution consisting of 150 mL of 0.1 M H_2SO_4 and 10 mL of $\text{K}_4\text{Fe}(\text{CN})_6$ at 250°C.

The dimensions of the pores are usually so small that they cannot be seen by the naked eye or even under a microscope. The porosity can be determined, however, by artificially induced corrosion, as a result of which, ions of the basis metal pass through the pores into the solution and form colored insoluble compounds with a specific reagent. The points of coloration indicate the pore dimensions.

The porosity of cathode deposits on iron, for example, is tested in solutions of potassium ferricyanide that forms a previously mentioned, colored compound with the iron ions. A detailed investigation of the kinetics of the appearance of pores, the influence of reagents on the dissolution of the deposit and the formation of new pores, plus the influence of various addition agents on the sensitivity of reagents containing potassium ferricyanide was carried out.¹⁵ Also determined were the variations with time of the electrode potentials of iron, copper, and nickel in solutions of $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ with and without sodium chloride. These investigations showed that iron is an anode when in contact with nickel. The largest initial differences between the potentials of nickel and iron (0.70 V), copper and iron (0.36 V), and nickel and copper (0.34 V), are obtained in a solution containing 10 g/L of $\text{K}_3\text{Fe}(\text{CN})_6$ and 20 g/L of NaCl.

For pre-indicating reagents to be effective, the following conditions must be fulfilled:

- maximum potential difference between the base metal and the deposit;
- maximum polarization and ohmic resistance;
- easy penetration of the pores by the electrolyte;
- rapid flow of the products of corrosion from the pores;
- easy reaction of the reagent with the corrosion products;
- no chemical dissolution of the deposit;
- no damage of the deposit at the outlet of the pores.

Before testing, the parts must be degreased, rinsed and dried. The solutions recommended for determination of the porosity and operating procedures are listed in the table.

As can be seen from the table, the pores in nickel deposits on steel and copper, and in chromium deposits on steel, copper, or nickel are indicated by the same solutions. The high sensitivity of reagents that contain no protective colloids results from the large difference between the initial potentials of the metals and the concentration of the electrolyte being sufficiently high to bring about precipitation of the reaction products formed in the pores.

For the detection of pores in deposits plated on copper, copper alloys, or nickel, the soaked filter paper which is removed from the deposit is subsequently treated with a solution of $\text{K}_4\text{Fe}(\text{CN})_6$ or with an ammoniacal solution of dimethylglyoxime. This treatment is recommended instead

of direct addition of $[\text{Fe}(\text{CN})_6]^{4-}$ to the solution because the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ ions hampers the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ ions.

A prolonged series of porosity tests carried out on nickel on the same area of the specimen reveals a continuously increasing number of pores because of dissolution of the deposit by the reagent. The largest pores are revealed at first, after which continued action of the reagent reveals smaller pores which either existed in the deposit before or were created by the action of the reagent. The duration of the test for thick deposits is arbitrary, therefore, and must always be stated in the test specification.

The relationship between electroplating overpotential and porosity of the thin (0.2 μm) electrolytic nickel deposits was shown to be dependent on the deposit structure, which is determined by the electroplating overpotential. A lower porosity can be achieved by using a relatively high overpotential, resulting in deposition of nickel with finer grains.¹⁶

Electrolytic and electroless plating exhibits the following general relationship between porosity (p) and plating thickness (t): $p \propto t^n$ where n is a constant that depends on deposition conditions, including preplating factors

Unsound base metal properties can be identified by metallographic examinations. In the case of engineering part failure, this analysis can pinpoint the spotting-out consequence of the basis metal, processing problem or intrinsic property of electrodeposited metal. A metallographic procedure known as *failure analysis* is available to solve rejected parts mysteries.³

Peeling, Laminations & Cracking

Among various electroplating defects that are still besetting electroplaters, despite immense technological and scientific progress, peeling and related phenomena as delamination and cracking are frequently the most exasperating. Although pitting often assumes a quantitatively leading position, peeling is, or can be, the product of so many factors and eventualities, that it is difficult to troubleshoot and solve quickly.

The most common cause for all these problems can often be traced to improper surface preparation of the basis metal. Cleanliness of the basis metal surface and the bath itself is a basic requirement of a trouble-free electroplating operation, particularly with acid copper, zinc or nickel baths. Presence of oil, oxides, scale, inclusions, passive substrate surface and their role as promoters of adhesion problems is obvious. If for example, the surface of the part, during immersion in the electroplating bath becomes partly or completely covered with oil or other types of interfering films, this film can serve as an isolating layer between the basis metal and subsequent deposits. If those films are present only on certain areas of the parts in sufficient quantity to interrupt electrodeposition reactions, pores or pits may result. Often those films are not heavy enough to interfere with normal electroplating conditions, but sufficient to reduce the degree of adhesion so as to cause peeling of the deposits as plated or sometimes afterward.

Laminations can occur (a) naturally, as a part of a particular deposition mechanism, (b) caused by operator or equipment, (c) by excessive addition of brightening and/or leveling additives, and (d) by faulty electroplating conditions, such as presence of metallic impurities, wrong pH, excessive current densities, excessive electroplating thickness, incorrect concentration of metal salts and buffers etc.

In the first case (a), naturally occurring laminations are not necessarily harmful.⁹ They are the result of naturally occurring current and ion concentrations in the vicinity of the cathode surface. In the second case, laminations can be

produced by incidental (*e.g.*, temporary loss of electric contact with rack, or equipment failure) or intentional current interruptions (*e.g.*, pulse electroplating). In the case of (c), excessive concentrations of brightening and/or leveling additives, to compensate for less than optimum smoothness of the substrate or shortened electroplating time, can be detrimental. The resulting decrease in ductility and increase of the hardness can produce highly stressed deposits, reduced adhesion and, in extreme cases, catastrophic cracking, delamination, and peeling.

Corrective Steps

Nothing serves better to substantiate the widely held conviction that electroplating and metal finishing are still art rather than science, than the collective tendency to blame the solutions whenever results do not meet expectations. This is, above all, obvious with the spotting-out problems. Platers often appear to accept no blame for having pitted and spotted deposits along with perfect electroplating of the same metal parts of the same assembly, or to ask why are unsatisfactory results limited to certain batches. It by no means appears to some that something other than solutions can be a culprit. To them we offer the *First Law of Electroplating*: "Electroplating solutions cannot think."

We often read about or even plate "difficult-to-plate metals" (*e.g.*, titanium or inconel alloys). On the other hand, die-castings have been in use for so many years that everyone considers them a "common" basis metal. By everyone, that is, except the plater! Because of this misconception, he is at fault wherever the finish fails to meet quality standards and, as a result, is often engaged in a running battle with purchasing, production and inspection personnel, not necessarily in that order.

Zinc-based and other die castings are a "difficult" metal to plate if the plater does not receive all the necessary cooperation. It becomes a "common" basis metal only if the electroplating process is the focus of interest of all other departments and all involved plant personnel. The plater is in the unenviable position of having to perform the final operation that turns semi-processed objects into the finished product. He is aware that failure often means scrapping of the part and complete loss of all the work that previously has gone into it. Worse, he may not find out that something went wrong until days have passed and delayed spotting-out or blistering appears. During that time, he has been blissfully processing many more parts the same way.

In any plant with a large percentage of this kind of reject, one will generally find one or more of the following conditions: The designer considers his work at an end when he has originated a part of suitable strength and shape for the application; the die-caster considers his responsibility ended with the removal of a smooth casting from the dies, without cold-shuts or other obvious surface defects; the machine operator thinks his job is only to machine, drill, tap, and slit the casting; and, last but not least, the polisher looks no further than the production of a highly buffed, shiny surface.

More than once, a pile of rejects has been blamed on "poor electroplating" when the following have been seen: Staining at the parting line, where removal of the flash has exposed the porous substructure of the casting; black streaks, arising from burrs left in drilled holes; peeling near deep crevices, which should never have been designed into the part, resulting from packed-in buffing compound that only a sharp pick or a powerful ultrasonic cleaning unit could remove; blisters on unbuffed areas, as a result of using a different mold-release compound without first determining whether it can be re-

moved in the cleaning line. By correcting these conditions, the rejection rate often drops from ten percent to below one percent.

The spotting-out conditions are completely unpredictable. They can come and go, while the afflicted plater wonders if the particular panacea he administered was the reason he obtained the relief, or was possibly a result of the weather, or maybe from the process chemistry or processing cycle, perhaps allied to the basis metal, or it is related to which side of the bed the die-caster got up from that morning. In some instances they are related to the weather (humidity).

It must be taken into account that for spotting-out, both moisture and salt are necessary. By eliminating the moisture, the dry salt will not spot-out. The essential, when applicable, is to lacquer the surface before the moisture is reabsorbed. A more recent and more powerful method¹⁹ is to use ultrasonics in water rinse tanks because the cavitation is distinctly helpful.²²

Anyone who has a foolproof method of preventing spotting-out has his future all set. It can be alleviated only to a certain extent. It seems to be a function of the pore size because spotting-out occurs only within a certain range of pore sizes. Few avenues of action are available, however. Although not guaranteed cures, they have been proven to be most effective to date in minimizing spotting-out. Probably the first treatment based on the exercise of the logic is to alternate hot- and cold-water rinses that the old-timers used to swear by. The bubble burst, however, when the late Dr. J. Kushner²³ figured, on the basis of expansion and contraction, that by rinsing between boiling and cold water ten times, 70 percent of the original solution remains in the pores. On the theory of neutralizing the cyanide and other alkalis, various mild acid dips have been suggested and tried over the years, including every mild organic or inorganic acid that would not attack the surface. Because the minute holes were already filled with solution, however, access to the acid was blocked and, although platers sometimes swear by the effectiveness of such dips, it is more likely that the results obtained were the result of a run of less-porous metal and by dry climate.

The cavitation produced by ultrasound is well known to drive the packed dirt from blind holes during cleaning and degreasing. This sound approach attracted a number of progressive finishers, inasmuch as this principle is also applicable to the matter entrapped in the pores, and this has been confirmed in practice. The cost of the necessary equipment will limit adoption of this method in many cases, especially when large parts are being processed. Nevertheless, it appears the best approach so far suggested. Slight amelioration to spotting-out of zinc and aluminum die castings has been obtained by the use of chromate dips and phenolic lacquers.

An array of wetting agents and sequestering agents has been claimed effective, but none produced complete relief. For those who have baking facilities the next best alternative for reducing or minimizing spotting-out is to give the part a good bake for 15 min at as high a temperature as the finish will stand. For brass, that is about 220 °F, before it starts to discolor, followed with lacquering as soon as the part cools. This serves to dehydrate the pores and, if baked parts are given a good coat of lacquer immediately after cooling and before hygroscopic salts have opportunity to absorb moisture from the air, spotting-out can be effectively minimized.

Conclusions & Moral

When the electrodeposit is spotty, pitted, cracked or blistered, search for the cause is in order. It can be the result of faulty bath chemistry, surface contamination, pores in the electrodeposits, pores in the substrate metal, or a combina-

tion of all of these. After the origin of the problem is known, one can speculate on why it is there and what best set of corrective measures can be implemented.

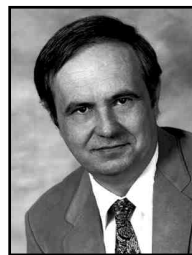
Spotting is an old problem. Although from the play, we cannot suppose that Shakespeare was referring to pre- or post-electroplating problems, Lady Macbeth did say "Out, damned spot!"²⁵

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