Troubleshooting Decorative Electroplating Installations, Part 5: Plating Problems Caused By Heat & Bath Temperature Fluctuations

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In previous parts of this series, emphasis was given to troubleshooting of the sequences for pre-plating and electroplating over metals, Parts 1 and 2;[1] the causes, symptoms and troubleshooting for pores, pits, stains, blistering and "spotting-out" phenomena, Part 3;[2] and troubleshooting plating on plastic systems, Part 4.[3] Here in Part 5, causes and some typical examples of problems that occur in electroplating as a result of a) thermal, mechanical surface treatments, b) the metallurgy of the part to be plated or c) effects of plating bath temperature on plating variables and quality of the deposits are discussed.

Nearly every plater has at one time or another had the experience of trying to plate parts that simply would not plate. The usual assumption is that the parts are not clean. If parts pass a water-break test, conventional wisdom then suggests that the likely cause is that one or more solutions are not as they should be. After all, if the parts cannot be properly plated it is the plater's fault, right? Wrong!

The plater is often the scapegoat even if the problem is caused by the condition of the basis metal before the part enters the first plating solution. Some problems cannot be completely prevented by the best solutions and the finest techniques currently known to the electroplating industry. Often the most difficult problems for the plater to solve come from heat-treating, polishing and buffing or barrel finishing operations. Nevertheless, it is important for the plater to be able to identify these problems correctly, if for no other reason than to protect his or her own interests. In some cases the defects can be solved by suitable pretreatment, if the plater identifies what is causing the particular problem.

Influence of Heat Treatment & Mechanical Preparations

Heat Treatment

Steel is frequently plated with functional chromium or sometimes with hard nickel for improved wear resistance. It is vital that the substrate be hard enough to withstand the pressure that will be applied to the top chromium electrodeposit. If this substrate is too soft, it may "cave-in," causing failure of both the electroplated deposit and the part. One way to get a surface hard enough for such applications is to use deep-hardening steels that are heat-treated to produce the desired mechanical properties. This would be no problem if only a few parts are required. Where the application requires large numbers of parts, fast-machining soft steels are generally preferred.

The fast-machining steels must then be carburized or case-hardened to obtain a surface with the hardness required to support the top chromium electroplate. *Case hardening* is the generic term covering several processes applicable to steel or ferrous alloys. It changes the surface composition of the top layer, or case, by adsorption of carbon, nitrogen or a mixture of the two. By diffusion, a concentration gradient is created. The heat-treatments and the composition of the steel are additional variables that should be addressed and taken into account in the electroplating procedure.

When discussing the effect of heat-treatment on subsequent electroplating processes it is necessary to zero in on the type of heat-treatment involved. We can define the heat-treatment process as changing the characteristics of the parts by heating above a certain temperature and quenching it in a suitable media, generally water or oil. A secondary process is then used to achieve the desired hardness range. This type of heat-treatment, commonly called neutral hardening or through hardening, depending on the alloying characteristics in the steel or its properties, gives platers few problems since the surface has not been chemically changed to any significant degree.

Most heat-treatment problems occur when the surface of a material is changed to achieve certain, prescribed characteristics. There are a few ways of doing this:

1. In *nitriding*, the part is subjected to nascent nitrogen and the nitrogen is absorbed into the surface of the solid ferrous alloy to obtain defined hardness characteristics. Quenching is not needed to produce a hard case.
2. In *carbonizing*, the part is exposed at a high temperature to a source of carbon that is absorbed into the skin of the part surface.
3. *Carbonitriding* is a case-hardening process in which a suitable ferrous material is heated above the lower transformation temperature in a gaseous atmosphere of such composition as to cause simultaneous absorption of carbon and nitrogen by the surface and by diffusion create a concentration gradient. Cooling at a rate that produces the desired properties in the workpiece completes the heat-treating process. This process seems to give platers the greatest amount of difficulty. The hardness is relatively shallow. The penetration generally is less than 500 µm (0.020 in.) and in commercial practice, it generally is 75–250 µm (0.003-0.010 in.) deep. It produces a very hard, abrasion-resistant surface, while preserving the ductility of the core.

4. *Decarburizing* is a loss of carbon on the surface layer of the carbon containing steel. It occurs by the reaction of carbon with one or more chemical substances from the medium that contacts the surface. The process is another source of trouble for the suspecting or unsuspecting plater. Heat-treating case-hardened parts that are to be hard chromium plated, for instance, may decarburize the surface. When chromium is plated on this surface, a three-layer structure results. The underlayer is hardened steel, the middle is the decarburized surface and the overlayer is hard chromium. The decarburized surface is rather soft, and the hard chromium will not take the load nor will it have good adhesion. Poor adhesion is a general problem with all steel that has been decarburized. Problems also arise when the decarburized layer is rather thick [500 – 750 µm (0.020-0.030 in.)] and 125 µm (0.005 in.) is removed in the grinding step to obtain a sound clean surface. The ground surface appears smooth and plates properly, but the resultant product often does not have good physical properties.

In hard chromium electroplating the surface metallurgy of the steel is rather important, if not the most important parameter. Change in electrical resistance is an example of properties, which are influenced by metallurgical factors. Electrical resistance changes with the carbon content of the steel. Data from the literature[4] shows that pure iron has a resistance of 10 µΩ•cm; steel, a mixture of pure iron and carbon, has a resistance of 16 µΩ•cm. The amount of current required in electroplating varies with electrical resistance. Hardening of steel causes a marked change in resistance. Heating above the critical temperature and quenching raises the resistance from 16 µΩ•cm to 46 µΩ•cm. Obviously the carbon content of steel is an important variable in electroplating.

Since hardening is often necessary, and given that the resistance is noticeably changed as a result, subsequent processing must take into account these changes. Current density can be increased or other appropriate changes made that can improve throwing power to compensate for the increased resistance. Compensating for other changes caused by heat-treating, is unfortunately not quite so simple.

Perhaps the best example of the other variables introduced by heat-treating is scaling. Parts heat-treated without a proper protective atmosphere are oxidized and scaled. The common practice of reverse-current (anodic) electrocleaning will not remove this type of surface contamination, and parts cannot be correctly plated in this condition.

Additional mechanical cleaning such as shot blasting, vapor honing, glass beading or grinding may be necessary to salvage such parts. Mechanical finishing is an additional expense, and it is cheaper to avoid the scaling rather than to correct it later with further processing. The surface can be protected and oxidation prevented in one of two ways. The part can be heat-treated in a molten salt bath, or in a controlled-atmosphere furnace.

Controlled-atmosphere furnaces are more widely used. Passing a mixture of natural gas and air over a hot catalyst generates these atmospheres. This produces an atmosphere of carbon monoxide, hydrogen and nitrogen. Natural gas can be added in the furnace to increase the carburizing potential. Adding ammonia increases corrosion resistance and hardness.

Under ideal conditions, the controlled-atmosphere furnace delivers parts that have a clean, dove-gray color after washing. They will plate readily after a simple, anodic alkaline electrocleaning.

What if conditions are not ideal? If there are leaks in the furnace or in the lines feeding the furnace, soot may be deposited. This can range from a faint trace to a heavy layer. Anodic electrocleaning will not remove the soot, causing serious problems in subsequent electroplating steps. Fine shot blasting, glass beading, vapor honing or grinding is necessary to salvage such parts. Again, this is a costly additional step that should be avoided.

All platers are discontent with the presence of soot, smut, heavy oxides, greases or oil that have been baked on the part during heat-treatment. When parts are adequately cleaned before they go into the heat-treat furnace, the plater's job is definitely made easier. One way to accomplish this, wherever possible, is to make the heat-treat foreman the supervisor of the electroplating department as well. This may often be impractical and there will always be some baked-on soils to be removed.

Cleaning such parts in a solvent degreaser is not the best practice. It removes, by dehydration, the last trace of anything that could be solubilized, making cleaning more difficult. It is preferable to use a solvent emulsion cleaner as the first cleaning step.

Oxides on heat-treated parts are also a source of problems. They are nearly always the result of improper furnace operation. Removal of an oxide film requires careful techniques to avoid damaging the parts.

At times it is difficult to nickel plate a nitrided surface and cover it properly. Nitriding has an effect similar to that of a fine sand blasting. The effective area of this mildly rougher surface may be larger than the visual area by a factor of two or three. In addition, the surface becomes more difficult to clean. In the pickling or acid treatment steps, with this larger effective surface area, there is more acid attack and a tendency to leave an insoluble smut on the surface. This in turn leads to poor metal coverage and poor adhesion in subsequent electroplating.

Proper pretreatment of a nitrided surface uses mechanical cleaning methods. In chemical cleaning steps, some scrubbing or mechanical action is desirable, *e.g.*, tumbling the parts in cleaning solution. Strong acids must be avoided, as they will form a weak, brittle surface that will not properly plate or not plate at all.

In producing a carbonitrided case on steel parts, it is possible that cyanide may concentrate in localized spots on the part surface producing a solid nitride. Plating these spots is difficult. The usual pickling procedure for such parts is a double-alkaline anodic electrocleaner followed by a 50-percent hydrochloric acid pickle. Overpickling must be avoided. In practice, a properly applied 50-percent hydrochloric acid should not cause overpickling. The problem with spots can be solved either by using a cyanide copper strike, or a low-pH nickel strike (pH 2.0) and enough initial surge current to initiate nickel plating. The parts could then be transferred into a bright nickel bath.

Surface stresses induced in heat-treating can also affect subsequent electroplating. For instance, when socket wrenches are hardened before nickel electroplating, the surface stresses in the steel will lead to stresses in the nickel deposit. These stresses are much greater than normal in bright nickel deposits. Such highly stressed nickel plate can crack.

Yet other parts being plated in the same system, even ones that might be plated and then formed, may not be cracking.

One may be tempted to blame the cracking on "brittle nickel," but the real cause of this stress is the epitaxial tendency of electrodeposits to match the structure of the basis material. The first few millionths of an inch, perhaps no more than the first 50 millionths, of an electrodeposit tends to match the crystal structure of the surface being plated upon. This becomes troublesome if that surface is stressed.

In electroforming, this problem is often easily identified. When using a low-stress nickel bath *(e.g.*, sulfamate) to plate nickel on a hardened mandrel that has high surface stresses, one will find that the deposited nickel has high stress that causes difficulties.

Mechanical Preparation

Buffing and burnishing may cause problems that are even more difficult to detect and correct. During buffing operations, surface can be smeared in such a way that imperfections are hidden. The parts will appear fine immediately after buffing, but after cleaning and acid treatment, the flaws will show. By this time, however, it is too late. The parts are on their way through the plating cycle and the defective surfaces are being plated. In burnishing, there is a tendency to produce hammered-over corners and edges. The metal is actually folded over and seams are present, resembling a lap joint. Such parts are hard to rinse and it is difficult to produce good plating on such a surface.

Grinding Slivers

When present on the metal surface, grinding slivers can cause acute problems. In hard chromium plating, the slivers can be pulled up from the basis metal by the highly-stressed top chromium layer. If slivers are present on the surface and a stressed electrodeposit is applied, the slivers will be raised to cause roughness and bumps. Probably 15-25 percent of all ground surfaces that are hard chromium plated have grinding slivers remaining that can lead to this kind of roughness. This type of roughness will not be hidden until the parts are plated with as much as 500 µm (0.020 in.) of chromium. The weak leveling ability of the chromium bath is not adequate to compensate for this effect.

One possible solution to this problem is electropolishing. If the sliver problem is extended to a depth of 25 µm (0.001 in.), this affected zone could be removed. Of course, the part or plating specification may not permit the removal of 0.001 in. from the surface. In hard chromium, it may be either too difficult or too costly to plate an extra thousandth when 0.005-0.006 in. are already called for. Many platers choose to ignore grinding slivers, to their later dismay.

Polishing Slivers

These can also cause problems. For example, pits in a deposit from an acid copper bath have been traced to polishing slivers. The typical pit had a "fish tail" appearance. After cross sectioning and looking at it under the microscope, the culprit was found to be a polishing sliver from a 140-grit belt. The cyanide copper strike did not fully cover the entire sliver. Further, a surface streaking formed in this area, which resembled a typical gas-plating pit. Instead, it was caused by a micron-size metal sliver.

Grinding Burns

These are difficult to recognize. Sometimes grinding wheels or belt polishers are operated in a way that will leave powdered metal or a heat-checkered surface. Obviously this is not a satisfactory surface for hard chromium plating.

The techniques used in removing scratches from a surface are also important. Previous research[5] on the buffing of zinc and aluminum die-castings has shown this. Different sized scratches were scribed and the wheel work necessary to remove those scratches was measured. Aluminum was buffed with a surface speed above 7,000 ft/min. It was found that the scratch still remained on the surface and was 2½ times wider than originally. It was found that, at such a high speed, the wheel came to ride atop the V-groove. The wheel widened the groove, instead of getting to the bottom of it and flattening or removing it. Clearly, proper polishing and buffing techniques are of major importance in proper scratch or pit removal.

Field Examples

Careful selection of buffing compounds and cleaners is important. Some cleaners just do not chemically attack certain materials that are used in the polishing and buffing compounds. If the plating plant does its own buffing and polishing, one can make sure that cleaner and the compound are compatible. If on the other hand, the polishing and buffing is outsourced, one may want to investigate the polishing and buffing compounds being used on a job that is particularly difficult to clean, and make necessary accommodations.

An example of one of the more difficult cleaning jobs involved plating a strip of steel that was finished flat. The final polishing operation was carried out with a 240-grit belt to produce a satin finish. However, it was impossible to obtain a smooth plated finish no matter what was tried. High leveling nickel did not eliminate the roughness, nor did leveling copper. Filtering the bath did not help either. Finally the search for problems was focused toward cleaning of the basis metal. The cleaning operation turned out to be the problem.

The reason for poor cleaning was that the metal was magnetized. The polishing department held the strip flat during belt polishing with magnets underneath. Each part that was polished became magnetized. Anyone who has ever tried to remove polishing dust from magnetic steel, can imagine how hopeless it was going through cleaners and acid pickle with the intent of getting an absolutely clean surface. Using a simple demagnetizer,[6] the parts were passed through a magnetic field that removed residual magnetism. After that, it was rather straightforward to clean the part.

The same thing can happen with parts that are horizontally ground on a magnetic chuck, or that have been lifted by a magnet. Occasionally, this problem can happen in a barrel, where the parts have simply run up a track with a magnetic carrier or where the parts have been picked up in bulk with an electromagnet. Particles that are magnetically attracted can be in the form of chips, powders and oxides. These contaminants will adhere to magnetized parts during the cleaning operation and then show up as roughness after electroplating.

Another example is a case where the basis metal was unfairly blamed. Cross-sectioning of particular die-castings revealed the presence of chill shot in the casting at every spot where there were blisters in the electroplated deposit. The manufacturer was considering the purchase of a new die caster to obtain better quality castings. Then the logical question was raised. How had these parts been plated previously with no trouble? Further inquiry found that the change had been made from previous practice.

When electroplating these porous die-castings, in order to increase the throwing power, the free cyanide in the copper strike was reduced to about 2.0 g/L (0.3 oz/gal), from the usual 11.0 g/L (1.5 oz/gal). With porous castings, extensive gassing in a highly inefficient cyanide copper bath caused the trouble. The pores filled with hydrogen, which would later expand and escape, causing the blisters.[3]

The obvious question is how to recognize some of these problems caused by the condition of the basis metal. In job shops, one should be suspicious any time one particular job among others is running into trouble. A jobshop has an advantage because it is plating a variety of work and can isolate and focus attention on a particular job that is causing trouble.

Influence of Temperature on Plating Bath Performance

The magnitude and control of temperature is a critical variable in all plating baths, and it is essential for the consistent performance of any deposition bath. For best results, it must be controlled within ± 1ºC from the optimum.

Unsuspected temperature fluctuations, appreciable, but not appreciated, can occur when the electroplating baths are operated with faulty or marginal heating and/or cooling equipment. Too wide a temperature range can have a considerable influence both on the operating conditions of the bath and on the structure of the deposit. At low temperatures, the deposits will tend to become brittle and it will be found difficult to operate at the normal current densities, as edge burning will occur.

In general, it is possible to apply higher current densities in hot as opposed to cooler plating baths. The advantages of higher operating temperatures are interrelated with several factors, such as:

(a) higher solubility of basic plating bath components (with some exceptions),
(b) higher ionic mobility and therefore increased bath conductivity that allows the use of higher current densities,
(c) in most baths, reduced anodic and cathodic polarization (*e.g.*, nickel baths),
(d) increased cathode current efficiency (a notable exception is chromium baths),
(e) improved anode corrosion,
(f) the ability to operate more dilute baths without loss of performance, and
(g) reduced power consumption due to lower voltage needed.

However, as a trade-off there are possible disadvantages to higher solution temperatures, such as:

(a) an increased tendency for hydrolysis and precipitation (*e.g.*, metallic impurities in nickel, iron or zinc baths, leading to pitting),
(b) an increased tendency to decompose organic brightening and leveling agents,
(c) production of passive deposits that will need additional activation,[7]
(d) reduced throwing power,
(e) excessive evaporation that can lead to notable changes in bath composition and/or difficulties in rinsing, and
(f) shortened plating equipment life.

These two opposing sets of factors make it difficult to predict the best temperature for any given bath at a given installation. It therefore must be obtained experimentally or semi-empirically. In general, the resistivity of most aqueous solutions decreases by about 2 percent for each increase of 1ºC or 1 percent for each increase of 1ºF. Therefore, a lower voltage is required to produce the same current density at the same temperature.

In the case of alloy deposition, an increase in temperature affects:

(a) the partial polarization curves of alloying metals (the deposition potential of metals usually becomes more noble with higher temperatures),
(b) the respective cathode efficiencies, and
(c) the tendency of the metals to form an alloy.

In general, increased temperature aids the deposition of the more noble metal. It has same effect as agitation. For example, it increases the proportion of copper in brass electrodeposits. However, the effect is actually more complicated since temperature changes may alter the degree of dissociation of the metal complexes and have various effects on polarization factors.

A number of other relevant factors are involved in connection with the effect of temperature on the plating baths:

- The crystal structure will be coarser when the temperature is raised without changing any of the other electroplating conditions. As a consequence, to obtain the same fine-grained structure at the higher temperature it is necessary to increase the applied current density.
- The deposit hardness usually falls with an increase in temperature.
- Temperature clearly affects the hydrogen content of the deposit. In a very early study,[8] for the metals of iron group, an increase in solution temperature from 1ºC to 75ºC caused a marked reduction of the hydrogen content. For sulfate-based nickel-plating bath, an increase in from 20ºC to 63ºC decreased the hydrogen content to 1/3 of its original value.[9]
- Cathodic reactions are influenced by temperature fluctuations. For example, in an acid zinc bath, the variation of the hydrogen overvoltage leads to coarser deposits that also cover the surface more irregularly than when the bath is worked at a higher temperature. In the case of nickel baths, the complex cathodic reactions give rise to basic products (hydroxides and oxyhydroxides) that can be occluded in the deposit and modify the properties of the plated metal. Temperature is one of the factors that modify these reactions. Below 30ºC, the nickel deposit tends to break into small hard patches that poorly adhere to the basis metal (“burning”). On the other hand, at 55 - 60ºC, the deposits are more ductile and softer and have less tendency toward flaking.
- The dependence of throwing power on temperature is a rather complex phenomenon. It is the result of two opposing influences. The temperature rise serves to increase the bath conductivity. In addition, by facilitating the diffusion of the ions, it reduces the cathodic polarization. According to whether the first or the second of these phenomena is the dominant influence, the throwing power is either increased or reduced. Often these effects will cancel each other out. In nickel baths, therefore, the variation of the throwing power with temperature will also depend on the pH value. The

variation is not noticeable when the pH is high enough, but it is quite significant with a lower pH bath. In the case of chromium baths, the throwing power will be better around 35ºC than towards 55ºC.

- Electrodeposits obtained from electrolytes operating at higher temperatures, have as a rule, lower internal stresses.

Temperature changes in the plating bath will most often necessitate modification of other bath factors to obtain a balanced working result. Therefore, increasing the temperature will allow higher salt concentrations to be used, which in turn allow higher current densities and consequently higher plating speeds. Other factors must also be modified. For this reason, higher temperature operation in a nickel bath requires that the pH and the concentration of the boric acid and metal salts be modified. In a chromium bath, the content of chromic acid must be increased to accommodate higher temperatures. With alkaline zinc baths, increased temperatures require changes in the values of hydroxide and free cyanide.

In general, with bright plating baths, the temperature considerably effects the current density range over which bright deposits are obtained. At lower temperatures, the bright plating range will be narrower. This renders the bright plating of deeply recessed and contoured parts rather difficult. An irregular blotchy finish may result, some parts of the surface being brighter than others. Even a dull deposit may result in places. It is well known, for example, in chromium plating, that the bright range is much more restricted at 10ºC than at 35ºC. This is the reason why totally trouble-free operation cannot be easily obtained from a cold chromium bath, at least for decorative plate, regardless of the noticeable increase in plating speed and some increase in the hardness.

Controlling & Monitoring Solution Temperature

In the early days of electroplating, a gas flame was usually lit under the tank and that was it. The flame was adjusted by eye and the temperature detected by touching the solution gingerly with a finger if a thermometer was not available (or the operator was too lazy to use it). Nowadays, temperature is automatically controlled in the plating bath within one degree or better by appropriate sensing and heating devices.

Solution temperature can be maintained with the thermocouples, thermistors, resistance temperature detectors or integrated circuit devices. In addition, many sensors used for the automatic control of other plating variables (*e.g.*, automatic brightener additions, pH, etc.) are temperature-sensitive and must be temperature-compensated for accurate measurements.

Conclusions

The problems related to heat-treatment, basis metal preparation or fluctuations in bath temperature should be positively identified. Once identified, search for cause is in order. Once it is established that the problem is related to heat-treating or basis metal conditions, the preplating process can be modified and something can be done about it.

After it is recognized where the origin of the problem lies, one can speculate on why it is there and what best set of corrective measures can be contemplated and implemented.[10]

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