Plating onto High-strength and Leaded Alloys

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Introduction

Quality plating with good adhesion, no star dusting and no pitted deposits is the goal of all platers. Poor adhesion can result in complete failure of the device. Often the smallest blister in a plated deposit results in failure. Pitted deposits often fail quickly and detract from the finish appearance.

Troublesome alloys include Kovar®, Invar®, stainless steels, brass, leaded steel, leaded copper, leaded-brass bronze, case-hardened steel and high-strength steels all require special preparation treatments different from those for mild steel and copper alloys which do not contain lead. In addition, the treatments are different for each of these materials, often requiring many different chemical treatments.

High-strength, low alloy steels have posed problems for platers. In order to achieve good adhesion, an extensive number of process steps are required. Some of the steps involve strong acids and a low pH nickel strike. These acid preparation steps contribute to hydrogen embrittlement of the basis metals plated. Hydrogen embrittlement can be catastrophic when stresses are applied. It can also reduce fatigue life. It is difficult to remove hydrogen from electroless nickel-plated high-strength steels because the deposit is amorphous (without crystal structure). Hydrogen relief takes place more easily when there are grain boundaries for the hydrogen to follow during the baking process. To release hydrogen from electroless nickel plated parts, slow ramping of the temperature should be done and longer baking time at the final temperature is the preferred procedure. If the temperature is too high during the beginning of the heat cycle, blisters may result from the extreme pressure under the deposit, causing fractures of the basis metal or the plated deposit. It is, therefore, best to limit the amount of hydrogen exposed to the metal during chemical processing and plating.

An important advance in good adhesion has been made. Additionally, the same chemical treatment can be used for all the basis materials mentioned above. It does not contribute to hydrogen embrittlement.

Pickling and conditioning

Most pickling and activating solutions are strong acids having pH levels near or below 0.5. Most high-strength steels and stainless steel alloys are activated using strong acids, such as hydrochloric acid or hot sulfuric acid. Hot hydrochloric acid is often used for preparation / activation of Kovar® and Invar®. I suggest that there is a citrate-based activator / conditioner / pickle that will prepare all of the above mentioned metals for adherent, pit-free plated deposits.

The typical pH of the new pickle / conditioner solution is 3.2. It is not considered corrosive by D.O.T. standards. Although the citric acid pickle / conditioner solution is not as corrosive as other pickling acids, it rapidly removes rust and light scale, leaving a very reactive, clean surface ready for subsequent finishing. The citric acid solution can be utilized for many so-called difficult-to-plate metals.

Citric acid forms chelates with metals which change their solubility characteristics, usually making the metal soluble where it normally is insoluble in the form of its chloride, sulfate, hydroxide or other salt. This is an advantage for cleaning operations, since metals can be dissolved at less corrosive pH levels.[1] Metal oxides are more easily removed using citrate-based solutions. There is less tendency to re-deposit metals by chemical replacement (immersion deposits) when citrates are present at the right pH. Citric acid solutions are subject to mold growth if they do not have an antimicrobial compound added to the solution. Adjusting the pH to 3.2 - 3.4 using ammonium hydroxide adds to the effectiveness of the treatment process. It is used at room temperature to 70°C (158°F). The typical temperature used is 24°C (75°F) for 6 to 7 minutes. Waste treatment is easy.

The pickle / conditioner process was developed primarily to prepare 4130 and 4100 series as well as 4340 and 4300 series low alloy high-strength steels for electroless nickel and sulfamate nickel plating. For these alloys the adhesion results are excellent. The process for preparation is greatly simplified by eliminating steps normally included in the typical preparation process.

Traditional process

Alkaline cleaning or vapor degreasing is followed by a mechanical surface treatment such as bead blasting, sand blasting, shot peening, vapor blasting or grinding. Grinding may leave metal splinters which should be removed by electropolishing or mechanical polishing. Further cleaning is required prior to plating. Anodic electrocleaning or periodic reverse, exiting on the anodic current cycle is preferred. Many different pickling and activation treatments have been used with some success in the past. Hot sulfuric acid, very strong hydrochloric acid and fluorides have been used, followed by a desmutting step. Another anodic clean, another acid treatment is often used. DO use inhibited acids if strong acids are to be used to minimize hydrogen embrittlement. DON'T forget to bake soon after plating.

Citrate process

The use of the citrate-based pickle/conditioner simplifies the procedure and assures good adhesion. A Woods nickel strike or low pH sulfamate nickel strike is often required to promote adhesion of plated deposits to these HSLA steels.

The citrate process has been tried experimentally with cast iron with equally satisfactory results. This led to its use on case-hardened steel and leaded steel, both of which resulted in good adhesion and good quality deposits. Using mineral acids, such as hydrochloric acid or sulfuric acid to prepare leaded steels and brass, results in leaving insoluble compounds on the surface that result in star dusting when bright nickel plating is used. Lead sulfate and lead chloride are insoluble. Since soluble compounds of lead are formed by the citrate solution, it is possible to process these metals satisfactorily. In addition, it is suitable for processing copper, copper alloys, zinc and zinc alloys. The results were excellent, with good adhesion and no blisters (including minute blisters of 5 to 100 μm in size) that often appear when these alloys are treated by conventional mineral acid preparation solutions. Alternate acids which produce good adhesion are fluoboric acid and sulfamic acid. However, fluoborates introduce waste treatment problems and sulfamic acid hydrolyzes to form sulfuric acid. Since lead appears in copper and brass castings as discrete globules, and in the casting process, lead is concentrated at or near the surface, the formation of insoluble salts can result in blistered plated deposits.

Electroplated nickel and many electroless nickel deposits quickly form oxide films which must be removed to assure adhesion of subsequent plated deposits. The longer the exposure to air, the more difficult it is to remove the oxide film and to keep oxides from reforming long enough to produce quality plated deposits. Oxide films can and do form in rinse water. It is important to have short but adequate rinses after activation of the nickel.

In the laboratory, to our amazement, the citric acid solution allowed adherent electroless nickel and sulfamate nickel to be plated over electrodeposited sulfamate nickel, bright nickel, Watts nickel and most electroless nickels without the use of a low pH strike such as a Woods nickel strike [240 g/L (32 oz/gal) nickel chloride in 10% hydrochloric acid] or a low pH activating sulfamate nickel strike (pH 1.0 to 1.2).

The adhesion of nickel-on-nickel deposits has been tested by various methods: bend, grinding and bulge tests. It should be noted that when low pH nickel strike solutions of proper formulation that are free from contaminants, including iron, chromium, lead, etc., are used over nickel, nickel-plated deposits and nickel alloys, excellent adhesion is obtained. When in doubt about the nickel alloy to be plated, use a proper low pH strike prior to subsequent plating. The low pH sulfamate strike is preferred because it is somewhat more tolerant of impurities, has somewhat better throwing power and will work on a larger variety of alloys. The strike consists of a nickel sulfamate solution with the nickel metal at 45 to 75 g/L (6 to 10 oz/gal), with the pH lowered to about 2.0, using sulfamic acid (very pure grade), then lowered further to pH 1.0 to 1.5 using hydrochloric acid. Following that, 30 g/L (4.0 oz/gal) boric acid is added to the solution. The solution is used at room temperature and at high current density.

Processing cycles

The processing cycles and operating data shown below are for typical applications and may have to be modified for specific applications. Factors influencing modified operation are the condition of the basis metal, including porosity, extreme roughness with entrapped foreign matter in the surface, metal splinters, etc., type and extent of soil(s) to be removed, part configuration, equipment and space considerations and plating requirements.

High-strength, low alloy steels (HSLA 4130 and 4100 series)

1. Soak clean.
2. Water rinse.
3. Anodic (reverse current) electroclean; 71 to 79°C (160 to 174° F), 58 to 76 A/dm^2 (60 to 75 A/ft^2) for 2 min.
4. Water rinse.
5. Pickle / condition; 60 g/L (8 oz/gal), ambient temperature for 3 to 6 min of immersion.
6. Water rinse.
7. Repeat step 3.
8. Water rinse.
9. Immerse in 0.5 vol% ammonium hydroxide, (no rinse for electroless nickel). Omit this step for plating deposits other than electroless nickel.
10. Plate.
11. Rinse and dry.

High-strength, low alloy steels (HSLA 4340 and 4300 series)

1. Soak clean.
2. Water rinse.
3. Anodic (reverse current) electroclean; 71 to 77°C (160 to 170°F), 58 to 72 A/dm^2 (60 to 75 A/ft^2) for 3 min.
4. Water rinse.
5. Pickle / condition, 60 g/L (8 oz/gal) at ambient temperature.
6. Water rinse.
7. Immerse in 0.5 vol% ammonium hydroxide, (no rinse for electroless nickel). Omit this step for plating deposits other than electroless nickel.
8. Plate.
9. Rinse and dry.

Note: Usually after cleaning in a separate line, HSLA steels are glass-beaded, shot-peened, sand-blasted or ground prior to nickel plating processes. Post-baking is often required, which is important for hydrogen relief.

Test Your Plating I.Q. #428

By Dr. James H. Lindsay

Electrocleaning

1. In mechanical plating, the workpiece is:
   (a) anodic
   (b) cathodic
   (c) pulse plated
   (d) uses no electrical current

2. In mechanical plating, the mechanism of plate adhesion is _____________

3. How does the process work?

4. What metals can be mechanically-plated?

5. What is the greatest advantage of mechanical plating over its electroplated counterpart?

Answers on page 26.

Cast iron

1. Soak clean.
2. Water rinse.
3. Anodic clean as above for HSLA steels.
4. Water rinse.
5. Pickle / condition, 60 g/L (8 oz/gal.) for 3 to 5 min.
   Note: Temperatures of 49 to 71°C (120 to 160°F) will speed the pickling action and remove red rust more quickly.
6. Water rinse.
7. Immerse in 0.5 vol% ammonium hydroxide for 30 sec. Omit this step for plating deposits other than electroless nickel.
8. Plate.
9. Rinse and dry.

Case-hardened steel

1. Anodic electroclean (reverse current).
2. Water rinse.
3. Pickle / condition, 30 vol%, 49°C (120°F) for 2 min.
4. Water rinse.
5. Immerse in 0.5 vol% ammonium hydroxide. Omit this step for plating deposits other than electroless nickel.
6. Plate.
7. Rinse and dry.

Leaded steel (free-machining steels) or leaded brass

1. Soak clean.
2. Water rinse.
3. Cathodic clean (direct current) followed by 15 to 30 sec anodic in separate solutions.
4. Water rinse.
5. Pickle / condition, 60 g/L (8 oz/gal) at ambient temperature for 3 min.
6. Water rinse.
7. Immerse in 0.5 vol% ammonium hydroxide for 30 sec. Omit this step for plating deposits other than electroless nickel.
8. Plate.
   Note: For leaded brass a copper strike is recommended before nickel plating to cover the lead in the surface. The nickel plating solution will form lead sulfate resulting in "stardusting".
9. Rinse and dry.

Nickel and nickel-plated deposits

1. Direct current (cathodic) electroclean for 1 min.
2. Water rinse.
3. Pickle / condition, 20 vol%, 49 to 54°C (120 to 130°F).
4. Water rinse.
5. Plate with electroless nickel or electroplated nickel.
   Note: This cycle can be used for bumper replate operations. Longer cleaning cycles to remove buffing compound are usually required for bumpers.

Leaded bronze

The cycle is the same as for case-hardened steel.

Kovar

Many process cycles for the activation of Kovar include alkaline permanganate and mineral acid steps. The pickle / conditioner solution is used to replace these steps. The pickle / conditioner is used at 15 vol%, 49°C (120°F) for 5 to 6 min.

Tarnished brass

1. Alkaline soak clean.
2. Water rinse.
3. Anodic (reverse current) electroclean for 20 sec at low current density.
4. Water rinse.
5. Pickle / condition, 20 vol%, 24°C (75°F). Use anodic (reverse) current, 6 V for 0.5 to 2.0 min.

Note: Portions of this column were presented at the EN '95 Conference, sponsored by *Products Finishing* magazine. P&SF

Answers to I.Q. Quiz #428

1. (d) uses no electrical current
2. The cold welding of fine metallic particles to the metal (usually steel) substrate
3. Glass beads, fine metal particles in suspension and parts are rotated in an oblique barrel. The impact energy imparted by the glass beads cold welds the metal fines to the substrate.
4. Zinc, tin, cadmium, other ductile metal and mixtures thereof
5. Hydrogen embrittlement and the requirement for post-plate baking are significantly reduced with cathodic hydrogen from electroplating. Hydrogen arising from cleaning and pickling is still a lesser factor.

Advice & Counsel

Continued from page 23

Discolored cadmium plate

Dull and dark deposits may be caused by conditions other than metallic contamination, including organic breakdown products, high carbonate content, high DC ripple and low metal content. Geduld reported a temporarily dull deposit caused by adding too much caustic over too short a time period (more than 0.5 oz/gal over 8 hours). No explanation for this was provided.

Organic contamination from additive breakdown products and other organics that may have been brought into the solution via drag-in can be removed by carbon treatment or carbon filtration.

Cyanide cadmium plating solutions are exceptionally sensitive to carbonate content and require more frequent carbonate removal than other cyanide-based solutions. High carbonate content can cause a narrowing of the bright range and dark streaky deposits. Very high concentrations can cause anode polarization and roughness.

Cadmium plating solutions are also sensitive to rectifier ripple. Ripple greater than about 5% can result in dull deposits or a shift in the bright range to the higher current density ranges. Even if a tap switch rectifier is in good shape, it can produce unacceptable ripple if the taps are improperly set (notches between taps exceeding 1).

Low cadmium metal content typically results in a hazy deposit at low current densities and may yield burning at high current densities in rack plating operations.

If a cadmium deposit is bright immediately after plating, but dulls up or yellows after bright dipping in a chromic acid based bright dip, the following possible causes are noted in the literature:

1. The bright dip is contaminated with copper, nickel or other heavy metals.
2. The rinse ahead of the bright dip is contaminated with heavy metals.
3. The cadmium plating solution is contaminated with heavy metals

Immersion in a dilute nitric acid solution ahead of the chromate can reduce the tendency for discoloration in the chromate.

More next month ….. P&SF