PLATING ONTO “DIFFICULT-TO-PLATE” METALS

Introduction

I receive phone calls and e-mails from time to time asking about how to plate on some of the more unusual metals and materials. This paper deals with some of the inquiries I have encountered. The procedures are identified as to the source. Included is leaded steel and leaded brass and bronze, piezoelectric ceramics containing lead. Zirconium, Niobium and beryllium copper, I hope one or more can be useful to you.

I  Leaded steel (“free machining”) and leaded brass

Ledeed steel and brass are difficult because of the nature of lead. The use of more traditional acids for metal preparation is not good for leaded metals. Lead forms insoluble compounds with sulfate as in sulfuric acid dips. The same is true for hydrochloric acid. Lead chloride and lead sulfate are both insoluble. They leave a film tightly adherent to the lead. There can be some slight loss of adhesion, but another result is "stardusting' and dulling of bright deposits. "Stardusting" can be from pits or small areas of insoluble salts causing rough plating. Lead is present in small globules on the surface of these metals. Particularly in brass since lead migrates to the surface when brass castings cool.

What to do about lead in the surface? Use one of three acids for the preparation instead of sulfuric or hydrochloric acid.

1. Use Fluoboric acid. This acid will deoxidize and leave no film. Note that there is an increased danger in using fluoride. With repeated exposure, fluorides tend to accumulate in the body. After repeated exposure or one larger exposure will adversely affect fingernails, bones and other parts of the body. Comment: a very small amount of fluoride is very beneficial in strengthening teeth, prevent cavities and preserve enamel, etc. Fluorinated drinking water is well below the toxic level, and is in the beneficial level. These very small amounts accumulate only in the teeth and fingernail area helping both. The toxic level will not be reached drinking fluorinated drinking water.

2. Sulfamic acid works very well. It is very activating to most metals. The sulfamate very slowly hydrolyzes to sulfate over time. It is good to test for sulfate and when the level becomes significant, change the bath. Small amounts of sulfate will not form the insoluble films because the sulfamate dominates; therefore the sulfamic acid dip is long lasting. Sulfamate activates many metals found in alloying constituents of steel and brass.

Fluoboric acid and sulfamic will attack lead leaving tiny pits that can cause some minor star dusting if left too long in the acids. A copper strike will cover these areas and protect the basis metal from reacting to nickel plating solutions. The sulfate in nickel-plating solutions will cause stardusting without the copper strike.

3. The third acid is citric acid. Citric acid is very activating and leaves no residue. It has the additional advantage that it deoxidizes the lead and steel or brass very well without any chemical attack. I have found it useful for high strength steels, stainless steels and numerous other alloys. The problem with citric acid is that it can grow mold. And therefore needs an antimicrobial material added to the citric acid solution to prevent mold from forming. There are proprietary citric acid solutions with the antimicrobial material included. It works even better if the pH is raised slightly to 3.6 using ammonia. Since citric does not attack lead there is no danger of stardusting from the process step. The copper strike may still be necessary for bright nickel plating to prevent the nickel solution containing sulfate from attacking the lead and result in stardusting.

II Piezoelectric Ceramics.

Piezoelectric ceramics are used for transducers, weight measuring and a number of other applications. Compressing these ceramics produces electricity. Piezoelectric materials contain lead and other similar materials as a part of the matrix. In this case we want to attack the lead at the grain boundaries to provide a tooth for adhesion of electroless nickel deposits.

Process 1. By Dr. Charles Baumgartner

1. Alkaline clean.
2. Rinse
3. Etch the grain boundaries using a solution of 0.5% Fluoboric acid and 5% by volume nitric acid (42 Be) for 90 seconds.
4. Rinse in DI water
5. Sensitize using stannous fluoroborate at about 100 ppm for 10 minutes.
6. Rinse In DI water.
7. Catalyze using palladium chloride, 50 ppm + 0.1 molar hydrochloric acid (HCl) 0.36 g/L.
8. Rinse in DI water.
Process 2. By Don Baudrand

1. Clean in alkaline cleaner. Steel cleaners are ok.
2. Roughen (mostly in the grain boundaries where lead accumulates) using a solution consisting of 60 g/L potassium chromate, or chromic acid, plus 100 ml concentrated sulfuric acid and 100 ml hydrofluoric acid. Use at 80°C for 5 to 15 minutes.
3. Rinse in DI water then in boiling DI water and if possible using ultrasonic agitation. This is to expand the pores and open the grain boundaries so that rinsing is complete and all the chrome is removed.
4. Sensitize using 11 g/L stannous chloride and 15 ml/L hydrochloric acid for 5 minutes at room temperature.
5. Rinse in DI water, preferable warm.
6. Catalyze using 2 g/L palladium chloride for 5 minutes.
7. Rinse in DI water
8. Electroless nickel plate.

Although all of the process work, I like chuck’s method best. It is gentler, has no chromium to waste treat and works just fine. Baumgartner did a lot of work on this to come up with the final process. It is a good idea to read his paper. Reference 1.

Process 3. X. Shi, Y. Liu, X. Li, Q. Zheng and J. Fang

These people published in “plating & Metal Finishing, March 1997, referencing Baumgartner’s paper. Their process is presented below in simplified form.

1. Clean and rinse
2. Roughen using 6 g potassium dichromate in 10 ml concentrated sulfuric acid and 10 ml of 27.6 molar hydrofluoric acid then diluting the mixture to 100 ml with DI water. Heat to 80°C and treat for 20 to 30 minutes.
3. Rinse using DI water
4. Boil in DI water for 15 minutes, then ultrasonic rinsed for 45 minutes then dried
5. Sensitize using 2.26 grams stannous chloride in 8.4 ml of 37% by wt. Hydrochloric acid, then diluted to 80 ml. Treatment time is 10 minutes, then bake dry.
6. Activation (catalyze) using 0.2 grams palladium chloride in 2 ml of 37% by wt. Hydrochloric acid, then diluted to 80 ml using DI water. Treatment time is 10 minutes, then bake dry
7. Electroless nickel plate.

No comments

III Zirconium

Zirconium is used where severe chemicals must be in contact with something that will withstand them. Zirconium resists attack by sulfuric acid at all concentrations up to 75%. It is not attacked by 40-60% boiling sulfuric acid. A common use is heat exchangers and heaters for sulfuric acid processes. There have been occasions where plating is needed on some part of a zirconium device. Two preparation processes are presented here. There is some efficacy to using them in tandem.

Process 1.

1. Cleaning a mild alkaline cleaner
2. Rinse
3. Pickle in a mixture of 3-6% hydrofluoric acid and 30% nitric acid in water.
4. Rinse quickly.
5. Electroless nickel plate starting with electrical current that is “on” when entering the plating solution. That has an anode already in place in the electroless nickel plating solution connected to a rectifier + side. Make the minus side connection to the zirconium to be plated. Leave the current on for 10-20 seconds then disconnect the current source. Check to see that the EN is plating without current by observing the bubbles coming off the item.

Process 2. Zirconium

1. Treat with 30% Nitric acid (42 Baume) using anodic current (the + side of the rectifier). 10-30 amps/sq ft. for 30 seconds to 1 minute.
2. Rinse
3. Electroless nickel plate using cathodic current to start the plating as in the process number 1 above.

IV Niobium

1. Clean in an alkaline cleaner.
2. Rinse and dry.
3. Abrasive blast using 50-micron alumina media in an argon atmosphere using 80 psi pressure uniformly over all the surfaces.
4. Rinse preferably using ultrasonic energy.
5. Activate using 5-6 oz/gal sulfamic acid with 4-6 oz/gal ammonium bifluoride. Treat for 2-4 minutes.
6. Drain. DO NOT RINSE
7. Nickel strike (low pH sulfamate or Woods strike) (sulfamate strike is preferred because it leaves no chlorides on the surface.
8. Nickel or electroless nickel plate going into the bath with current on as in the zirconium procedure.

The sulfamate nickel strike is made as follows: 10 oz/gal nickel added as liquid sulfamate nickel solution. (Nickel sulfamate is available having 24oz/gal Nickel. Use 42% by vol.)

4 oz/gal boric acid
Add sulfamic acid to pH 2-1.6, and then add a small amount of hydrochloric acid to pH 1 –1.5. Maintain the pH at that level using sulfamic acid and a little HCl.

V Beryllium Copper

Beryllium copper is used instead of pure copper for applications requiring more strength and hardness. Its unusual properties make it desirable for many electronic applications. Beryllium copper can be heat-treated to increase hardness to a figure greater than many other copper alloys. Common products are Beryco 10 and Beryco 24.

Process

1. Degrease if necessary. Alkaline clean using anodic current in a moderately strong anodic alkaline cleaner. Usually proprietary cleaners are used. Treat at about 27 amps/sq.ft. for 1 minute.
2. Rinse
3. Hydrochloric acid dip using 18% HCl for 1-2 minutes.
4. Rinse
5. Sulfamate nickel plate.
6. Alternate: If electroless nickel is to be the finish, it is best to first plate a thin layer of sulfamate nickel to promote better adhesion. The sulfamate nickel-plating solution can be either a sulfamate strike or a sulfamate plating solution.
7. Other plated deposits such as copper, zinc, cadmium, silver and gold can be plated. However if silver of gold is selected it is best to have a diffusion barrier of plated nickel or electroless nickel. Silver requires a silver strike. And some gold solutions require a gold strike. For adhesion before silver or gold plating. Contact your supplier for strike solutions and proprietary silver or gold plating solutions.

Reference


You may download this article FREE in .pdf form, save it or share it with a colleague. Click here.