Plating & Surface Finishing Retrospective

Originally conributed by John Laurilliard, CEF
Compilied by Dr. James H. Lindsay, AESF Fellow

Based on an original article from the early "Finishers Think Tank" series
*[Plating & Surface Finishing, **68**, 18 (July 1981) and **68**, 25 (August 1981)]*

Nickel on Kovar

Q: Would you please give me a procedure for preparing Kovar sheets for direct plating from a nickel sulfamate bath?

A: Kovar, an iron-base alloy with a nominal composition of 29% nickel and 17% cobalt, may be prepared for plating by the following method:

1. Cathodic electroclean for 3 to 5 min at 4.6 to 7.0 A/dm^2 (50 to 75 A/ft^2) in a heavy-duty alkaline steel cleaner.
2. Cold water rinse.
3. Activate in 40 to 60% by volume of 22°Be' hydrochloric acid for 3 to 5 min at room temperature.
4. Cold water rinse.
5. Strike in a Wood's nickel solution for 24 min at 7.0 to 9.2 A/dm^2 (75 to 100 A/ft^2).
6. Cold water rinse.
7. Sulfamate nickel plate to specified thickness.

A cathodic activation at 7.0 A/dm^2 (75 A/ft^2) for 30 to 60 sec in a solution of 75 g/L (10 oz/gal) of potassium cyanide and 7.5 g/L (1.0 oz/gal) of nickel sulfate hexahydrate has been suggested as a substitute for the Wood's nickel strike.

When plating sheet material it is very important - especially for large, thin-gage sheets—to provide adequate contact area to conduct the high current during activation. Small contact areas present a high ohmic resistance and result in high temperatures—high enough to burn a hole through or warp the sheet.

Molybdenum etchant

Q: Would you please give me a formula for a molybdenum etchant that has a pH greater than 7 but less than 9 (the closer to 7, the better). The etchant is for photochemical milling.

A: In a limited cursory search of the literature, I have not been able to uncover any etchants or pickling solutions for molybdenum with formulations in the pH range of 7 to 9. In fact, there is hardly an etchant or pickling solution for any metal or alloy that is not highly acidic or alkaline in composition. The reason is that the high concentration of hydroxide or hydrogen ions greatly accelerates the speed of the reaction.

The most common etchants for molybdenum, whether for photofabrication, preparation prior to plating or metallographic examination. are those based on alkaline ferricyanide formulations.

One recommended solution is:

Potassium ferricyanide	200 g/L (26.6 oz/gal)
Sodium hydroxide	20-25 g/L (2.7-3.3 oz/gal)
Sodium oxalate	3.0-3.5 g/L (0.4-0.5 oz/gal)

Other similar solutions are higher in ferricyanide and sodium hydroxide or potassium hydroxide.

For photochemical milling, the solution is usually applied by spraying rather than by immersion for uniformity of metal removal. The high-velocity spray increases the rate of metal removal by sweeping away the byproducts of etching and continuously bringing fresh solution in contact with the surface. Spraying also reduces the extent of image undercutting that otherwise would occur with immersion etching.

To achieve a uniform etching depth over the entire surface, especially for very shallow etching, it is extremely important that the surface of the molybdenum be chemically clean. This can be accomplished mechanically by pumice scrubbing or chemically by the following method:

1. A 3-min immersion in 20 vol% sulfuric acid with 5% potassium tartrate at 76.5°C (170°F).
2. A 5- to 10-min immersion in 80% hydrogen peroxide and 10% formic acid at room temperature.
3. Electropolishing for 30 sec at 155 to 217 A/dm^2 (1440 to 2020 A/ft^2).

One primary disadvantage of the ferricyanide-type etchants is waste treatment. Ferricyanide cannot be destroyed by the standard chlorination treatments used for the less-refractory sodium, potassium, zinc, cadmium or copper cyanides. Successful treatment requires (1) high-temperature alkaline chlorination or (2) chlorination or ozonation in the presence of ultraviolet radiation.

If the ferricyanide solution is concentrated, another possibility would be to use a process similar to the distillation method for the analysis of total cyanide. The ferricyanide would be acidified with sulfuric acid and boiled under a

partial vacuum in the presence of magnesium chloride. The distilled hydrogen cyanide would be collected by absorbing in dilute sodium hydroxide for a later standard treatment with chlorination, or could be absorbed in a concentrated sodium hypochlorite solution for immediate chlorination. Of course, great care would be needed to prevent the escape of hydrogen cyanide.

None of the etchants in the literature meets your original pH requirements. I did come across an etch solution proposed for titanium that may be worthwhile checking out for molybdenum. The etchant has neither acid nor alkalis but contains a powerful oxidizing and complexing agent.

The formulation is:

Ammonium persulfate, $(NH_4)_2S_2O_8$	114 g/L (15 oz/gal)
Sodium fluoride, NaF	21 g/L (2.8 oz/gal)
Temperature	88-96°C (190-205°F)

Although you didn't specify why you are seeking a neutral etchant, I suspect that you may be having a problem with your photoresist. If that is the case, a different type of etchant probably won't solve your problem. Most resists are plenty capable of standing up to the harshest of chemicals.

Plating aluminum pistons

Q: We would like you to help us with our lead "conversion" plating process on aluminum pistons. Our plant in Mexico is similar to our facility in West Germany, but we are unable to find a source for lead fluosilicate and fIuosilicic acid. Our pickling bath contains 0.25 vol% hydrofluosilicic acid (H_2SiF_6) and the plating solution contains the following: 13.0 vol% lead fluosilicate ($PbSiF_6$) at a specific gravity of 2.0; 3.2 vol% stannous fluoborate [$Sn(BF_4)_2$] at a specific gravity of 1.59; 2.0 vol% of a sugar solution at a specific gravity of 3.38 and a bath temperature of 22 ± 2°C (64 to 72°F). If you know of some laboratory that makes these products - especially lead fluosilicate - please let me know. If you know of another type of lead "conversion" plating, please send us the information.

A: The *Oil, Paint and Drug Chemical Buyers Directory* lists nine suppliers of fluosilicic acid (also known as hydrofluosilicic). A list of company names, addresses and phone numbers is being sent to you. However, the directory does not list any suppliers of lead fluosilicate.

Lead fluosilicate ($PbSiF_6$) may be prepared by dissolving either lead oxide (PbO) or "white lead" [$Pb(OH)_2{\cdot}2PbCO_3$] in an excess of fIuosilicic acid. Since the fluosilicate bath may present a problem with chemical availability, makeup additions and bath operation, it may be advantageous to consider the fluoborate bath as a substitute. The fIuoborate bath is much easier to prepare and maintain, gives finer-grained, denser deposits and is not subject to decomposition.

The following formulation for a lead-tin fluoborate bath is suggested as a substitute for your application. The bath composition and operating conditions will produce 6% tin / 94% lead, an alloy typically used for piston break-in lubrication.

Tin (stannous)	6.0 g/L (0.8 oz/gal)
Lead	94.0 g/L (12.6 oz/gal)
Free boric acid	22.5 g/L (3.0 oz/gal)
Free fluoboric acid	30.0 g/L (4.0 oz/gal)
Glue	0.4 g/L (0.053 oz/gal)
Temperature	16-38° C (60-100°F)
Optimum cathode C.D.	2.3 A/dm^2 (25 A/ft^2)

Tin and lead fluoborate are available from several U.S. metal finishing suppliers, a list of which is also being sent to you.

Adhesion tests on sockets

Q: We need a quantitative method of determining the adhesion of nickel/chromium plate on hardened and case-hardened steel sockets to RC 42-50. Inside adhesion is more important than exterior, although we are interested in both.

A: Adhesion to the basis metal is probably the most important property of an electrodeposit. A deposit that separates from the basis metal when a mild physical force is applied is worthless. It won't be in place to function when needed.

Many ingenious methods and techniques have been developed over the years to ascertain the degree of adhesion. Most tests involve mechanical, physical or electrochemical techniques. Most are qualitative, some are semi-quantitative, and a few are quantitative. As you might expect, the qualitative tests are the simplest, easiest quickest, while the quantitative tests are involved, time-consuming and expensive. The most common adhesion test performed in the average shop is a bake test, usually at 190°C (375°F). The parts are then examined for blistering.

Somewhat more severe and destructive is the scrape test. Using a penknife, the blade contacts the plated surface at approximately a 45° angle. Enough force is applied to pierce the coating to the basis metal and examine at four-diameter magnification to determine whether removal has been caused by the cutting away of an adherent plate or by the lifting of a nonadherent deposit. The drawback to this test is that it only reveals the adhesion where scraped and only on those pieces selected for analysis. It's not the type of test you would use when plating just a few costly items.

Another common practice is the tape test. A strip of tape* is firmly pressed onto the surface of the plated deposit. The tape is pulled from the surface in one abrupt perpendicular motion. The tape and part are examined at four-diameter magnification to determine if the deposit has detached. The tape test is used on deposits and coatings that, by their very nature, have a relatively low degree of adhesion. These include painted and vacuum-deposited coatings, and some plated deposits on relatively inactive basis metals. Parts that fail the bake or scrape tests may very easily pass the tape test. Failure of the tape test indicates an extremely low degree of adhesion.

Along with the scrape test, the most common examination for adhesion called out in federal and military specifications is the bend test, in which a 25 × 100 × 1 cm (1 × 4 × 0.04 in.) test panel of the same basis metal, similarly heat treated and otherwise prepared, is plated along with the production parts. After plating, the test panel is repeatedly bent through an angle of 180° on a diameter equal to the panel thickness until fracture occurs. The fractured edge is then examined for evidence of non-adhesion. If the plate cannot be detached by a sharp "C" instrument, adhesion is acceptable. The bend test is cheap, quick and non-destructive to the production parts, but it indicates only the adhesion of the deposits on the panels. You must assume that if the adhesion is good on the panels, it is also good on the production parts.

Other qualitative or semi-quantitative tests mentioned in the literature are many and varied. Most involve the application or inducement of stress on the deposit or coating. The following list indicates the variety available:

1. Bending or twist tests
2. Impact or hammering tests
3. Burnishing, buffing and abrasion tests
4. Erichson cup test
5. Scratch test
6. Chisel test
7. File or saw tests
8. Grinding-wheel test

* 3M No. 250 (or its equivalent), 3M Co., St. Paul, MN.

9. Peel test (can-opener test)
10. Push-out or push-in tests
11. Ultrasonic test
12. Whirl or rotor tests
13. Shot-impingement and shot-peen tests
14. Cathodic treatment and electrochemical methods and
15. Heat-quench test.

Quantitative tests include:
1. The Burgess method
2. The Ollard method
a. Ring and plug test
b. Roehl modification
c. Sheet-test modification
d. Tapered conical-pin modification
3. Nodule test
4. Scratch test

With the above information, you can see that it is difficult to identify a meaningful quantitative adhesion test for both internal and external surfaces of hardened sockets. A great deal of preliminary testing of various methods may be required. If I were you, however, I would take a look at the whirl test, which could be adopted for both external and internal surfaces. The cylindrical shape of the socket makes it ideal for this test method.

The whirl test consists of spinning a plated object about its axis at extremely high speeds up to 35,000 to 40,000 rpm. In this test, the centrifugal stress developed in the coating causes blisters to form in areas with poor adhesion and complete detachment of deposits in large defective areas. No evidence has been found that a good bond is adversely affected by this test, even at speeds that permanently deform the basis metal.

Lower speeds might be possible if specimens were to be plated with nickel several thousandths of an inch thick to increase the centrifugal stress on the deposit/basis-metal interface. Internal surfaces are tested by mounting several parts some distance from the center of rotation. The centrifugal force tends to detach the coating from the sides nearer this center.

Another approach open to you would be to correlate adhesion on test specimens with that of production parts. Quantitative values could be obtained by utilizing the Jacquet test. Using the simplest form of this method, a steel panel similar to that used in the bend test is masked along its edges. One half inch (1.27 cm) of one end is dipped in a protein solution or otherwise passivated to prevent an adherent deposit. The entire panel is then plated to the required thickness. After plating, the panel is held in a suitable fixture and the deposit at the passivated end of the panel is pried loose. A measuring device is attached to the loose flap of metal and force is applied to pull away the adherent part of the deposit. Weights or even a tensile machine could be used. The amount of force required to remove the deposit is a measure of the degree of adhesion.

One last recommendation would be to use a functional test. For your application, this might consist simply of torquing the socket to failure (reaming or splitting) on a slightly undersize mandrel. If the deposit passes this test, it is more than adequate regardless of what values you might get on a quantitative test.

Editor's Note: *The edited preceding article is based on material compiled and contributed by John Laurilliard, CEF, as part of the "Finishers Think Tank" series, which began its long run in this journal 25 years ago. It dealt with everyday production plating problems, many of which are still encountered in the opening years of the 21st century. As we have often said, much has changed … but not that much. The reader may benefit both /from the information here and the historical perspective as well. For many, it is fascinating to see the analysis required to troubleshoot problems that might be second nature today. In some cases here, words were altered for context.*