P&SF Retrospective

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Based on an original article from the early Finishers Think Tank series
[Plating & Surface Finishing, **70** (9), 18 (1983)]

Contaminants in Woods bath

Q: ***What is the maximum permissible level of metal contamination in a Woods nickel strike and how often should it be checked?***

A: The basic reason for using a Woods nickel strike is to activate difficult-to-plate metals and, in doing so, to deposit a very thin nickel layer. Because the bath pH is very low (nearly 0), a lot of gassing takes place, indicating the process is very inefficient, but any surface oxides are removed and the new nickel is easily plated over. To my knowledge, most of the metal contaminants tend to build up in these baths and never codeposit enough to cause a problem as long as the parts are put into and removed live (with current) from the bath. Without current, you may get an immersion coating of these impurities, which may give poor adhesion. Copper is one of these metallic impurities that may result in adhesion problems. Fortunately, the copper can be removed fairly easily using electrolysis at a low current density (2.0 to 3.0 A/ft^2; 0.2 to 0.3 A/dm^2) on dummy, nickel-plated cathodes.

Test method for acids

Q: ***In a solution that contains 25 vol% sulfuric acid (H_2SO_4) and 5 vol% hydrofluoric acid (HF), what is the best way to test both acids in order to determine the exact concentration?***

A: Any of the usual test methods for acid would tell you only the total hydrogen ion concentration. With these strong acids, a simple titration using a pH meter or suitable indicator may be used. Remember that the HF will dissolve glass and that most pH probes are made of glass. It will also bleach some indicators, giving poor results. *Standard Methods for the Examination of Water and Wastewater, 21st Edition* (2005) (ISBN 0-87553-047-8; 1365 p.), prepared by the American Public Health Association, American Waterworks Association and the Water Environment Federation, is a good place to start. It's available from the American Public Health Association, 800 I (Eye) Street NW, Washington, DC 20001 (See www.aphabookstore.org). To determine the fluoride ion concentration, distillation is generally a preliminary step. However, the fluoride-selective electrode has also shown good results when the sample is properly prepared. The sulfate ion can be determined gravimetrically after it is precipitated, washed and dried. Details for these procedures are spelled out in "Standard Methods …," cited above.

Frank Altmayer of Scientific Control Labs., Chicago, has adapted another procedure from information provided in *Analysis of Electroplating and Related Solutions*, by Langford and Parker and published by Robert Draper Ltd. He says it requires the "least sophisticated equipment." Mixed acids are quantified by first analyzing the total acidity and then analyzing for one individual component and subtracting to determine the other. The procedure is as follows:

1. Pipette a 2-cc sample into a 250-mL Erlenmeyer flask and add approximately 25 cc of deionized water.
2. Add 3 to 5 drops of methyl orange indicator and titrate with 1N (Normal) sodium hydroxide to a yellow endpoint. Call this titration volume "A."
3. Pipette a 1-mL sample into a second 250-mL Erlenmeyer flask and add approximately 25 cc of deionized water and 1N sodium hydroxide equal to that added in Step 2.
4. Add 2.5 mL "buffer" solution.
5. Add 3 to 5 drops of sodium alizarin sulfonate indicator and titrate with 0.05N thorium nitrate to a pink endpoint. Call this volume "B."
6. Calculate the percent by volume HF as follows: %vol HF = B × 0.1.
7. Calculate the percent by volume H_2SO_4 as follows: %vol H_2SO_4 = [A - (B × 0.1)] × 1.335.

The buffer solution is made as follows: Dissolve 19 g of monochloracetic acid in 200 mL of water and divide the solution into two equal portions. Neutralize one portion with 1N sodium hydroxide to phenolphthalein endpoint. Mix both portions and dilute to 500 mL.

Definition, please

Q: ***We have received a request to apply 80 µm (0.0032 in.) of electrogalvanized zinc on some pipe. Is there a distinction in the definition of "electrogalvanized" and ™electroplatedî zinc?***

A: No, there is no difference. Electroplating is defined in ASTM B374-06, "Standard Terminology Relating to

Electroplating," as "the electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the basis metal." Electrogalvanizing is defined as "electrodeposition of zinc coatings." Galvanized iron is produced by dipping the steel substrate into a bath of molten zinc. Unlike electrogalvanizing, galvanizing steel by hot dipping produces a zinc-iron alloy layer between the zinc coating and the substrate. This alloy layer is brittle and accounts for differences in the performance of hot-dipped and electroplated zinc.

Peeling on high-carbon steel

Q: ***We are facing a problem of nickel/chromium plate peeling off of bicycle spokes upon bending. We use a steel containing 0.35% carbon and employ a Watts nickel bath. We clean the parts both cathodically and anodically and use a sulfuric acid etch afterwards. Why do we have this peeling problem?***

A: Any steel with a carbon content of 0.35% is considered a high-carbon steel and is very susceptible to hydrogen embrittlement in the cleaning or acid-dipping stage before plating. These hydrogen-producing steps should be kept to a minimum. Refer to ASTM B242-99(2004)e1, "Standard Guide for Preparation of High-Carbon Steel for Electroplating" - for guidance.

Perhaps heating the parts after plating for at least 30 min at 204°C (400°F) may save what is already plated, but care should be taken not to affect the hardness of the steel.

Stressed deposits can occur from any nickel bath due to metallic contaminants (*e.g.*, chromium, copper and iron), excess brightener or other organics, nitrate contamination or an out-of-range pH. The best way to check the pH range is with a spiral contractometer. Inadequate cleaning may also be contributing to your problem.

Lou Gianelos ot The Harshaw Chemical Co., Cleveland, suggests you look into eliminating the cathodic cleaning step. Says Mr. Gianelos, "It is not clear whether you're using current with the sulfuric acid etch. If not, then sulfuric acid should not be used as an acid dip because it can promote smut on the surface. Hydrochloric acid is preferred, and the strength may be anywhere from 30 to 50 vol%. However, it is important that the time of immersion be kept to an absolute minimum (probably on the order of 15 sec) in order to avoid hydrogen embrittlement and obtain adhesion. If smut persists, it may be necessary to follow the hydrochloric acid with a reverse- current sulfuric acid etch using high current density (10 A/dm^2; 100 A/ft^2), high concentration (greater than 80%) and low temperatures (less than 24°C; 75°F)." ***P&SF***

The edited preceding article is based on material compiled by Mr. Ronald Kornosky, then of Hager Hinge Co., in Montgomery, AL, as part of the Finishers Think Tank series, which began its long run in this journal 26 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.