# Troubleshooting Plating Problems From a Laboratory Perspective

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Troubleshooting plating problems from high-quality automotive shops presents some challenges to the laboratory personnel who need to solve these problems. Discussions will center on the following: Defining the problem; identifying the problem on the parts; identifying the problem in the plating solutions; controlling the problem; eliminating the problem; and prevention of the problem. Discussion will include the types of analysis, instrumentation used, and plating tests used to discover the source of the problems.

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When one is producing high quality plated parts, whether on a plastic or metal substrate, solving plating problems in a relatively short period of time becomes most important due to production requirements.

I will demonstrate what a typical laboratory technician may have available to him, to solve these plating problems.

A typical plating line for automotive exterior parts may have as many as five processes such as bright acid copper, duplex nickel, microporous nickel and hexavalent chromium baths. There may also be an acid copper strike or a nickel strike incorporated in a plating on plastics (POP) line or a nickel strike incorporated in an aluminum substrate line. In both situations there are a variety of plating baths that may be the source of the problem.

How does one begin to troubleshoot these solutions to determine the type and source of the problem?

First and foremost, the solutions must be analyzed for the inorganic constituents. In the case of the acid copper solution, copper sulfate, sulfuric acid and chloride concentrations are analyzed by simple titrations that should be well known to all technicians in the plating laboratory. These components or constituents must be in the range of concentrations set forth by the chemical suppliers. A standard formulation may be as follows:

| | |
|---|---|
| Copper sulfate, $CuSO_4.5H_2O$ | 210 g/L (28 oz/gal) 1 |
| Sulfuric Acid $H_2SO_4$ | 75 g/L (10 oz/gal) |
| Chloride | 60ppm |

Problems Associated with Acid Copper

| **Problem** | **Cause** | **Remedy** |
|---|---|---|
| Burning | low copper sulfate | make addition |
| | low sulfuric acid | make addition |
| | low temperature | adjust temperature |
| | low H.C.D. additive | make addition |
| Dull deposits | low brightener conc. | make addition |
| | high temperature | adjust temperature |
| | organic contamination | carbon filter |
| Roughness | particle contamination | filter |
| | incorrect anode | use Hi Phos anode |

| Problem | Cause | Remedy |
|---|---|---|
| Striations | high chloride | zinc dust treat |
| | low chloride | adjust level |

All of the nickel solutions must be analyzed for their respective concentrations of the inorganic constituents. The standard Watts type nickel formulation is utilized as follows:

| | |
|---|---|
| Nickel sulfate $NiSO_4 \cdot 6H_2O$ | 300 g/L (40 oz/gal) 1 |
| Nickel chloride $NiCl_2 \cdot 6H_2O$ | 75 g/L (10 oz/gal)* |
| Boric acid $H_3BO_3$ | 45 g/L (6.0 oz/gal) |
| PH | 4.2 - 4.5 |

* Note that the semi-bright nickel in a duplex nickel system will have a lower nickel chloride concentration, somewhere in the range of 33 g/L. This is done to keep stresses low especially in a plating on plastics line.

Problems associated with Nickel

| Problem | Cause | Remedy |
|---|---|---|
| Burning | nickel metal low | analyze and adjust |
| | chloride low | analyze and adjust |
| | boric acid low | analyze and adjust |
| | pH too high | add sulfuric acid |
| | temperature too low | adjust |
| | current density too high | adjust |
| Pitting | organic contamination | carbon filter |
| | low wetter | adjust |
| Roughness | iron contamination | filter |
| | particle matter | filter |
| | boric acid too high | analyze and adjust |
| Brittle deposits | organic contamination | carbon filter |
| | high secondary brightener | carbon filter |
| | low primary brightener | make addition |
| Dull deposits | low brightener | make addition |
| | low pH | make addition |
| | organic contamination | carbon filter |

The pH is checked using a standard pH meter common to all plating laboratories.

The final plating solution to be analyzed is the hexavalent chromium process which can be analyzed as follows: the chromium content, hexavalent as well as trivalent chromium can be titrated, and the sulfate catalyst can be analyzed by precipitation method. The concentration of these components should be within the suppliers recommended range and usually is as follows:

| | | | |
|---|---|---|---|
| Chromic acid | 240 g/L | (32 oz/gal) | 1 |
| Sulfate | 0.75 g/L | (0.10 oz/gal) | |
| Trivalent chrome | 7.5 g/L | (1.0 oz/gal) | |

Most hexavalent chromium baths contain a secondary catalyst, fluoride compound, that is usually analyzed using a F selective ion meter. This concentration can be within the 500-800 ppm range. In recent years hexavalent chromium processes have been developed using a third catalyst which may also be analyzed.

Problems Associated with Chromium

| **Problem** | **Cause** | **Remedy** |
|---|---|---|
| Poor coverage | Low chromic acid | analyze and adjust |
| | High sulfate | analyze and adjust |
| | Passive nickel | Reduce pH in nickel, decrease brightener conc., carbon filter |
| | High temperature | reduce temperature |
| | Low cathode CD | increase to 150 ASF |
| | Inactive anodes | remove and clean anodes |
| | High chloride | electrolyze to reduce |
| Burning | Current density too high | adjust current density |
| | Temperature too low | adjust upward |
| | Chromic acid too low | make addition |
| | Low sulfate | make addition |
| | Bipolar condition | check for bipolar |
| Whitewash | Low sulfate | analyze and adjust |
| | Low fluoride catalyst | analyze and adjust |
| | Passive nickel | Reduce pH of nickel.<br>Carbon filter nickel. |
| | Current interrupted | Check rectifier, cathode rails, etc. |

| | | |
|---|---|---|
| Rainbow | Low sulfate | analyze and adjust |
| | Low fluoride | analyze and adjust with F catalyst |

Once all of the appropriate inorganic constituents of the plating baths have been analyzed by titration, the organic components must be analyzed. These organic components, or brighteners, are usually analyzed by instrumentation methods. In the case of the nickel brighteners, HPLC seems to be the preferred method of analysis. HPLC, high pressure liquid chromatography, analyses are able to give accurate analytical results for nickel brighteners.

The organic components or brighteners of acid copper are not so easily analyzed by means of HPLC instrumentation and the use of other instrumentation methods have not been widely accepted. The use of a CVS (cyclic voltametric stripping) instrument has been used to analyze organic components in an acid copper bath tank-side but not in the laboratory. Organic additives in acid copper can be determined by plating test cell evaluation discussed later. There are no organic additives in hexavalent chromium solutions and therefore no analysis is required.

Now that the major organic and inorganic components have been analyzed, adjusted or corrected, one must analyze for tramp metallics and tramp organics.

Tramp metallics are analyzed by an atomic absorption spectrometer, commonly referred to as an A.A. As a general rule all tramp metals, Cu, Fe, Zn, Sn, etc., must be kept below 5 ppm.

Another useful instrument to help solve plating problems is the Total Organic Carbon, TOC, instrument which has the capability to analyze the total amount of organic carbon that is in most plating baths (chromium being the exception). This TOC number can be used to determine the relative cleanliness of a plating bath. And one can use this number as a tool to give an indication that a plating bath requires a carbon treatment to clean up tramp organics.

Once all of the chemical analyses are completed, the next step in troubleshooting these plating baths in the laboratory is to perform plating tests. These plating tests are usually performed in a Hull cell or equivalent type plating cell or sometimes in a beaker or jiggle cell. The purpose of this type of testing is to plate a cathode in order to duplicate the working parameters of the specific process and duplicate the problem that is occurring on that plating line. One should duplicate the operating conditions of the plating bath.

Operate test cell at the bath temperature, similar agitation, etc. Once the problem is duplicated, the source of the problem can be determined and the proper remedy implemented. In a multi plating process line such as a duplex or triplex nickel/chrome line it may be advantageous to plate a test cell with sulfur-free nickel and then plate the bright nickel directly over the sulfur-free nickel deposit in an effort to duplicate what is happening on the plating line. Plating a cathode panel with nickel and then chromium is a common procedure to find problems on a nickel/chrome plating line.

Hull cell panel tests will become the most important tool in finding the source of the problem. Metallic contamination, organic contamination, and bath imbalances can be determined by performing this simple plating test. Corrective action to solve a problem can be performed in this plating test cell without fear of ruining the production bath.

Once the chemistry of the plating baths are analyzed and they are in the proper range, the other laboratory tests that may be required to solve a problem are thickness testing, S.T.E.P. test to determine the mv potential between deposit layers in a decorative copper duplex nickel chrome plating line, ductility evaluation and stress testing may be required.

The last troubleshooting tool that I want to mention is the use of microscopy. There are times when standard analytical procedures and plating test cells cannot pinpoint the source of the problem and it is at this point that one has to turn to the microscope. One can use a simple 10 X loop to identify a pit rather than a particle or at times a larger scope is needed such as a microscope that allows 1000 X magnification. The scanning electron microscope with Xray detector (SEM/EDAX) will be able to find an analyze most defects.

In conclusion, the number of analyses that are required in order to troubleshoot the many plating baths may appear to be overwhelming but with the proper discipline and knowledge of each of the processes the task can be managed.

REFERENCE

1. F.A. Lowenheim, Electroplating, McGraw-Hill Book Co., New York, New York, 1974 edition. Several chapters.