Shop Talk

Some Production Plating Problems & How They Were Solved—Part 1

By Dr. Samuel Heiman Updated by Dr. James H. Lindsay, AESF Fellow

Technical editor's note: *The following introduction is no less true today than it was in 1965.*

For many years, there has been a clamor by production people, who constitute a sizable and important segment of AES membership, for more practical articles in the Society's publications. A large number of the papers now published are certainly practical but the demand still exceeds the supply. Efforts which have been made to satisfy the demand include picture stories of various plating departments, a Question-and-Answer Box and a Tricks of the Trade Department. Currently, *Plating Topics* is designed to help fulfill this need.

Appeals by the editors of *Plating* for more material have been less than completely successful. I believe that one type of article which should interest production people and of which there is an almost inexhaustible supply is the problem-solution story or production problems and how they were solved. Every production man in the course of swapping stories can always recall a number of problems with which he has been faced and his method of solving them, and these could certainly be written up and published. With the introduction of new processes and equipment and new demands for quality and productivity, production problems are constantly being generated (and eventually solved, although never quite quickly enough). These stories could always be instructive, interesting and even sometimes entertaining.

It has been difficult to obtain this kind of practical problem-solution article. Perhaps one reason is that they often do not appear to merit publication, and from the purely scientific point of view may be rather elementary. To the scientist, writing up and publishing the results of his researches is part of the job, and the outcome is a paper. To the practical production man, solving the immediate problem is the prime objective and writing about it later may earn him no kudos. Nevertheless, such stories could be prime reading for production people, and interesting production people is one of our primary objectives.

The fact that some stories may be elementary should not discourage their publication. Young platers may be facing

these problems for the first time and may find much help in these stories. Indeed, many of these platers are working in small shops or departments, and have to grapple with production problems without the benefit of more experienced technical personnel.

Production people must not only make their processes and equipment work but they must make them work economically. They are caught between expediters who primarily want to get the work out and quality control people who concentrate on meeting the requirements. Production people are faced with many problems beyond the neat and tidy processes described in articles and instruction sheets. These include such problems as unpredictable contaminations, insufficient equipment, labor, the human element and accidents.

To meet these problems often requires ingenuity, common sense, keen observation and detective work of a high order. From experience, production people are inclined to believe in Chisolm's (or Murphy's) Laws which state that if anything can happen, it will happen; and when things are going well, something will go wrong. What I am leading up to is this: *If production people want more "practical" articles or material in Plating, they must write them themselves.* And if the reader at this point feels some sort of involvement in the matter, more specifically that he is being asked to contribute, he is correct.

To illustrate what I am driving at, I have put down a number of problem-solution stories. In some cases full details are not available. Work is often done on a problem to get out of trouble - no more; no less. Time does not permit fuller investigations. It could be that the reader himself is in a position to supply further details. By the same token, these stories may supply subjects to those who are seeking problems for research work. I should welcome these comments.

These stories need not follow any rigid format but certainly they should be built around the following general sequence of events:

- 1. A statement of exactly what the trouble or problem was.
- 2. Some background information regarding the basis metal, the process used, etc.
- 3. A listing of the things tried which did not work (don't tell us you found the answer on the first try).

Based on an original article from the "Plating

Topics" series [Plating, 52, 1040 (October 1965)]

- 4. A statement of how the problem was finally solved.
- 5. General conclusion or moral of the story.

If enough of these production-solution stories are received, they could be made a regular feature of *Plating* [again].

Phosphate Coating On Steel: Failure To Meet The Required Salt Spray Requirement

This case refers to the failure of parts which had been processed per MIL-P-16232; Type Z - Zinc phosphate base; Class 3 - No supplementary treatment; to meet the required two hour salt spray test. The parts were phosphated in a barrel. They failed in the salt spray test after about one hour. The phosphating solution had the proper analysis and the process was in good condition. Steel panels were processed through the facility and the phosphate coating easily passed the two hour salt spray test.

Tracing the history of the parts, it was found that they had been deburred by a dry tumbling operation. The soil and fine iron particles had been literally beaten into the metal. The parts looked clean and were free from water breaks after the cleaner. However, the presence of smut on the piece was revealed by wiping the part with clean tissue. Interestingly enough, the area which had been wiped with the tissue produced a smoother and finer-grained phosphate coating than the areas which had not been wiped with tissue.

Parts which were cleaned by a pumice scrub and then phosphated easily passed the two-hour salt spray test. After the customer deburred the parts with the proper compounds which prevented the soil from becoming impacted on the work, no further trouble was experienced in producing the required phosphate coating.

Zinc Plating: Increasing The Metal Content Of a Zinc Bath

Operating a zinc bath with insoluble anodes causes a decrease in zinc content of the bath. The cheapest way to replenish the zinc content is from the anodes. Chemical solution of the anodes overnight or over weekends in some cases may not be sufficient to maintain the required zinc metal content of the bath. One convenient way to raise the metal content of the bath is to electrolyze the tank with cast iron cathodes which have a plating efficiency of zero. In other words, the anodes dissolve, but no zinc plates out during this process.

Cadmium Plating: Tank Material

A steel tank containing cadmium plating solution leaked, resulting in a considerable loss of solution before its discovery the following morning. The remaining solution was pumped out and the tank carefully examined. It was found that the tank had an outlet near the bottom and this outlet was fitted with a cast iron plug. The solution had leaked through the cast iron plug which was found to be spongy and porous. The tank was in the anode circuit. The anode bar was submerged and welded to the ends of the tank. Apparently, the iron in the cast iron plug had dissolved in the cyanide bath under the chemical and electrochemical processes involved. A forged steel plug was then used and this resisted further attack.

Tin Plating: Poor Adhesion On Steel

This case concerns poor adhesion of tin on certain areas of a steel part. The tin was plated from a conventional stannate bath. The part was a solid steel cylinder 0.5 in. long X 0.5 in. diameter. The tin

Table 1 Analysis of Two Grades of Zinc Oxide (wt%)		
	Technical grade	U.S.P. grade
Zinc oxide	99.1	99.8
Lead oxide	0.2	0.001
Cadmium oxide	0.04	0.005
Copper oxide	0.004	0.002

flaked off the edges only. Examination of the materials and process used in cleaning and pickling disclosed no clues. The parts looked perfectly clean before plating.

Examination of the plated parts under a low power microscope disclosed that the tin flaked off when probed with a needle and that the steel appeared dark in these areas. Variations in the cleaning and pickling processes were tried to no avail.

An investigation of the customer's procedures for manufacturing the parts was then made. The parts were made of hardened steel and were tumbled in order to round the sharp edges. During the course of this operation the soil was packed on the surface, particularly on the edges where the impact was greatest. This soil on the edges was not removed in the course of the ordinary cleaning and pickling operations.

A tumbling operation with a lime compound was able to remove the impacted soil. The parts were then readily cleaned in the conventional manner and the deposited tin adhered properly. Subsequently, the original deburring operation was modified to prevent impacting the soil in the first place.

Pitting In Nickel Plating

White nickel plated on steel rods was found to be pitted. Pitting was not occurring on any other parts plated in this particular tank. This indicated that the basis metal was involved. The pitting ran the length of the rod. The steel was AISI-C-1213 which had a nominal composition of 0.13% carbon (max), 0.07 to 0.12% phosphorus, 0.90% manganese and 0.08 to 0.33% sulfur. Investigation disclosed that the rods as received were free from pits. However, pitting was observed after the anodic cleaning operation. By changing to a cathodic cleaner, the pitting was eliminated. Apparently, inclusions and segregations which ran along the length of the rod were oxidized in the anodic cleaner and dissolved out, leaving the pits.

Bright Nickel Plating: Skipping In Low Current Density Areas

A stubborn case of "skipping" in low current density areas was encountered. No plating took place in recesses. This is sometimes caused by chromium in the solution or by an excess of secondary brightener, but these were ruled out in this case. An insidious factor was the fact that the skipping "came and went." For example, skipping was eliminated after the tank had stood idle over the weekend or had been dummied for several hours. It recurred after the tank had been worked normally for a period of time. A sample of the solution was sent to the vendor of the brighteners but he was unable to duplicate the skipping in the laboratory.

This tank had a history of stray current behavior such as nickel plating on the lead coils, etc., and it was reasoned that lead was introduced into the bath by this bipolar action. The skipping phenomena could also be explained by this bipolar activity. The skipping was duplicated in laboratory tests by adding a soluble lead salt

¹Zhur. Priklad. Chem., **37**, 2387 (1964).

to a bright nickel bath. After a period of time, lead sulfate slowly formed, precipitated out and the skipping no longer occurred. The tank was inspected to eliminate possible sources of stray currents and the lead coils were replaced by a carbon heater. This completely eliminated the skipping in the shop bath.

Room Temperature Operation

"Room temperature" in a plating shop varies considerably from summer to winter and allowances for this should be made for most efficient operation. Solutions operated at room temperature such as chromate conversion coatings, acid pickles and the zincate dip for plating on aluminum are certainly more active when warm than cold. Adjustments may be made by the operator. For example, the time of immersion may be shortened to compensate for a higher temperature. For chromate solutions, the pH may be raised to slow the reaction in warm weather and lowered to speed the reaction in cold weather. Rinsing in cold water in winter is not as effective as rinsing in warmer water in summer and therefore provision and allowance should be made for more thorough rinsing with cold water. A very cold rinse following a soak cleaner may "set" the soaps in the cleaner and leave a stain on the work which would remain through the plating operation.

A warm rinse following the phosphoric acid / nitric acid bright dip for aluminum is a necessity.

Panel For Soil Spray Qualification Tests

One procedure for qualifying a facility for anodizing or applying a chromate conversion coating on aluminum is to process a test panel and check the salt spray resistance of the coating. For example, according to MIL-A-8625: *Anodic Coatings for Aluminum*, aluminum alloy panels shall conform to specification QQ-A-355, condition T. In MIL-C-5541A: *Chemical Films and Chemical Film Materials for Aluminum and Aluminum Alloys*, the test panels for Class I treatment (where the application of a paint finish is not required) are 2024-T3 or 7075-T6 aluminum. It was found that panels which were cut from a large sheet of the proper alloy of aluminum failed to meet the salt spray requirement, while special panels which were purchased for this purpose passed the salt spray requirement, although both panels were processed at the same time and in an identical manner.

The difference lay in the "quality" of the special panels. They were carefully selected to be substantially free from scratches and pits. Furthermore, they were checked to verify that they had the proper temper. If the heat treat was not properly carried out, copper could precipitate in the grain boundaries and contribute to accelerated corrosion of the finished panel.

Metal Whiskers

Some troubles occur for which a satisfactory explanation never seems to be found. One example is as follows: an alloy deposit of 85 percent tin/15 percent zinc was plated satisfactorily for several months. On one occasion, however, a shipment of this alloy deposit on steel chassis was returned because of the presence of whiskers in the deposit. No satisfactory explanation could be found. Work processed later in this solution was satisfactory.

An article by Glazunova *et al.*,¹ on the subject of whiskers indicated that copper contamination in the tin bath greatly accelerates the formation of whiskers. The tin-zinc alloy plating tank was located near a pyrophosphate copper plating tank and thus could have been accidently contaminated by copper.

Poor Deposits From Impure Or Improper Additions To The Plating Solution

Impurities in a plating solution are a major cause of poor deposits. Some sources of impurities are the chemical additions, anodes and anode bags. During periods of scarcity the plater may be under pressure to buy anodes from unusual or foreign sources. In one case foreign cadmium anodes were used. Within a short time, the cadmium deposits became rough. A spectrographic analysis of an anode disclosed the presence of antimony in an amount far exceeding tolerable limits. When this was called to the attention of the jobber, he disclaimed all responsibility, pointing out that he himself had purchased the anodes on the basis of a certified analysis. The plater had no redress for the loss in rejects and the necessary rework.

Impurities can be introduced into a plating solution through chemical additions. On one occasion a considerable amount of zinc plating was being done which required an insoluble inside anode. As a result, the zinc content of the bath constantly decreased and had to be replenished. One method was to add zinc cyanide or zinc oxide. A fairly large addition of zinc oxide to this solution caused the zinc deposit to become dull gray. Additions of sodium sulfide gave temporary relief but only a zinc dust treatment finally restored the brightness to the zinc deposit. It was found that the technical zinc oxide had the analysis given in Table I. The analysis of a U.S.P. grade zinc is also given in this table.

Obviously, the larger percentages of lead, cadmium and copper in the technical grade caused the dull deposits. After this incident, U.S.P. grade zinc oxide was used with no recurrence of this difficulty.

Color Anodizing: One Way To Prevent Spotting Out

Anyone who has color anodized porous aluminum castings is familiar with the white spots which develop at the pore sites in the metal after the part has been processed and dried. Color anodizing refers to the process of anodizing aluminum and then coloring the anodic film by immersing the part in a dye bath. The white spots are caused by the bleed-out of residual sulfuric acid from the pores or seams, which bleaches the dye at that spot or area. Procedures which minimize but usually do not eliminate this difficulty are to:

- a. Rinse the part thoroughly after anodizing;
- b. Soak the part in a dilute ammonia or sodium bicarbonate solution after anodizing;
- c. Impregnate the porous aluminum with plastic before anodizing.

Another method which has been useful in some cases has been to anodize the part in an oxalic acid bath after the sulfuric acid anodizing process. This serves to replace the strong acid in the pores with a weak acid. Consequently, no bleaching of the dye occurs. The oxalic acid anodizing is carried out under the standard conditions for a short time. A typical example would be 50 g/L (6.7 oz/gal) oxalic acid, 29°C (85°F), 1 A/dm² (9.3 A/ft²), 50 V; one to ten min. The reader should evaluate and modify this process, however, to suit his own particular conditions.

Chromic Acid Anodizing: Case of Burning

Burning occurred during the chromic acid anodizing of an assembly made of 2024 aluminum alloy. The burning occurred in and

In Memoriam: Dr. Samuel Heiman

Dr. Samuel Heiman of the AESF Philadelphia Branch died June 7, 2003. He was 93. He was born and raised in the Olney section of Philadelphia, an old and traditional neighborhood. He was always very proud of his roots there. After he married, he and his wife, Belle, chose to live in the same neighborhood where they raised two children. According to his son,



William, he always marveled at the progress he witnessed in the city over the years.

Dr. Heiman graduated from South Philadelphia High School and attended the University of Pennsylvania, where he earned a BS (1930) and a PhD (1948) in chemistry.

After working for a few years in the petroleum industry, Dr. Heiman joined the former Graham, Savage & Associates in 1935 as an electroplating researcher.

During World War II, Dr. Heiman worked for two years at the Battelle Memorial Institute. At that time, it was a chemical and biological defense research lab in Columbus, OH. Following the war, the U.S. Navy honored him with the Ordnance Development Award for his work at Battelle.

From 1943 to 1961, Dr. Heiman was employed at Philadelphia Rust-Proof Company as technical director. From 1961 until 1973, he worked at General Electric Company as a consultant in the fields of electroplating, surface treatments and coatings.

All during his career in surface finishing, Dr. Heiman taught classes in electroplating at Temple University (1950 to 1966), and served as a guest lecturer at the University of Pennsylvania.

Highly respected among his peers in the plating industry, Dr. Heiman was a pillar of the Society. He served as national president of AES in 1956-57. He also was an author or co-author for many technical articles published in *Plating & Surface Finishing*, and he regularly contributed practical articles on electroplating. In 1939, one of his papers earned an AES Gold Medal for "Best Paper." Active in the Philadelphia Branch, he held most offices during his career, and served as its president from 1949 to 1951.

In 1966, Dr. Heiman received the Charles Henry Proctor Leadership Award, one of the highest honors given by the Society. In 1968, he was made a National Honorary Member.

Dr. Heiman was also a member of American Society of Metals, the Electrochemical Society and the Franklin Institute. near a seam or faying (adjoining) surface. Burning in an anodizing process means that the aluminum has dissolved away, leaving the part completely spoiled. A number of possible causes were considered but after further investigation were rejected as the cause of the burning. These included high current density at the burned area, overheating within the seam from insufficient circulation, the presence of flux or lubricant on the aluminum which was not removed before fabrication and excessively high chloride or fluoride ion in the anodizing bath.

The burning was eventually found to be caused by the caustic cleaning of the parts before anodizing. This was ordinarily not done, but in this case, the parts had burnt-in soil which did not yield to the solvent degreasing operation and this gave the anodized coating a poor appearance.

The caustic within the faying surface was apparently not completely rinsed out or neutralized when the part entered the chromic acid anodizing tank. The absence of chromic acid at the surface of the aluminum within the crevice prevented the formation of the anodic film and the metal dissolved.

Chromate Conversion Coating On Aluminum: Pitting Of The Aluminum

The parts were semi-circular forgings about 4 ft in diameter. Since they had been machined in several areas, the built-in cost was fairly high at that stage. Aluminum had been chromated in this set-up for several years and this was the first time pitting had ever occurred. A surprising thing was that the pitting occurred only on these particular parts. Many other parts were processed without any trouble.

The cycle consisted of an inhibited cleaner, a deoxidizer and the chromate conversion solution with adequate rinses and a final warm water dip. The solutions had been made up recently and the analyses were well within operating range. It was noticed that the pitting occurred at stressed areas in the metal such as at countersunk holes and along a ridge which had been rolled. The basis metal was suspected and the fabricator of the part was called in to explain what he had done wrong. At the same time all the unfinished parts on hand were carefully inspected for pits in the metal. These time-consuming efforts yielded negative results.

The degreaser was suspected since under some unusual circumstances etching or pitting of aluminum could be caused here. This investigation, however, showed that the maintenance work on the degreaser could stand some improving but did not solve the problem at hand.

Laboratory tests were made in an effort to duplicate the pitting. Since the parts just about fitted in the tanks they rested on the bottom. Galvanic effects caused by the aluminum touching the stainless steel deoxidizer tank were tested without being able to produce or duplicate the pitting.

In the meantime, processing of these parts had been held up in the shop pending the above investigation. With pressure from the production people building up it was finally decided to process a few parts. At this time it was noticed that the steel bracket holding the aluminum drip pan between the deoxidizer tank and the rinse was missing. It had fallen into the deoxidizer tank the last time this solution had been made up. The galvanic effect between the steel bracket and the aluminum part (whenever it touched the steel) corroded the aluminum in a typical pitting fashion in the areas of its stressed condition. *Pass*

Technical Editor's Note: The preceding article is based on material contributed by Dr. Samuel Heiman, as part of the Plating Topics series that ran in this journal. This one deals with everyday production plating problems in the mid-1960s, many of which are still encountered in the opening years of the 21st century. Much has changed ... but not that much. The reader may benefit both from the information here and the historical perspective as well. In some cases here, words were altered for context. The bottom line is the challenge that Dr. Heiman gives in the introduction; perhaps it needs to be heeded once again.