

## **Servicing a Hard Chromium Plating Operation**

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Proper maintenance and operation of both chemistry and equipment is essential to obtaining predictable deposits from any plating operation. It is particularly important in hard chromium plating operations, since many plating problems can be caused by any one, or a combination of, several different process variables. The following paper is a practical guide, which will highlight a process for troubleshooting the most common plating problems and provide practical advice for eliminating these problems in the first place.

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Whenever the deposit properties of a plating process do not meet specifications or previous results, it is necessary to employ some good detective skills in order to determine and eliminate the root cause of the problem. This is especially true when troubleshooting hard chromium plating installations. On the surface, troubleshooting a hard chromium plating operation does not seem like a difficult matter, since the chemistry in a typical hard chromium plating process involves simply, chromic acid, sulfate, and a secondary catalyst, if one is utilized. However, due to the fact that the same deposit defect can be caused by several different process variables, alone or in combination and due to several unique features of a hard chromium plating operation, finding the root cause of a hard chromium plating bath can be quite challenging. This paper will attempt to provide the reader with a systematic approach to determining the root cause of the most common plating problems experienced by hard chromium platers, such as:

- Poor Coverage
- Burnt Deposits
- Slow Plating Speed
- Nodular or Rough deposits
- Pitted Deposits
- Poor Adhesion
- Dull Deposits

**Finally, this paper will offer practical advice for eliminating these problems in the first place.**

Troubleshooting a hard chromium plating operation can be a challenge because a particular deposit defect can be caused by multiple process variables and/or opposite extremes of the same process variable. For example, a dull deposit can be caused by the temperature of the plating solution that is either too high or too low. In addition, rough deposits can be caused by a chromic acid to sulfate ratio that is too high or too low. In other words, it is not possible to observe a deposit defect and immediately identify the root cause of the problem. Identifying the problem will simply provide a clue as to where to start the process of uncovering the root cause. This paper will provide you with a method of troubleshooting that eliminates the obvious, or the simple to correct, first, before proceeding to more complicated and time consuming analyses.

When troubleshooting a hard chromium plating installation, the possible causes of the defect can be distilled into four basic categories: chemistry, equipment, part preparation, or substrate. As was mentioned earlier, the chemistry components of a hard chromium plating operation are limited and are relatively easy to analyze. So to begin with, I always recommend you make sure that the chemistry is within operating parameters recommended by the supplier before you begin to look elsewhere for a root cause. Having said that, if the chromium deposit is bright and smooth, the defect is usually not caused by the chemistry.<sup>1</sup> It is more likely an equipment issue or a problem caused by the substrate itself (or preparation of the substrate prior to plating).

Before we begin, it is important to note several unique features of a hard chromium plating operation when compared to other typical plating processes such as zinc or nickel.

1. Chromium metal will not deposit from a hard chromium plating processes unless a specific concentration of sulfate catalyst is present. It is extremely important to follow your suppliers recommendations for maintaining the proper chromic acid to sulfate ratio based on the type of hard chromium plating process you operate. Typical ratios for the different types of plating processes available can be found in Table 1.
2. Cathode current efficiencies in a typical hard chromium plating operation are low, ranging from 12 to 28 percent, depending on the type of hard chromium plating process utilized and the current density at which it is operated, compared to nearly 100 percent in plating processes such as acid copper, acid zinc, or bright nickel. In other words, only 12-28 percent of the current supplied to the system is used to deposit chrome metal at the substrate. The rest of the energy is used to generate hydrogen, and heat the solution. These factors must be taken into consideration when specifying the proper equipment for the operation such as exhaust, rectification, bussing, fixtures, and heating/cooling coils.
3. A hard chromium plating operation utilizes insoluble lead alloy anodes. Chromium ions are supplied to the hard chromium plating system as chromic acid, instead of metal anodes that dissolve into solution to replenish soluble metal ions that are deposited at the cathode. In addition, to completing the electrical circuit, these anodes play a key role in the proper operation of the bath by reoxidizing the trivalent chromium that is normally generated as a by product of the reaction that reduces  $Cr^{6+}$  to chromium metal at the cathode.
4. Hard chromium plating operations require extremely high current densities, in some cases, up to 10 times the current densities required for plating other metals. In fact, the average current density for most plating operations ranges from 7.8 to 15.6 A/dm<sup>2</sup> (72 to 144 A/ft<sup>2</sup>) whereas typical current densities in hard chromium plating operations range from 23.3 to 101.1 A/dm<sup>2</sup> (1.5 to 6.5 ASI). It is important to factor these extreme current densities into account when sizing rectification, bussing, and heating/coiling requirements for the operation.
5. It is critical to maintain the proper operating temperature of the hard chromium plating solution. Follow the recommendations of the supplier for the type of plating process utilized and maintain the temperature within  $\pm 1.1^{\circ}C$  ( $2^{\circ}F$ ).<sup>2</sup>

Table 1

<b>Typical Hard Chromium Plating Process Ratios</b>			
	<b>Conventional Chrome</b>	<b>Mixed Catalyst</b>	<b>High Efficiency Non Fluoride</b>
Chromic Acid:	240 g/L (32 oz/gal)	240 g/L (32 oz/gal)	240 g/L (32 oz/gal)
Sulfate:	2.4 g/L (0.32 oz/gal)	1.2 g/L (0.16 oz/gal)	2.6 g/L (0.35 oz/gal)
Ratio (CrO <sub>3</sub> /SO <sub>4</sub> ):	100:1	200:1	90:1
Fluoride:	None	2-4 g/L (0.25-0.5 oz/gal)	None

**Authors note:**

This troubleshooting guide is organized by plating problem. Find section of the paper which describes the hard chromium plating problem you are experiencing and check each of the possible causes in the order they are discussed. The order is determined, not by the most likely cause of the problem, but by the ease of analysis for each troubleshooting step. Each section of the paper can be considered a separate troubleshooting guide, therefore, a complete explanation of the possible remedy is provided in each section so that it is not necessary to refer to previous sections when attempting to address a particular plating problem.

**Poor Coverage***Chemistry*

Poor coverage in a hard chromium plating operation can be caused by high operating temperature of the bath. Make sure that the bath has been thoroughly mixed prior to measuring the temperature of the solution. If the temperature is too high adjust to the range recommended by the supplier.

Poor coverage can also be caused by low chromic acid content of the plating solution. Low chromic acid content decreases the conductivity of the solution which leads to poor coverage in low current density areas and lower plating thicknesses across the entire current density range. Make sure that the plating solution is at operating temperature and solution level, and that the solution has been thoroughly mixed prior to removing a sample for analysis. Take a baumé reading and or perform a titration on the solution to determine the concentration of chromic acid in the solution. If the concentration is low, adjust with the proper replenishment chemistry to the optimum concentration recommended by the supplier. Note, if the chromic acid concentration from the baumé reading is higher than the concentration determined by wet analysis, metallic impurities are contributing to the specific gravity of the solution. You should determine the concentration of impurities in the bath and address that problem separately.

Poor coverage can be caused by a low chromic acid to sulfate ratio. Analyze the sample that was previously taken from the bath for the concentration of sulfate, using a sulfate precipitation method or the Kocour centrifuge method. To calculate the ratio of the bath, divide the concentration of sulfate into the concentration of chromic acid to determine the chromic acid to sulfate ratio. If necessary, adjust the sulfate concentration, raising it with sulfuric acid or lowering it with barium carbonate, to the optimum concentration recommended by the supplier. If you are utilizing a self-regulating plating process, follow the recommendations of the supplier for hoeing the solution in order to adjust the sulfate to the proper concentration.

Poor coverage can be caused by high or low concentration of secondary catalyst (if utilized). Analyze the sample to determine the concentration of secondary catalyst in the bath and adjust it to the optimum concentration recommended by the supplier. If you are utilizing a self-regulating mixed catalyst plating process, follow the recommendations of the supplier for hoeing the solution in order to adjust the fluoride to the proper concentration.

Poor coverage can be caused by a build up of metallic impurities, including trivalent chromium. Analyze the sample for common metallic impurities found in hard chromium operations, such as: iron, copper, and trivalent chromium and, if necessary, for zinc and aluminum. If the bath is high in trivalent chromium, over 3.75 g/L (0.5 oz/gal), you should immediately investigate the cause of this build up. An increase in the concentration of trivalent chromium indicates either insufficient anode area in the bath or organic contamination of the solution. Insufficient anode area can be due to the fact that there are not enough anodes in the tank. Whenever possible you should maintain an anode to cathode area of greater than 1.5—2.0 to 1. Insufficient anode area could also be the result of anodes that have been insulated from the solution by poor contact with the anode buss or are scaled with lead chromate. When lead alloy anodes are in contact with a chromic acid solution and no current is being applied to them, they immediately begin to scale with lead chromate. Lead chromate is an orange-yellow scale that is a familiar site to all experienced chromium platers. Lead chromate scale does not conduct electricity, therefore, if it becomes too thick the anode will be insulated from the solution and will behave as if it does not exist. Anodes that are working properly will have a brown, black coating of lead peroxide. If organic contamination is the cause of the build up of trivalent chromium, you should determine and eliminate the source of the contamination. No matter the source, trivalent chromium is easily reduced by dummy plating the solution using an anode to cathode ratio as high as possible (an anode to cathode ratio of 30 to 1 is optimum) at 6 volt potential, at operating temperature. If the concentration of metallic impurities such as iron, copper, zinc, or aluminum, exceeds 7.5 g/L (1.0 oz/gal) you should reduce these impurities via ion exchange, electro dialysis, porous pots, solution dilution, or other suitable method.

Poor coverage can be caused by chloride contamination of the solution. Chloride can affect the hard chromium deposit at concentrations as low as 0.023 g/L (0.003 oz/gal). Chloride contamination in a hard chromium plating operation is typically caused by the drag in of hydrochloric acid from a pretreatment pickling step, but chloride can also be introduced to the chromium bath via make up water. If you detect chloride contamination in the solution check the make up water for chloride content. If chloride is present, you should consider a water purification system for any water that is added back to a chromium plating tank. If the source water is free of chloride, you should increase rinsing between the hydrochloric pretreatment steps and the chromium plating tank. If chloride contamination is resulting in poor coverage on parts being processed, you can remove chloride in one of two ways. First, chloride can be precipitated from the solution as insoluble silver chloride (AgCl) by additions of silver oxide (Ag<sub>2</sub>O). Determine the amount of silver oxide needed to remove the chloride contamination using the following formula:

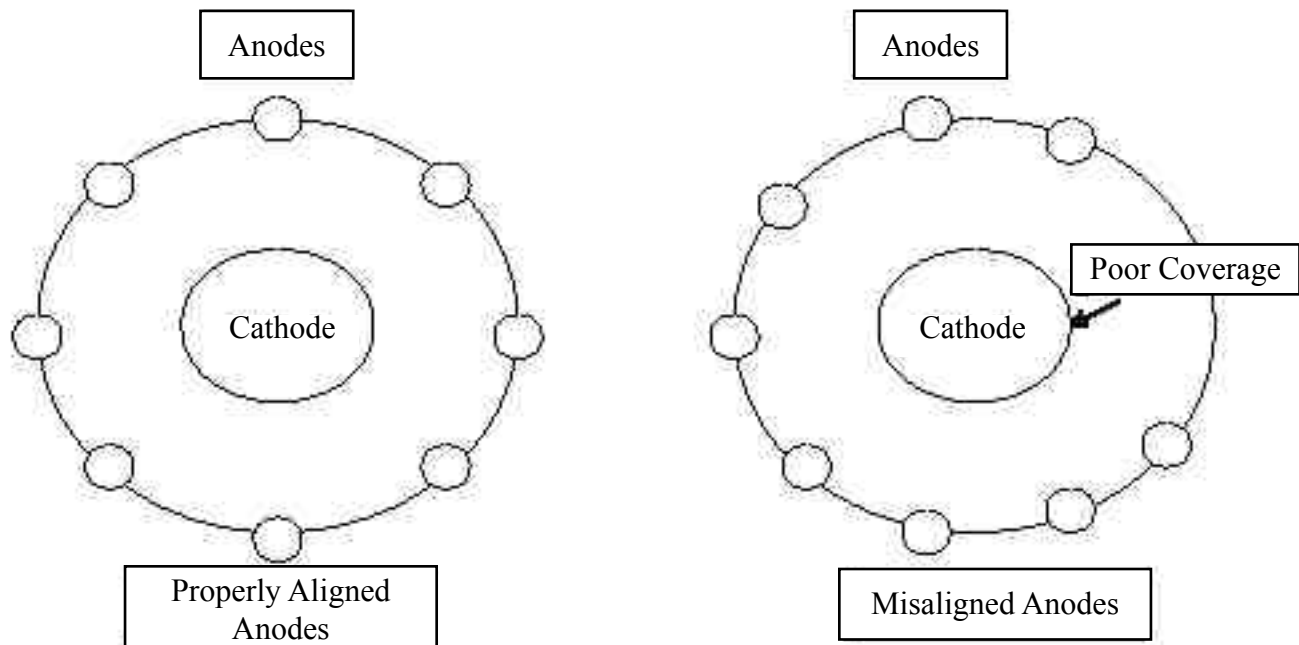
$$\text{g/L of Cl}^- \times 3.3 = \text{g/L of Ag}_2\text{O needed}$$

Chloride contamination can also be removed from a chromium plating bath by electrolysis. The bath is dummy plated using the same operating procedures described for the removal of trivalent chromium above. A word of caution is advisable at this point, chlorine gas is liberated from the solution during electrolysis, therefore, steps should be taken to ventilate the tank throughout this process.

### *Equipment*

Poor coverage can be caused by low current density. It is important to accurately determine the number of square meters of surface area to be plated so that the correct current density, in A/dm<sup>2</sup>, can be applied to the part. Once surface area and resulting current density have been determined, the current applied to the part should be controlled in amperes, not volts. Voltage in a hard chromium plating operation will vary based on the conductivity of the solution and the concentration of metallic impurities in the bath. Since metallic impurities act as resistors to current flow in the system, as their concentration increases in the bath, it will require more volts to push the same number of amperes through the bath. Therefore, if you set the current density for the part using volts instead of amperes, as the bath ages and builds in metallic impurities, the effective current density on the parts will decrease. As a result, you may experience poor coverage. Low current density can also be caused by rectifiers and bussing that are undersized or are experiencing poor contact. As was mentioned earlier, hard chromium plating operations require extremely high current densities, in some cases, up to 10 times the current densities required for plating other metals. It is important to remember these current density requirements in order to determine the physical limitations of your equipment when bidding large jobs. It is a good idea, as part of a routine maintenance program, to inspect bussing connections for loose fitting joints and/or parts of the bussing that are warm to the touch. Bussing that is properly sized and is well connected will remain at ambient shop temperature. Bussing that is warm to the touch has resistance to current flow—the bussing is undersized for the part being plated or there is a loose connection in the system. Finally, low current density can be caused by fixtures that are built up with metal from the plating operation. If rack tips become plated up, they should be stripped on a regular basis in order to ensure that there is no resistance to current flow in the fixtures themselves.

Poor coverage can also be caused by scaled or passive anodes or anodes that are misaligned. As was mentioned before, lead alloy anodes that are in contact with a chromic acid solution when no current is being applied to them, will immediately begin to scale with lead chromate. If it is not too thick, this lead chromate scale can be removed by dummifying the plating bath at operating temperatures and current densities for approximately 15 minutes at the beginning of each shift. After extended periods of down time, however, it is possible that the lead chromate film becomes too thick to remove by dummy plating. If that is the case, it will be necessary to remove the anodes from solution and chemically clean them using a proprietary anode cleaner. Anodes that are scaled with lead chromate should not be cleaned mechanically since, lead chromate dust is hazardous. In addition, mechanically cleaning anodes can create grooves on the surface that can affect the current density applied to the parts. If the anodes are active they will be coated with a brown, black coating of lead peroxide. Next, check to see that the anodes are aligned properly. Current flows in the system using the path of least resistance. Therefore, it is necessary to space anodes in a way that all areas of the part receive the same current distribution from the anodes.



Poor coverage can be caused by thieves that are too large or too close to the work piece. Design and use of thieves is one part of the hard chromium plating business that still requires some trial and error to perfect. It may be necessary to redesign or reposition thieves that are used to rob the high current density areas of a part if they also shade the low current density area or an adjacent part. Parts that are racked too close together can also act as thieves for adjacent parts. If a dense grouping of parts exhibit poor coverage, try running the rack package with fewer pieces to determine if coverage improves.

Finally, poor coverage can be caused by high ripple. Ripple is AC Voltage divided by DC Voltage, expressed as a percentage.

$$\frac{\text{AC Voltage}}{\text{DC Voltage}} \times 100 = \% \text{ Ripple}$$

Ripple should be controlled as low as possible for any chromium plating installation, but it should not be allowed to exceed five percent. If ripple is present, you should immediately have a qualified electrician service the rectifier to replace defective diodes or add additional capacitors if necessary.

## **Burnt Deposits**

### *Chemistry*

Burnt deposits in a hard chromium plating operation can be caused by low operating temperature of the bath. Make sure that the bath has been thoroughly mixed prior to measuring the temperature of the solution. If the temperature is too low adjust to the range recommended by the supplier.

Burnt deposits can also be caused by low chromic acid content of the plating solution. Make sure that the plating solution is at operating temperature and solution level, and that the solution has been thoroughly mixed prior to removing a sample for analysis. Take a baumé reading and or perform a titration on the solution to determine the concentration of chromic acid in the solution. If the concentration is low, adjust with the proper replenishment chemistry to the optimum concentration recommended by the supplier. Note, if the chromic acid concentration from the baumé reading is higher than the concentration determined by wet analysis, metallic impurities are contributing to the specific gravity of the solution. You should determine the concentration of impurities in the bath and address that problem separately.

Burnt deposit can be caused by a high or low chromic acid to sulfate ratio. Analyze the sample that was previously taken from the bath for the concentration of sulfate, using a sulfate precipitation method or the Kocour centrifuge method. To calculate the ratio of the bath, divide the concentration of sulfate into the concentration of chromic acid to determine the chromic acid to sulfate ratio. If necessary, adjust the sulfate concentration, raising it with sulfuric acid or lowering it with barium carbonate, to the optimum concentration recommended by the supplier. If you are utilizing a self-regulating plating process, follow the recommendations of the supplier for hoeing the solution in order to adjust the sulfate to the proper concentration.

### *Equipment*

Burnt deposits can be caused by high current density. It is important to accurately determine the number of square meters of surface area to be plated so that the correct current density can be applied to the part. If you determine that the correct current density was applied and you still experience burning, it may be necessary to utilize thieves or robbers to direct current away from the high current density areas of the part.

Burnt deposits can also be caused by scaled or passive anodes or anodes that are too close to the work piece. As was mentioned before, lead alloy anodes that are in contact with a chromic acid solution when no current is being applied to them, will immediately begin to scale with lead chromate. If it is not too thick, this lead chromate scale can be removed by dummied the plating bath at operating temperatures and current densities for approximately 15 minutes at the beginning of each shift. After extended periods of down time, however, it is possible that the lead chromate



film becomes too thick to remove by dummy plating. If that is the case, it will be necessary to remove the anodes from solution and chemically clean them using a proprietary anode cleaner. Anodes that are scaled with lead chromate should not be cleaned mechanically since, lead chromate dust is hazardous. In addition, mechanically cleaning anodes can create grooves on the surface that can affect the current density applied to the parts. If the anodes are active they will be coated with a brown, black coating of lead peroxide. If the anodes are working properly and the deposit is burnt, the anodes may be too close to the work piece. Redistribute the anodes and/or move the anode bussing in order to obtain the correct current density on the part.

Burnt deposits may be caused by intermittent contact during plating. If parts loose contact with the cathode bussing they can burn. Clean all electrical contacts, including anode and cathode bussing on a regular basis in order to ensure good electrical contact between all parts of the system. Consider utilizing a conductive grease and/or clamping work fixtures to the cathode bussing.

Burnt deposits may be caused by plating parts too close to the solution interface. Parts should be plated at least 7.6 centimeters (3 inches) below the surface of the solution. Hard chromium plating is an inefficient process that is plated at high current densities. As a result, there is a large amount of hydrogen that is generated at the cathode. If the parts are too close to the surface of the bath, the hydrogen evolved at the top of the work piece does not allow fresh chromic acid solution to the deposit interface. The solution in that area becomes low in chromic acid concentration and the part burns.

Burnt deposits may be caused by inadequate solution agitation. Similar to the discussion in the previous paragraph, if fresh plating solution does not get to the deposit interface, the solution becomes depleted of chromic acid and the part burns. In addition to providing fresh plating solution at the deposit interface, solution agitation prevents temperature stratification of the solution, especially in deep plating tank. It is important, however, to use a low pressure blower or mechanical agitation, not compressed air, to provide solution movement. Compressed air system will introduce oil into the plating solution, which will immediately generate trivalent chromium and cause additional plating problems.

Burnt deposits can be caused by high ripple. Ripple is AC Voltage divided by DC Voltage, expressed as a percentage.

$$\frac{\text{AC Voltage}}{\text{DC Voltage}} \times 100 = \% \text{ Ripple}$$

Ripple should be controlled as low as possible for any chromium plating installation, but it should not be allowed to exceed five percent. If ripple is present, you should immediately have a qualified electrician service the rectifier to replace defective diodes or add additional capacitors if necessary.

### *Part Preparation*

Burnt deposits can be caused by parts that are colder than the bath temperature when plating begins. It is especially important when plating large parts to allow them to heat to the operating temperature of the bath prior to commencing plating in a hard chromium plating operation.

### **Slow Plating Speed**

#### *Chemistry*

Slow plating speed can be caused by high operating temperature of the bath. Make sure that the bath has been thoroughly mixed prior to measuring the temperature of the solution. If the temperature is too high adjust to the range recommended by the supplier.

Slow plating speed can also be caused by low chromic acid content of the plating solution. Make sure that the plating solution is at operating temperature and solution level, and that the solution has been thoroughly mixed prior to removing a sample for analysis. Take a baumé reading and or perform a titration on the solution to determine the concentration of chromic acid in the solution. If the concentration is low, adjust with the proper replenishment chemistry to the optimum concentration recommended by the supplier. Note, if the chromic acid concentration from the baumé reading is higher than the concentration determined by wet analysis, metallic impurities are contributing to the specific gravity of the solution. You should determine the concentration of impurities in the bath and address that problem separately.

Slow plating speed can be caused by a high chromic acid to sulfate ratio. Analyze the sample that was previously taken from the bath for sulfate, using a sulfate precipitation method or the Kocour centrifuge method. To calculate the ratio of the bath, divide the concentration of sulfate into the concentration of chromic acid to determine the chromic acid to sulfate ratio. If necessary, adjust the sulfate concentration, raising it with sulfuric acid or lowering it with barium carbonate, to the optimum concentration recommended by the supplier.

Slow plating speed can be caused by a build up of metallic impurities. Analyze the sample for common metallic impurities found in hard chromium operations, such as: iron, copper, and trivalent chromium and, if necessary, for zinc and aluminum. If the concentration of these metallic impurities exceeds 7.5 g/L (1.0 oz/gal) you should reduce these impurities via ion exchange, electrodialysis, porous pots, solution dilution, or other suitable method.

#### *Equipment*

Slow plating speed can be caused by low current density. It is important to accurately determine the number of square meters of surface area to be plated so that the correct current density, in A/dm<sup>2</sup>, can be applied to the part. Once surface area and resulting current density have been determined, the current applied to the part should be controlled in amperes, not volts. Voltage in a hard chromium plating operation will vary based on the conductivity of the solution and the

concentration of metallic impurities in the bath. Since metallic impurities act as resistors to current flow in the system, as their concentration increases in the bath, it will require more volts to push the same number of amperes through the bath. Therefore, if you set the current density for the part using volts instead of amperes, as the bath ages and builds in metallic impurities, the effective current density on the parts will decrease. As a result, you may experience poor coverage. Low current density can also be caused by rectifiers and bussing that are undersized or are experiencing poor contact. As was mentioned earlier, hard chromium plating operations require extremely high current densities, in some cases, up to 10 times the current densities required for plating other metals. It is important to remember these current density requirements in order to determine the physical limitations of your equipment when bidding large jobs. It is a good idea, as part of a routine maintenance program, to inspect bussing connections for loose fitting joints and/or parts of the bussing that are warm to the touch. Bussing that is properly sized and is well connected will remain at ambient shop temperature. Bussing that is warm to the touch has resistance to current flow—the bussing is undersized for the part being plated or there is a loose connection in the system. Finally, low current density can be caused by fixtures that are built up with metal from the plating operation. If rack tips become plated up, they should be stripped on a regular basis in order to ensure that there is no resistance to current flow in the fixtures themselves.

Slow Plating speed can be caused by passive or scaled anodes. As was mentioned before, lead alloy anodes that are in contact with a chromic acid solution when no current is being applied to them, will immediately begin to scale with lead chromate. If it is not too thick, this lead chromate scale can be removed by dummifying the plating bath at operating temperatures and current densities for approximately 15 minutes at the beginning of each shift. After extended periods of down time, however, it is possible that the lead chromate film becomes too thick to remove by dummy plating. If that is the case, it will be necessary to remove the anodes from solution and chemically clean them using a proprietary anode cleaner. Anodes that are scaled with lead chromate should not be cleaned mechanically since, lead chromate dust is hazardous. In addition, mechanically cleaning anodes can create grooves on the surface that can affect the current density applied to the parts. If the anodes are active they will be coated with a brown, black coating of lead peroxide.

Slow plating speeds can be caused by plating rectifiers, bussing, and/or fixtures that are improperly sized for the operation. Once you determine the number of square meters of surface area for a particular part, it is necessary to determine if the physical limitations of the system will allow you to apply the proper current density. The current carrying capacity of copper bussing and fixtures is 1,000 amperes per 6.45 cm<sup>2</sup> (1 in<sup>2</sup>). Therefore, if a part requires 500 amperes, all fixtures must contain at least 3.23 cm<sup>2</sup> (0.5 in<sup>2</sup>) in cross sectional area.

Slow plating speeds can be caused by high ripple. Ripple is AC Voltage divided by DC Voltage, expressed as a percentage.

$$\frac{\text{AC Voltage}}{\text{DC Voltage}} \times 100 = \% \text{ Ripple}$$

Ripple should be controlled as low as possible for any chromium plating installation, but it should not be allowed to exceed five percent. If ripple is present, you should immediately have a qualified electrician service the rectifier to replace defective diodes or add additional capacitors if necessary.

### **Nodular or Rough Deposits**

#### *Chemistry*

Nodular or rough deposits in a hard chromium plating operation can be caused by low operating temperature of the bath. Make sure that the bath has been thoroughly mixed prior to measuring the temperature of the solution. If the temperature is too low adjust to the range recommended by the supplier.

Nodular or rough deposits can be caused by a high chromic acid to sulfate ratio. Analyze the sample that was previously taken from the bath for the concentration of sulfate, using a sulfate precipitation method or the Kocour centrifuge method. To calculate the ratio of the bath, divide the concentration of sulfate into the concentration of chromic acid to determine the chromic acid to sulfate ratio. If necessary, adjust the sulfate concentration, raising it with sulfuric acid or lowering it with barium carbonate, to the optimum concentration recommended by the supplier. If you are utilizing a self-regulating plating process, follow the recommendations of the supplier for hoeing the solution in order to adjust the sulfate to the proper concentration.

Nodular or rough deposit can be caused by a build up of metallic impurities, especially iron and trivalent chromium. Analyze the sample for common metallic impurities found in hard chromium operations, such as: iron, copper, and trivalent chromium and, if necessary, for zinc and aluminum. If the bath is high in trivalent chromium, over 3.75 g/L (0.5 oz/gal), you should immediately investigate the cause of this build up. An increase in the concentration of trivalent chromium indicates either insufficient anode area in the bath or organic contamination of the solution. Insufficient anode area can be due to the fact that there are not enough anodes in the tank. Whenever possible you should maintain an anode to cathode area of greater than 1.5—2.0 to 1. Insufficient anode area could also be the result of anodes that have been insulated from the solution by poor contact with the anode buss or are scaled with lead chromate. When lead alloy anodes are in contact with a chromic acid solution and no current is being applied to them, they immediately begin to scale with lead chromate. Lead chromate is an orange-yellow scale that is a familiar site to all experienced chromium platers. Lead chromate scale does not conduct electricity, therefore, if it becomes too thick the anode will be insulated from the solution and will behave as if it does not exist. Anodes that are working properly will have a brown, black coating of lead peroxide. If organic contamination is the cause of the build up of

trivalent chromium, you should determine and eliminate the source of the contamination. No matter the source, trivalent chromium is easily reduced by dummy plating the solution using an anode to cathode ratio as high as possible (an anode to cathode ratio of 30 to 1 is optimum) at 6 volt potential, at operating temperature. If the concentration of metallic impurities such as iron, copper, zinc, or aluminum, exceeds 7.5 g/L (1.0 oz/gal) you should reduce these impurities via ion exchange, electro dialysis, porous pots, solution dilution, or other suitable method.

Nodular or rough deposits can be caused by particulate matter in the solution. It may be necessary to filter the solution in order to remove particles from solution. If the particulate matter is steel filings, they can be removed by passing a magnet through the solution until they are completely removed.

#### *Equipment*

Nodular or rough deposits can be caused by high current density. It is important to accurately determine the number of square meters of surface area to be plated so that the correct current density can be applied to the part.

#### *Part Preparation*

Nodular or rough deposits can be caused by over aggressive reverse etching. Reverse etching is used in most hard chromium plating operations to condition the substrate, in order to improve adhesion of the chromium deposit to the basis metal. This process actually produces a microetch on the surface of the part. If the reverse etch current density is too high or the part is reverse etched for too long, the surface roughness produced can cause nodular or rough deposits in the final finish. Ideally, the reverse etch process step should be carried out in a reverse etch tank, not the plating tank. Reverse etching in the plating tank will contaminate the plating solution with iron. In addition, if the plating bath utilizes a secondary catalyst, it is easy to over etch the work piece.

#### *Substrate*

Nodular or rough deposits are most often caused by rough base material prior to plating. A hard chromium deposit does not have the ability to level surface roughness, like a bright nickel or acid copper plating process. The chromium deposit will mirror the surface finish prior to plating. In fact, depending on the thickness, the chromium deposit may exaggerate an uneven surface finish. It is always a good idea to check the surface roughness of a part prior to plating in order to determine if an acceptable surface roughness can be achieved after chromium plating.

### **Pitted Deposits**

#### *Chemistry*

A pitted hard chromium deposit can be caused by the improper concentration of secondary catalyst (if utilized). Analyze the sample to determine the concentration of secondary catalyst in the bath and adjust it to the optimum concentration recommended by the supplier. If you are

utilizing a self-regulating mixed catalyst plating process, follow the recommendations of the supplier for hoeing the solution in order to adjust the fluoride to the proper concentration.

A pitted hard chromium deposit can be caused by the build up of oils or solvents in the plating solution. Of course, organic contamination of a chromium plating solution will lead to an increase in the concentration of trivalent chromium. Care should be taken during the process of part preparation to ensure that oils and solvents are not dragged into the plating tank.

#### *Part Preparation*

A pitted hard chromium deposit can be caused by insufficient cleaning prior to plating. Parts that are properly cleaned prior to chromium plating will be free of “water breaks” in the surface film. A “water break” indicates that oil or solvents have not been completely removed from the surface of the part and additional surface preparation should take place until the proper surface film is achieved.

A pitted hard chromium deposit can be caused by over aggressive reverse etching. Reverse etching is used in most hard chromium plating operations to condition the substrate, in order to improve adhesion of the chromium deposit to the basis metal. This process actually produces a microetch on the surface of the part. If the reverse etch current density is too high or the part is reverse etched for too long, the surface roughness produced can cause pits in the final finish. Ideally, the reverse etch process step should be carried out in a reverse etch tank, not the plating tank. Reverse etching in the plating tank will contaminate the plating solution with iron. In addition, if the plating bath utilizes a secondary catalyst, it is easy to over etch the work piece.

A pitted hard chromium deposit can be caused by carbon smut on the surface of the part prior to plating. Make sure that part preparation minimizes the carbon smut generated at the surface of the part. If carbon smut forms during part preparation, remove completely prior to chromium plating.

A pitted hard chromium deposit can be caused by gas bubbles adhering to the surface of the part during plating. Hard chromium plating is an inefficient process that is plated at high current densities. As a result, there is a large amount of hydrogen that is generated at the cathode. If a gas bubble adheres to the surface of the part, the chromium will deposit around the bubble and a pit will form in the deposit. One way to decrease the ability of gas bubbles to adhere to the part during chromium plating is to improve the surface finish of the part prior to plating. If the surface finish of the part is smooth, the bubble will have nothing in which to adhere. If improving the surface finish of the part is not possible or practical, another way to decrease adhesion of gas bubbles to the work piece is to occasionally agitate the part while plating.

A pitted hard chromium deposit can be caused by nodules that are “picked out” of the deposit during post plate finishing operations. This problem should be addressed by eliminating the nodules.

### *Substrate*

A pitted hard chromium deposit is most often caused by pits or inclusions in the basis metal prior to plating. As you recall in our discussions regarding surface roughness of the substrate, a hard chromium deposit will mirror the surface finish prior to plating. If the base substrate is pitted, the chromium deposit will be pitted.

Finally, a pitted hard chromium deposit can be caused by a part that is magnetized. Demagnetizing the part prior to plating should eliminate the problem.

### **Poor Adhesion**

#### *Chemistry*

Poor adhesion in a hard chromium deposit can be caused by low operating temperature of the plating bath. Make sure that the bath has been thoroughly mixed prior to measuring the temperature of the solution. If the temperature is too high adjust to the range recommended by the supplier.

Poor adhesion in a hard chromium deposit may be caused by low chromic acid content of the reverse etch solution. Make sure that the reverse etch solution is at operating temperature and solution level, and that the solution has been thoroughly mixed prior to removing a sample for analysis. Take a baumé reading and or perform a titration on the solution to determine the concentration of chromic acid in the solution. If the concentration is low, adjust with chromic acid to the optimum concentration recommended by the supplier.

#### *Equipment*

Poor adhesion in a hard chromium deposit can be caused by intermittent contact during plating. If parts loose contact with the cathode bussing, chromium deposited after the current interruption may not adhere to the prior deposit. Clean all electrical contacts, including anode and cathode bussing on a regular basis in order to ensure good electrical contact between all parts of the system. Consider utilizing a conductive grease and/or clamping work fixtures to the cathode bussing.

Poor adhesion in a hard chromium deposit can be caused by high ripple. Ripple is AC Voltage divided by DC Voltage, expressed as a percentage.

$$\frac{\text{AC Voltage}}{\text{DC Voltage}} \times 100 = \% \text{ Ripple}$$

Ripple should be controlled as low as possible for any chromium plating installation, but it should not be allowed to exceed five percent. If ripple is present, you should immediately have a qualified electrician service the rectifier to replace defective diodes or add additional capacitors if necessary.

### *Part Preparation*

Poor adhesion in a hard chromium deposit is most often caused by insufficient cleaning prior to plating. Parts that are properly cleaned prior to chromium plating will be free of “water breaks” in the surface film. A “water break” indicates that oil or solvents have not been completely removed from the surface of the part and additional surface preparation should take place until the proper surface film is achieved.

Poor adhesion in a hard chromium deposit can be caused by insufficient reverse etching. Reverse etching is used in most hard chromium plating operations to condition the substrate, in order to improve adhesion of the chromium deposit to the basis metal. If the deposit is not adhering to the basis metal, you may need to increase the current density or the time of the reverse etch.

### *Substrate*

Poor adhesion in a hard chromium deposit can be caused by excessively hardened basis metal. Hardened steels usually require longer reverse etch times at higher current densities in order to obtain proper adhesion of the deposit to the substrate.

## **Dull Deposits**

### *Chemistry*

Dull deposits in a hard chromium deposit can be caused by high or low operating temperature of the bath. Make sure that the bath has been thoroughly mixed prior to measuring the temperature of the solution. If the temperature is too low adjust to the range recommended by the supplier.

Dull deposits in a hard chromium deposit can be caused by a high chromic acid to sulfate ratio. Analyze a plating bath sample for the concentration of sulfate, using a sulfate precipitation method or the Kocour centrifuge method. To calculate the ratio of the bath, divide the concentration of sulfate into the concentration of chromic acid to determine the chromic acid to sulfate ratio. If necessary, adjust the sulfate concentration, raising it with sulfuric acid or lowering it with barium carbonate, to the optimum concentration recommended by the supplier.

Dull deposits in a hard chromium deposit can be caused by a low concentration of secondary catalyst (if utilized). Analyze the sample to determine the concentration of secondary catalyst in the bath and adjust it to the optimum concentration recommended by the supplier. If you are utilizing a self-regulating mixed catalyst plating process, follow the recommendations of the supplier for hoeing the solution in order to adjust the fluoride to the proper concentration.

Dull deposits in a hard chromium deposit can be caused by a build up of metallic impurities, including trivalent chromium. Analyze the sample for common metallic impurities found in hard chromium operations, such as: iron, copper, and trivalent chromium and, if necessary, for zinc and aluminum. If the bath is high in trivalent chromium, over 3.75 g/L (0.5 oz/gal), you



should immediately investigate the cause of this build up. An increase in the concentration of trivalent chromium indicates either insufficient anode area in the bath or organic contamination of the solution. Insufficient anode area can be due to the fact that there are not enough anodes in the tank. Whenever possible you should maintain an anode to cathode area of greater than 1.5—2.0 to 1. Insufficient anode area could also be the result of anodes that have been insulated from the solution by poor contact with the anode buss or are scaled with lead chromate. When lead alloy anodes are in contact with a chromic acid solution and no current is being applied to them, they immediately begin to scale with lead chromate. Lead chromate is an orange-yellow scale that is a familiar site to all experienced chromium platers. Lead chromate scale does not conduct electricity, therefore, if it becomes too thick the anode will be insulated from the solution and will behave as if it does not exist. Anodes that are working properly have a brown, black coating of lead peroxide. If organic contamination is the cause of the build up of trivalent chromium, you should determine and eliminate the source of the contamination. No matter the source, trivalent chromium is easily reduced by dummy plating the solution using an anode to cathode ratio as high as possible (an anode to cathode ratio of 30 to 1 is optimum) at 6 volt potential, at operating temperature. If the concentration of metallic impurities such as iron, copper, zinc, or aluminum, exceeds 7.5 g/L (1.0 oz/gal) you should reduce these impurities via ion exchange, electrodialysis, porous pots, solution dilution, or other suitable method.

Dull deposits in a hard chromium deposit can be caused by chloride contamination of the solution. Chloride can affect the hard chromium deposit at concentrations as low as 0.023 g/L (0.003 oz/gal). Chloride contamination in a hard chromium plating operation is typically caused by the drag in of hydrochloric acid from a pretreatment pickling step, but chloride can also be introduced to the chromium bath via make up water. If you detect chloride contamination in the solution check the make up water for chloride content. If chloride is present, you should consider a water purification system for any water that is added back to a chromium plating tank. If the source water is free of chloride, you should increase rinsing between the hydrochloric pretreatment steps and the chromium plating tank. If chloride contamination is resulting in poor coverage on parts being processed, you can remove chloride in one of two ways. First, chloride can be precipitated from the solution as insoluble silver chloride (AgCl) by additions of silver oxide (Ag<sub>2</sub>O). Determine the amount of silver oxide needed to remove the chloride contamination using the following formula:

$$\text{g/L of Cl}^- \times 3.3 = \text{g/L of Ag}_2\text{O needed}$$

Chloride contamination can also be removed from a chromium plating bath by electrolysis. The bath is dummy plated using the same operating procedures described for the removal of trivalent chromium above. A word of caution is advisable at this point, chlorine gas is liberated from the solution during electrolysis, therefore, steps should be taken to ventilate the tank throughout this process.

### *Equipment*

Dull deposits in a hard chromium deposit can be caused by low current density. It is important to accurately determine the number of square meters of surface area to be plated so that the correct current density can be applied to the part. Once the measure of surface area to be plated has been determined, and the current density, in A/dm<sup>2</sup>, applied to the part should be controlled in amperes, not volts. Voltage in a hard chromium plating operation will vary based on the concentration of metallic impurities in solution. Since metallic impurities act as resistors to current flow in the system, as their concentration increases in the bath, it will require more volts to push the same number of amperes through the bath. Therefore, if you set the current density for the part using volts instead of amperes, as the bath ages and builds in metallic impurities, the effective current density on the parts will decrease. As a result, you may experience dull deposits. Low current density can also be caused by rectifiers and bussing that are undersized or are experiencing poor contact. As was mentioned earlier, hard chromium plating operations require extremely high current densities, in some cases, up to 10 times the current densities required for plating other metals. It is important to remember these current density requirements in order to determine the physical limitations of your equipment when bidding large jobs. It is a good idea, as part of a routine maintenance program, to inspect bussing connections for loose fitting joints and/or parts of the bussing that are warm to the touch. Bussing that is properly sized and is well connected will remain at ambient shop temperature. Bussing that is warm to the touch has resistance to current flow—the bussing is undersized for the part being plated or there is a loose connection in the system.

Dull deposits in a hard chromium deposit can be caused by intermittent contact during plating. If parts loose contact with the cathode bussing, chromium deposited after the current interruption may appear dull. Clean all electrical contacts, including anode and cathode bussing on a regular basis in order to ensure good electrical contact between all parts of the system. Consider utilizing a conductive grease and/or clamping work fixtures to the cathode bussing.

Dull deposits in a hard chromium deposit can be caused by high ripple. Ripple is AC Voltage divided by DC Voltage, expressed as a percentage.

$$\frac{\text{AC Voltage}}{\text{DC Voltage}} \times 100 = \% \text{ Ripple}$$

Ripple should be controlled as low as possible for any chromium plating installation, but it should not be allowed to exceed five percent. If ripple is present, you should immediately have a qualified electrician service the rectifier to replace defective diodes or add additional capacitors if necessary.

### *Surface Preparation*

Dull deposits in a hard chromium deposit can be caused by over aggressive reverse etching. Reverse etching is used in most hard chromium plating operations to condition the substrate, in order to improve adhesion of the chromium deposit to the basis metal. This process actually produces a microetch on the surface of the part. If the reverse etch current density is too high or the part is reverse etched for too long, the surface roughness produced can cause the final finish to appear dull. Ideally, the reverse etch process step should be carried out in a reverse etch tank, not the plating tank. Reverse etching in the plating tank will contaminate the plating solution with iron. In addition, if the plating bath utilizes a secondary catalyst, it is easy to over etch the work piece.

### *Substrate*

Dull deposits in a hard chromium deposit can be caused by rough base material prior to plating. A hard chromium deposit does not have the ability to level surface roughness, like a bright nickel or acid copper plating process. The chromium deposit will mirror the surface finish prior to plating. If the surface finish of the work piece prior to plating is rough and dull, the chromium deposit will be rough and dull. It is always a good idea to check the surface roughness of a part prior to plating in order to determine if an acceptable level of brightness can be achieved after chromium plating.

### **Preventative Maintenance**

Now that we have reviewed the causes of the most common defects in a hard chromium plating operation, I will suggest some practical steps you can take to prevent these problems from occurring in the first place.

### *Chemistry*

As is evident from the proceeding discussions, proper maintenance and control of the key operating parameters of the chemistry can eliminate the majority of the defects experienced in a typical hard chromium plating operation. Key chemistry operating parameters to control include:

- Operating temperature of the plating solution
- Chromic acid concentration in the plating and reverse etch solutions
- Sulfate concentration in the plating solution
- Chromic acid to sulfate ratio in the plating solution
- Metallic impurities, including trivalent chromium, in the plating solution
- Concentration of the secondary catalyst (if utilized) in the plating solution
- Concentration of chloride contamination in the plating solution

Documentation of key operating parameters of the process chemistry using SPC or other control mechanism can identify operational trends. These trends can be used to identify and eliminate problems before they occur.

I also recommend routine maintenance of the equipment, such as:

- Inspect bussing for loose contacts. Remember if any part of the anode or cathode bussing or fixtures is warm to the touch, it is undersized or there are loose contact points.
- Inspect anodes for the build up of lead chromate. Anodes that are operating properly will be covered with a brown, black coating of lead peroxide. Anodes that are covered with a yellow-orange lead chromate scale should be removed from the plating tank and cleaned in a proprietary anode cleaner.
- Strip contact points to remove metal build up from racks and fixtures.
- Have a qualified electrician check rectifier for ripple.

Finally, know your substrate:

- Determine surface roughness of part prior to plating. If the surface is rough or pitted, improve surface roughness prior to plating.
- Make sure that the surface film of the part is “water break free” prior to plating.
- Make sure that the work piece receives the proper time and current density in reverse etch process tank prior to chromium plating.

I have included a recommended preventative maintenance schedule:

Daily Checks:

1. Determine plating bath temperature and adjust to range recommended by supplier.
2. Inspect plating racks and fixtures and repair as necessary.
3. Adjust the operating level of the bath.
4. Stir solution thoroughly, using low-pressure air agitation.
5. Analyze solution for chromic acid, sulfate, and ratio and adjust to optimum concentration recommended by the supplier.
6. Put dummy cathodes in tank and electrolyze solution at maximum voltage for 15 to 30 minutes at start of each day.
7. After electrolyzing the solution check the anodes to ensure that they have a chocolate-brown appearance (lead peroxide). If the anodes are orange-yellow (lead chromate) continue to electrolyze them or remove them from the tank and immerse them in a lead anode cleaner until the lead chromate scale is removed.
8. Visually check meters, automatic feeders, temperature controls, and solution agitation—make sure that it is evenly distributed across the entire tank.

Weekly Checks:

1. Visually check anodes for proper activation.
2. Check and clean all electrical contacts.
3. Remove all loose parts from bottom of the tank.

#### Monthly Checks:

1. Clean and straighten anodes.
2. Analyze solution for metallic impurities, including trivalent chromium.
3. Calibrate amperage and voltage meters.
4. Analyze plating solution for secondary catalyst (if utilized) and adjust to optimum concentration recommended by the supplier.

#### Every Six to Twelve Months:

1. Pump bath into storage tank and remove sludge.
2. Examine tank and coils for cracks and leaks.
3. Clean all electrical contacts.
4. Inspect all temperature controls.
5. Check exhaust equipment for proper operation. Clean and repair hoods and ducts.
6. Clean and repaint outside of all tanks.
7. Inspect anodes; clean, straighten or replace as necessary.
8. Have a qualified electrician perform a complete maintenance check of the rectifier.

#### References

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