Troubleshooting Decorative Chromium Solutions

Anthony J. Varuolo MacDermid Inc. Waterbury, Connecticut, U.S.A.

Troubleshooting chromium plating solutions will be reviewed. The discussion will center on solving plating problems not only from a chemical standpoint, but from a total plating line standpoint. Chemical, physical, electrical and human conditions will be investigated. Trivalent chromium solutions will also be investigated and there will be a comparison between the two systems.

For more information contact:

Anthony J. Varuolo MacDermid Inc. Waterbury CT 06702 Phone: 203-575-7912 Fax: 209-575-7990 E-mail: tvaruolo@macdermid.com When one is producing high quality plated parts, whether on a plastic substrate or a metal substrate, solving chrome plating problems in a relatively short period of time is most important due to production requirements. The following discussion will help in identifying, and correcting many of the problems on a decorative chrome plating line.

Decorative Hexavalent Chrome

Hexavalent chrome plating rejects can be difficult to troubleshoot because with chrome defects it may be difficult to identify the problem. If one can not identify the problem, it is almost impossible to correct the problem. This is true with hexavalent chrome because unlike most plating solutions the are many external factors that effect the chrome deposit. We will investigate these factors later in this discussion. Therefore one must identify the problem, locate the origin of the defect and initiate the corrective action.

The chemistry of the chrome plating solution is important and must be kept within the parameters set forth by the chemical supplier. The external factor that effect the chrome deposit can be electrical, mechanical or human. I will reference these factors in the following discussion and one should keep these external factor in mind when troubleshooting chrome.

TROUBLESHOOTING CHART

Careful inspection of the defective parts will allow one to place the defects into one of the types listed below:

Problem	Cause	Correction
Poor Coverage	Low chromic acid High sulfate concentration High temperature Passive nickel	Analyze and adjust Analyze and adjust Reduce temperature Reduce Ni pH, carbon filter and decrease brightener
	Low current density Inactive anodes High chloride impurity	Increase current density Remove and clean anodes Remove chlorides

Burning, rough, gray deposits	Current density too high Temperature too low Chromic acid too low Low sulfate	Adjust current density Adjust temperature upward Analyze and adjust Analyze and adjust with sulfuric acid
	Bipolar condition	Check for bipolar
White-wash, dull gray	Low sulfate	Analyze and adjust
deposits, irregular white	Low catalyst	Analyze and adjust
blotches	Passive nickel	Reduce pH, carbon filter nickel
	Current interruption	Check rectifier, cathode rails, connections etc.
	Mechanical problems	Check live entry,
Iridescent or brown staining	Low sulfate	Analyze and adjust with sulfuric acid
	Low catalysts	Analyze and adjust F or other catalyst

At this point, each defect will discussed, the source determined and the possible root cause uncovered.

Poor chrome coverage or nickel show: complete coverage of the nickel plated part with little or no indication of a leave-off mark is the ideal situation. The chemistry of the chrome solution should be analyzed and adjusted as required. Low chromic acid concentrations and/or high sulfate concentration can be the cause of poor chrome coverage which is referred to as nickel show. The corrective action is straight forward, add chromic acid if low in concentration and reduce sulfate concentration by adding barium carbonate. Adding barium carbonate is done by making a slurry of barium carbonate and adding to the chromium tank with agitation. Barium carbonate takes about eight hours to react so it is best to make this addition after the work shift is over and agitation can be kept on the tank to help with the reaction. Please note that air agitation should not be used while plating hexavalent chrome.

Chloride contamination from drag-in of nickel solution or from city water supply can be the cause of nickel show. The reduction of chloride can be accomplished by electrolyzing the chrome bath at an anode current density of 200-250 ASF or by adding silver oxide to precipitate the chloride.

Mechanical or physical sources of nickel show can be traced back to improper racking or poor anode maintenance. Parts must be racked in such a manner that the parts do not shield each other. Anodes must be constructed of the proper material usually lead alloyed with 7% tin. Anodes that are working properly are ones that are gassing while the tank is operational. If an anode is not gassing, it must be removed and inspected. A chocolate brown coating, lead peroxide, is preferred. A yellow coating, lead chromate, is not acceptable. It is actually an insulator and must be removed by using a anode cleaner. Once cleaned and rinsed the anode may be returned to the plating tank. Anode and cathode rails and connections must be kept clean to insure proper current flow.

Passive nickel deposits can be a major cause of poor chrome coverage and unless one knows to investigate the nickel solution, it can be overlooked. After analyzing the chrome solution and determining that the anodes are active, the nickel should be investigated. This investigation is helped by plating Hull cell panels or other small scale testing of the solutions in question.

The panel testing of hexavalent chrome solutions usually is performed under the following conditions: 267ml Hull cell or equivalent cell, 108 °F, 5 amperes for 3 minutes plating time. Using a ruler, a measurement is made to determine how far across the cathode panel the chrome has deposited. The cathode panel is 100 mm in length and when the chrome deposits 75-80mm (or %) from the high current area to the low current area this is considered good coverage. Conversely, anything less than 75% coverage is not acceptable and may be the cause of nickel show on the work.

If the chemistry of the chrome solution is in range, the anodes are active, electrical issues are correct and the temperature is in range and the chrome coverage is poor, one needs to investigate the nickel deposit's activity. A nickel solution that is "dirty" with organic breakdown products will not readily accept a chrome deposit and will yield poor chrome coverage. This nickel is commonly referred to as passive nickel. Carbon filtering or batch treatment may be required to reduce the organic contamination in order to obtain a cleaner nickel commonly referred to as active nickel. Tracking the amount of organics in a decorative nickel can be accomplished by tracking the total organic carbon (TOC) level. TOC level is an excellent method to determine the cleanliness of a nickel bath. The chemical supplier of the nickel process will be able to inform the user of the optimum TOC level and the level at which a carbon treatment is required. Generally, a bright nickel may have a TOC of 10-15,000 ppm and if the TOC climbs to 25-30,000 ppm the solution needs to be treated to reduce the organics.

Nickel plating a Hull cell panel, followed by chrome plating the nickel plated panel can give a good indication of passive nickel if the TOC level is not available. Proper rinsing of the nickel panel is desirable prior to chromium plating.

There are times when a carbon treatment is not feasible and production must continue. Installing a chromic acid pre-dip directly prior to the chrome solution may activate the nickel surface

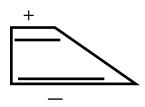
enough to increase the chrome coverage. Chromic acid pre-dips consist of 0.3-0.5 oz/gal chromic acid or varying combinations of chromic acid and sulfuric acid. In extreme cases an electrolytic pre-dip can be installed. The composition of these electrolytic pre-dips can vary by the manufacturer but they usually contain chromic acid and sodium bisulfate at concentrations that will carry 4-7 volts.

Burning: This defect is characterized by a dark, rough, gray deposit that occurs in the high current density of the part. Finding the root cause or source of burning should be straight forward. Analyzing the chrome solution and bringing the chromic acid and sulfate to optimum concentration is easy to do. Temperature and current density should be verified. Anodes must be active, i.e. gassing uniformly. Check for parts on the bottom of the tank to insure that a bi-polar condition does not exist.

Whitewash: This defect is characterized by white gray deposit that can be anywhere on the part. Whitewash is also referred to as false burn because it can be mistaken as a true burn when it occurs in the high current density area. It may be streaky or blotchy in nature. Low catalyst, fluoride, sulfate or other organic catalyst, may be the cause of white-wash but once these bath components are adjusted and the white-wash is still present, the source is either passive nickel or electrical in nature.

Although passive nickel has been discussed previously, we need to devote a little more time to it at this point. Many service people have spent countless hours troubleshooting the cause of white-wash and passive nickel. The Hi/Lo Plating Test is an excellent tool to help determine the cause of white-wash. This relatively simple test is described below.

The Hi/Lo panel test uses a standard nickel plating hull cell or equivalent test cell to plate a nickel panel at a "high" current density and a panel at a "low" current density. Both panels are subsequently chrome plated in a standard chrome cell. The theory behind this test is that the purity of the nickel deposit at the high current is better than the purity of the nickel plated at the low current, there are more organics co-deposited with the nickel than at the high current. The more organics that are co-deposited, the more passive the nickel deposit.



The nickel cell is set-up as illustrated and the chrome cell is set-up in the standard configuration.

- Panel #1 is nickel plated at 3 amperes for 10 minutes with no air agitation. It is rinsed and chrome plated at 5 amperes for 3 minutes. This is the Hi panel.
- Panel #2 is nickel plated at 3 amperes for 4 minutes to seal the panel then lowered to 0.25 amperes and continue to plate for 3 minutes. This panel is rinsed and chrome plated for 5 amperes for 3 minutes. This is the Lo panel

Evaluation of panels

- 1. A chemical imbalance in the chrome plating solution will produce defects (whitewash, rainbow or poor coverage) in both the Hi and Lo panels.
- 2. High organics (passive nickel) in the nickel will result in whitewash in the Lo panel because the impurities have been dummied out on the surface over which the chrome was plated.
- 3. If both panels show good chrome coverage without whitewash, both the nickel and chrome are free of defects. Therefore, the source of the whitewash is either electrical or poor quality rinsing between the nickel and chrome tanks on the plating line.
- 4. Repeating the test is beneficial.
- 5. If the Lo panel exhibits whitewash, the nickel solution can be carbon treated and the test rerun. A reduced TOC nickel solution should yield a whitewash free deposit.

If both Hi and Lo panels are defect free, one must investigate the quality of the rinse waters between nickel and chrome. The rinses must be flowing at a rate that will produce active nickel surfaces. This flow rate will vary from plant to plant. The time cycle between nickel and chromium must be minimal.

The chrome rectifier must produce DC current that is low in ripple. Rectifiers should be rated at 5% ripple or less at full output. High ripple will cause whitewash. A simple ripple meter can be used to check ripple. If a ripple meter is not available, ripple can be checked by using a VOM meter and a 0.1mfd capacitor. Measure the DC voltage with the VOM meter and then measure the voltage with the capacitor inline. This second voltage reading is the AC leakage, ripple.

Current interruption will cause whitewash. Insure that there are no "make and breaks" as the racks travel along cathode rails on return type machines. Cathode rails must be greased with conductive grease. Entry and exit shoes must be smooth in their operation. The use of a Tong Tester, clamp on ammeter, to track racks is a good method to investigate a break in the current.

Bi-polar is another condition that will produce whitewash. A bi-polar effect will happen when a part or rack becomes slightly anodic. This anodic charge will make the nickel plate passive and the subsequent chrome plate will exhibit whitewash.

The causes of bi-polar conditions are documented in several articles and will not be described

here. Suffice it to state that cathodically charged parts can become anodically charged if they come within close proximity to an anodic charge. This is the condition of bi-polar effect.

To prevent a bi-polar from happening live entry and live exit is used in the nickel plating tank and live entry is used in the chrome plating tank. It is best to use separate entry and exit rectifiers so that the current can be controlled at about 1.5 to 3.0 volts. The nickel anode baskets must be keep full and anode bags must be clean. Plugged anode bags and empty baskets can cause a bipolar effect as the racks exit the nickel tank.

Remove any fallen parts from the bottom of the tank to insure that the parts do not become part of the circuit.

Chrome pre-dips must be kept clean of organics and metals from the nickel rinses. Live entry into the chrome solution is required as mentioned before. There are ramp-up rectifiers that will transition from the live entry voltage to plating tank voltage automatically.

The last factor to take into consideration when investigating chrome plating problems is the human factor. Operators, platers, laboratory technicians, supervisors, maintenance people and managers must be trained in the art and science of plating so that everyone can contribute to solving the problem.

Trivalent Chrome Plating

The techniques used to service trivalent chrome defects are the same as hexavalent chrome: identify the problem, determine the source and root cause of the problem and implement the corrective action. The types of problems are somewhat different and will be discussed in this section.

Once again trivalent chrome plating problems can be caused by chemical imbalance or defects, mechanical issues, but unlike hexavalent chrome, electrical issues do not effect the trivalent chrome deposits. The chemistry of trivalent chrome solutions are similar to nickel plating chemistry and this may be why electrical issues are not critical. Trivalent chrome baths have organic additives for brightness that are similar to nickel brighteners. The pH is on the lower end of the range used for bright nickels. And the current density range is also similar, 30-40 amps/sq. ft.

Plating defects from a trivalent chrome bath are listed in	n the chart below.
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Defect	Possible Cause	Remedy
Dark Deposits	Excessive carrier or	Reduce additions and work
Ĩ	brightener Excessive chromium	solution Reduce additions
	concentration	
	Low pH	Raise pH
HCD Defects	Lack of boric acid	(See Note A) Analyze and adjust
(Burning, Missing)	Low chromium conc.	If possible, analyze and adjust using chrome liquid concentrate
	Lack of complexant	(See Note B)
	Lack of wetter	Analyze and complexant
	Lack of wetter	Add 0.05% wetter
	High pH	(See Note C) Lower pH
	Excessive C.D.	(See Note A) Reduce current
		(35-40 ASF)
LCD Darkness	Lack of boric acid	Analyze and adjust
	Lack of complexant	Analyze, and add 0.05% complexant
	Lack of wetter	Add wetter
		(See Note C)
	Metallic contamination	Dummy plate
	Lack of carrier	Analyze, and add 0.05% carrier
		(See Note D)
Staining	Poor rinsing after nickel plating	Improve rinsing
	Lack of wetter	Add wetter (See Note C)

	Low pH	Raise pH (See Note A)
White Streaks	Low pH	Raise pH (See Note A)
	Low C.D.	Raise current
	Lack of wetter	Add wetter (See Note C)
Blue Haze	Poor rinsing after nickel plating	Improve rinsing
	Lack of carrier	Analyze and adjust
Dark Streaks	Low pH	Raise pH
	Lack of boric acid	(See Note A) Analyze and adjust
	Lack of complexant	Analyze, if possible, otherwise add 0.05-
	Carrier has been added too quickly	0.1% complexant Work solution (See Note D)
Gray mark at nickel/ chrome boundary	Lack of wetter	Add wetter
chrome boundary	Lack of complexant	Analyze and add 0.1% complexant
	Lack of carrier	Analyze and add 0.05% carrier (See Note D)
Brown tint to deposit	Lack of carrier	Analyze, if possible, otherwise add carrier
	Poor rinsing	(See Note D) Improve rinsing (Use air agitation)
Low plating rate (Thin/Chrome deposit)	High pH	Lower pH (See Note A)
	Low chromium conc.	analyze and adjust with liquid concentrate
	Lack of complexant	Analyze and adjust

	Low brightener Lack of wetter	Add 0.1% brightener Add wetter (See Note C)
Poor Coverage	Low pH	Raise pH (See Note A)
-	Excessive C.D.	Reduce current
	Insufficient C.D.	Raise current
	Lack of boric acid	Analyze and adjust
	Lack of complexant	Analyze and make addition
	Low chromium.	0.1% complexant analyze and adjust with liquid concentrate
	Lack of wetter	(See Note B) Add wetter (See Note C)
Defect	Possible Cause	Remedy
Variable pH	Lack of boric acid	Analyze and adjust
High Voltage	Poor electrical contacts	Inspect and clean contacts
	Low conductivity of solution	Analyze solution, add plating salts
	Anode coating worn	Replace anodes
Random or no chromium in plated areas	Poor rinsing after nickel plating	Improve rinsing
NOTES		

NOTES:

A. The pH of the trivalent chrome solution is maintained at 3.0 to 3.7 electrometric.

When a correction is necessary, bring the solution back to the optimum pH of 3.4 with

either 10% sulfuric acid solution or 10% sodium hydroxide solution as appropriate.

Any additions to correct pH should be made SLOWLY with VIGOROUS AGITATION each addition not more than 0.01 %.

At a pH above 3.4, a loss of efficiency is experienced.

- B. An addition of 2.0% of liquid concentrate will raise the chromium concentration by 1 g/L.
- C. Wetter should be added at 0.05 % increments. If no improvement is observed, then further additions should not be made.
- D. Additions of more than 0.5 ml/L per day of carrier may induce dark streaking in the deposit.

If larger additions are required then solution should be thoroughly worked in prior to plating.

Discussion of the individual defects

Dark trivalent chrome color is one of the most common defect. High chrome metal concentration due to over additions is the most common cause of this defect. Chrome concentrate should be added and maintained by chemical analysis. The next most common cause for dark deposits is low pH. Installing a caustic pre-dip of 2-5 % by volume sodium hydroxide may be required. Raising the pH to the optimum is accomplished by making an addition of 20 % v/v of liquid caustic soda. Additions are made slowly and with vigorous agitation. Excess carrier or brightener component can darken the deposit.

High current density skip or miss is a defect that is characterized by having no plating in the high current density. This defect is caused by one or more of the bath components being low in concentration. Low chrome, low plating salts, wetter or complexant. Excessive current density will also cause the high current skip.

Low current density darkness. This defect is caused by metallic impurities from drag-in of nickel rinse water. Nickel, copper and zinc as metallic impurities must be dummy plated to an acceptable level or the bath can be treated with a purifier to precipitate the metallics. Also low boric acid, brighteners, wetter and complexant can cause low current density darkness.

Staining and white streaks as a defect is caused by insufficient rinsing between nickel and chrome. Lack of wetter and low pH are additional causes of this defect. The corrective action is to insure that the bath parameters are within operational range and that the rinses are flowing adequately. Filtering the chrome solution through activated carbon is beneficial.

Dark streaks and gray leave off at Ni/Cr boundary These two defects are caused by low wetter, low complexant and lack of carrier brightener. Organic impurities will contribute this defect. Carbon filtering will help in this situation.

Low plating rate is a defect that is manifested by thin chrome deposits and is usually caused by the pH being above the acceptable range. Sulfuric acid is used to reduce the pH value. Care must be used when reducing the pH. Add 25% by volume sulfuric acid carefully with air agitation. Low concentration of the bath components will also contribute to this defect.

Poor coverage is the inability to plate into the recess areas. Excessive current density will reduce the coverage and cause this defect. Reducing the current density is the corrective action. Trivalent chrome installations use insoluble anodes; either carbon anodes or iridium coated DSA anodes. Check for coating thickness for DSA anodes or anode area for carbon anodes. Defective anodes can cause poor coverage.

Fluctuating pH may be due to low boric acid concentration. Installing a pre-dip of 5% by volume liquid caustic soda can be helpful to stabilize the pH.

High voltage requirement may be caused by poor or dirty electrical connections. As with any plating tank the electrical connections must be kept clean. Low conductivity salts can also contribute to this problem.

Random or no chrome coverage can be caused by poor rinsing of the nickel deposit. Adequate rinsing between nickel and chrome is required.

The identification of defects in trivalent chrome deposits is straightforward. Electrical problems do not cause defects as they do with hexavalent chrome. That being stated, we still want to have low ripple from the trivalent chrome rectifier and we want to have clean electrical connections. Whitewash is not a defect that happens with trivalent solutions, but good housekeeping techniques will always produce the better quality deposit.

Although passive will not produce a whitewash defect, coverage of the trivalent chrome deposit will be reduced if the nickel is passive. The TOC of the nickel solution should be monitor to insure that the most active nickel deposit is attained as is possible. Actually a Hi/Lo panel test can be performed using a trivalent chrome to determine the organic load in the nickel. The defect will not be whitewash but will be poor coverage if the nickel is passive.

There have been reports that the Hull cell panel testing of trivalent solutions is not representative of what is happening in the plating tank, but using a plating test cell is still the best option. It may be that a liter beaker panel test is more representative of what is actually happening in the tank. This is just a twist in the troubleshooting technique that must be developed. Determining what is fact and what is not can be a challenge.

In conclusion, good service techniques must be employed when solving chrome plating problems. One must be methodical and investigate all of the parameter of the specific process as well as the parameters of the complete cycle. Investigate the chemistry, the electrical issues, mechanical issues and of the human factor. This human factor must not be overlooked. There are times when plating problems are caused by an individual's actions that may be either accidental or intentional.

Keeping the plater, foreman and machine operator informed and educated may give an insight as to the cause of a specific problem and more importantly may help solve a problem and prevent its reoccurrence.

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