A Review of Trivalent Chromium Electroplating

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Abstract

Over the last 20 years, trivalent chromium electroplating has been an environmentally friendly and productive process in comparison with hexavalent chromium plating. The factors contributing to this success will be discussed.

History of Trivalent Chromium Plating

Ecological considerations have spurred increased interest in development of trivalent chromium electroplating solutions as an alternative for conventional hexavalent chromium plating solutions. Initial work on chromium plating, ironically, started with a trivalent chromium electrolyte in 1854 by Professor Robert Bunsen.(1) This process required the use of a membrane electrode to separate the anode from the catholyte. The membrane system contributed to a reduced interest in conducting further research in trivalent chromium plating. In 1856 a hexavalent chromium process was reported in the literature by Guther (2). Probably this deposit was superior to the trivalent chromium deposit. Since then most of the reported research was based on hexavalent chromium deposits.

A renewed interest in trivalent chromium research in the 1930's produced many patents and papers. Probably because of limited knowledge of the chemistry of trivalent chromium complexes used in the proposed systems, none of the early processes gained commercial acceptance. Some of the problems with these processes included:

1) Diaphragms (membranes) are necessary to separate the anode from the cathode to eliminate the formation of hexavalent chromium and the formation of noxious and poisonous gases produced at the anode. Also the chromium deposits from these systems were dark in color compared to hexavalent chromium.

2) The trivalent chromium complexes required for successful chromium electroplating within the cathode film are slow in forming and is not stable requiring electrolysis to maintain the complex.

3) The processes have slow plating rates and could not produce deposits with thickness greater than 0.25-0.38 microns.

Probably the most significant development in trivalent chromium was the use of carboxylic and/or hydroxy carboxylic acids to form complexes with the trivalent chromium species. Cr^{3+} forms a very stable complex with water and substitution exchange rates is on the order of 10^{-6} whereas Ni^{2+} exchange rates of 10^{+4}.(3) The Cr^{3+} exchange rate is 10 billion times slower than Ni^{2+}. This slow exchange rate makes the Cr^{3+} hexaaqua complex ion very stable and this is why a ligand other than water is required to electrodeposit chromium from the trivalent state. The coordination chemistry of chromium and particular trivalent chromium is very complex and it is beyond the scope of this paper. For more information on the coordination chemistry of trivalent chromium see Cotton and Wilkinson. (6)

Commercially viable trivalent chromium processes use coordination complexes. A list of selected Cr^{3+} complexors is in Table 1.

Table 1

Species	**Formation Constant (log K)**
H_3PO_3	1.32 (45°C)
F^-	4.34
Cl^-	-.5
IO_3^-	2.11
NH_3	4.4
H_2CO_2	1.93 (25°C) 2.01(35°C) 2.10(50°C)(4)
$H_4C_2O_2$	4.63 (25°C) 4.68 (50°C) 4.70(75°C)(5)
$H_6C_3O_2$	4.70(6)
HSCN	1.09
$C_2H_5NO_2$	4.2

The trivalent chromium electrolyte must be tolerant to a reasonable amount of dragged in impurities. The covering and throwing power must be as good as and preferably better than hexavalent chromium processes. Also the bath chemistry should be stable and rapid in forming the required complex and should not be sensitive to make up procedure. In addition, the trivalent chromium electrolyte should be nontoxic and treatable by conventional waste treatment procedures. The desired process would be a system that did not require an expensive and difficult to control separate anode compartment.

Twenty years ago a process was developed based on trivalent chromium salt that substantially met these requirements. Over the years modifications have been made to the chemistry and operation of the process which made it progressively easier to use. Recent environmental legislation in the USA has altered the regulations concerning chromium plating. As of January 25, 1996, decorative hexavalent chromium platers have to monitor the following parameters:

- Emission limits
- Work practice standards
- Initial testing
- Ongoing Monitoring
- Record keeping
- Reporting.

Whereas, trivalent chromium, because of its low environmental hazard, requires electroplating shops only to maintain records and reports.(7)

Chemistry of Trivalent Chromium

In the history of trivalent chromium electroplating, the most successful trivalent chromium plating processes used complexors. Two basic chemistries have achieved commercial success. One is based on patents from Albright&Wilson (8) and the other chemistry is based on patents from I.B.M.(9) The differences between the two chemistries are in the complexor and anode. The I.B.M. chemistry uses a membrane anode that separates the anode from the electrolyte so hexavalent chromium is not produced at the anode. In addition the I.B.M. patents are based on a thiocyanate and/or amino acid complexor. The Albright & Wilson patents are based of carboxylic acids and do not use a membrane anode. The Albright & Wilson chemistry was introduced more than 20 years ago. Since its introduction, many improvements have been made to the basic chemistry to lighten the color and to improve the operating parameters. The color and operating changes will be discussed in a later section of this paper.

To understand the chemistry and how the chemistry affects the operating parameters an experimental design experiment was carried out to evaluate the main variables and their interactions. The main variables are pH, temperature, Compound A*, Compound B* and wetter. A modified Box-Behnken experimental design plan was used. Throwing or covering power, color and efficiency are the factors which were measured. These factors are the most important in evaluating the commercial viability of a trivalent chromium process.

Covering or throwing power is the ability of the metal to plate at a low current density. Figure 1 shows the results in relationship to temperature and pH. At lower temperature and higher pH better covering power is achieved and higher temperature and lower pH produces poor covering power.

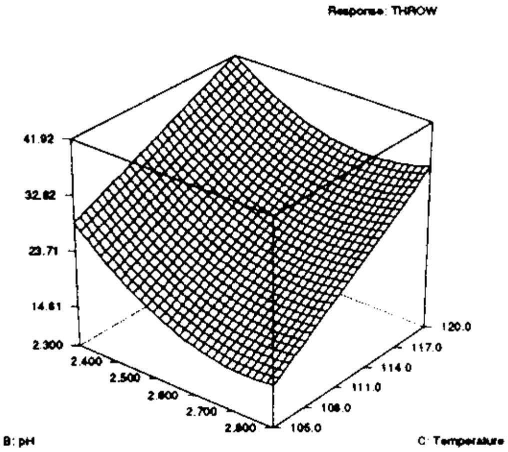

Figure 1

The main variables influencing cathode efficiency are the concentrations of compound A and Compound B. High concentrations of Compound A decreases the efficiency whereas Compound B concentration shows a nonlinear effect on the efficiency. At low and high concentrations of Compound B there is a decrease in efficiency and maximum efficiency is obtained in the middle of the range of concentration. (Fig. 2).

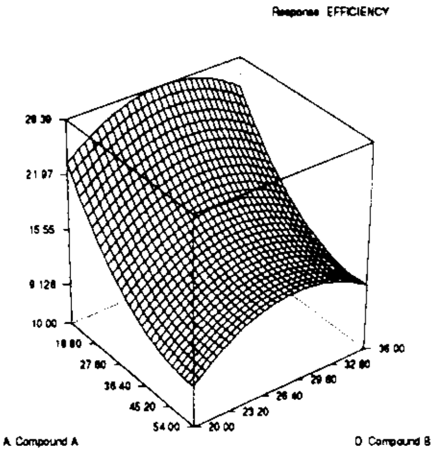

Figure 2

For decorative applications, color of the deposit is an important consideration. Color is very complex phenomenon and is related to the visual perception of tone and hue at various wavelengths of reflected light. (10) The color of the deposit was measured by a color spectrophotometer. This instrument, frequently used in the paint and coating industry for color formulation, has been useful in quantifying and objectively rating color of the deposit.

Results of the experimental design show Compound A, Compound B and temperature affect the color. Figure 3 shows the results of

* Compound A- Complexor 1
* Compound B - Complexor 2

color response temperature versus Compound A. As Compound A is increased the color becomes darker (higher number on the vertical scale). Also as the temperature is increased, the color becomes lighter.

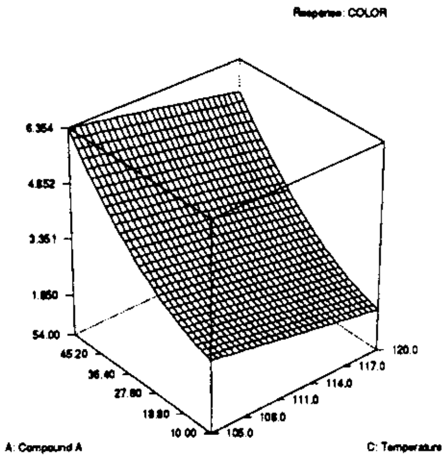

Figure 3

Understanding the various interactions of components and operating parameters provides the information to optimize the commercial application of the trivalent electrolyte.

Properties of Trivalent Chromium Deposits

Over the last 20 years testing has been done to evaluate deposit properties of trivalent chromium and to compare them with those of hexavalent chromium. Numerous papers describe the wear and corrosion properties of trivalent chromium. [11-13]

Comparing the wear resistance, as measured by Taber Abrasive Wear Tester, of the trivalent chromium to the hexavalent chromium deposit shows a small difference. (Figure 4)

The trivalent chromium coating has a micro hardness of 950 -1050 HK_{100} depending on the plating conditions. The hexavalent chromium coating has a micro hardness between 900 and 1100 $HK_{100.}$

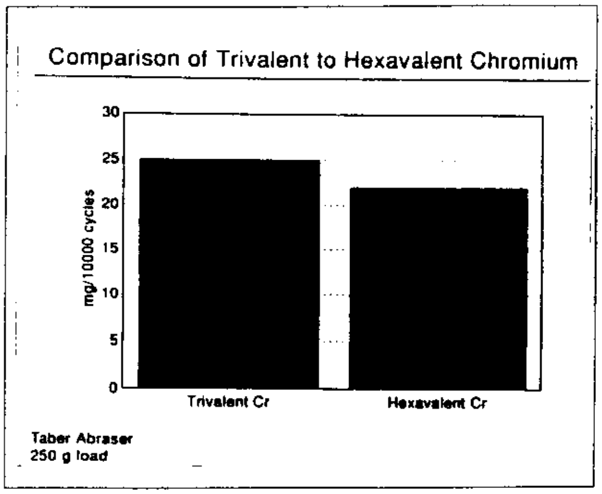

Figure 4

Corrosion properties of trivalent chromium for decorative thickness is more dependent on the nickel thickness in the system than is the case for hexavalent chromium deposits over nickel. Trivalent chromium electrodeposits are microporous in nature whereas hexavalent chromium deposits need special treatment to produce either microcracks or micropores. Considerable work shows that microcracked or microporous chromium has better corrosion protection than non-microcracked or microporous chromium.(11) Microdiscontinous (microporous or microcracked) chromium deposit distributes the corrosion potential over the small discontinuities in the deposit, reducing the rate of corrosion at each site.

For decorative application there should be a minimum of 2.5 microns, 0.25 mils, of nickel. At thicknesses less than 2.5 microns the nickel tends to be porous and since the trivalent chromium deposit is microporous itself there is a probability that some pores could be aligned creating a site for rapid corrosion in a corrosive environment. This is the reason for maintaining the proper nickel thickness in products which require maximum corrosion protection when using trivalent chromium deposits.

Hexavalent chromium chemistry has the advantage of being able to passivate the nickel and steel whereas the trivalent chromium cannot. This passivation offers short term corrosion protection on thin nickel deposits. In mildly corrosive environments there is a reduced amount of moisture to produce a corrosion enhancing electrolyte therefor the probability of rapid corrosion of the thin nickel with the microporous trivalent chromium is reduced. In addition trivalent chromium suppliers can recommend post dips to help protect the unplated areas.

Color

A frequently cited difference between trivalent and hexavalent chromium deposits is the color. Early versions of trivalent chromium coatings were darker than hexavalent chromium deposits. The trivalent chromium deposit does not have the blue white color of hexavalent chromium. Figure 5 shows the spectral analysis of the various perturbations of the trivalent chromium deposit. This graph shows that over the years the color of the trivalent chromium deposit has been lightened by the use of process optimization cited earlier to look similar to hexavalent chromium. Trivalent chromium 1 is the first generation of the non-membrane trivalent chromium electrolyte. The color of this deposit is visually darker than the hexavalent chromium deposit. Trivalent chromium 2 is the second generation of the non-membrane trivalent chromium electrolyte which shows a color more like the hexavalent chromium. When measuring the color any value less than two, 2, you cannot perceive this difference with the human eye.

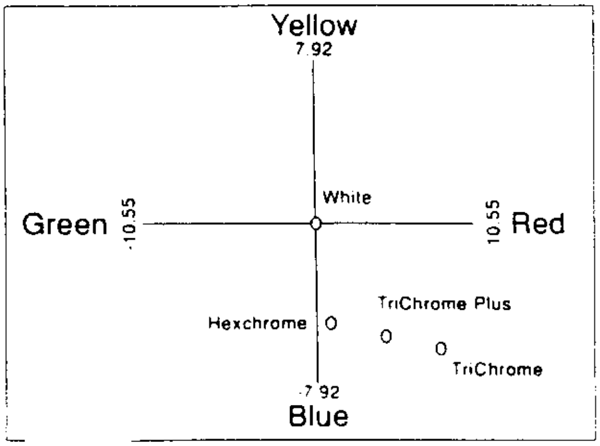

Figure 5

Process Parameters

There are several trivalent chromium electroplating chemistries commercially available. One commercial trivalent process is based on using a membrane anode system to separate the anode from the electrolyte. This prevents the formation of hexavalent chromium at the anode. The other trivalent chromium system uses graphite anodes with a soluble proprietary additive to prevent the formation of hexavalent chromium at the anode. The trivalent chromium system which uses the graphite anode is referred to as a single cell process. The operating parameters discussed in this paper will be based on the single cell process.

The electrolyte is based on the following chemistry:

1) Chrome 3^+ salt
2) Complexor
3) Conductivity Salt

This chemistry is similar to a nickel electrolyte except for the complexor. In addition, inorganic impurities that affect nickel have a similar effect to the trivalent chromium electrolyte. These inorganic impurities are mainly metals, Cu, Zn and Ni, and the problems that they cause are dark deposits and staining of the deposit. There are three ways in which the metallic impurities can be removed: electrolysis, precipitation and ion exchange.

Electrolysis (dummying) requires time and expense. The production tank is out of service while treating the solution unless there is an auxiliary tank.

With metal removed by precipitation a hazardous sludge is formed which requires filtration and disposal. In addition if to much of this material is added to precipitate the metals out it could ruin your solution. The most recent development in purification of trivalent chromium electrolytes is ion exchange. (14) A proprietary ion exchange technology which removes divalent cations but not trivalent, permits close operation of the plating solution. In addition there is no down time like electrolysis or chemical purification. The main benefits of ion exchange are the metallic contamination concentration is far below danger level, color of deposit and consistent product quality.

Environmental Factors

Hexavalent chromium is a suspected carcinogenic agent to humans whereas trivalent chromium salts have no known or suspected harmful effects. Other environmental benefits of the trivalent chromium electrolyte are no misting and reduction of sludge. Waste treatment of the trivalent chromium solution and rinse water is simpler than hexavalent chromium. The hexavalent chromium solution must go through a reduction step to convert it to the trivalent state. Since the trivalent chromium solution is already in this reduced state, treatment chemicals, equipment and time are not needed. These chemicals add cost and sludge volume.

Trivalent chromium solutions, contain approximately 20 g/L of metal whereas hexavalent chromium solutions contain 125 g/L of metal, drain significantly faster and more completely than hexavalent chromium solutions. Therefore, less chromium is carried on the plated part into the rinse tank which require waste treatment. Better drainage properties also results in less solution being trapped and adhering to welded and crimped areas. Not only does this reduce the amount of solution to be waste treated, but also reduces staining of the part.

Another source of hexavalent chromium which must be waste treated is from the fume scrubbers. Trivalent chromium processes do not mist as do hexavalent chromium processes. For this reason scrubbers are not presently required for trivalent chromium solutions. This eliminates the large capital costs and the expenses associated with operating, maintaining and record keeping associated with scrubbers. The lack of misting from trivalent chromium solutions has many beneficial effects. It dramatically improves the air quality for workers inside the plating shop and eliminates stains and sores which hexavalent chromium ions are capable of producing on human skin. In addition this lack of misting makes it easier to keep the tanks and other equipment adjacent to the chromium plating tank cleaner and safer.

Because of the many environmental, health and safety advantages of trivalent chromium electroplating processes, local, state and federal governments are encouraging the use of this process through regulatory measures which increase the severity of controls on hexavalent chromium electroplating processes.

Recent Developments

There is significant work in the literature over the past few years on different applications of trivalent chromium plating. Since this chemistry can tolerate current interruption better than hexavalent chromium could lend itself for barrel plating. A recent paper on barrel plating from a trivalent chromium electrolyte summarized the requirements to produce acceptable chromium plated parts in a barrel.(15)
Another development is the production of a chromite coating, Cr_2O_3, on various metallic substrates. The theory behind this technology is to poison the trivalent chromium electrolyte with peroxide, nitrate, phosphate, polyamines and formaldehyde. This poisoning inhibits the deposition of chromium metal and produces and oxide.(16)
Most of the recent literature with trivalent chromium chemistry is with producing thick, functional coatings. Several patents have been issued on the subject. For further information about functional plating from a trivalent chromium see references. (17-20)

Future of Trivalent Chromium

Decorative trivalent chromium plating processes have been commercially available and used since 1975. The primary benefits for conversion from hexavalent chromium to trivalent chromium are environmental issues, better coverage and higher rack density. With a better understanding of the chemistry and ease of operation and waste treatment and environmental regulation more shops will convert over to trivalent technology. In addition with the recent work on functional trivalent chromium it is only a matter of time before a commercial process is available.

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