Alternative to Hexavalent Chromium Coatings: Decorative & Functional Trivalent Chromium Plating

Donald L. Snyder, Ph.D. Atotech GMF Rock Hill, SC 29730 - USA

Trivalent chromium electroplating processes have been commercially used for over 25 years as an alternative process to decorative hexavalent chromium electroplating while offering environmental and productivity advantages. Deposits ranging from near-hexavalent to grayblack in appearance are available. Trivalent processes that produce deposits similar to functional hexavalent chromium are available but are considered experimental due to their inability to meet or surpass all the properties of hexavalent deposits. The status of these processes will be reviewed.

For more information, contact:

Dr. Donald L. Snyder Atotech GMF Rock Hill, SC 29730 Phone – (803) 817-3639 Fax – (803) 817-3624 E-mail: Dsnyder@atousa.com Because of HES concerns and public attitude, there is an ongoing discussion about the pros and cons of continuing usage of hexavalent chromium electrolytes to produce decorative and functional chromium electrodeposits. Very successful hexavalent chromium processes and deposits have been used for many years to meet critical service requirements. During this time, no alternative process has acquired a significant percentage of the market. Even with all of the regulations that are placed on the use of hexavalent chromium ions, the majority of platers have chosen to spend their money to install the necessary equipment and change their operating practices to meet the regulations instead of converting to alternatives.

Tighter OSHA regulations are currently being proposed for hexavalent chromium platers in the United States. Similar regulations are anticipated elsewhere in the industrial world. Platers, environmentalists, consumers, regulators, politicians and others have increased their dialog on the merit of converting to alternatives or spending additional money to meet these new regulations. For those who choose to continue to spend money to meet these regulations, will more money need to be spent later to meet tighter and more expensive regulations? And, in the end, will hexavalent chromium be banned as is being discussed in several places worldwide.

Trivalent chromium processes are one of several potential alternatives to hexavalent chromium. Because of trivalent chromium's reduced HES concerns, there are considerably fewer regulations compared to hexavalent chromium processes. Also, successful decorative trivalent chromium processes have been used worldwide for years. Established alternative processes for functional chromium deposits are limited.

Decorative Trivalent Chromium

Twenty-five years after the introduction of decorative trivalent chromium processes in the United States, it is being used by less than one third (approximately 200 accounts) of the potential platers. The percentage is even lower in most other countries. However, even with the small percentage, supplier surveys have shown that decorative trivalent chromium has been used on essentially every part being plated with decorative hexavalent chromium.

Trivalent chromium processes plate much further into the low current density areas of the part with less difference in thickness between the low and high current density areas than hexavalent chromium processes. It does this while plating 2 to 4 times faster at less than half the current density required for hexavalent chromium processes. Trivalent processes have no problems with current interruptions and normal ripple. White wash and burning are almost completely eliminated. These factors usually increase the overall productivity of the nickel/chromium plating operation. And, even though the actual plating chemistry is more expensive, the cost per plated part is usually less expensive than hexavalent plating. This low cost operation is obtained by being able to put more parts on the rack, fewer rework/rejects due to plating problems, and lower costs related to waste treatment, ventilation and fulfilling the regulations.

The maintenance of trivalent chromium solutions is more like a bright nickel than a hexavalent chromium process in that additives are added a little at a time based upon the number of amp-hours used. If maintained properly, the anodes of some trivalent chromium processes will last indefinitely and cost less to purchase than the lead anodes that are slowly consumed in hexavalent chromium process. Carbon on a filter and a long-lived ion exchange resin will remove all of the organic and metallic contaminants normally encountered. With some

supplemental evaporation to decrease solution volume, most of the dragged out trivalent chromium solution can be returned to the bath without concern for a build up of contaminants.

Converting to Decorative Trivalent Chromium

There are two major concerns for those who consider converting to decorative trivalent chromium. The one most often mentioned is color. "Trivalent chromium deposits do not look like hexavalent chromium deposits." This is generally true but some trivalent chromium processes produce deposits that are close enough in appearance that they are being placed adjacent to hexavalent chromium deposits on the same part without the end user noticing any difference. There are other processes that produce darker deposits. Some users prefer the darker appearance because of its unique, very eye appealing appearance. A color difference is really not a valid concern today.

Some users are utilizing the different colors of trivalent chromium deposits as an advantage when designing their parts. Figure 1 shows a color analysis of trivalent chromium deposits obtained from actual plating installations. A daylight light source is used with a pure white standard. A bright nickel deposit with its yellow/green hue is included for comparison.

Hexavalent chromium deposits are close to white with a blue hue mixed with a little red. One of the trivalent chromium samples, referred to as Near Hexavalent Appearance, is very close in appearance to hexavalent chromium deposits. It has slightly less blue and a little more red but it is hard to distinguish this with the eye. This deposit is used commercially on assemblies where trivalent and hexavalent chromium plated parts are attached adjacent to each other on the part. Another deposit, referred to as Standard Appearance, is from the trivalent chromium process most commonly used in North America. By itself, it appears like a hexavalent chromium deposit but if placed adjacent to a hexavalent chromium deposit it would appear darker. The Pewter Appearance deposit is darker with even more red and blue. It has a very pleasing appearance that some companies use to distinguish some of their products from others. Another trivalent chromium process that produces a deposit that is too dark to be shown in Figure 1 is used for its decorative gray/black appearance. Figure 2 shows plated nylon automotive door handles with this black trivalent deposit.





Figure $1 - L^*A^*B^*$ Methodology color analysis of commercially obtained trivalent chromium deposits

Figure 2 – Black trivalent chromium plated PA (nylon) plastic automotive door handles

The second concern that some people have when considering converting to decorative trivalent chromium is corrosion resistance. Because trivalent chromium chemistry is different, very extensive and long-term corrosion studies have been conducted on the deposits from one commercial trivalent chromium process to determine what differences there are, if any. There are two properties of trivalent chromium that hexavalent chromium processes do not possess that influence the corrosion resistance of all decorative trivalent chromium deposits. Trivalent chromium deposits are micro-porous as plated. Hexavalent chromium deposits require a pre or post operation to obtain the corrosion resistance enhancing benefits of micro-porous chromium. Automotive specifications require micro-porous chromium for exterior applications. Many corrosion studies have established that where micro-porous chromium over nickel is beneficial, trivalent chromium deposits offer equal or better corrosion resistance than hexavalent chromium made micro-porous. Under these conditions, hexavalent chromium deposits that were not made micro-porous would corrode much faster than micro-porous hexavalent or trivalent chromium deposits.

Where micro-porous chromium is not beneficial, such as over thin (less than 7.5 microns) nickel, trivalent chromium deposits might not perform as well as hexavalent chromium deposits. Hexavalent chromium solutions "chromate" metal that is not chromium plated offering some short-term corrosion resistance that trivalent ions cannot offer. Also, the pores in trivalent chromium deposit might line up with the pores in the thin nickel forming a direct path to the substrate for corrosion. As-plated, low porosity hexavalent chromium deposits along with its "chromating" effect retard the corrosion in these nickel pores/defects. However, many parts with thin nickel are satisfactorily plated with trivalent chromium. Post-trivalent chromium treatments have been developed, when needed, that make trivalent chromium acceptable in most thin nickel applications.

The physical properties (color, corrosion, etc.) of modern trivalent chromium deposits, under most conditions, are equal to or better than hexavalent chromium deposits. Trivalent processes are almost always better as far as productivity and HES are concerned. Many papers have been published reviewing the properties of trivalent chromium processes and their deposits. Then, why haven't more platers converted? Many reply:

"Why should I, I am comfortable with hexavalent and I meet the regulations."

"What do I do with all of my old hexavalent chromium solution?"

"All of my customers might not accept the change."

"I am not convinced it is as good as I have heard/read."

More than 25 years of successful performance on almost every chromium plated part has not convinced the majority of platers to switch to any of the HES friendly trivalent chromium processes available from several suppliers. HES concerns alone have only converted a few platers. Productivity increases have been more of a motivator than HES. Like a pair of comfortable old shoes, decorative hexavalent chromium will continue to be used unless they are forced to change.

Functional Trivalent Chromium

Hundreds of platers and end users have experienced the benefits of decorative trivalent chromium processes for numerous years. Processes are available from several suppliers with years of technical experience to back up their products. This is not the case for functional trivalent chromium processes.

A few research groups (university, research centers, and suppliers) report that they are working on functional trivalent chromium processes. A number have published some results while keeping pertinent information proprietary. One trivalent chromium brush plating process that can be used for functional chromium applications has been commercial for several years. Another company is in the process of qualifying their trivalent chromium rack process for a commercial functional chromium application. A couple of research/development organizations are reviewing experimental functional trivalent chromium chemistries obtained from other developers. Their intent is to commercialize a process even if acceptable for only a limited market. At least one of these organizations is using EU funding to conduct research/development to try to enhance their preferred process. Using functional hexavalent chromium deposits as the standard, they are evaluating corrosion resistance and wear of the deposits. These are the two most important physical properties of functional chromium deposits. Plating efficiency, high to low current density thickness ratio, hardness, post plating operations and HES concerns are also important. A significant advantage in one factor might overcome a minor deficiency in another.

Three generic functional hexavalent chromium chemistries are used worldwide. Using chromium trioxide, commonly called chromic acid, as the source of chromium ions, they use different catalysts to enhance the plating conditions and the resulting deposits. The oldest process, but still widely used, is referred to as the Conventional bath. It uses sulfate ions as the catalysts. Even though the physical properties of the deposits from this process are not as good as the other two, they more than meet the requirements of many applications. A process that produces deposits at a faster plating rate and with better physical properties is called a Mixed Catalyst system because it uses sulfate and fluoride ions as catalysts. There are far more platers using these two types of chemistries than the third, an Organic Catalyzed process. The Organic Catalyzed process is primarily used in large volume applications where wear, corrosion resistance and plating rate are especially important.

All functional hexavalent chromium deposits contain micro-cracks. The crack density and depth of the micro-cracks vary among the three generic types of processes. Figure 3 shows a surface view and cross-sectional views of these deposits. The Conventional deposit has less cracks but many of them penetrate completely through the deposit. This offers a site for corrosion of the substrate. The Mixed Catalyst deposit has more micro-cracks but they are shallower. Very few micro-cracks penetrate complete through the deposit. This improves the deposit's resistance to substrate corrosion. The Organic Catalyst deposit has many times more micro-cracks but they "heal" during the plating operation and do not penetrate completely through the deposit. As with micro-porous decorative chromium deposits, these microdiscontinuities spread out the corrosion current and greatly retard corrosion penetration to the substrate.



Figure 3 – Top surface and cross sectional views of functional hexavalent chromium deposits showing the micro-crack patterns

The chemistries of trivalent chromium processes are much more complex than hexavalent chromium. The literature describes a couple generic ways of producing their operating solutions. One starts with hexavalent chromium and reduces it in such a way that generates an operating trivalent chromium process. The other starts with trivalent chromium salts and adds the necessary ingredients to produce an operating process. The chromium ions concentrations, plating current densities, plating rates, bath chemistry, pH and some of the physical properties of the deposits also differ.

In order to simplify a comparison between trivalent and hexavalent chromium deposits, only the deposit properties from one trivalent chromium process will be reviewed. This process uses trivalent salts as its source of trivalent ions. The process maintains a constant plating rate of between 25 and 50 microns per hour at 43 to 49 C and a pH of approximately 2.2. The graphite anodes can last indefinitely, do not need to be conditioned, and will not form hazardous lead/chromium sludge as in hexavalent chromium operations. The operating solution can be maintained indefinitely by making adds to replace the consumables. Ion exchange removes all of the metallic impurities commonly present in functional chromium applications such as iron, copper, nickel, and zinc. Organic contaminants are removed by carbon placed on a filter. Hexavalent chromium contamination is immediately converted back to trivalent chromium solutions is usually more expensive than disposing of the solution. Some literature reports that at least some of the hexavalent chromium solutions must be removed about every five years to "purify" the solution. If the volume is large enough, it could be sent to a treatment plant that uses the chromium content as a raw material for stainless steel or other applications.

To reduce the replenishment cost of the chromium salt, a common large volume trivalent chromium salt containing sodium sulfate is used. Excess sodium sulfate has no detrimental effect upon the bath operation. However, if solution drag out is reduced to almost zero, sodium sulfate will reach its solubility limit and form large crystals that are easy to filter out. These

crystals can be easily rinsed to remove chromium ions. Waste treatment of the solution is much easier and produces considerably less sludge than hexavalent chromium solution because it is already in the trivalent state and contains about one-tenth the chromium ion concentration. The solutions used to regenerate the trivalent chromium's ion exchange unit can be mixed with the trivalent chromium rinse water and treated together.

To obtain good adhesion between the substrate and the chromium, it is typical for hexavalent chromium platers to reverse etch their steel parts in the plating bath. This builds up iron contamination that eventually makes the process inoperable if not removed. To reduce iron contamination, some use a separate solution to etch the part outside of the plating bath. Functional trivalent chromium platers can also etch their parts in a separate tank when required for adhesion. Others plate a thin nickel deposit on the part prior to trivalent chromium plating. This nickel layer produces excellent adhesion between the substrate and the chromium and also helps improve the part's corrosion resistance. The major disadvantage of all known functional trivalent chromium deposits, except for the brush plated process, is that they contain micro-cracks when plated. Many of these cracks go all the way through the deposit similar to the cracks produced from Conventional hexavalent chromium processes, Figure 3. Without the nickel deposit or some post treatment, thick trivalent chromium deposits do not retard substrate corrosion as well as the Mixed or Organic type hexavalent chromium deposits.

Figure 4 shows these micro-cracks in a magnified top view of an eighteen-micron thick trivalent chromium deposits with and without a brightening additive. This additive also produces about 10 % leveling which is unique for chromium deposits. Without the brightener, the deposit contains nodules as can be seen at 500 X magnification in Figure 4A. Hexavalent chromium deposits also produce some nodules when plated thick. Figure 4B shows a deposit with the brightener. Even at 5 times the magnification of Figure 4A, no nodules are visible. However, the micro-cracks are visible in both pictures. Trivalent chromium deposits have a much lower high current to low current density thickness distribution. The lack of nodules, the leveling effect and the lower current density thickness distribution reduces or eliminates the need for mechanical post treatments. However, since post treatments many times improve the corrosion resistance of hexavalent chromium deposits, trivalent deposits might also benefit.



Figure 4A – 500 X magnification of an 18-micron thick trivalent chromium deposit without a brightener



Figure 4B – 2500 X magnification of an 18-micron thick trivalent chromium deposit with a brightener

Thick trivalent chromium deposits appear to be amorphous in structure in contrast to hexavalent's body-centered-cubic (bcc) structure. Annealing at 350 to 400 C for 15 minutes converts the amorphous structure to bcc. This conversion also slowly takes place while the part is in service, depending upon the amount of heating. The conversion also increases the hardness but, due to shrinkage of the structure during transformation, it increases the width of the micro-cracks. Table 1 gives some typical laboratory obtained micro hardness values. A unique property for trivalent chromium deposits is that they harden when heated while hexavalent chromium deposits can soften.

Figures 5 and 6 contain some standard wear test data comparing trivalent with hexavalent chromium deposits. Using a Taber Abraser, Figure 5, the wear of both deposits is about equal even after aging the deposits for up to 8 weeks. The Falex Wear Test, Figure 6, indicates that a trivalent chromium deposit has much better wear resistance. Heat-treated, trivalent chromium deposits are even better.

	Trivalent	Hexavalent
	Chromium	Chromium
As-Plated	1000 KHN ₁₀₀	1000 KHN ₁₀₀
Heat Treated 400 ^o C for 15 min	1600 KHN ₁₀₀	800 KHN ₁₀₀
Heat Treated 800 °C for 15 min	1400 KHN ₁₀₀	300 KHN ₁₀₀

Table 1 – Typical micro-hardness values for as-plated and heat-treated functional trivalent chromium deposits



Figure 5– Taber Abraser Wear Test results for hexavalent and trivalent chromium deposits over time



Figure 6 – Lubricated Wear Test (Falex) results for hexavalent, trivalent, and heat-treated trivalent chromium deposits

The Status of Trivalent Chromium Processes Today

Decorative trivalent chromium processes have been successfully used for over 25 years on many applications over a wide variety of nickel thicknesses. When the productivity advantages of trivalent chromium processes can by utilized, the cost per part can be less expensive than plating from hexavalent chromium processes. There is also a great advantage in HES issues.

The status of functional trivalent chromium processes is less clear. Many of the requirements for functional chromium deposits have been obtainable in the laboratory. However, uncertainty remains about the impact that trivalent's different deposit structure and the micro-cracks will have on long-term serviceability. The EU project (Ecochrom), the most comprehensive study being conducted today, might answer some of these questions. If they commercialize a process after their study, as planned, the service experience will go a long way to help understand what is required from a functional trivalent chromium deposit.