Trivalent Chrome Overview

Q. In the last year, the industry has moved rapidly to change over to decorative trivalent from hexavalent. As an applicator, we find there is no shortage of information, but the topic is so complex, we don't even know where to begin, specifically when deciding between chloride and sulfate-based systems. Can you provide an overview of the topic and a review of what factors we may want to consider as we evaluate our choices?

A. It is quite common to be at a loss for where to begin when sifting through the large volume of information available regarding this transition. When talking with other applicators in your situation, I have found it helpful to provide an overview that offers a basic history on the usage of trivalent chromium, the important industry testing that has occurred to validate its usage, and then offer a comparison of the two types of systems and factors to consider when selecting what is right for your situation.

Due to the amount of focus currently on this topic in the industry, I would be remiss if I did not first address a common misunderstanding between decorative trivalent plating and hard chrome plating. Decorative trivalent chromium is not the same as hard chrome plating, nor is the availability of technology the same. That is a topic in and of itself. For the purposes of this article and your question, we will discuss information related only to decorative chrome plating.

To begin with a basic history, many people don't realize that decorative trivalent chromium has been used in exterior applications for decades. Specifically, it has been used in the over-the-road trucking industry for well over 30 years, with the heaviest usage being on truck bumpers and stacks. In the beginning, trivalent chromium was chosen primarily for its operational efficiencies as it offered better coverage and less burning than hexavalent chromium. From an appearance standpoint, the earlier versions of decorative trivalent chrome were quite a bit darker (average L* value of 74-75) than hex chrome (average L* value of 81-83) which unfortunately tarnished its reputation for a while. However, as with other plating processes over time, the technology has advanced and the color value and appearance of trivalent plating systems on the market today is much closer to hexavalent (with L* values ranging from 76-82, depending on which process you choose).

Over the years, extensive testing has been completed to gauge the performance of decorative trivalent plating in the field. In the mid-1970s, CASS testing and mobile performance tests were conducted by ASTM International (formerly

known as American Society for Testing and Materials). Plated in accordance with ASTM-B-456, testing was performed on steel 4 x 6 inch panels that were mounted on truck trailers traveling primarily in the rust belt. Extensive data is available for these tests, but a brief summary revealed microporous hexavalent chromium and trivalent chromium performed best in long-term outdoor exposure in these real-world tests and both performed identically in the protection and appearance ratings. As mentioned, the ASTM tests were conducted in the mid-1970s.

More recently, however, USCAR conducted a three-year field test study of trivalent chromium deposits. USCAR (United States Council for Automotive Research, LLC) is a collaborative automotive technology company whose member companies include Ford Motor Company, General Motors and Stellantis. Their primary goal is to strengthen the technology base of the U.S. auto industry with research and development. In 2020, USCAR released the findings of its "Final Assessment of Decorative Trivalent Chromium Exposure in Winter Environments" study. A summary of the study was published in the March 2020 issue of *Products Finishing*.

USCAR wanted to better understand the corrosion performance of trivalent chromium in CASS, calcium chloride and real-world winter conditions with a focus on general corrosion, high chloride corrosion, as well as color and color stability. The main goal was to identify whether sulfate or chloride should be used industry-wide for the U.S. car manufacturer's supply chain. As part of the three-year field study, chloride systems were tested against the sulfate systems, and the data determined chloride systems performed better in high chloride corrosive environments than the sulfate systems. With respect to the specific performance in high chloride regions, the study found that chrome loss was more prevalent on sulfate-based chemistries than on chloride-based chemistries. The study revealed that 13 of 14 chemistries with significant chrome loss were sulfate systems. Again, these test results are specific to the USCAR field study, but the information is worthy of reference and consideration for any decorative plater working with automotive OEMs.

Recently, heat exposure testing was performed by a third-party Tier 1 supplier on automotive exhaust tips. The testing compared hexavalent chromium against a popular trivalent chloride system, trivalent sulfate system, and a newer technology trivalent system with reclaim abilities. The results of the testing revealed that after heat cycling the sulfate system's color degraded to become less white and less blue than the chloride-based systems. In other words, the chloride systems behaved similarly to hexavalent chromium systems. The results were comparable to those obtained in the USCAR field study. Follow up salt spray testing post-heat exposure also showed delamination and pitting on the sulfate sample. It is worth noting that

the automotive sector is interested in the results of the heat exposure data and further testing will be completed.

Initially, trivalent chromium was used for its operational efficiencies, however, today we find it is primarily the regulatory drivers such as REACH, OSHA (employee exposure), and EPA (wastewater, emissions, PFAS) moving the process forward. This has led the automotive industry to further sharpen its focus and enhance testing on the performance of trivalent chromium plating. As a result, applicators are increasingly becoming aware of the color stability and corrosion performance differences between the two systems.

When evaluating the choice between chloride and sulfate-based decorative trivalent systems, there are several factors to consider. Appearance and corrosion performance, plating rate in microns per minute, and anode type and functionality are all central to the evaluation.

Appearance or color is often the first consideration. Though we know both sulfate and chloride trivalent are not quite as white as hexavalent chromium, the good news is both are very near in color, almost to the point of being indistinguishable to the average eye. Based on the supplier, different systems can offer varying levels of L*a*b* values, so we often recommend applicators send in samples to be processed in the actual chemistry, request finished samples for evaluation, or ask to visit shops using the process to see the production line. Again, we encourage any applicators doing heavy work with automotive OEMs to review the USCAR field study summary in depth when considering performance factors. In terms of color stability, when referencing the USCAR field study, the data shows chloride systems are more color stable than sulfate systems. A related critical performance characteristic is corrosion resistance, and the data from the field study revealed chloride systems ranked higher in providing better corrosion resistance, especially in high chloride corrosion environments.

The next thing to highlight is the operational comparison of the plating rate in terms of microns/minute. This is a key consideration for applicators when deciding whether to install sulfate or chloride. When making the switch from decorative hexavalent to trivalent, many shops look at their existing line layout and timing and want to be able to maintain as close to the same process and plating speed they had with hexavalent plating to maintain their efficiency. Chloride systems have a plating rate that is identical or slightly faster than hexavalent chromium, averaging 0.1 to 0.25 microns per minute. Sulfate systems plate at half the speed of a hexavalent system, averaging .04 to .08 microns per minute. For applicators with return automatic lines, the speed is a very important factor to consider when choosing a sulfate system, as a larger tank size or possibly a new line might need to be constructed to accommodate switching to the slower plating speed. With a hoist line, you would need to add additional stations to account for the longer plating time with sulfate. This can be a concern based on your building footprint and floor-space limitations. If choosing a chloride system, speed will be less of an issue as it does not require additional plating time when converting from hexavalent chromium, so you will not need to lengthen your plating tank on a return automatic line or add another station on your hoist line.

A final operational difference to consider is the anode type and functionality. Anodes for chloride baths are graphite and have an extremely long life. I am aware of a shop that has had the same graphite anodes for 25 years. Sulfate baths require mixed metal oxide anodes which are typically replaced every few years. These anodes can be quite expensive, and they are also more delicate and require special shielding to ensure they do not get damaged or scratched. If the surface does get scratched, the electrolyte can begin building slight amounts of hexavalent chromium which, in turn, will lower the efficiency of the bath drastically. If you go in this direction, it can be helpful to note that most high-volume trivalent sulfate applicators will keep an additional set of MMO anodes on hand to accommodate this concern and prevent downtime if the surface gets damaged.

With the increasing and ever-tightening regulations and controls on hexavalent plating for both environmental and worker exposure, the benefits of making the switch can quickly be realized by the applicator. All things being equal, when switching to either chloride or sulfate decorative trivalent baths from hexavalent, trivalent offers better throwing power, is extremely tolerant to current interruption, is not prone to burning or nickel show, offers increased production and decreased rejects, and will greatly enhance employee safety.

As indicated in your question, the industry is indeed moving rapidly on this front. It is important to be aware that OEMs are actively changing process standards and developing new color standards. Specs are being reviewed and revised regularly to specifically call out trivalent chromium. Collaborative efforts are also happening across the industry: AIAG is reviewing related quality requirements of the applicators, and a workgroup of ASTM's B08.10 subcommittee is in the process of developing new thickness testing standards for trivalent chrome. On a global level, we are aware of numerous decorative trivalent RFQs circulating and Tier suppliers and automotive OEMs that are seeking platers who have already made the conversion to decorative trivalent chromium. This industry movement has led applicators to begin rapidly installing baths and preparing to make line adjustments to accommodate the transition. Your review of this information as you evaluate your choices in this decision is well timed.

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