The Decorative Colors of Trivalent Chromium Deposits

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Trivalent chromium electroplating processes have been commercially available since the mid 1970s. Processes are available today offering deposits with colors varying from gray-black to almost the blue-white appearance of hexavalent chromium. Changes in bath operation and electrolyte formulation control the deposit's color, plating rates, and physical properties.

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Trivalent chromium processes have been used commercially in the United States since the mid 1970s. Based upon sales, it is estimated that approximately 40% of the proprietary decorative chromium sold in 2001 was trivalent. The health, safety, and environmental advantages of trivalent chromium processes are well known. Many platers have converted to trivalent processes because of these reasons. However, increased productivity is probably the main reason for conversions today. The cost per liter of trivalent chromium solutions is more expensive than hexavalent chromium solutions. However, for most platers, trivalent chromium electroplating is less expensive per plated part than hexavalent chromium. The lack of burning and whitewashing, tolerance to current interruption, and improved throwing and covering powers contribute to the increased productivity. The lower cost for waste treatment and EPA/OSHA compliance issues are also factors.

There are several different trivalent chromium processes, some commercially available while others presently have limited or no commercial availability. Two classes of processes distinguish the different methods uses to produce trivalent chromium electrolytes. They involve the source of the trivalent chromium ions and the method employed to apply electric current during plating.

1. Processes using trivalent chromium salt(s) mixed with chemicals that permit chromium to be electroplated.
    a. Processes using DC current at a current density within the range of nickel and decorative hexavalent chromium processes.
    b. Processes using DC current at a current density higher than decorative hexavalent chromium processes.
    c. Processes using "charge modulated electric field waveform" (pulse plating).
2. Processes using chemical reduction of hexavalent chromium ions to form trivalent chromium ion complexes. This procedure excludes the formation of the very stable hexa-aquo coordinated trivalent chromium complexes. These processes typically use current densities in excess of hexavalent chromium processes.

The processes that form the trivalent chromium ions and their complexes in situ, process 2, are primarily being developed to produce thick trivalent chromium deposits (functional chromium). Processes 1b and 1c are also being developed primarily to produce thick trivalent chromium deposits. Even though many of these processes can produce deposits as thick as hexavalent chromium processes, their deposits do not have all of the physical properties of traditional functional hexavalent chromium deposits. For example, at this time, the corrosion resistance of thick as plated trivalent chromium deposits is not as good as many functional hexavalent chromium deposits. This is commonly measured by the length of time the substrate is protected from corrosion during neutral salt spray corrosion testing. Cracks which permeate through the trivalent chromium deposit from the surface to the substrate are responsible for this reduced corrosion protection. With some processes, this can be overcome by nickel strikes prior to chromium plating or by post chromium treatments.

At least one trivalent chromium product line that fits process 1a above is being used extensively today for decorative chromium plating applications worldwide. Some of the processes within this product line can also produce thick trivalent chromium deposits. A review of the different processes within this product line follows.

The Many Colors of Trivalent Chromium Deposits

One method to distinguish among the different commercial trivalent chromium processes in this product line is to organize them by the color of the chromium deposits that they consistently produce. Historically, color has been used to distinguish between hexavalent and trivalent deposits.

- Pewter/Stainless Steel appearance
- Standard appearance (color of the most common commercial process)
    - Normal plating speed
    - High plating speed/Thick deposits
- Near hexavalent chromium appearance
- Gray-black appearance

A color analysis using the L*A*B* Methodology on commercially obtained deposits is shown in Figure 1. Day Light 65 is the reference light source for these measurements. Bright nickel is included as a reference because most decorative platers are familiar with its appearance. The gray-black deposit is off the scale in the blue/red quadrant and is not includ

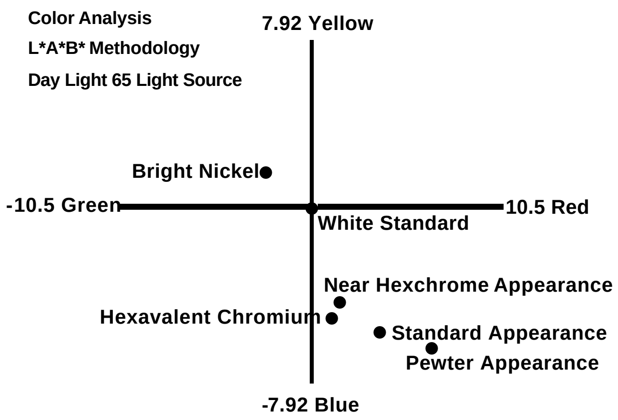

Figure 1 *– Color Analysis of commercially obtained deposits using processes designed to produced different colors*

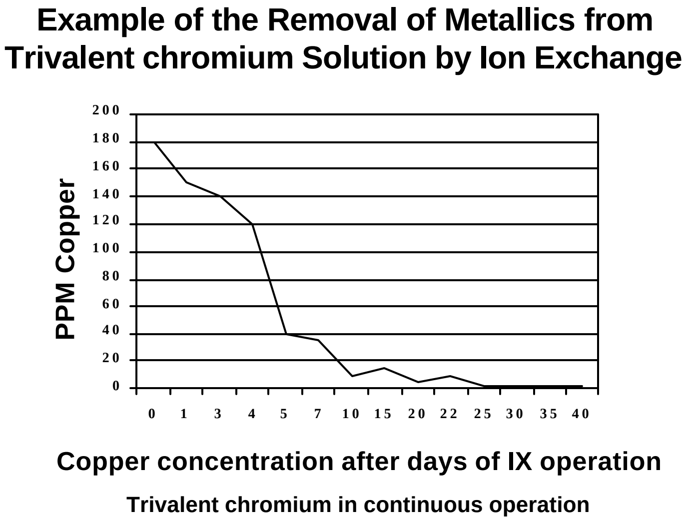

Figure 2 *– Removal of Copper by Ion exchange*

The operation of each of the trivalent chromium processes in this product line is very similar. Most platers report that the plating operations are comparable to their bright nickel process that precedes the chromium. With a few adjustments, they can also use the same equipment they used with their hexavalent chromium process. After cleaning the plating tanks (or reline), the ventilation system (scrubbers usually not required but check with local agencies) and other equipment that contain hexavalent chromium, they can be used for trivalent chromium processes. Most platers use their hexavalent chromium rectifiers but nickel rectifiers can also be used because ripple filters are not required. Special graphite anodes are required but they cost about the same as lead anodes and will never need to be replaced unless they are mechanically damaged. These trivalent chromium processes start plating about 5 A/dm^2 (50 ASF) instead of the10 A/dm^2 (100 ASF) for hexavalent chromium. No start-up or shutdown procedures are necessary.

The plating rate is consistent throughout the plating operation when additions are maintained by amp-hours.

The normal nickel waste treatment system can be used to treat trivalent chromium solutions because the chromium is already in its reduced trivalent state. However, less chromium per part is dragged out of the operating tank because trivalent chromium solution drains much faster and more completely than hexavalent chromium solution. Therefore, less solution per part is transferred to the rinse tanks. An added plus is that, on a dry basis, about one-seventh as much sludge is generated per liter of waste treated plating solution. Even though waste treatment is simplified, these trivalent chromium processes permit complete recycling of the solution. An atmospheric evaporator can be used to adjust solution volume if necessary. Carbon can be added to a filter to remove foreign particulate and organic contamination. A very unique ability of these processes is that their operating solutions can be treated with a special ion-exchange resin that lasts for many years. The resin removes metallic impurities such as iron, copper, nickel, and zinc directly from the plating solution without removing trivalent chromium ions. Figure 2 demonstrates this operation by plotting the removal of copper from an operating trivalent chromium solution simply by passing the operating solution directly through the ion-exchange unit and back into the operating tank.

Trivalent chromium solutions are tolerant to dragged in sulfate, chloride and boric acid from the preceding nickel process. Also, there are no additives that breakdown and accumulate in the electrolyte. Hexavalent chromium ions are not formed in the bath under normal operating conditions. Even the addition of moderate amounts of hexavalent chromium ions to the bath can be tolerated and results only in a change in consumption rates. These are all indications of the long-term stability of the processes.

Pewter/Stainless Steel Appearance Processes

A chromium deposit slightly darker than hexavalent chromium deposits, having an appearance close to polished pewter or stainless steel, is obtained from the original trivalent chromium process in this product line. The darker deposit is due to its deeper blue and red hues, Figure 1. For some manufacturers, the deposit’s rich appearance and the perception of depth in the coating are ideal to distinguish their parts from standard hexavalent chromium plated parts. Since this decorative deposit has the same physical properties as other trivalent chromium deposits, this process can give parts such as furniture, appliances and tools a rich distinctive appearance without a change in physical properties of the plated system.

The operating conditions for this process are given in Table 1. Additives are added based upon amp-hours of plating as they are for all trivalent processes within this product line. Figure 3 plots the thickness of the deposit with time. A consistent plating rate with an average of 6 millionths per minute at 10A/dm^2 (100 ASF) is obtained up to at least 1.3 microns (50 millionths) with total adhesion and cohesion. This thickness is approximately 5 times the thickness of typical decorative chromium deposits.

Table 1

Operating conditions for the
Pewter/Stainless Steel Appearance Process

- 2.7 to 3.5 pH
- 15 to 30o C (59 to 86o F)
- 8.6 to 10.7 A/dm2 (80 to 100 ASF)
- Mild air agitation (less than nickel)
- Graphite anodes
- 20 g/L Trivalent chromium

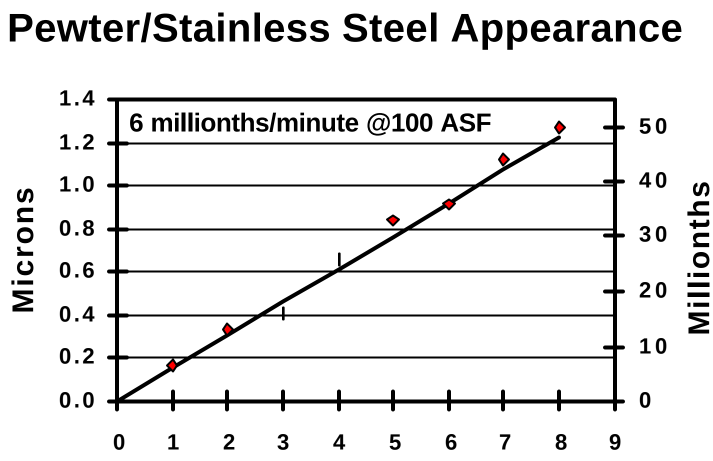

Figure 3 – Minutes of Continuous Plating

Standard Appearance – Normal Plating Speed Process

This process is the most widely used product worldwide for decorative trivalent chromium electroplating. The color of the deposit, Figure 1, is closer to that obtained from hexavalent chromium than the Pewter/Stainless Steel process but does not have as much pure blue hue. It has an average consistent plating rate of about 9 millionths per minute at 10 A/dm^2 (100 ASF), Figure 4. Adhesion and cohesion is as good as hexavalent chromium deposits up to at least 1.4 microns (54 millionths). This is about 5 times thicker than the typical decorative chromium deposit. The operating conditions are given in Table 2. Macrocracking starts at about 1.3 microns (50 millionths) while hexavalent chromium deposits marcocrack at about 0.6 microns (25 millionths).

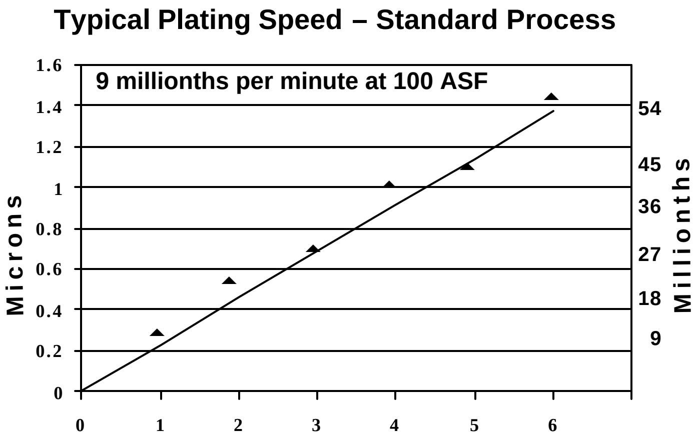

Figure 4 – Minutes of Continuous Plating

Table 2

Operating Conditions for the Standard
Appearance – Normal Speed Process

- 2.3 to 2.9 pH
- 27 to 49° C (80 to 120° F)
- 8.6 to 13.5 A/dm2 (80 to 125 ASF)
- Mild air agitation (less than nickel)
- Graphite anodes
- 20 g/L Trivalent chromium
- Approximately 30 to 33% plating efficiency

This process is being used on most, if not all, products that use decorative hexavalent chromium processes. The types of products range from original equipment truck bumpers to medical devices. Because this product has been used for over 30 years, an extensive amount of research has been conducted to determine its properties. For example, the deposit's corrosion properties have been studied for over 25 years using experimentally designed studies and actual parts in service. Figure 5 contains some of the experimentally designed corrosion results for panels that were plated with a plating system designed for exterior automotive original equipment parts, Service Condition 4. The panels all contain the same nickel systems (23 microns semibright and 7.5 microns of bright nickel) prior to either hexavalent or trivalent chromium deposits (0.3 microns).

The marine tests were conducted over a 15-year prior at Kure Beach, a recognized marine corrosion site in North Carolina. The 12-year industrial test was at a static site located in a highly industrial northern area of the United States, Cleveland Ohio, with an atmosphere containing sulfur and chloride. The mobile tests were conducted on delivery trucks driven for 7 years in the “rust belt” around the Great Lakes. All three outdoor exposure tests determined that microporous (MP) and microcracked (MC) hexavalent chromium and trivalent chromium (TV) deposits performed essentially equally. Microcracked hexavalent chromium (MC) corroded slightly faster than the other two microdiscontinious chromium systems. They all performed much better than the hexavalent chromium deposits that were not made microdiscontinous (SH).

Figure 6 contains the corrosion data from the same corrosion sites for plating systems designed for a less corrosive atmosphere, Service Condition 3. This service condition requires a minimum of 18 microns of semibright and 7.5 microns of bright nickel under 0.3 microns of chromium over a steel substrate. Examples of parts are bicycles, lawn furniture, and hospital fixtures. As expected, the corrosion rate to the substrate is slightly higher for these parts than for the Service Condition 4 parts, Figure 5. However, the relationship between the chromium systems is the same. All the microdiscontinious chromium systems (MC, MP, TV) have less base metal corrosion than the standard hexavalent chromium plated parts (SH). Also, the microcracked (MC) system is slightly more corrosive than the other two (MP, TV) microdiscontinious systems. The important information obtained from both Figures 5 and 6 is that trivalent chromium deposits resist base metal corrosion at least as good as microdiscontinous hexavalent chromium deposits and they are much better than standard hexavalent chromium deposits. Also, trivalent chromium is microporous as plated and so it does not have to be treated to become microdiscontinous as does hexavalent chromium deposits. This could eliminate one process step.

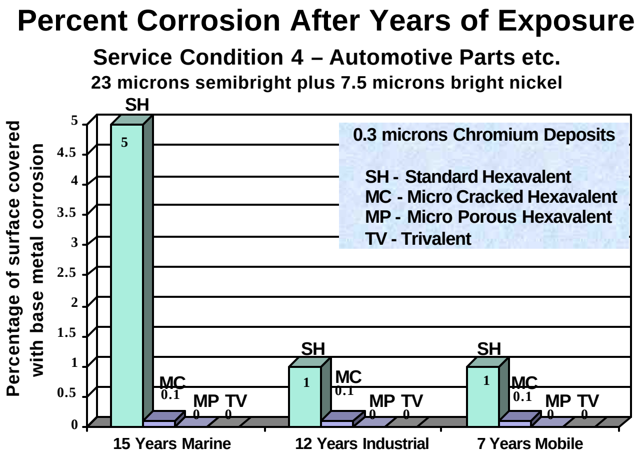

Figure 5 – Corrosion Studies – Trivalent versus Hexavalent Chromium

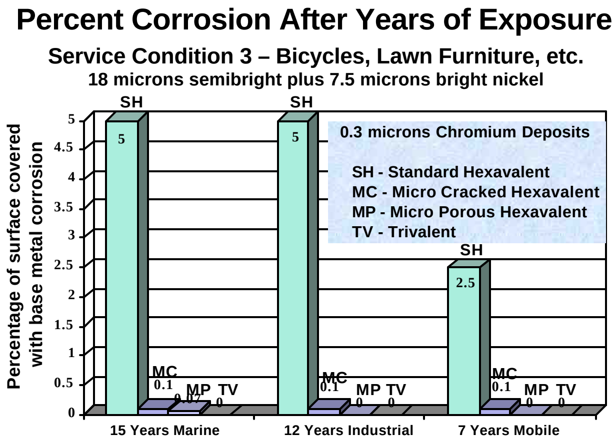

Figure 6 – Corrosion Study – Trivalent versus Hexavalent Chromium

Microdiscontinuous chromium is not typically used on parts with less than a total of 7.5 microns (0.3 mil) of nickel because nickel deposits under this thickness are usually porous. Microdiscontinious chromium over porous nickel usually produces pores that extend to the substrate creating a route through the nickel for rapid base metal corrosion. Hexavalent chromium ions offer some corrosion resistance for the exposed substrate by “chromating” the substrate. Trivalent chromium ions will not “chromate” the substrate and so this temporary protection is not produced. However, post treatments/dips can be used to produce an equivalent short-term corrosion resistance.

Standard Appearance – High Speed Plating Rate Process

A high speed plating process, producing deposits similar in appearance to the widely used “normal plating speed” process, is also available. Table 3 lists the operating conditions of this process. They are similar to the “standard plating speed” process except approximately 10% leveling is obtainable. Hexavalent chromium and traditional trivalent chromium processes do not reduce the roughness of the substrate (leveling) as is possible with this process. Another advantage of this high plating speed trivalent chromium technology is that thick deposits can be produced with good adhesion and cohesion. Figure 7 plots the thickness of the deposit obtained after the indicated hours of continuous plating. The average plating rate is 1.2 mil per hour at 125 ASF. This is significantly faster than the 0.4 mil per hour at 144 ASF that is obtained with conventional functional hexavalent chromium processes. However, it is slower than the 2.8 mil per hour at 575 ASF obtainable from organic catalyzed functional hexavalent chromium processes. However, the hexavalent chromium processes plates at 4.6 times the current density to obtain 2.3 times the plating rate.

Deposits over 10 mils thick have been successfully plated using this high plating speed process. A cross-section of a trivalent chromium deposit that is 17 microns (0.68 mils) thick is shown in Figure 8. This cross-section illustrates the microcracking that is typically observed in all thick trivalent chromium deposits. These cracks permit faster base metal corrosion than some thick hexavalent chromium deposits since hexavalent chromium deposits can be produced without cracks going completely through the deposit. Corrosion resistance with trivalent chromium deposits can be obtained if a thin nickel deposit precedes the trivalent chromium deposits or if a post chromium plating treatment is performed to “seal” the cracks.

Table 3

Operating Conditions for the Standard
Appearance
High Speed Plating Rate Process

2.1 to 2.3 pH
43 to 49^{o} C (110 to 120^{o} F)
12 to 15.5 A/dm$_2$ (115 to 145 ASF)
Mild air agitation (less than nickel)
Graphite anodes
20 g/L Trivalent chromium
10% Leveling

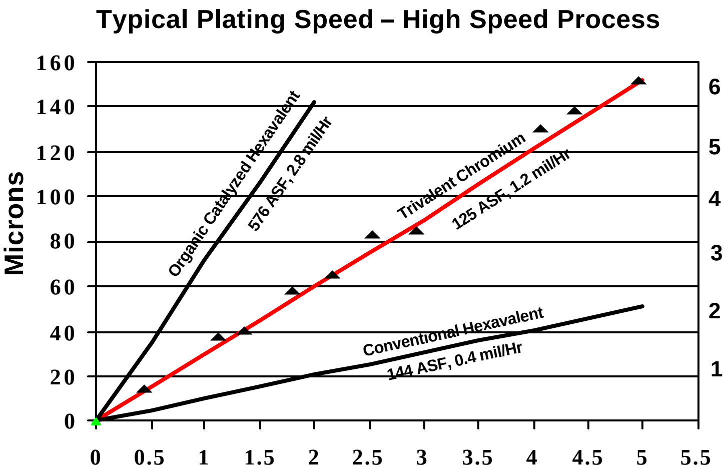

Figure 7 – *Hours of Continuous Plating*

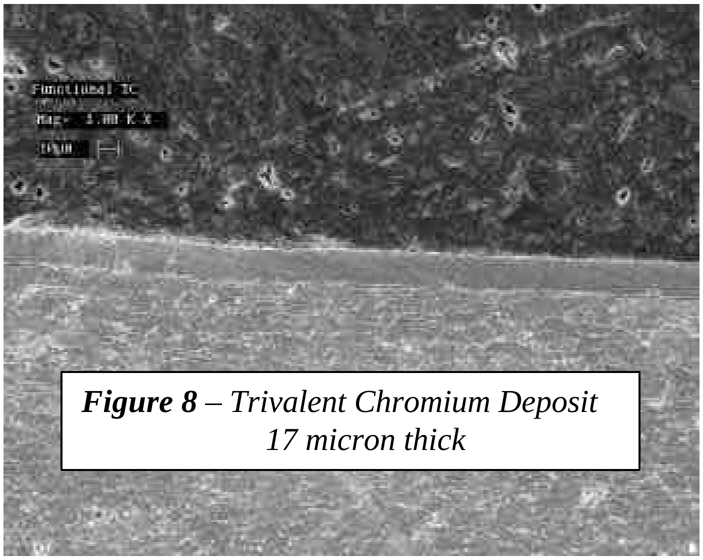

***Figure 8** – Trivalent Chromium Deposit 17 micron thick*

Table 4

Typical Chromium Deposit Hardness

	Trivalent Chromium	Hexavalent Chromium
As-Plated	1000 KHN_{100g}	1000 KHN_{100g}
Heat Treated 15 minutes at		
400^{o}	1600 KHN_{100g}	800 KHN_{100g}
800^{o}	1400 KHN_{100g}	300 KHN_{100g}

Since this high plating speed/high thickness process is a candidate for a functional trivalent chromium plating process, many of its physical properties have been investigated. The average hardness of 1000 KHN_{100g} for the as-plated trivalent chromium deposit is similar to the typical hardness for functional hexavalent chromium deposits, Table 4. However, when heated for 15 minutes at 400^{O} C, the trivalent chromium deposit increases in hardness to approximately 1600 KHN_{100g} while the hexavalent deposit decreases in hardness to approximately 800 KHN_{100g}. At 800^{O} C, trivalent deposits from this process still maintain a hardness of 1400 KHN_{100g} while the hardness of hexavalent chromium deposits drop to approximately 300 KHN_{100g}. It is also easy to co-deposit metals and particles such as carbides in a trivalent chromium deposit. In some cases, this increases the hardness and wear resistance of the trivalent chromium deposit.

There are many methods to measure wear but two common ones used for functional chromium deposits are Falex and Taber Abraser. The lubricated wear Falex test results for as plated, 25 micron plus (1+ mil) deposits are compared in Figure 9. There was less wear (weight loss) on both the trivalent chromium coated Pin and the unplated steel Vee than for the combination of a hexavalent chromium plated Pin and steel Vee. The trivalent chromium deposit and the steel Vee even had less wear when the trivalent chromium deposit was heat-treated at 400^{O} C for 15 minutes. Non-heat treated hexavalent and trivalent chromium deposits were much closer in wear resistance when tested by the Taber Abraser. Figure 10 contains the wear results after testing deposits as plated and 2 and 8 weeks after plating. Testing after ambient temperature aging was conducted to determine if this type of aging altered the wear resistance. The results for the trivalent and hexavalent chromium deposits were equal within experimental accuracy. Also, they both showed a slight loss in wear resistance after aging, as measured by an increase in weight loss. This aging study was not repeated and so the observed loss of wear resistance might actually be equal, within experimental error, to the weight loss for the as plated tests. In either case, the wear resistance values are equal for both hexavalent and trivalent chromium deposits.

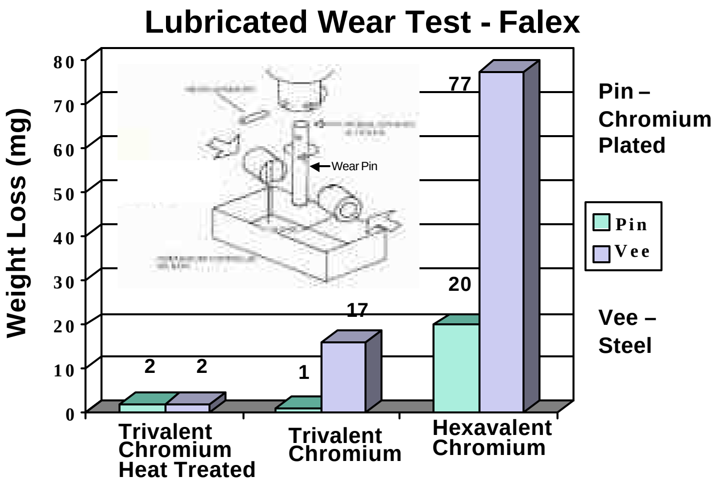

Figure 9 – Falex Wear Test Results

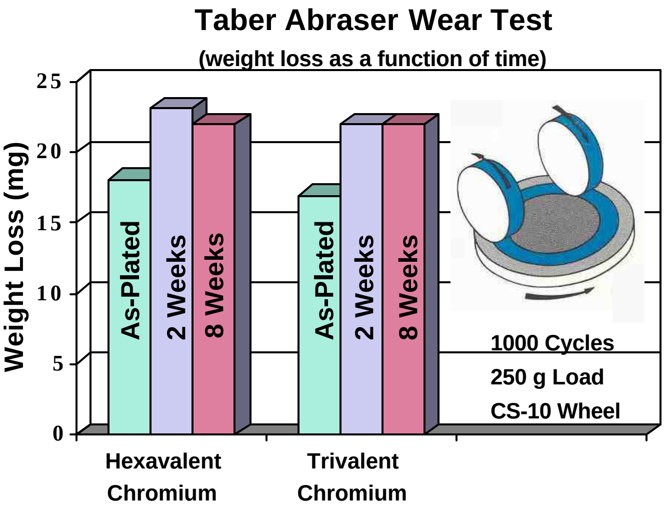

Figure 10 – Taber Abraser Wear Test Results

Another physical property of functional chromium deposits that might be important under some conditions is stress. Figure 11 plots the internal stress of trivalent and hexavalent chromium deposits as a function of thickness. The trivalent chromium deposits start out with a lower stress than hexavalent chromium deposits, as measured by a Sprial Contractometer. The trivalent chromium deposit's stress approaches zero stress at about 50 millionths. The lower stress is probably more important for thin, decorative chromium plated parts such as plated plastic than for parts with thick chromium deposits.

There are many organizations working on developing a trivalent chromium process that can produce a thick (functional) chromium deposit that has equal or better physical results than hexavalent chromium deposits. There are other groups willing to obtain the best trivalent chromium deposits that is avaible and then find parts that can use these deposits even if some of the physical properties might not be the same.

Near Hexavalent Chromium Appearance Process

This process produces trivalent chromium deposits with an appearance (color) very close to what is considered the standard appearance for plated chromium, hexavalent chromium deposits, Figure 1. If a standard trivalent chromium deposit is more than a few inches away from a hexavalent chromium deposit, most consumers would not be able to distinquish the "standard" trivalent deposit from the hexavalent chromium deposit. If the trivalent chromium deposit is placed adjacent to a hexavalent chromium deposit, manufacturers might prefer the "near hexavalent chromium appearance process". The operating conditions of this process are listed in Table 5. Figure 12 plots the thickness of the deposit after the continuous minutes of plating. The average plating rate is 17 millionths per minute at 100 ASF. The physical properties of these deposits are the same as the other decorative trivalent chromium deposits.

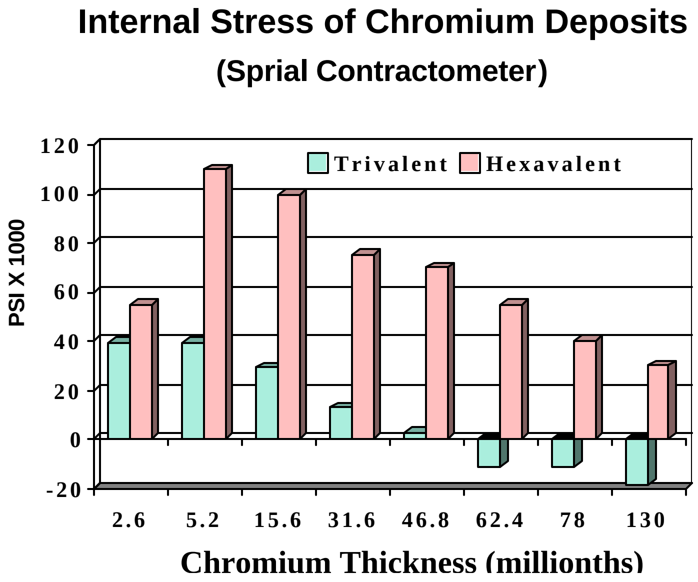

Figure 11 *– Stress as a Function of Chromium Thickness*

Table 5

Operating Conditions for the
Near Hexavalent Chromium
Appearance Process

2.3 to 2.9 pH
35 to 46o C (95 to 115o F)
8.6 to 10.8 A/dm^2 (80 to 100 ASF)
Mild air agitation (less than nickel)
Graphite anodes
21 g/L Trivalent chromium

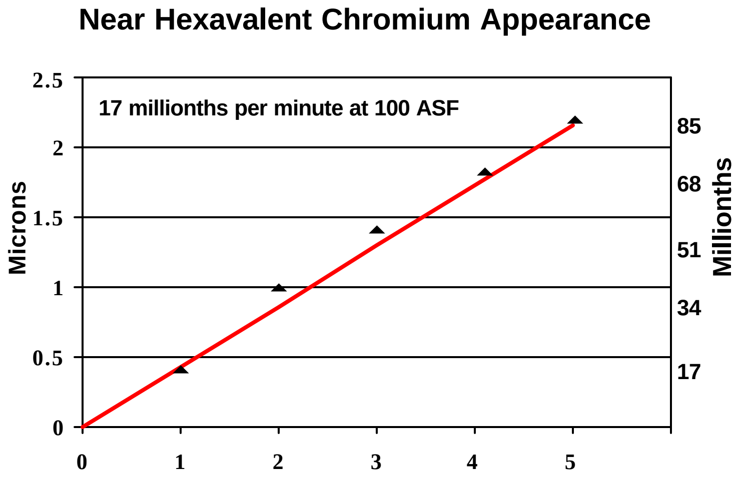

Figure 12 *– Minutes on Continuous Plating*

Table 6

Operating Conditions for the
Gray-Black Appearance Process

3.4 to 3.8 pH
35 to 40^{o} C (95 to 105 ^{o} F)
8.6 to 13.5 A/dm^2 (80 to 125 ASF)
Mild air agitation (less than nickel)
Graphite anodes
25 g/L Trivalent chromium

Gray-Black Chromium Appearance Process

Some designers use this process to produce decorative parts with a dark gray appearance. This color is lighter than the jet black appearance that is obtained with some black-hexavalent chromium processes. Table 6 contains the operating conditions for this process. As with black hexavalent chromium processes, the deposit is a high chromium oxide deposit that is self-limiting in thickness.

The abrasion resistance is similar to black hexavalent chromium deposits. They both have less abrasion resistance than conventional chromium deposits. To improve the abrasion resistance, platers can plate the Pewter/Stainless Steel Appearance deposit first with its slightly dark appearance and then the gray-black deposit. As the gray-black deposit is worn away, the more wear resistant under layer of chromium maintains some of the dark appearance. Because trivalent chromium processes are less sensitive to the passivity of the substrate, plating trivalent chromium over another trivalent chromium deposit is relatively easy.

Status of Trivalent Chromium Processes

Several decorative trivalent chromium processes are commercially used today around the world. At least one product line is easy to plate (similar to bright nickel) and has plating and physical properties very similar to the comparable hexavalent chromium processes. In most cases, they can be a “drop in” process when replacing hexavalent chromium processes with much lower health/safety/enviornmental and waste treatment concerns. They use very long life graphite anodes with conventional DC current (ripple and current interuption not being a problem) and have consistent plating rates. Their bath chemistries are stable and are tolerant to most of the impurities found in a nickel/chromium plating line. Metallic impurities are removed by ion-exchange. Carbon removes organic contamination.

Thick (functional) trivalent chromium processes have not yet been developed that are direct replacements for hexavalent chromium processes. Plating thickness, plating rates, and deposit hardness are comparable to hexavalent processes. With some wear resistance tests, trivalent chromium deposits are as good as or better than hexavalent deposits. Trivalent chromium deposits co-deposited with hard particles and other metals can be used to further enhance the properties of the trivalent chromium deposit. Corrosion resistance is not as good because of the microcracks that permeate through the deposit. However, methods such as nickel strikes and post treatments might be able to overcome this problem. Therefore, if thick (functional) trivalent chromium deposits are desired, it is best to test the deposit on the actual part.

Acknowledgement

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