Finishers' Think Tank

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Change is Good ... Change is Ongoing ... To Chrome or Not to Chrome

The title of this month's article helps to define the purpose of progressive action. A key factor is understanding the precarious balance that forms with respect to regressive action. Or, be certain that any implemented change or replacement will improve the particular condition or situation. Change occurs many times over on a daily basis. It can influence how we conduct business, enjoy recreation, health care, military defense, space exploration, transportation, and, yes, metal finishing.

How many people state "how could we have conducted business without a fax machine?" Sending e-mail has replaced a large amount of letter-writing. Inventories are maintained on a "just needed" basis, to meet supply and demand. Rock climbing and bungee jumping offer new recreational challenges. Cruise vacations have developed into a lucrative industry. Development of new vaccines and medicines, coupled with effective, yet minimally invasive surgical techniques, advance the progress of medicine. Missile technology refinements, electronic detection systems, and faster, more accurate vehicles, improve military defense capabilities. Space probes are gradually visiting all the rest of our solar system's planets. A new international space station is in the works. More fuel-efficient and less-maintenance vehicles are being introduced. What about metal finishing? Sure, tanks still prevail, and nothing rinses better than water. But surface preparation, plating baths, and post finishes are continually improving. The driving forces include: improved corrosion protection & extended service life of finished parts, environmental compliance, and economizing. Let's focus on the status of chromium.

Basic Facts

Chromium, derived from the Greek word "color," is a flashy contributor to the sparkle and appearance of emeralds, rubies, and sapphires. The metal, itself, is never found in the pure state. It predominantly exists in the Earth's surface as an oxide.

Chromium exists chemically in two preferential oxidation states: trivalent and hexavalent. For continued health and general well being, our bodies need chromium, for the necessary nutritional value it supplies. By following a recommended consumption of food sources, we consume 0.03-0.10 mg of trivalent chromium daily. Supplemental vitamins containing trivalent chromium are sold over the counter. Efforts have focused on replacing hexavalent with the trivalent form, or eliminating it altogether.

Target: Hexavalent Chromium

The crosshairs of industry, EPA, OSHA, and environmentalists are focused on specific toxicity problems associated with hexavalent chromium.

- Chromium is on a list of metals for lower emissions.
- Hexavalent chromium compounds are listed as carcinogenic by IARC and NTP.
- The chrome PEL is about 100 micrograms/cm^3. (There was litigation concerning the value in a suit by OCAW vs. OSHA).
- Hexavalent chrome compounds are substantially toxic compared to trivalent compounds.
- EPA studies (EPA 450/2-89-012A) indicate that hexavalent chromium contributes to 5.8 cases of cancer per one million population.
- EPA targeted chrome emissions for early regulation under the Clean Air Act.

This information mainly pertains to hard/decorative chrome plating and anodizing. Hexavalent chromates, by virtue of their chemistry, are also monitored. By comparison, many trivalent chromium compounds are:

- Non-regulated per hazard class or division.
- Not listed as carcinogenic by NTP, IARC, or OSHA.
- Not listed as extremely hazardous.

Trivalent chromium is safer and more compliant. Some related attributes include:

- The common form of ionized chromium in nature.
- Known harmful effects of chromium in humans are attributed to the hexavalent form.
- Trivalent chrome's passage through cell membranes is inhibited. However, hexavalent chromium is not.

Clarification

It may appear, at least from the information given, that use and application of hexavalent chromium is being phased out or scheduled for aggressive curtailment. This is not the case. We recall that change is good and ongoing. But, in certain respects "nothing else currently does it better" than hexavalent chromium chemistry. Hard chromium, as described in last month's article, provides the best deposit characteristics for a wide range of industrial applications. Decorative hexavalent chromium has been a staple for bright, hard, corrosion resistant top coats. Chromates, available in a range of colored finishes, maintain excellent service life corrosion protection for assorted zinc and zinc alloy plated parts.

Hexavalent chromium type process baths can meet strict EPA, OSHA, and municipal regulatory regulations by doing what many finishers acknowledge works, and certified evaluators confirm:

- Cover the bath surface with polypropylene balls to minimize misting.
- Add surface tension reducing agents (additive), dissipating bubbles before they reach the surface and burst.
- Add fume suppressant (additive), to maintain a stable surface foam blanket.
- Install pollution control devices, such as packed bed scrubbers, fiber bed mist eliminators, or composite mesh pad systems.
- Reduce solution drag out. Reduce working bath concentrations of hexavalent chromium compounds.
- Maximize bath efficiency by using best suited catalysts for hard & decorative chrome.
- Consider ion exchange purification technology.

In The Works

Chromate conversion coatings over zinc have produced acceptable conversions from hexavalent to trivalent types. Clear or blue trivalent chromates meet or exceed these critical coating parameters:

- Corrosion resistance* (24-100 hr to white rust, 250-750 hr to red rust).
- Self-healing characteristics.
- Relatively low abrasion resistance.
- Cold forming & good solderability.
- Compatible with organic top coats (lacquers, silicates, powder coats).
- Relatively constant surface conductivity (50-100 microhms/in.^{2}).

** over zinc-plated steel, approximately 0.0003 in. of deposit thickness.*

Trivalent blue chromates tolerate higher levels of metallic contaminants than comparable hexavalent blue chromate baths. Therefore, trivalent blue chromate baths may provide specification chromating activity up to three times longer, per service bath life. The polishing action of trivalent baths is slower, thus permitting longer immersion and transfer times, without aggressive stripping of the zinc deposit. Post trivalent chromated parts can also be heated to accentuate the blue color.

Decorative trivalent chromium plating offers acceptable finish requirements in place of hexavalent chromium. Finished parts cover a broad range of consumer and institutional goods, such as: personal care, plumbing, automotive, hand tools, garden & landscaping, and appliances. These finishes provide:

- 100% elimination of hexavalent chromium.
- Flash deposit coating thicknesses (4-20 millionths of an inch).
- Similar blue bright deposit color.
- Corrosion resistance per total standard total finishing cycles (ASTM B-117 salt spray, CASS, dropping sand abrasion, etc..).
- Exceptional throwing power, elimination of blow holes and high current density burning.
- Reduced power consumption (twice the efficiency).
- Not sensitive to current interruption.
- Greater tolerance to AC ripple.
- Ability to dummy electrolyze for removal of metallic contaminants (nickel, copper, iron, zinc).
- Improved efficiency, thereby increasing production throughput.
- Less drag out, lower concentration of chromium metal and as the trivalent form.
- Easier waste treatment (simple alkaline precipitation of trivalent chromium).
- Approximately 90% less sludge generation in waste treatment.

Decorative trivalent plating baths do not, however, passivate unplated steel (*e.g.*, inner surface areas of tubular stock). Nothing does this better than hex! However, postplate passivation dips are used. They usually react with the iron surface, to passivate and leave a mechanical surface barrier. Some plating specifications permit the application of decorative trivalent chromium. A great deal of finishing also includes non-specific application of decorative trivalent chromium.

Much applied work has been conducted to improve corrosion resistance of iron/zinc phosphatized parts and directly over metals and metal/alloys. Applications are compatible with single and multiple process lines (*e.g.*, 3-stage, 5-stage). New chemistries result in minimum burden on the waste stream and treatment system. They are economically feasible versus chromates, showing a last cost reduction comparative waste treatment.

Older systems are based on phosphoric acid and molybdates. Some of the newer chromate alternative sealers were developed using the elements hafnium, titanium, and zirconium. They chemically form unique conversion coatings that also provide very good paint adhesion properties. Working solution pH ranges from 2-6, with temperature from 75-120 °F. A variation of these sealers are formulated to be used in an alkaline solution, protecting unpainted aluminum exposed to acidic conditions.

Challenges Coming Our Way

The European Union is mandating the complete banning of hexavalent chromates in about two years. The awesome challenge is developing alternative top coat finishes that will replace hexavalent chromium. Specifically, these new coatings must at least meet the wear resistance, corrosion resistance, and general application of each hexavalent process. Big assignment? You bet! In fact, General Motors in the U.S. has already specified alternatives to be used. Ford is going a step further, recommending more stringent chromium use requirements. This is actually good news for the metal finishing industry, for suppliers and captive/job finishers. The challenge is to develop these new, feasible processes, while not skipping a beat with regard to protective functions, wear resistance, and service life. I think of it as all new hexavalent finishes on an airplane. A plane must experience thousands of take-offs, landings, and flight mileage, without nuts, bolts, support frames, and critical parts cracking or falling off. A most formidable challenge, considering the end product applications. **P&SF**

Trivia

- One ore of chromium is thermite. This material is used to line steelmaking furnaces.
- A tremendous lode of chromium ore was discovered in the Beartooth Mountains, in Montana.
- A large amount of chromium is used in the manufacture of stainless steel.