Hard at work

For years, hard chromium electroplating has been a trusted industry solution for erosion, corrosion, and wear resistance. On the bright side, it provides excellent hardness (typically 66 Rc), has an appealingly shiny appearance, and offers relatively good resistance to corrosive environments. What's more, it is easily applied and is low cost.

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Not so positive, however, is the fact that hard chromium plating is an environmentally unfriendly process. In fact, the Environmental Protection Agency (EPA) has found that even short-term exposure to chromium may cause skin irritation; long-term exposure can damage the liver, kidneys, circulatory system, and nervous system. It has therefore become critical to find alternative processes that offer similar characteristics to hard chrome plating, but without the consequent risks.

This article gives a brief overview of what the hard chromium plating process entails, explores some well-known alternatives to it, and describes how Velan is hard at work on developing its own innovative alternatives.

Four steps to perfect hard chrome plating

Typically, hard chromium plating ranges from 25 to 250 micrometers in thickness. In the traditional hard chrome plating process, these are four critical steps:

• Activation

This step prepares the parts to accept the plating by removing oxides from the appropriate surfaces. It does so by circulating a reverse electrical current from the part into the bath. This activation can either take place in a separate activation bath or in the electroplating bath itself.

• Electroplating

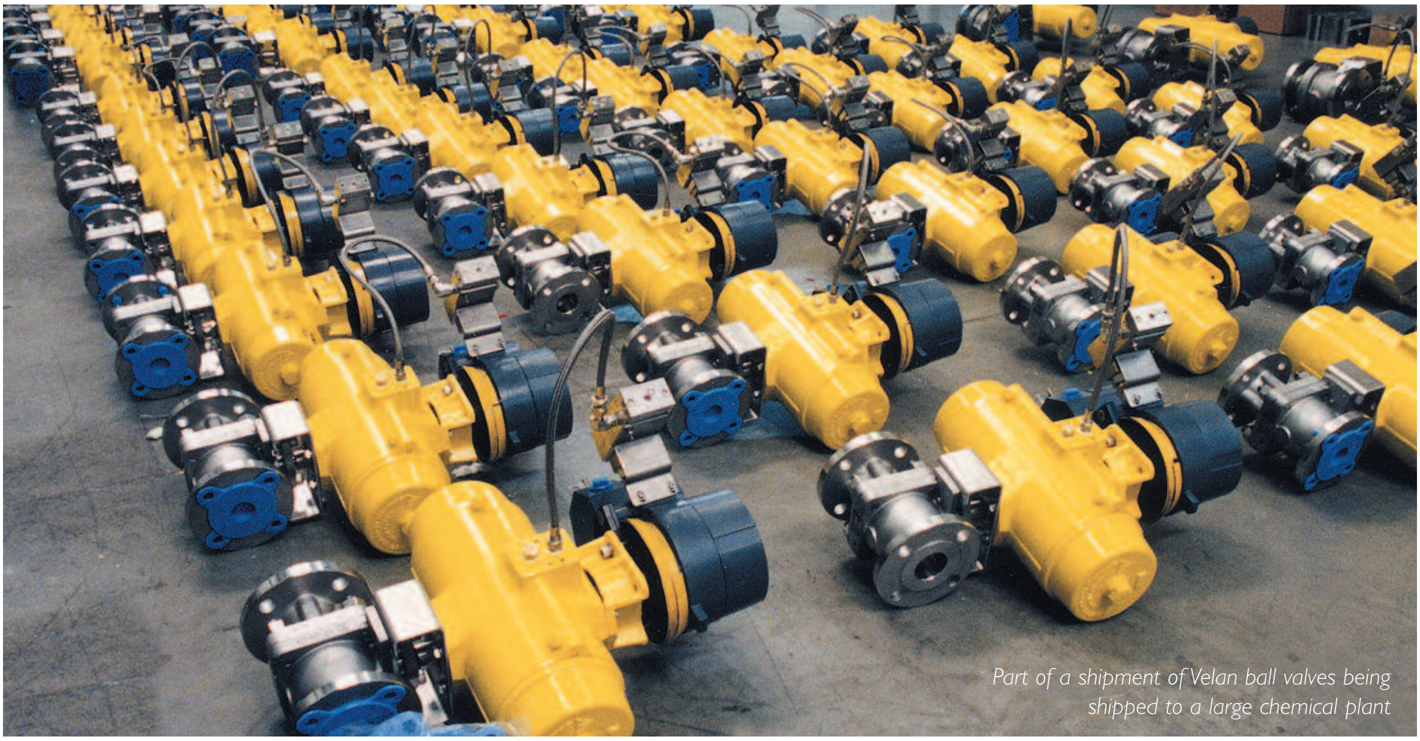
Electroplating is likewise performed in a highly acidic (pH near 0) chromium bath composed of chrome oxide ($CrO3$) and sulfate ($SO4$). An electrical current is applied and circulates from the bath into the part, effectively transporting and reducing the chromic acid from its original CrVI oxidation state to the desired Cr0 state. During the plating process, hydrogen and oxygen bubbles are produced, forming a mist that contains chromium and that can potentially escape into the shop environment. To prevent this, chromium air emissions are generally filtered using wet scrubbers, which pull the CrVI into the water.

• Rinsing

This essential step removes any particles that are not chemically bonded to the surface, such as the above-mentioned chromium particles –- a byproduct of the electroplating process itself -– and brings the CrVI from the controlled chemical tank into the shop's water system.

• Grinding/honing

Typically, the low cathode efficiency of the chromium plating process results in poor coverage at the edges of the part. What's more, chrome plated surfaces have a typical "cauliflower" surface finish, which is not acceptable in most applications. Consequently, the part usually has to be ground down to its final dimensions.



Part of a shipment of Velan ball valves being shipped to a large chemical plant

Alternatives to hard chrome plating

The following two coatings are widely considered in the valve industry to be the most natural alternatives to hard chrome plating:

- **Electroless nickel plating (ENP):** Widely used in the valve industry for over a decade, ENP uses conventional plating equipment that is similar to conventional hard chrome plating baths. It is important to note that only EOLVD- and RoHS-compliant process types (free from heavy metal stabilizers) should be used to meet this specification. The two major drawbacks of ENP are generally considered to be cost and a less robust wear behavior.
- **Thermal spray:** All forms of thermal spray are based on the same concept – metallic powder is heated close to melting and accelerated onto the surface that is to be coated. A large range of powder chemicals can be used, which makes it possible to customize coating options (e.g., ceramic or cermets).

The most popular thermal spray form is high-velocity oxy-fuel (HVOF). HVOF projects metal particles at a moderate temperature and high velocity onto a surface to produce a coating bond stress of around 10,000 psi and a porosity of above 1%. High-velocity oxygenated fuel is mostly used for severe service valve applications and its hardness and wear resistance are at least as good as hard chrome plating. In this case, HVOF's two drawbacks are once again high cost and the fact that the non-metallurgical bond with the substrate can lead to coating failure, such as crazing, cracking or delamination.

Velan's contributions to hard chrome plating alternatives

Velan has a long history of innovative valve design and commitment to R&D. Today, the company adheres to the Porter Hypothesis, which suggests that strict environmental regulations can trigger the discovery and introduction of cleaner, more innovative technologies, thereby improving a company's commercial competitiveness. In keeping with this vision, Velan's R&D team felt it made little sense to replace hard chrome plating (EP-HC) with the existing thermal spray technique since, while it might be

A non-exhaustive sampling of hexavalent chromium regulations in Europe and the United States*

The hexavalent oxidation state is the most toxic form of chromium. Within the European Union, the use of hexavalent chromium in electronic equipment is largely prohibited by the Restriction of Hazardous Substances Directive (RoHS). In the United States, it is classified by the EPA as one of 17 high-priority toxic chemicals for voluntary reduction through the 33/50 Program.

Restriction of Hazardous Substances Directive (RoHS) and other EU regulations

Hexavalent chromium is the toxic, carcinogenic by-product created when manufacturing, fabricating, or disposing of hard chrome plated products.

RoHS

In July 2006, the RoHS directive regulated hexavalent chromium use in electrical devices; a year later it also regulated its use in the automotive industry. The concern here is that RoHS currently focuses on final products that contain toxic elements and doesn't cover valves themselves since, according to the EU Commission, plating and coatings differ in composition from the substrate material and so are considered to be "homogeneous materials."

End-of-Life Vehicle Directive (EOLVD)

The EOLVD was adopted to address the waste associated with vehicles. This directive ensures the reuse, recycling, and recovery of vehicles. Hexavalent chromium is identified in the Directive as one of the hazardous materials used in the manufacture of vehicles. It has been banned from use in the manufacture of vehicles in EU states since 2003.

EPA and other US regulations

- Clean Air Act (CAA): Vapor produced during plating is regulated under the Clean Air Act Amendments of 1990. On January 1995, the EPA published the Final Rule for its "National Emission Standards for Hard and Decorative Chromium Electroplating and Chromium Anodizing Tanks." The EPA reduced the emission standards for chromium from 0.05 mg/m3 to 0.010 mg/m3.
- Clean Water Act (CWA): Chromium air emissions are controlled using wet scrubbers, which transfer chromium from the air into the water. The EPA regulates chromium as a "priority pollutant" under the CWA; typical discharge concentrations for chromium in wastewater range from 0.1 up to 1.0 ppm max.
- Safe Drinking Water Act (SDWA): Under the SDWA, a maximum contaminant level (MCL) is set for drinking water that comes from a public water system. For hexavalent chromium, the MCL is set at 0.1 ppm.
- Resource Conservation and Recovery Act (RCRA): Under the RCRA, chromium is also classified as a "hazardous constituent" and is categorized as a hazardous waste when concentration exceeds 5 mg/L. The chromium plating baths themselves must be handled as hazardous waste.
- Comprehensive Environmental Responsibility, Compensation, and Liability Act (CERCLA): Under CERCLA, chromium is categorized as a "hazardous substance." Users are liable for damages resulting from any release of it into the environment. A company remains liable for its waste, even if the release to the environment occurs at a licensed disposal facility.
- Occupational Safety and Health Administration (OSHA): On February 2006, the OSHA published the most recent Hexavalent Chromium CrVI US Standard. The new permissible exposure limit for CrVI is 5μg/m3.

* *www.newmoa.org*

more environmentally friendly, it is also a much more expensive alternative and so is unsustainable from a business point of view.

After much hard work both in the lab and in the field, we've found two chromium-free nanostructured coatings that offer high hardness, good wear resistance, and attractive corrosion behavior. These two promising nanostructured coatings (A and B) were studied in collaboration with the Functional Coatings and Surface Engineering Laboratory (FCSEL) in Engineering Physics Department of the École Polytechnique de Montréal. Graph No. 1 below shows a brief overview of this technical study and highlights the positive behavior of the two coatings. Subsequent testing included scratch and adhesion tests, Young's modulus test, and a corrosion test in a salt water environment. Both the A and the B coatings had consistently better results than did the hard chrome plating coating in all of these tests. Furthermore, costs associated with the two nanostructured coatings were comparable to standard hard coating costs (Graph No. 2).

Next, Velan R&D tested the A and B nanostructured coatings in a 3" ball valve using superheated steam at 600 F and 600 psi. During this tough test, torque and seat leakage levels were monitored over cycles; the test was stopped when the seat leakage was judged to be unacceptable (>100ml/min) and visual inspection showed that the coating had been damaged. Graph No. 3 illustrates the performance of coating A and B versus hard chrome plating in these tests.

Coating A and B outperformed hard chrome plating in this test as well.

About the authors

Luc Vernhes is Design Manager of Velan Securaseal Ball Valves. He is a professional Engineer with two Master's degrees: one in mechanics from the École Nationale d'Ingenieurs (France) and one in physics from the École Polytechnique de Montréal (Canada). Luc is currently pursuing graduate studies on nano-coating and has seven years of experience at Velan, focusing on metal-seated ball valve design and project management.

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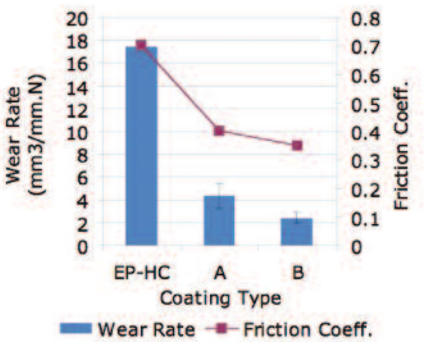
Summary

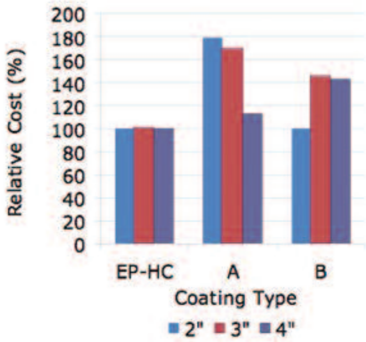
In conclusion, nanostructured coatings clearly have the potential to be the best alternative to hard chrome plating. Velan is now actively identifying interested customers to collaborate with us to develop the potential of these chromium-free solutions.

This article briefly describes the hard chrome plating process itself and mentions some of the many regulations that have been put in place to limit the use –- and potential damage to people and the environment -– of this hazardous material. And, although a number of well-known alternative coatings exist, none is yet available that perfectly meets the varied requirements of every possible application.

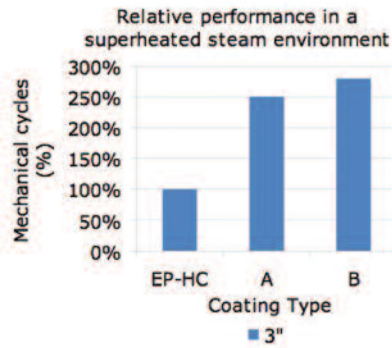
What is clear, however, it that as laws and regulations such as the EPA, the Council Directive on End-of-Life Vehicles, and RoHS are increasingly passed, there's more impetus than ever to find reasonable alternatives to hexavalent chrome plating.



Graph No. 1



Graph No. 2



Graph No. 3