Alternatives to Hexavalent Chromium to Comply with European Union's Directives (ELV, RoHS and WEEE)

by Harish Bhatt

The deadline for the European Union's Directives is approaching. RoHS (Restriction of Hazardous Substance) is effective July 1, 2006, WEEE (Waste Electrical and Electronic Equipment) is effective December 31, 2006 and the ELV (End of Life Vehicle) directive is effective July 1, 2007 for hexavalent chromium. Industry is working hard to find a suitable alternative for compliance. Ideally a drop-in replacement, at a reasonable cost that meets engineering specification would be preferred. This paper describes various options that are commercially available to comply with these directives.

Introduction — The Directives

This paper will outline three major directives from European Union — ELV, RoHS and WEEE. It will address replacement of hexavalent chromium for all three directives.

ELV
(End of Life Vehicle) Directive —
Directive 2000/53/EC of the European Union and the Council of European Union, September 18, 2000.

A mandate was proposed in 1997 to restrict the usage of heavy metals in motor vehicles by the European Union (EU). The four heavy metals included are cadmium, lead, mercury and *hexavalent chromium*. The bill was introduced in the EU parliament in May 2000, and in September 2000 it became EU directive 2000/53/EC. This directive aims to prevent wastes from vehicles and aims at the reuse, recycling and other forms of recovery so as to reduce the disposal of waste, while at the same time improving the environmental performance of all of the economic operators involved. This directive restricts the total content of hexavalent chromium to 2.0 grams per vehicle prior to shredding, incineration or recycling. The usage of hexavalent chromium is only for corrosion protection purposes. For all other purposes, the limit is 0.0 gram.

Annex II of the directive has been periodically revised (6/2002, 1/2005, 6/2005 and 9/2005). Annex II is revised based on new technology and available alternatives. Annex II defines specific heavy metal limits and provides information on acceptance allowances, and also its exceptions. The revision of Annex II is Commission Decision (6/2005, 2005/438/EC) and it amends that "spare parts put on the market after July 1, 2003 which are used for vehicles put on the market before July 1, 2003 are exempted from the provisions of Article 4(2)(a)."

The latest revision of Annex II (9/20/2005, 2005/673/EC) is a European Union Council Decision and amends the scope and expiry dates of the exemption — "Hexavalent Chromium - corrosion preventive coatings, 1 July 2007, corrosion preventive coatings related to bolt and nut assemblies for chassis applications, 1 July 2008 and absorption refrigerators in motor caravans are to be labeled or made identifiable in accordance with Article 4(2)(b)(iv)." This directive is effective July 2007 for hexavalent chromium with a limit of 0.00 grams.

RoHS
(Restriction of Hazardous Substance) Directive —
Directive 2002/95/EC of the European Parliament and the Council of the European Union, 27 January 2003.

The hazardous substances covered in this directive are mercury, lead, cadmium, hexavalent chromium, PBB (polybrominated biphenyls) and PBDE (polybrominated diphenyl ether). The purpose of this directive is to approximate the laws of the Member States on the restrictions of the use of hazardous substances in electrical and electronic equipment and to contribute to the protection of human health and the environmentally sound recovery and disposal of waste electrical and electronic equipment. This directive does not apply to spare parts for the repair, or to the reuse of electrical and electronic equipment put on the market before July 1, 2006. Member States shall ensure that, from July 1, 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, PBB or PBDE. The Annex to this directive applies to lead, mercury, cadmium and hexavalent chromium, which are *exempted* from the requirement of Article 4(1) — "hexavalent chromium as an anti-corrosion agent of the carbon steel cooling system in absorption refrigerators."

* *Corresponding author:*
Harish Bhatt
Vice President, Technology
METALAST International, Inc.
2241 Park Place
Minden, NV 89423
Phone: (775) 782-8324
Fax: (775) 782-2498
Email: hbhatt@metalast.com

A decision - 2005/618/EC: Commission Decision of 18 August 2005 amending Directive 2002/95/EC of the European Parliament and of the Council - was promulgated for the purpose of establishing the maximum concentration values for certain hazardous substances in electrical and electronic equipment. In the Annex to Directive 2002/95/EC the following note was added: "For the purpose of Article 5(1)(a), a maximum concentration value of 0.1% by weight in homogeneous materials of lead, mercury, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) and of 0.01% by weight in homogeneous materials for cadmium shall be tolerated." This decision applies from July 1, 2006. Deca-BDE (decabromodiphenyl ether) is a brominated flame retardant used in a variety of applications because of its compatibility with component materials and its effectiveness in preventing fires. A ten-year long risk assessment of all deca-BDE's potential environmental and human health impacts carried out by the European Union government chemical authorities was closed in May 2004. It concluded that there were no identifiable risks and no restrictions on use of deca-BDE. That conclusion led directly to the European Union Commission's exemption of deca-BDE from the RoHS directive on October 15, 2005.

The term "homogeneous" means "of uniform composition throughout." Examples of "homogeneous materials" are individual types of plastics, ceramics, glass, metals, alloys, paper, board, resins and coatings. A plastic cover is a "homogeneous material" if it consists of one type of plastic that is not coated with or has attached to it or inside it any other kinds of materials. In this case the limit values of the directive would apply to the plastic. An electric cable that consists of metal wires surrounded by non-metallic insulation materials is an example of a "non-homogeneous material" because mechanical processes could separate the different materials. In this case the limit values of the directive would apply to each of the separated materials individually. A semi-conductor package contains many homogeneous materials, which include plastic molding material, tin-electroplated coatings on the lead frame, lead frame alloys and gold-bonding wires.

The Republic of China has a similar directive (2/2006), "Administrative Measure on the Control of Pollution caused by Electronic Information Products." It takes effect March 1, 2007 and covers the same six hazardous substances.

The Republic of Korea, Ministry of Environment has drafted (4/2006) a similar directive, "The Act for Resource Recycling of Electrical/Electronic Products and Automobiles." This act will enter into force from July 1, 2007 onward.

For the purpose of this directive "dependent" means the equipment must be dependent on electric current or electromagnetic fields. In other words, electricity is the primary energy. It also means that when the electric current is off, the appliance cannot fulfill its basic (primary) function. If electrical energy is used only for support or control functions, this type of equipment is <u>not</u> covered by Directive 2000/96/EC. Examples of products outside the scope of RoHS are: piezoelectric ignition, combustion engines with ignition, gasoline driven lawnmowers, pneumatic tools, gas cookers with electric clocks, teddy bears with batteries, high-voltage switchgear, medical equipment and measurement and control equipment. The criterion, "equipment, which is not covered by specific community waste management legislation," exempts car radios. Military equipment is excluded from the categories of Annex 1A of the WEEE directive, and therefore not covered by the RoHS directive. This directive (RoHS) covers spare parts for the repair, or the reuse, of electrical and electronic equipment put on the market from July 1, 2006. However, the directive does not apply to parts for use in equipment put on the market before July 1, 2006 with the purpose of extending its life by updating its functionalities or upgrading its capacity.

The RoHS directive does not differentiate between households or professional EEE, so the RoHS directive covers products for professional use.

WEEE
(Waste Electrical and Electronic Equipment) Directive — Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003.

The purpose of this directive is the prevention of waste electrical and electronic equipment (WEEE), and the reuse, recycling and other forms of recovery of such wastes so as to reduce the disposal of waste. It also seeks to improve the environmental performance of all operators involved in the life cycle of electrical and electronic equipment, *i.e.*, producers, distributors and consumers and in particular those operators directly involved in the treatment of waste electrical and electronic equipment. The product registration date was August 13, 2005. This directive is effective December 31, 2006.

"Electrical and Electronic Equipment" (EEE) means equipment which is dependent on electric currents or electro-magnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields falling under the categories set out in Annex 1A and designed for use with a voltage rating not exceeding 1,000 V for alternating current and 1,500 V for direct current.

Categories of electrical and electronic equipment covered by this directive are: large household appliances, small household appliances, IT and telecommunications equipment, consumer equipment, lighting equipment, electrical and electronic tools (with the exception of large-scale stationary industrial tools), toys, leisure and sport equipment, medical devices (with the exception of all implanted and infected products), monitoring and control instruments and automatic dispensers.

Directive 2003/108/EC of the European Parliament and of the Council of 8 December 2003 (is) amending Directive 2002/96/EC on waste electrical and electronic equipment (WEEE).

This amendment covers Articles 1 and 2 addressing financing with respect to WEEE from users other than private households. It also mentions that Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with this Directive by August 13, 2004.

The WEEE directive contains provisions that cover WEEE from households and WEEE from users other than private households.

All three directives (ELV, RoHS and WEEE) have been directly or indirectly derived from the original waste directive 75/442/EEC, July 15, 1975.

Hexavalent chromium replacements

Hexavalent chromium (Cr^{+6}) is found in corrosion preventative (chromic acid, zinc chromate, calcium chromate, sodium chromate) and conversion coatings on numerous key vehicle components. Hexavalent chromium can be found in finishes on metallic parts such as fasteners, brackets, levers, etc. It is also widely used on hardware parts, electronics, household appliances and consumer items. It is also found in polymer pigments, inks and plastics (lead chromate, zinc chromate, barium chromate). Hexavalent chromium is also present in stainless steel (Cr^{+6} is released during casting, welding or torch cutting), textile dyes (ammonium dichromate, potassium chromate, potassium dichromate, sodium chromate), wood preservatives (chromium trioxide) and in leather tanning (ammonium dichromate). Zinc chromate and chromium chromate are carcinogenic substances. Besides being classified as carcinogenic, hexavalent chromium compounds are extremely corrosive, exhibit strong and potentially hazardous oxidative strength and in plating, yield poor chromium plating efficiency. The PEL (permissible exposure limit) for hexavalent chromium and all other hexavalent chromium compounds is five micrograms per cubic meter of air as an eight-hour time-weighted average (OSHA, February 2006).

One widely-used application of hexavalent chromium (for metal parts) is as a layer for corrosion protection over zinc-coated steel surfaces. It is a wet, gelatinous film, drying on the surface. Subsurface moisture provides self-healing and lubricity properties. Cr^{+6} also offers torque/tension properties to meet fastener finish requirements. Zinc chromate and chromium chromate are used in manufacturing as anti-corrosion coatings with active corrosion preventive properties. Hexavalent chromium is used in two main fields: (1) cathodic corrosion prevention applied mainly on smaller steel parts and (2) rinsing solutions containing hexavalent chromium used in paint shops following a phosphatization pretreatment as an adhesion layer (or fixation ground) before additional layers of paint are applied. Protective coatings based on hexavalent chromium are very effective because of their sacrificial nature (self healing).

The End of Life Vehicle directive is for manufactured vehicles and vehicle components sold in EU Member Nation States (twenty five countries at present, two more to join in 2007 with an estimated population of 490 million people). According to the automotive industry, 4 to 8 grams of hexavalent chromium are used per car on average though some will contain more than 10 grams. Every year, end-of-life vehicles in the EU Community generate between 8 and 9 million tons of waste, which must be managed correctly. It is a further fundamental principle that waste should be reused and recovered, and that preference be given to reuse and recycling.

It is technically possible to produce vehicles without hexavalent chromium in most applications. Hexavalent chromium is used for corrosion prevention on numerous steel parts in the form of zinc dichromate. In addition to corrosion protection, some parts must fulfill requirements like disconnectability even after several years of use or special sealing or similar functions in high-pressure liquid system applications (*e.g.*, high-pressure fuel injection, brake liquids). For these applications, which are also safety relevant, extensive time for introduction of alternative corrosion or sealing systems will be needed. In some other cases, it cannot be excluded that certain parts are chromated for merely aesthetic purposes today (*e.g.*, to yield a blue, black or yellow chromate surface).

A wide variety of strategies to substitute for hexavalent chromium have been developed, including thick layers based on zinc combined with an organic coating, and zinc powder alloys in duplex lamina, which offer a better corrosion protection. There are several trivalent chromates available to replace hexavalent chromates. In most cases, their performance is enhanced with a final coating of a topcoat or a sealer. There are also some non-chromium alternatives available though the applications and availability are limited due to the nature of the deposit. The substitutes are readily available for rinsing solutions after phosphatizing and are in widespread use for car bodies.

Several trivalent chromates are commercially available. Their performance is at least as good as hexavalent chromates in meeting the current specifications, and in most cases, the performance is enhanced with a topcoat or a sealer following immersion in a heated chromate bath. In recent years there has been a tremendous amount of development work to obtain performance and color finish in a trivalent chromium coating. Corrosion resistance has been improved with the use of a topcoat and/or a sealer. Most color finish applications require a process step that includes a color dye. Trivalent systems meet the End of Life Vehicle (ELV) and RoHS directives. It is important to run test samples for evaluation to meet your engineering specifications. The final finish and color of a trivalent chromated part depends on the proprietary formulation of the chemical supplier. Some suppliers offer a color dye as a final immersion in the plating process, which facilitates laser marking on the part surface. In most cases, an individual metal finishing job shop may have two or three chemical suppliers' chemistries to perform zinc plating with a trivalent chromate and a sealer/topcoat followed by a dye.

The Department of Defense and United States Navy have developed a trivalent chromium pretreatment called TCP and has licensed it to supplier companies for commercial applications.[**] This unique process is based on a formulation that contains trivalent chromium and zirconate for performance that exceeds any conventional trivalent chromium in meeting the requirements of many military and industrial specifications. The Navy had spent over two and a half years to develop this process and has compiled extensive data on various characteristics of the process. TCP can be applied as an immersion, spray or wipe application. It can be applied over aluminum, zinc-plated steel and over just about any other substrate. It is a simple drop-in replacement for hexavalent chromium that can be operated at room temperature (in most cases), is environmentally-friendly and complies with all three (ELV, RoHS, WEEE) EU directives. It provides harder and denser deposits (as compared to a conventional trivalent chromium) and offers corrosion resistance that meets or exceeds performance of hexavalent chromates. It can be baked following application without degradation or loss of performance, is electrically conductive and most importantly, it requires no topcoat or sealer to enhance its performance. It is an ideal undercoat for cured coatings such as powder coat or paint applications.

Non-chromium substitutes are also available, as more research and development have taken place in recent years. In most cases, the application involves more than one coat, and is limited to either a spray and spin or dip and spray operation. This prohibits its usage for any finer thread size fasteners. The colors are also limited to gray, black or silver finishes. Chromium-free substitutes are desirable and offer excellent performance. However, typical chromium-free alternatives are more expensive than a conventional trivalent chromium application due to process chemistry and requirements for more than a one-coat application.

The Annex II of the ELV directive defines specific heavy metals and provides information on the acceptance allowance of a particular heavy metal with a definite date. Annex II has been periodically revised from time to time (almost every two years) based on new technical developments and available alternatives. The most recent revision (2005/673/EC) occurred on September 20, 2005. This stepwise phase-out should enable the market to change in an appropriate time scale. Taking into account the time required for diffusion of information, retooling of plating shops, creation of full capacity, qualification and validation of parts and components for series manufacturing phase-out on a case-by-case basis is a reasonable route. Okopol (Institute for Environmental Strategies, Hamburg, Germany) suggests differences to the phase-out plan proposed by the experts from industry for those systems where alternatives are well established and already in use.

The main concerns about hexavalent chromium are related to occupational safety and health issues, and to production waste and discharge waters. For these reasons, car manufacturers have already significantly reduced its use in recent years. Zinc chromate and chromium chromate are carcinogenic substances, which upon inhalation cause cancer to the bronchial tract. Skin contact may cause sensitization towards allergic reactions. Human exposure can occur mainly during production, in repair shops during grinding and in recycling processes.

As the European Union revised Annex II of the ELV directive, vehicle manufacturers also have revised their targets for compliance to zero grams of hexavalent chromium. Some of the major manufacturers have established earlier dates (at least a year or two ahead of July 2007), while others have also extended in line with

[**] *METALAST TCP-HF, METALAST International, Minden, NV.*

the European Union's dates. Some vehicle manufacturers have selected dichromates by the color finish and corrosion protection for a gradual elimination process. Most OEMs have established a task force and budget to address this issue.

Tier I and Tier II suppliers have the responsibility to comply with their customer's requirements regardless of the dates established by the European Union. At times, it makes it difficult for them to meet different due dates for more than one OEM customer.

There are other important directives from the European Union that have direct or indirect impact on the ELV directive. WEEE (Waste of Electric and Electronic Equipment) and RoHS (Restriction of Hazardous Substance) have a tremendous impact on the ELV. The ELV directive restricts four heavy metals (cadmium, lead, mercury and hexavalent chromium), RoHS restricts these four plus (PBB and PBDE), while WEEE requires prevention, reuse/recycle and its disposal. The European Council and the European Parliament have reached reconciliation on the text of this pair of directives. These directives became law on December 31, 2002 with transposition into national legislation within 30 months (latest by June 2005) with material restrictions applying from January 1, 2006 at the point of sale to a consumer. The WEEE directive is the first true "producer responsibility" directive. In other words, the producer must finance the total cost of disposal (including collection from the last user) of the product at the end of its life and prove that implemented recycling targets have been met. These requirements started on December 31, 2004. There is now a real incentive for every manufacturer to create products from which more parts can be recycled more completely.

Summary and conclusions

It must be acknowledged that corrosion protection needs to be tested on a long-term basis. The widespread usage of hexavalent chromium in the automotive and other industries makes this elimination program very complex. The different functions of hexavalent chromium in addition to corrosion protection and the safety and human health issues make a phase-out of hexavalent chromium following a case-by-case process reasonable.

It is suggested that hexavalent chromium be replaced with a suitable trivalent chromium coating. There are several commercially available substitute trivalent chromium chemistries on the market; the most recent development being TCP, now commercially available. It offers outstanding advantages over conventional trivalent chromium systems. Most trivalent chromates are offered with a topcoat or a sealer to enhance the performance in order to meet engineering specifications. Some products have a pale and lighter finish that can be darkened with a dye. One should consider a non-chromium finish wherever possible to avoid future replacements of interim coatings based on trivalent chromium based chemistry. Non-chromium substitutes are available for limited applications. There are color or finish limitations and the number of suppliers is small. It may also be a good time to evaluate your specifications as well as manufacturing process; either could be modified to an appropriate level.

Two major critical factors are the timing and cost of the program. The magnitude of the program is rather large. The timing to run samples, evaluation of test data to meet engineering specifications and the acceptance by the customer would perhaps take four to six months or even longer. The dates established for these directives are: July 2007 for ELV, July 1, 2006 for RoHS and December 31, 2006 for WEEE. The OEMs have set up their own dates as the time line for acceptance of components with no hexavalent chromium. The cost may depend on several factors, most importantly the selection of a particular process and the supplier's capability. Production volume also plays an important role in determining cost. In general, higher raw material cost, shorter bath life and higher concentration are the contributing factors for higher cost of trivalent chromium. Limited availability of non-chromium substitutes and higher raw material costs are the major factors for the higher cost of non-chromium deposits.

The replacement of hexavalent chromium for the compliance of EU directives is a tremendous environmental task that will require a team approach among chemical suppliers, the electroplaters (applicators) and manufacturers. This is not an option. It is a legal requirement by the European Parliament and the Council of the European Union. Even though the ELV directive is implemented for the sale of motor vehicles within the EU member nation states, and RoHS and WEEE for consumer and household goods, they have expanded globally due to global manufacturing. The objective is to re-use and recover with a preference to re-use and recycle wherever possible. This reduces waste, while at the same time improving the environmental performance by related industries.

References

1. F. A. Lowenheim, *Electroplating*, McGraw-Hill Book Co., New York, NY, 1978.
2. M. Schlesinger, *Modern Electroplating*, John Wiley and Sons, Inc. New York, NY 2000; p. 293, 299.
3. P.C. Wynn and C.V. Bishop, *Product Finishing*, 2 (2001).
4. S.F. Rudy, *Plating and Surface Finishing*, **93** (6), 34 (2006).
5. Official Journal of the European Union, L 269/34, 21.10.2000.
6. Official Journal of the European Union L 25, 28.1.2005, p.73, Commission Decision, 2002/525/EC.
7. Official Journal of the European Union L 25/73, 28.1.2005, Commission Decision, 2005/63/EC.
8. Official Journal of the European Union L 152/19, 15.6.2005, Commission Decision, 2005/438/EC.
9. Official Journal of the European Union L 254/69, 30.9.2005, Council Decision, 2005/673/EC.
10. Official Journal of the European Union Common Position (EC) No. 19/2002, (2002/C90 E/02).
11. Official Journal of the European Union L 37/19, 13.2.2003 Directive 2002/95/EC (RoHS).
12. Official Journal of the European Union L PE — CONS 3662/ 02.
13. Official Journal of the European Union L 37/24, 13.2.2003 Directive 2002/96/EC (WEEE).
14. OSHA Final standard on Hexavalent Chromium National News Release 06-342-NAT 2.27.06.
15. H. Bhatt, "Status Update for End of Life Vehicle Directive," *Proc. AESF/EPA Conference 2003*, AESF, Washington, DC, 2003.

About the Author

Harish Bhatt is Vice President, Technology at METALAST International, Minden, NV. Internationally respected and former Senior Technical Specialist for Visteon Automotive and Ford Motor Company for 16 years, Harish has over 30 years experience in the metal finishing industry. He served as an active member of SOC (Substance of Concern) committee for US CAR (United States Council of Automotive Research), which was founded by Ford, General Motors and Chrysler as the auto industries leading technology and environmental association consisting of 33 of the top automotive companies in the United States. Additionally, for over 15 years, he has been the speaker at various technical conferences around the world including the SAE (Society for Automotive Engineers), AESF (American Electroplaters and Surface Finishers Society), NAMF (National Association of Metal Finishers), MFSA (Metal Finishing Suppliers' Association) and the AAC (Aluminum Anodizing Council). As Vice President of Technology for METALAST, Harish directs and manages all metal finishing and technical support-related operations, including research and development, training and education, as well as new and existing product/technology validation.