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

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The deadline for European Union's Directives is approaching. RoHS (Restriction of Hazardous Substance) is effective July 1, 2006, WEEE (Waste of Electric and Electronic Equipment) is effective December 31, 2006 and 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.

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Introduction

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 the 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 a EU directive 2000/53/EC. This directive aims at the prevention of wastes from vehicles and 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 purpose; for all other purposes, the limit is 0.0 gram. The Annex II of the directive has been periodically revised (6/2002, 1/2005, 6/2005 & 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 allowance, and also its exception. The revision of Annex II is Commission Decision (6/2005, 2005/438/EC) and it amends "spare parts put on the market after 1 July 2003 which are used for vehicles put on the market before 1 July 2003 are exempted from the provisions of Article 4(2)(a). The latest revision of Annex II (9/20/2005, 2005/673/EC) is European Union Council Decision and amends 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 chrome 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 chrome, 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 electric 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 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, PBB or PBDE. Annex to this directive – application of lead, mercury, cadmium and hexavalent chromium, which are exempted from the requirement of Article 4(1) – "hexavalent chromium as an anti-corrosion of the carbon steel cooling system in absorption refrigerators".

2005/618/EC: Commission Decision of 18 August 2005 amending Directive 2002/95/EC of the European Parliament and of the Council 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 is 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 shall apply from 1 July 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 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-electroplating coatings on the lead frame, the lead frame alloy and gold-bonding wires.

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

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 shall 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 not covered by Directive 2000/96/EC. Examples of products outside the scope of RoHS are – piezo-electric ignition, combustion engine with ignition, gasoline driven lawnmower, pneumatic tools, gas cooker with electric clock, teddy bear with batteries, high-voltage switchgear, medical equipment, and measurement and control equipment. Criteria "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 covers spare parts for the repair, or the reuse, of electrical and electronic equipment put on 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, e.g. producers, distributors and consumers and in particular those operators directly involved in the treatment of waste

electrical and electronic equipment. Product registration date was August 13, 2005. This directive is effective 31 December 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 1000 Volt for alternating current and 1500 Volt 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 article 1 and 2 addressing financing in respect of 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 13 August 2004.

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

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

Body

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. Hex chrome can be found in finishes on metallic parts such as fasteners, brackets, levers, etc. Cr^{+6} is also widely used on hardware parts, electronics, household appliances and consumer items. It is also 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 cut), textile dyes (ammonium dichromate, potassium chromate, potassium dichromate, sodium chromate), wood preservation (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, strong and potentially hazardous oxidative strength, and poor chrome 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).

Typical application of hexavalent chromium (for metal parts) is as a layer for corrosion protection over zinc coated steel surface. It is a wet, gelatinous film, drying at the surface. Subsurface moisture provides self-healing and lubricity properties. Cr^{+6} also offers torque and tension to meet fasteners' finishing requirement. 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: The cathodic corrosion prevention which is applied mainly for smaller steel parts and the rinsing solutions containing hexavalent chromium which are used in paint shops following a pretreatment with phosphatization 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 of deposit (self healing).

End of Life Vehicle directive is for vehicle and its component manufacturing that are 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 is used per car as an 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 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 function 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 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 no-chrome alternatives available though the applications and availability are limited due to the nature of deposit. The substitutes are readily available for rinsing solutions after phosphatizing and are in widespread usage for car bodies.

Several trivalent chromates are commercially available. Their performance is at least as good to meet the current specifications with hexavalent chromates, and in most cases, (the performance) is enhanced with a topcoat or a sealer following an immersion in a heated chromate bath. In recent years there has been a tremendous development for the performance and color finish of a trivalent chrome 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 a 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 supplier's chemistries to perform zinc plating with a trivalent chromate and a sealer/topcoat followed by a dye.

The Department of Defense, United States Navy has developed a trivalent chromium pretreatment called TCP and has licensed (to companies such as METALAST International) for commercial applications. This unique process is based on formulation that contains trivalent chromium and zirconate for performance that exceeds any conventional trivalent chromium to meet requirements of many MIL and industry 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 immersion, spray or wipe application. It can be applied over aluminum, zinc plated steel and over just about any 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 meets compliance to all three (ELV, RoHS, WEEE) EU directives. It provides harder and denser deposit (as compared to a conventional trivalent

chrome), offers corrosion resistance that meets or exceeds performance of hexavalent chromates, it can be baked following TCP application without degradation or loss of performance, it is electrically conductive, and most importantly, TCP does not require any topcoat or a sealer (like most commercially available trivalent chromates) to enhance its performance. It is an ideal undercoat for cured coatings such as powder coat or paint applications.

No-chrome 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. Chrome free substitutes are desirable and offer excellent performance. However, typical chrome free alternatives are more expensive than a conventional trivalent chromium application due to its chemistry and requirement for more than a one-coat application.

The Annex II of the ELV directive defines specific heavy metals and provides information on 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 20 September 2005. This step-wise 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 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 of 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 ELV directive. WEEE (Waste of Electric and Electronic Equipment) and RoHS (Restriction of Hazardous Substance) have tremendous impact on ELV. The ELV directive restricts four heavy metals (cadmium, lead, mercury & hexavalent chromium), RoHS restricts these four plus (PBB & 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 have became law by December 31, 2002 with transposition into national legislation within 30 months (latest by June 2005) with material restrictions applying from January 1, 2006 at 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 (laid down) have been met. These requirements started December 31, 2004. There is now a real incentive for every manufacturer to create products of which more parts can be recycled more completely.

Summary and Conclusions

It has to 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 the 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 to replace hexavalent chromium with a suitable trivalent chromium coating. There are several commercially available substitute trivalent chrome chemistry in the market; the most recent development is TCP, and now the commercially available version METALAST TCP-HF, which offers outstanding advantages over a conventional trivalent chrome system. Most of

trivalent chromates are offered with a topcoat or a sealer to enhance the performance in order to meet your engineering specifications. Some products have a pale and lighter finish that can be darkened with a dye. One should consider a no-chrome finish wherever possible to avoid a future replacement of interim coating of trivalent chromium based chemistry. No-chrome substitutes are available for limited applications. There are color or finish limitations and the number of suppliers. 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 this program. The magnitude of the program is rather large. The timing to run samples, evaluation of test data to meet your 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 – major factors are the selection of a particular process and the supplier's capability. Production volume also plays an important role for the cost. In general, higher raw material cost, shorter bath life, and higher concentration are the contributing factors for higher cost of trivalent chrome. Limited availability for no-chrome substitutes and higher raw material cost are the major factors for higher cost of no-chrome deposits.

The replacement of hexavalent chromium for the compliance of EU directives is a tremendous environmental task that will require a team approach among the 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 European Union. Even though ELV directive is implemented for the sale of motor vehicles within the EU member nation states, 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 is to reduce waste, while at the same time improving the environmental performance by related industries.

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