Massachusetts Chemical Fact Sheet

Hexavalent Chromium Compounds

This fact sheet is part of a series of chemical fact sheets developed by TURI to help Massachusetts companies, community organizations and residents understand the chemical's use and health and environmental effects, as well as the availability of safer alternatives.

Hexavalent chromium compounds are a toxic form of chromium and are used in a variety of industrial processes and products.

Hexavalent chromium compounds are human carcinogens, mutagens and developmental toxicants and are acutely toxic. Non-hexavalent chromium compounds do not pose the same level of concern with regard to either chronic or acute toxicity.

Until 2011, all chromium compounds were treated as a single category under TURA. Beginning with reporting year 2012, hexavalent chromium compounds are reportable under TURA as a separate category and are designated as a Higher Hazard Substance, which lowers the reporting threshold to 1,000 lb/year.

Terminology

Chromium (Cr) is a naturally occurring metal that exhibits a range of possible forms or oxidation states ("valence states"). The most commonly found forms are:

- **Zero valence.** Metallic chromium or Cr(0) is found in metal alloys.
- **Trivalent.** Chromium compounds are stable in the trivalent form (III or +3).
- **Hexavalent.** The hexavalent (VI or +6) form is the second most stable state. Hexavalent chromium rarely occurs naturally; it is usually produced from industrial activity. Cr(VI) can also be generated through hot work, such as welding of stainless steel or other metals alloyed with Cr.

A number of commonly used hexavalent chromium compounds along with their chemical formulas are listed in Table 1.

Hazards

Cr(VI) compounds are toxic to both humans and wildlife. Human health hazards include respiratory, gastrointestinal, immunological, hematological, reproductive, and developmental toxicity, as well as eye and skin irritation.[1]

Table 1: HEXAVALENT CHROMIUM COMPOUNDS: SELECTED EXAMPLES*

Compound	Chemical Formula	CAS #
Ammonium chromate	$(NH_4)_2Cr0_4$	7788-98-9
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	7789-09-5
Barium chromate	$BaCrO_4$	10294-40-3
tert-Butyl Chromate	$[(CH_3)_3CO]_2CrO_2$	1189-85-1
Calcium chromate	$CaCrO_4$	13765-19-0
Chromic acid	H_2CrO_4	7738-94-5
Chromium VI chloride	$CrCl_6$	14986-48-2
Chromic trioxide	CrO_3	1333-82-0
Hexavalent chromium ion	Cr^{6+}	18540-29-9
Lead chromate	$PbCrO_4$	7758-97-6
Lead chromate oxide	$PbCrO_4$-PbO	8454-12-1
Potassium chlorochromate	$KCrO_3Cl$	16037-50-6
Potassium chromate	K_2CrO_4	7789-00-6
Potassium dichromate	$K_2Cr_2O_7$	7778-50-9
Silver chromate	Ag_2CrO_4	7784-01-2
Sodium chromate	Na_2CrO_4	7775-11-3
Sodium dichromate dihydrate	$Na_2Cr_2O_7 \cdot 2H_2O$	7789-12-0
Sodium dichromate	$Na_2Cr_2O_7$	10588-01-9
Strontium chromate	$SrCrO_4$	7789-06-2
Zinc chromate	$ZnCrO_4$	13530-65-9
Zinc dichromate	$ZnCr_2O_7$	14018-95-2

*Note: List is not comprehensive of all hexavalent chromium compounds.

Acute (Short-Term) Health Effects

Cr(VI) exposure can cause several short-term and intermediate effects including, but not limited to, respiratory irritation, nosebleeds, running nose, nasal ulcerations, asthma exacerbations, skin burns, and pneumonia.[1]

Chronic (Long-Term) Health Effects

Cr(VI) compounds can cause cancer. The International Agency for Research on Cancer (IARC) classifies Cr(VI) compounds as Group 1 (carcinogenic to humans). Exposure to Cr(VI) is associated with lung cancer, nasal and sinus cancers.[2] Inhalation is the main route of exposure understood to induce cancer. Evidence is also emerging regarding cancer risks associated with ingesting Cr(VI) compounds, and human and animal studies document links to other types of cancers (skin, oral, and intestinal).[3]

Intermediate and chronic respiratory exposure (i.e., more than 15 days) can cause: damage to the nasal mucous membrane, perforation of the nasal septum, decreased pulmonary function and asthma.[4] If inhaled through the mouth, Cr(VI) can cause periodontitis and gingivitis.

Effects of chronic Cr(VI) skin exposure include skin sensitization (contact dermatitis), hypersensitivity reactions, eczema, and kidney or liver damage. The characteristic lesions resulting from hexavalent chromium exposure are referred to as "chrome holes" or "chrome ulcers." Chronic eye exposure can result in conjunctivitis.[4]

Both hexavalent chromium compounds and non-hexavalent chromium compounds are associated with asthma.[5]

Occupational Exposure

The primary sources of occupational exposure to hexavalent chromium compounds are associated with three scenarios: as a byproduct when other forms of Cr are used in processes or operations that occur at high temperatures, during the manufacture of Cr(VI) compounds from other forms of Cr, and when using products or substances containing Cr(VI) during the production or manufacture of other products.[4]

According to the Occupational Safety and Health Administration, the majority of workplace exposures to Cr(VI) compounds occur during:

- Welding and other types of "hot work" on stainless steel and other metals that contain Cr;
- Use of pigments, spray paints, and coatings containing Cr(VI); and,
- Operating chrome plating baths.[6]

Additional industries where Cr(VI) occupational exposures can occur include:

- Construction
- Textile production (textile dyeing)
- Glass production
- Leather tanning
- Steel mills
- Production and use of plastic colorants [4]
- Chemical production
- Wood products production (wood preserving)
- Printing
- Electroplating
- Iron and steel foundries

In 2006, it was estimated that 558,000 U.S. workers were exposed to airborne Cr(VI) compounds while another 1,045,500 workers experienced dermal exposure to Cr(VI) compounds in cement, primarily in the construction industry.[4]

Community-Based Exposure

Specific populations may be at greater risk for exposure to Cr(VI). Individuals living near manufacturing operations involving chromium or near hazardous waste sites contaminated by Cr(VI) can be exposed by ingesting or inhaling contaminated soils, food, drinking water or while bathing.[1] Dermal exposure to Cr(VI) can occur from skin contact with contaminated soil or ash from contaminated hazardous waste sites or from consumer products that contain Cr(VI) compounds.[1] Some consumer products known to contain Cr(VI) compounds include certain wood preservatives, cement, textiles, and improperly tanned leather.[1 7] Home-based exposures can also occur in the families of workers who are in contact with Cr(VI) compounds.[1] Exposure to Cr(VI) compounds can also occur from home hobbyist uses (for example, gum bichromate photo processing or home electroplating.)[8]

Recent concern has emerged regarding levels of Cr(VI) in municipal drinking water, with Cr(VI) detected in the majority of U.S. tap water samples tested by a nonprofit organization in 2010.[9] However, recent testing (2011) of water treated by the Massachusetts Water Resources Authority demonstrate levels below California's public health goal of 0.02ppb.[10 11]

Environmental Fate and Hazards

Cr(VI) can be found in air, soil, and water after release from industries that use or produce Cr(VI) compounds, including industries involved in electroplating, leather tanning, textile production, and the manufacture of chromium-based products. Other smaller sources of Cr(VI) emissions include cement producing industries, incineration of municipal refuse and sewage sludge.[1] Cr(VI) compounds can also be released into the environment from the burning of natural gas, oil, or coal.[1]

The toxicity of Cr(VI) to organisms varies. In aquatic environments, algae, saltwater polychaete worms, freshwater and marine crustaceans, rainbow trout, lake trout and some catfish species are relatively sensitive to Cr(VI). The presence of Cr(VI) in irrigation water can kill some types of earthworms. Ingestion of Cr(VI) compounds by mammals can be lethal or can result in severe developmental effects. Ingestion by birds can cause deformities in embryos or reduced survival rates of chicks.[12]

Cr(III) can be oxidized to Cr(VI) in air or water in the presence of manganese oxide or in other oxidizing environments.[1] In general, Cr(VI) levels in soil are favored by higher pH, aerobic conditions, low amounts of organic matter, and situations where there is manganese or low iron.[1 13] Transformation of Cr(VI) to Cr(III) tends to occur in acidic, anoxic soils with high organic content.[13] Studies have observed that most of the uptake in plants is retained in roots, and only a small fraction is translocated to the above-ground part of edible plants.[1]

It is generally believed that chromium (both hexavalent and trivalent) does not bioconcentrate in fish and there is no indication of biomagnification of chromium along the aquatic or terrestrial food chain.[1]

Uses of Hexavalent Chromium

Cr(VI) compounds are used in a range of industrial processes and consumer products. They are widely used as corrosion inhibitors, in the manufacture of pigments, in metal finishing, in chrome plating, in stainless steel production, in leather tanning, and in wood preservatives. For example:

- **Plating.** Cr(VI) may be used in decorative chrome plating (e.g., on some furniture items). It is also used in hard chrome plating (e.g., in jet turbine engines, providing resistance to corrosion, high temperatures, and wear).

- **Coatings.** Anti-corrosion coatings containing hexavalent chromium compounds are widely used. Hexavalent chromium coatings are "self-healing," meaning that ions migrate to fill in areas where the coating is damaged. They are particularly useful in marine applications due to their resistance to salt spray.
- **Pigments.** Hexavalent chromium-based pigments are valued for their vivid colors and resistance to weathering; they have historically been used in traffic paints for those reasons.
- **Wood preservatives.** The biocidal properties of hexavalent chromium compounds are key to their use in wood preservatives (e.g., chromated copper arsenate (CCA)).[8] The use of CCA was phased out in 2004 for residential and consumer uses, and has largely been replaced by other preservatives.

Use & Environmental Releases of All Chromium Compounds in Massachusetts

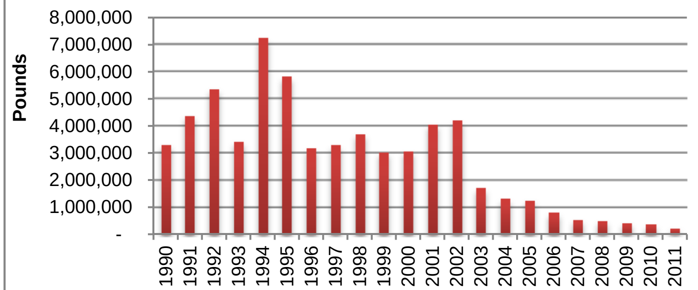
In Massachusetts, from 1990 to 2011, companies reported data under TURA using the chromium compounds category, which can include both Cr(VI) and Cr(III) forms. Thus, historical data trends are available only for this broad category. **Beginning with reporting year 2012, facilities using Cr(VI) compounds will report these specifically as hexavalent chromium compounds.**

Companies reporting chromium compounds in the greatest quantity in Massachusetts have been involved in the production of pigments, metal finishing, electroplating, and the manufacture of abrasives and asphalt roofing shingle granules. Since 1990, more than 70 facilities have reported chromium compounds use at some point.

From 1990 to 2011, use of chromium compounds among facilities reporting to the TURA program declined 93%, from 3.3 million pounds in 1990 to 243,974 pounds in 2011 (Table 2 and Figure 1). The 1994 and 1995 spike in use was due to one manufacturer of refractory and abrasive materials who reported large quantities of chromium compounds in those 2 years. A large part of the decline in use between 2002 and 2004 is due to the phase-out of CCA as a wood preservative by the wood products industry.

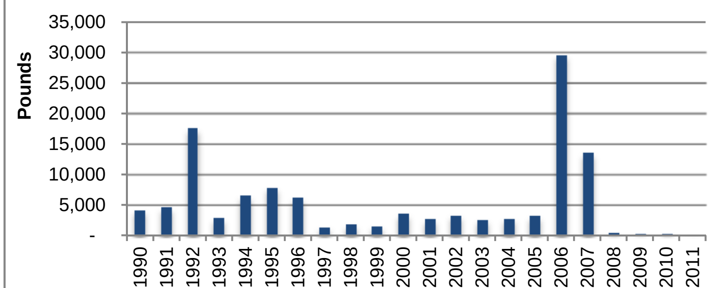
Releases to the environment declined 95% from 4,275 pounds in 1990 to 213 pounds in 2011 (Table 2 and Figure 2). The spikes in releases in 1992, 2006 and 2007 were due to on-site land treatment and surface impoundment, by a leather tanner in 1992, and by an electricity generating plant in 2006 and 2007.

Figure 1: Chromium Compounds Use, 1990-2011, TURA Program



This chart shows use of chromium compounds, and does not include zero valence chromium (chromium metal). Where possible, reported quantities have been adjusted to reflect this distinction.

Figure 2: Chromium Compounds Environmental Releases, 1990-2011, TURA Program



This chart shows use of chromium compounds, and does not include zero valence chromium (chromium metal). Where possible, reported quantities have been adjusted to reflect this distinction.

Table 2 summarizes the uses of chromium compounds in Massachusetts in 1990 (first year of the TURA data) and 2011. These data reveal:

- Seven facilities reported using chromium compounds in 2011, a decrease from 29 facilities in 1990.
- As of 2011, metal finishing and pigments continue to be important sectors using chromium compounds. Electricity generation is also significant, due to Cr(VI) in fuel, and represents the principal source of environmental releases.
- Use of CCA for the manufacture of treated wood has been eliminated in Massachusetts, both as a result of voluntary action by the industry, as well as U.S. EPA regulations that restrict its use in a majority of residential use applications.[15] The three wood products companies that reported in 1990 have phased out their use of CCA. Newer products include copper azole and alkaline copper quaternary preservatives.[14]

Table 2: SUMMARY OF CHROMIUM COMPOUNDS USE IN MASSACHUSETTS (1990-2011)[a]						
	1990			2011		
Use Category	Use (lbs.)	Releases (lbs.)	# Filers	Use (lbs.)	Releases (lbs.)	# Filers
Electricity generation	-		0	72,308	187	1
Leather tanning	107,439	0	2	-	-	0
Metal finishing						
Facilities that plate or treat with Cr	51,728	5	3	2,532	0	1
Manufacturers of metal finishing chemistries	251,226	5	3	72,386	0	1
Metal products	123,997	515	3	-	-	0
Photography and audio film	813,239	260	3	-	-	0
Pigments						
Resins and coatings	1,213,531	725	10	83,111	13	3
Laminated paper	19,650	0	1	-	-	0
Textile dyes	62,000	2,750	1	-	-	0
Wood preservatives	671,090	15	3	-	-	0
Waste recyclers	-	-	0	13,582	13	1
TOTAL	**3,313,900**	**4275**	**29**	**243,974**	**213**	**7**

[a] This table shows use of chromium compounds, and does not include zero valence chromium (chromium metal). Where possible, reported quantities have been adjusted to reflect this distinction.

Availability of Alternatives

Applications of Cr(VI) that continue to be relevant in Massachusetts and for which safer alternatives are available include: surface treatments, paints, sealants, electroplating, and pigments.

Surface treatment

Chromate solutions provide specific performance benefits related to corrosion resistance and other surface treatment performance objectives. The primary characteristic of chromate surface treatment is the ability of the surface to "self-heal" when damaged. When a metal surface is scratched, for instance, the hexavalent chromium ions travel within the surface finish matrix to "heal" the damaged surface.

Passivation

Citric acid is a viable alternative for the use of chromic acid for passivation (corrosion resistance) of stainless steel. Citric acid can be used for all stainless steel alloys, though this may be limited by the geometry or performance needs of the part being treated. Other options for passivation in some cases include nitric acid and plasma oxidation. Nitric acid is a TURA listed chemical.

Anodizing

Chromic acid is also used for anodizing – a passivation process that builds up an oxide layer and is often used on aluminum surfaces.

Sulfuric acid anodizing is an alternative to the Cr(VI) process and is more widely used than chromic acid. However, for some critical applications, the properties of the Cr(VI) process continue to be preferable. For complex geometries, if sulfuric acid becomes entrapped, it can cause corrosion during the product's service life, while chromic acid does not. This limitation helps to account for the continued use of chromic acid anodizing for protective coatings in the aerospace and defense sectors. [16]

Aluminum and zinc conversion coatings

Conversion coatings inhibit corrosion on metal parts and prepare the surface for adhesion of primers and other coatings. These coatings are important in military, nautical and aerospace applications.

Traditional Cr(VI) conversion coatings are being replaced by Cr(III) alternatives for some applications, including a material developed and patented by the U.S. Naval Air System Command. These Cr(III) alternatives are now called for in some military and aerospace specifications. However, there are limitations and barriers for adopting the non Cr(VI)-based processes, including:

- The non-Cr(VI) materials are more susceptible to contamination and require tighter operating windows, different pre-treatment and post-treatment processes (e.g., the use of a deoxidizing bath), and more careful bath maintenance. In addition, some customers require that the non-Cr(VI) process be certified by the National Aerospace and Defense Contractors Accreditation Program (NADCAP).
- Military and aerospace specifications for specific colors can be difficult to achieve with non Cr(VI) alternatives. Some color-matching success has been achieved through use of dyes; however, use of these chemicals could raise other health and environmental concerns. There is an ongoing need for work throughout the supply chain to achieve solutions in this area, including revising color specifications when possible.

Etching

Chromic acid is used to etch plastic products prior to plating a metal surface onto the products. This process requires a relatively high concentration of Cr(VI) in solution. Alternatives include alkaline etch chemistries or plasma etching. Use of plasma etching is not possible for all types of plastics.

Anti-Corrosion Sealants and Paints

Sealants

Sealants containing soluble Cr(VI) compounds are used in a variety of aerospace/defense manufacturing applications. They are used to fill gaps and recesses to prevent water intrusion and collection, in an effort to prevent corrosion of the base metal. Cr(VI) sealants are most commonly used on aluminum assemblies and are often over-coated with a variety of primers and topcoats that, for aerospace/defense applications, commonly do not contain hexavalent chromium.

Alternative sealants without Cr(VI) are now commercially available. These sealants use zinc phosphate and phosphate salts as corrosion inhibitors. TURI is working with aerospace/defense industry leaders and federal government agencies to conduct further research on the corrosion prevention efficacy of these sealants under the most demanding applications in corrosive environments.[17]

Paints and Primers

Alternatives to chromated primers include praseodymium, a rare earth element; zinc-rich and magnesium-rich coatings; as well as some powder coats and e-beam cured coatings. The effectiveness of alternatives depends on the use environment, substrate material, and performance requirements, such as product life, adhesion, and corrosion protection. There are additional human and environmental health impacts associated with the life cycle of metals that are in many of the alternatives.

Pigments, Colorants and Dyes

Pigments containing Cr(VI) are used for coloring both plastics and paints. In paints, Cr(VI) not only serves as a pigment, but also provides corrosion protection. In the early 1990's, many businesses found that they were able to replace chromium in the majority of pigments in which it had been used previously.

A variety of alternatives are available for Cr(VI) compounds in pigments. Some alternatives also pose significant health and environmental hazards, while others are superior from a health and environmental perspective. Alternatives include inorganic pigments based on acid solutions of synthetic oxonitrides,[18] iron oxide pigments,[19] bismuth vanadate pigments,[20] organic/inorganic pigment blends using titanium dioxide, mixed metal oxide titanites and/or iron oxide, rutile tin zinc compounds, and others.[21]

Electroplating

Decorative plating

For decorative chromium electroplating applications, switching from a Cr(VI) compound to a Cr(III) compound is technically straightforward. Comparison testing shows that the trivalent plating process has many advantages over the hexavalent process, and the finished product performs similarly.

Important advantages to switching to a Cr(III) process from a Cr(VI) process include greater material efficiency (less off-gassing occurs and, thus, less aerosol is produced), as well as greater energy efficiency. Primary limitations include: concern about slight differences in color, which can be an issue for facilities that produce replacement parts (e.g., for faucets or other household equipment); and in some cases, the need for additional passivation techniques to ensure durability and corrosion resistance.

Some Massachusetts metal finishing companies have phased out the hexavalent process; however, many continue to offer a choice of processes in order to meet customer requirements.

Hard (functional) chromium electroplating

Replacing Cr(VI) in hard/functional chromium electroplating applications is more difficult. One of the challenges to the adoption of alternatives is the prevalence of military specifications that specifically require the use of Cr(VI).

The U.S. Department of Defense (DoD) and others have increased efforts to adopt alternatives to Cr(VI). Based on an alternatives assessment conducted by TURI, available options include: metallic (e.g., tungsten carbide) high velocity oxygenated fuel (HVOF) thermal sprays, weld facing methods, heat treatments and plasma nitriding, electrodeposited nanocrystalline cobalt-phosphorus coating, physical and chemical vapor deposition, and Cr(III).[8] All of the alternatives have the potential to offer equivalent or better performance, as well as environmental and human health improvements compared to hard chrome plating.[8] However, some of the alternatives also use materials that pose health concerns.

Opportunities

Research into alternatives for the various uses of Cr(VI) continues. For instance, TURI is working with companies across the aerospace and defense industry supply chain to promote the adoption of safer alternatives for specific applications (www.turi.org/aerospace_defense_research). The Department of Defense has also created a useful database of alternatives information (www.assetsdefense.org).

The hazards associated with the continued use of Cr(VI) are significant and there is an urgent need to minimize risk for workers and the environment. However, in key sectors such as the aerospace and defense industries, the primary users of the chromate solutions are often smaller facilities (job shops) whose choices of technology and chemistry depend largely on customer requirements. For this reason, continued collaboration throughout the supply chain is critical for long-term decisions to specify safer alternatives. In the case of specifications for specific color requirements, direct conversation between the job shops and their customers must be prioritized to identify and implement acceptable changes. The solutions require cooperation and training to assure appropriate adoption of alternatives.

Regulatory Context

Due to their serious adverse health effects, Cr(VI) and its compounds are subject to multiple regulations at the state, federal, and international levels. The tables below summarize pertinent regulations that affect the use of Cr(VI) in Massachusetts (Table 3), as well as nationally (Tables 4-5) and internationally (Table 6).

Table 3: MASSACHUSETTS REGULATIONS	
Toxics Use Reduction Act	• Effective in reporting year 2012, designated as a Higher Hazard Substance and subject to reporting and planning requirements for use at or above 1,000 lb/year
Environmental & Public Health	• Ambient air guidelines, threshold effects exposure limit (24-hr average), 0.003 $\mu g/m^3$ • Allowable Ambient Limit (annual average), 0.0001 $\mu g/m^3$ • Drinking water standard: same as U.S. EPA SDWA standard (all chromium compounds)
Waste Clean-up	• Under the MA Contingency Plan (MCP), a concentration of 30 $\mu g/m^3$ in soil is considered protective of current and future uses of the remediated property, including the potential to leach into ground water used as a drinking water source. MCP also outlines other standards for Cr(VI), such as standards for protection of ecological receptors.

Table 4: U.S. REGULATIONS	
Emergency Planning and Community Right-to-Know Act	• Subject to TRI Sec. 313 reporting, under the "chromium compounds" category • Included on the list of extremely hazardous substances and subject to Tier II reporting requirements
Clean Air Act	• A listed Hazardous Air Pollutant • Facilities using chromium & chromium compounds are subject to the National Emission Standards for Hazardous Air Pollutants (NESHAP) area source standards for nine metal fabrication and finishing source categories and for plating and polishing facilities (40 CFR Part 63 Subparts XXXXXX and WWWWWW).
Clean Water Act	• Chromium is listed as a toxic pollutant with guidelines set for Cr(VI)
Occupational Safety and Health Act	• 8-hr time weighted average permissible exposure limit, 5 $\mu g/m^3$ (recent NIOSH Recommended Exposure Limit, 0.2 $\mu g/m^3$)
Safe Drinking Water Act	• Maximum Concentration Level (MCL) 0.1mg/L (set in 1991 for all Cr compounds) • EPA is currently considering setting a separate MCL for Cr(VI)
Federal Drug Administration	• Amount of chromium (total chromium) in bottled water limited to 0.1mg/L
Department of Defense - DFARS	• For Department of Defense contracts, prohibits the use of more than 0.1% Cr(VI) in any homogeneous material where acceptable substitutes are available. (Defense Federal Acquisition Regulation Supplement [DFARS], 76 FR 25569)

Table 5: OTHER U.S. STATE REGULATIONS (*not comprehensive*)	
California	• Cr(VI) compounds regulated as carcinogens and developmental toxicants under the Safe Drinking Water and Toxics Act of 1986 (Proposition 65) • Cr(VI) public health goal, 0.02 ppb in drinking water • Proposed drinking water standard for Cr(VI) of 10 ppb (August 2013)
19 states	• Toxics in packaging laws that limit the total concentration of Cr(VI) to 100 ppm

Table 6: INTERNATIONAL REGULATIONS (*not comprehensive*)	
European Union	• Use in electrical and electronic equipment restricted under the Restriction on Hazardous Substances (RoHS) • As of January 2014, a number of Cr(VI) compounds or categories are subject to Authorization requirements under REACH – use will be prohibited unless authorization is granted for a specific application. Sunset dates range from 2015 to 2017. • Toy Safety Directive sets limits for Cr(VI) and Cr(VIII) in accessible parts of toys • Dangerous Substances Directive regulates chromium in several different applications
China	• Regulation of Hazardous Substances in Electrical and Electronic Equipment (known as China RoHS)
Korea	• Korea RoHS (or the Act for Resource Recycling of Electrical and Electronic Equipment and Vehicles) restricts the use of Cr(VI) in electronic equipment and vehicles, including component parts
India	• E-waste (Management and Handling) Rules 2011 restricts use of Cr(VI) in new electronic products

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