Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name: Dichromium tris(chromate)

EC Number(s): 246-356-2

CAS Number(s): 24613-89-6

Submitted by: FRANCE[1]

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[1] Dossier drafted by Anses (French agency for food, environmental and occupational health safety) on behalf the French competent authority on REACh.

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PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CATEGORY 1A OR 1B CMR, PBT, VPVB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name: Dichromium tris(chromate)

EC Number(s): 246-356-2

CAS Number(s): 24613-89-6

- The substance is proposed to be identified as a substance meeting the criteria of Article 57 (a) of Regulation (EC) 1907/2006 (REACH) owing to its classification as carcinogen category 1B according to CLP Regulation[2] (which corresponds to classification as carcinogen category 2[3])

Summary of how the substance meets the CMR (1A or 1B) criteria

Dichromium tris(chromate) is covered by index number 024-010-00-X of Regulation (EC) No 1272/2008 and classified in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: “May cause cancer”). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen, Carc. Cat. 2 (R45: “May cause cancer”).

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogen in accordance with Article 57 (a) of REACH.

Registration dossiers of the substance submitted: yes

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[2] Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances.

[3] Classification in accordance with Regulation (EC) No 1272/2008, Annex VI, part 3, Table 3.2 List of harmonised classification and labelling of hazardous substances (from Annex I to Council Directive 67/548/EEC).

PART I

JUSTIFICATION

1. IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

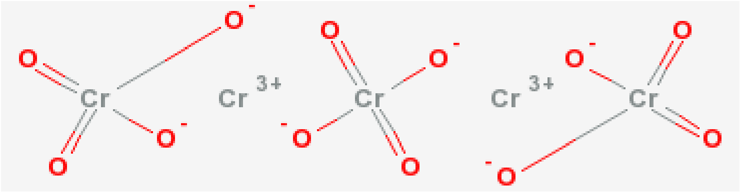
A common background description of chromium and chromate compounds is provided in annex I and annex II.

1.2 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	246-356-2
EC name:	dichromium tris(chromate)
CAS number (EC inventory):	24613-89-6
CAS name:	Chromic acid (H_2CrO_4), chromium(3+) salt (3:2)
IUPAC name:	Dichromium(3+) trichromate
Annex I index number:	024-010-00-X
Molecular formula:	Cr_5O_{12} $CrH_2O_4 \cdot 2/3Cr$
Molecular weight range:	452
Synonyms	Chromic chromate, Chromium (III) chromate, Dichromium trischromate
Main trade names	Accomet C; other trade names are confidential

Structural formula:



1.3 Composition of the substance

Name: Dichromium tris(chromate)

Description: Mixed chromium III, chromium VI salt formed when chromic acid solution is partially reduced.

Degree of purity: ≥ 80 % (w/w), ≤ 97 % (w/w)

Table 2: Constituents

Constituent	**Typical concentration**	**Concentration range**	**Remarks**
Dichromium tris(chromate) EC n°: 246-356-2	ca. 90 % (w/w)	80 ≤ [C] ≤ 97 % (w/w)	

Table 3: Impurities

Impurities	**Typical concentration**	**Concentration range**	**Remarks**
/	/	/	/

Table 4: Additives

Additives	**Typical concentration**	**Concentration range**	**Remarks**
none	/	/	/

1.4 Physico-chemical properties

Table 5: Overview of physicochemical properties

Property	**Value**
Physical state at 20°C and 101.3 kPa	Freeze-dried dichromium tris(chromate) is a dark purple/black granular solid, with an amorphous non-crystalline structure.
Melting/freezing point	The substance melts above 300°C
Boiling point	n/a
Vapour pressure	n/a
Relative density	2.269 g/cm^3 at 20°C
Water solubility	96.6 g/L at 20°C.
Partition coefficient n-octanol/water (log value)	n/a inorganic compound
Dissociation constant	n/a
Oxidising properties	Oxidizing solid according to the CLP (Ox. Sol. 1)
Granulometry	Not known

2. HARMONISED CLASSIFICATION AND LABELLING

Dichromium tris(chromate) is covered by index number 024-010-00-X in Annex VI, part 3, Tables 3.1 and 3.2 of Regulation (EC) No 1272/2008 as follows:

Table 6: Classification according to part 3 of Annex VI, Table 3.1 (list of harmonised classification and labelling of hazardous substances) of Regulation (EC) No 1272/2008

Classification		**Labelling**		**Specific Conc. Limits, M-factors**	**Notes**
Hazard Class and Category Code(s)	**Hazard statement Code(s)**	**Pictogram, Signal Word Code(s)**	**Hazard statement Code(s)**		
Ox. Sol. 1 Carc. 1B Skin Corr. 1A Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H271 H350 H314 H317 H400 H410	GHS03 GHS08 GHS05 GHS07 GHS09 Dgr	H271 H350 H314 H317 H410		T

Key:
Ox. Sol. 1 : Oxidising solids
Carc. 1 B: Carcinogenicity
Skin Corr. 1A : Skin corrosion
Skin Sens. 1 : Skin sensitisation
Aquatic Acute 1, Aquatic Chronic 1: Hazardous to the aquatic environment

H271: May cause fire or explosion; strong oxidiser
H350: May cause cancer
H314: Causes severe skin burns and eye damage
H317: May cause an allergic skin reaction
H400: Very toxic to aquatic life
H410: Very toxic to aquatic life with long lasting effects
GHS03: Flame over circle
GHS08: Health hazard
GHS05: Corrosion
GHS07: Exclamation mark
GHS09: Environment
Dgr: Danger

Note T : This substance may be marketed in a form which does not have the physical hazards as indicated by the classification in the entry in Part 3. If the results of the relevant method or methods in accordance with Part 2 of Annex I of this Regulation show that the specific form of substance marketed does not exhibit this physical property or these physical hazards, the substance shall be classified in accordance with the result or results of this test or these tests. Relevant information, including reference to the relevant test method(s) shall be included in the safety data sheet.

Table 7: Classification according to part 3 of Annex VI, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Council Directive 67/548/EEC) of Regulation (EC) No 1272/2008

Classification	**Labelling**	**Concentration Limits**	**Notes**
O; R8 Carc. Cat. 2; R45 C; R35 R43 N; R50-53	O; T; C; N R: 45-8-35-43-50/53 S: 53-45-60-61		
Key: O: Oxidising properties Carc.: Carcinogenic C: Corrosion N: Dangerous for the environment R8: Oxidising; Contact with combustible material may cause fire R45: May cause cancer R35: Corrosive; Causes severe burns R43: May cause sensitisation by skin contact R50-53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment S53: Avoid exposure - obtain special instructions before use S45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible) S60: This material and its container must be disposed of as hazardous waste S61: Avoid release to the environment. Refer to special instructions/Safety data sheets			

3. ENVIRONMENTAL FATE PROPERTIES

Not relevant for this dossier

4. HUMAN HEALTH HAZARD ASSESSMENT

Please refer to Annex III to get an informal overview of the human health hazard assessment on 5 chromium compounds covered by the Risk Assessment Report (E.C., 2005) (chromium trioxide, sodium dichromate, sodium chromate, ammonium dichromate and potassium dichromate) and from other sources regarding the irritation, corrosion and sensitisation effects. This risk assessment report is mainly based on reviews from Cross et al (1997) and Fairhurst and Minty (1989).

Contrary to five other hexavalent chromium compounds (potassium dichromate, ammonium dichromate, sodium chromate, chromium trioxide, and sodium dichromate) dichromium tris(chromate) was not placed on the third list of substances for assessment within the European Union's (EU) Existing Substances Regulation (ESR) 793/93 and consequently was not subjected to a risk assessment.

5. ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant for this dossier.

6. CONCLUSIONS ON THE SVHC PROPERTIES

6.1 PBT, vPvB assessment

Not relevant for this dossier.

6.2 CMR assessment

Dichromium tris(chromate) is covered by index number 024-010-00-X of Regulation (EC) No 1272/2008 and classified in Annex VI, part 3, Table 3.1 (the list of harmonised classification and labelling of hazardous substances) as carcinogen, Carc. 1B (H350: “May cause cancer”). The corresponding classification in Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008 is carcinogen, Carc. Cat. 2 (R45: “May cause cancer”).

Therefore, this classification of the substance in Regulation (EC) No 1272/2008 shows that it meets the criteria for classification as carcinogen in accordance with Article 57 (a) of REACH.

6.3 Substances of equivalent level of concern assessment

Not relevant for this dossier.

PART II

INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

7. INFORMATION ON MANUFACTURE, IMPORT/EXPORT AND USES – CONCLUSIONS ON EXPOSURE

Contrary to five other hexavalent chromium compounds (potassium dichromate, ammonium dichromate, sodium chromate, chromium trioxide and sodium dichromate), dichromium tris(chromate) was not placed on the third list of substances for assessment within the European Union’s (EU) Existing Substances Regulation (ESR) 793/93 and consequently was not subjected to a risk assessment.

Data reported hereafter on manufacture, uses, volumes, etc. have been collected from a review of the available literature and the registration dossiers, then checked with results from a French consultation of stakeholders performed in June 2011. Comments and contributions were received from civil and military aeronautic/aerospace sector (GIFAS - French aerospace industries Association) and steel industry (FFA - French Steel Federation).

Given confidentiality reasons, only public data from the registration dossiers are reported hereafter.

7.1 Manufacturers

Dichromium tris(chromate) is still produced in Europe by manufacturers located in France, Spain, Germany, Italy and United-Kingdom.

7.2 Manufacturing process

According to HSDB, a method of manufacturing dichromium tris(chromate) consists of an incomplete reduction of chromium trioxide and a precipitation of trivalent chromium with chromate anion.

Dichromium tris(chromate) is also produced by reduction of a chromic acid solution in water. The substance has chromic acid (CAS No. 7738-94-5) as main impurity.

Potential identified sources of occupational exposure within the manufacturing process are the following: use in closed continuous process but with occasional exposure (during sampling, maintenance...), transfer (charging, discharging, mixing) of substance or preparation from/to containers and vessels (manual or automatic), handling.

7.3 Quantities manufactured, import and export

The worldwide production and consumption of dichromium tris(chromate) is not known. Data from the registration dossiers are confidential.

In the frame of ECHA’s approach for prioritisation of SVHC for inclusion in Annex XIV of REACh (recommendation process), the annual quantity manufactured within the EU meets the tonnage band of 10-100 tons (“relatively low” volume supplied in the EU).

SPIN database of substances in preparations in Nordic countries gives some information concerning the total use of dichromium tris(chromate) in Finland between 2002 and 2008 (see figure 1 below). The use of this substance is not reported in other Nordic countries.

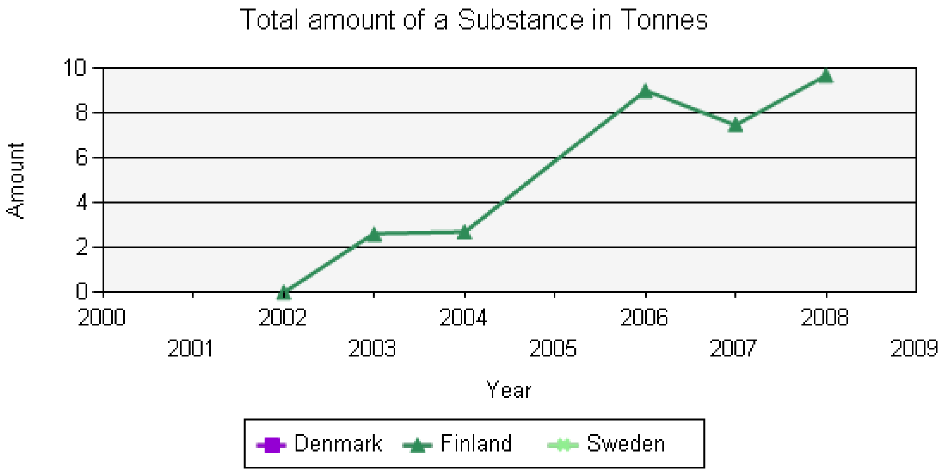


Figure 1: Total use of dichromium tris(chromate) in Finland between 2002 and 2008 [KEMI, 2011]

7.4 Functions of the substance according to its properties; mechanisms of action

As other chromates, dichromium tris(chromate) provides excellent corrosion protection to metal substrates (especially steel and aluminum). In addition, chromates often form good bonding layers, improving the bond between a paint system and a surface, which also helps to improve corrosion resistance.

According to GIFAS (French aerospace industries Association) dichromium tris(chromate) is used as chromate conversion coating of aluminum in anticorrosive preparations, following a first step of chemical conversion or chromic anodizing (that use other chromate compounds). The use of dichromium tris(chromate), especially in the surface finishing sector and steel industry, to formulate bath solutions for aluminium anodizing (using usually chromium trioxide / chromic acids oligomers in solution) may be expected but is not confirmed neither in the registration dossier neither through consultation.

Conversion coating is a chemical passivation process which generates an oxide film on the metal surface that protects it from white corrosion by enhancing rust resistance. Chemical passivation can be used on various metals. Chromate conversion coating is widely used because of its effectiveness and low cost. The chromate coating acts like a paint, protecting the zinc from white corrosion, this can make the part several times more durable depending on chromate layer thickness. It is commonly used on aluminum alloy parts in the aircraft industry where it is often called chemical film. As for a classical primer, it has additional value as a primer for subsequent organic coatings, as untreated metal, especially aluminium that is difficult to paint or glue

Anodising of aluminium is an electrolytic passivation process (forced passivation) used to increase the thickness of the natural oxide layer on the surface of metal parts (natural passivation in oxidant conditions). Anodising increases corrosion resistance and wear resistance, and provides better adhesion for paint primers and glues than bare metal. The most widely used anodising specification, MIL-A-8625, defines three types of aluminium anodisation: Type I is chromic acid anodisation, Type II is sulfuric acid anodisation and Type III is sulfuric acid hardcoat anodisation. The oldest anodising process uses chromic acid which does not lead to the deposition of chromium but uses chromic acid as electrolyte in the solution. It is widely known as the Bengough-Stuart process. Chromic acid produces thinner, 0.5 µm to 18 µm more opaque films that are softer, ductile, and to a degree self-healing. They are harder to dye and may be applied as a pretreatment before painting. Once again, the use of dichromium tris(chromate) for this purpose is not confirmed and available data are not sufficient to conclude.

Annex IV gives an overview of metal surface treatments and metal finishing processes using chromate compounds.

7.5 Types of uses

Identified uses from the registration dossiers are:

- formulation of metal treatment products;
- industrial surface treatment of metals- reactive anti-corrosion primer for steel and aluminium;
- laboratory reagent (minor use).

Because of its corrosion inhibitor property, dichromium tris(chromate) is used in mixtures for specific uses such as chemical conversion against corrosion, post-treatment in hot dip galvanizing, pretreatment of organic coating, passivation (of galvanized steel sheets for instance).

Examples of sectors of use for such industrial surface treatment are construction and aeronautics.

Information from the Swedish Product Register:

The following non-confidential use categories (UC 62) have been communicated to the Swedish product register in the years 2008 and 2009 for dichromium tris(chromate) in preparations [KEMI, 2011]:

- surface treatment,
- corrosion inhibitors.

Another use identified in the literature is catalyst in the mordanting of yarns [HSDB, 2011].

7.5.1 Formulation of dichromium tris(chromate) containing mixtures/preparations

According to a review of the literature, formulations could contain dichromium tris(chromate) from 0.1 up to 20 %.

Preparations are used (as end use) by the different activity sectors, resulting in service life (for articles concerned by the application of such products: part of aircrafts, part of buildings ...) and waste stages (see parts 7.5.2 and 7.5.3).

7.5.2 Use in the industrial surface treatment

The dichromium tris(chromate) is supplied as part of formulated anticorrosive products for industrial surface treatment of steel and aluminum. As similar other anticorrosive chromate compounds, such products are expected to be marketed as primer paints and coatings.

The dichromium tris(chromate) in the formulation reacts on contact with the metal surface to form a thin metal oxide conversion layer on the surface of the metal. The surface of the treated metal will have an insoluble chromium (III) metal oxide layer (where metal is Fe or Al depending on the substrate) following treatment.

7.5.2.1 Use in the aerospace sector

According to GIFAS (French aerospace industries Association) dichromium tris(chromate) is used

- as chromate conversion coating in anticorrosive preparations for specific touch up of damaged aircraft metal parts, following a first step of chemical conversion or chromic anodizing,
- in stock solutions used to formulate metal pre-treatment mixtures for touch up of aircraft wings structure and engine blades following chromic anodizing.

According to Gifas, the consumption of dichromium tris(chromate) by members of Gifas is estimated around 2 tons/year in France and involves19 french sites.

Dichromium tris(chromate) in “ready-to-use” stick (for instance Touch-N-Prep Alodine, cf. figure 2) is used in chemical conversion treatment of aluminum alloys against corrosion (no-rinse conversion coating), preparation before painting and refinishing after treatment of corrosion, local corrosion protection in aircraft maintenance. The feasibility of using of another chromate for the same purpose is not known, but may be in theory achievable.

According to the manufacturer (Henkel), “the design of the stick allows repair of hard-to-reach places or the underside of aircraft. This application method controls the amount of coating applied to the surface, reduces the amount of chemical used and generates no secondary waste associated with other repair methods”.

Figure 2: Example of a Touch-N-Prep® pen

When the conversion coating solution is applied to aluminum, it converts the oxide on the aluminum to a chromium/aluminum oxide. This newly formed chromium/aluminum oxide layer provides increased corrosion resistance and improves paint adhesion. This oxide layer also provides a conductive corrosion resistant film for electrical bonding and grounding applications where low electrical contact resistance is required. Note that other methods of application are spraying, brushing and immersion.

According to the manufacturer (Henkel), advantages for using the Touch-N-Prep® pens include: increased shel-life compared to other methods of applying, reduced operator exposure to the conversion coating solution, logistics advantages such as in field repair to aircraft, reduced labor time, and the elimination of hazardous waste being generated. Applying conversion coatings using the Touch-N-Prep® pens does not require any rinsing or wiping. The solution simply dries in place. Occupational exposure appears to be limited, except during preparation of substrates already coated with this product (deburring, sanding, etc.).

Dichromium tris(chromate) is also used in stock solutions to formulate metal pre-treatment mixtures for touch up of aircraft wings structure and engine blades following chromic anodizing. This use is no more developed hereafter because of a lack of information. According to Gifas, this use involves one French site and represents 10 litres per year.

7.5.2.2 Use in the steel industry:

According to FFA (French Steel Federation), there are 3 main uses of dichromium tris(chromate):

- post-treatment in hot dip galvanizing;
- pretreatment of organic coating;
- passivation of galvanized steel sheets.

No more detailed information has been shared by Industry.

Different processes are used for metal passivation such as the chem-coater, primarily used in the aluminium and steel sectors. It is used to apply a variety of media in processes that do not involve rinsing.

The formulation is pumped to the chem-coater for use in metal passivation. Because this process involves the application of low viscous media at high speeds, total protection against splashes is needed. The chem-coater can be used for coils that are running either vertically (see example drawing in Figure 3) or horizontally.

Another possibility is metal surface treatment by spraying with spraying tunnels or spraying basins. Note that spraying generates aerosols and possible occupational exposure.

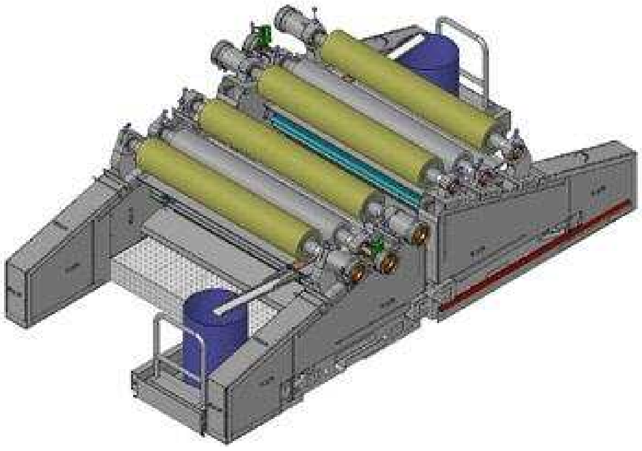


Figure 3: chem-coater vertical[4]

7.5.2.3 Picture of the metal finishing industry

Metal finishing covers a wide range of varied and complex processes carried out by industry and involve both chemical and physical processing. In the EU there are more than 18 300 installations known to carry out surface treatment of metals and plastics. Approximately 440 000 people are employed in the European surface treatment industry, most of these in small or medium enterprises (SMEs) typically employing 10-80 people [HSE, 2007]. In Germany approx. 45 000 employees are occupied in the metal finish industry, 38 000 of them in 1 500 SMEs [UBA, 2007]. However the part of plants that use chromate compounds, especially dichromium tris(chromate), is not known.

7.5.3 Laboratory use

Dichromium tris(chromate) is also used in laboratories for conducting analysis and performance or quality tests. Volumes are not known but are expected low, compared to the consumption of other industrial uses.

8. CURRENT KNOWLEDGE ON ALTERNATIVES

The toxicity and carcinogenic nature of hexavalent chromium has led to great international efforts to develop alternatives. Many R&D programs are under development, especially in the USA and Europe. However the current amount and accessibility of information on alternatives developed

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[4] http://www.coilcoater.de/english/products/chemcoater/index.html.

within the EU is low and few data have been shared through the French consultations[5]. Following information for each activity sector comes from a review of the literature on all chromate compounds. Alternatives to the specific substance dichromium tris(chromate) are not known. For a same or similar use between two chromate compounds, a substitution/alternative implemented for the one is expected to be effective for the other as well.

8.1 (Metal) surface treatment

Research in the replacement of hexavalent chrome from conversion coating started over 15 years ago, before environmental regulations were enacted [Prosurf, 2008a]. Directive 2000/53/EC on End-of-Life Vehicles (ELV Directive) [EC, 2000] and Directive 2002/95/EC on the Restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) [EC, 2002] were the most drivers for R&D activities for replacement of chromate compounds in metal surface treatment. By now the automotive industry has introduced chromate-free coating systems in most of the connecting elements [Rybka, 2008]. Currently, there are about 30 different alternatives for chromium (VI) coating systems available on the market [Mairhöfer, 2008]. **There is no drop-in solution in replacement of chromate based surface treatment technologies**; however individual solutions could be found for different applications and market segment. Some feasible alternatives, which have been found by literature and internet research, are described below.

Concerning **chromic anodizing**, industrial test is performed with baths based on sulfo-tartaric acid (TSA process); in specific cases hard anodizing or sulfuric oxydation with sulfuric acid instead of chromate solution could be efficient [CRAMIF, 2010]. It seems TSA process is not applicable to parts of aircraft susceptible to fatigue, for parts made from aluminum castings [INERIS, 2011].

Several alternatives show potential regarding chromic acid anodizing replacement as sulfochromic etching replacement (sulfo fluoro nitro ferric, phospho sulfonic, alkaline), dichromate sealing (molybdates salts, electrolytic, trivalent chromium, rare earth salts, Sol Gel), sulfuric acid anodizing (low thickness applications), diluted sulfuric acid anodizing, sulfo boric acid anodizing, sulfo tartaric acid anodizing [Eybel *et al.*, 2011].

Concerning **chemical conversion coating** on aluminium, several alternatives already on the market are based on chromium (III) and fluorure, or based on nickel, cobalt and chromium (III) alloy, or based on zirconium.

It is reported that CrIII based conversion coatings are increasingly being used in the practice as alternative for chromate conversion coatings (passivation) [Galvanotechnik, 2005]. Additional corrosion/wear protection level could be achieved by using the second barrier layer – sealer or Topcoats.

Surface modification can also be applied. Heat can diffuse elements into the near surface region of a substrate to form an alloy or compound layer with improved properties, such as hardness or lubricity. The names of some of the processes are derived from the type of element used: nitriding (nitrogen), boronizing (boron), and carburizing (carbon) plasma diffusion is the process whereby elements are introduced into the surface of the substrate by the use of a gas activated with the

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[5] French consultations conducted in 2010 and 2011 in the context of SVHC identification

desired element at elevated temperatures. Variations on this process include plasma nitriding, nitrocarburizing, and low pressure nitriding [TURI, 2006].

Several new technologies are under industrial development such as ceramic coating on aluminium (Ceratronic® process) [Eybel *et al.*, 2011].

Concerning the **pretreatment of organic coating in the steel industry**: if general substitution of that generic use is in progress, there are still some specific applications without short-term solutions, especially in the construction industry [FFA, 2011]. There is no more information available on this topic

8.2 Chromate alternatives researches for United States military uses

United States Department of Defense has been developing and testing chromate alternatives for a number of years. On April 8, 2009 the Under Secretary of Defense for Acquisition Technology and Logistics issued a memo restricting the use of chromates in military systems. As a result of this memo the effort to develop, test and approve alternatives has been accelerated. A number of alternatives are now available, or have been authorized, or implemented. More detailed information on the performance and implementation of alternatives is available on the searchable ASETSDefense database at http://www.asetsdefense.org/.

However, the pace of substitution is necessarily quite slow because these substances are critical to the safe operation of military equipment, particularly aircraft. The costs of corrosion in general are very high, and corrosion can lead to catastrophic failures such as environmental embrittlement and stress corrosion cracking. Alternatives must be thoroughly laboratory-tested and then evaluated in service over a number of years to ensure that they will function safely and effectively in the range of operational environments experienced by defense equipment.

US Department of Defense has already made significant investments to find alternatives for a variety of its uses of hexavalent chromium. Some are approved and some are still undergoing necessary rigorous tests to prove their utility for military applications (which need to operate in extreme environments, be fully reliable, and which tend to last a long time).

Two approaches have been used to provide the US military with Cr(VI) alternatives (Morris et al., 2007). One approach is the use of a Cr(III) based pretreatment, however, toxic forms of cobalt are sometimes used and present in waste streams. The other option is a system’s approach where the corrosion resistance of the conversion coatings (using other chromates like dichromates) are evaluated not as stand alone coatings, but rather as a complete paint coating system. One of several issues arising from this approach is that most of the commercially viable pretreatments are not conversion coatings, but rather adhesion promoters that do not provide inherent corrosion protection if the outer paint coatings are breached. Based on current corrosion protection mechanisms learned from successful rare earth-based primers, a pretreatment chemistry is being developed that is designed to provide inherent corrosion protection for the aluminum alloys and have improved interaction with the chrome-free primers to provide a higher state of the art chrome-free pretreatment and system. The design includes conversion coating composition, which in turn is based on similar chemistries as the chrome-free primer. No chromium is present in the proposed pretreatment or primers used in the coating system. Conclusion drawn from this study is that the chrome-free primer development and implementation in the fleet has been successful. These chrome-free primers have performed well during accelerated corrosion testing, as well as real world exposure conditions. They have demonstrated their ability to perform comparably to chromated primers over currently used military conversion coatings, anodized films, and aluminum alloys.

8.3 State of play of chromium-free alternatives development: technical and economic issues, approach for each activity sector

8.3.1 Technical alternatives and remaining difficulties

Since the decline in the use of lead and chromate containing anti-corrosive agents on toxicological and ecological grounds, the importance of phosphate containing pigments has grown dramatically. As they still cannot replace the traditional anti-corrosive pigments in every respect, efforts are being made to improve both their efficiency, by combining various phosphates or by adding other substances such as zinc oxide or zinc borate, and their reactivity. Some of the most important members of this group include zinc phosphate, chromium phosphate, aluminum triphosphate, barium phosphate and aluminum zinc phosphate.

Primary alternatives to chromate sealants are chrome-free of which there are many on the market. Alternatives are commercially available and some have been authorized and implemented, especially in vehicles and commercial aircraft. They are non Cr-sealants (faying and fillet sealants for edges and overlaps), Teflon tapes and polythioether sealants.

According to SNCZ (consultation conducted in 2010), substitution is not yet possible for the two following applications:

- coil coating metal surfaces for building under oceanic climate (harsh weathering conditions),
- aluminum alloys protection in the aerospace sector.

The global picture obtained from a French survey of recent literature and expert advice from industry and academics [INERIS, 2009] according to the information available at the present time, is that alternative technologies to uses of chromate compounds seem to be available for some applications. Substitution solutions are not universal and shall be developed on a case by case basis. But generally most issues raised by industry appear to be due rather to additional costs, delays of implementation / industrialization, testing, certification of new alternatives, etc. than to a real technical impossibility to substitute. Such difficulties remain more stringent for SMEs which still have problems to access to the core information on alternatives, and financial difficulties (and even impossibilities for very small companies) – low investment capacity to achieve substitution alone.

8.3.2 Economic issue

According to the industry, development of alternatives is costly. But on the other hand new severe rules on occupational exposure to chromates are expected to greatly increase the cost of compliance, due to lower exposure limits, increased cost of protecting workers and increased record keeping and reporting. Chromate containing treatments and primers may cause cost increases at maintenance facilities due to the worker's exposure to hazardous particulate waste generated from paint stripping processes and waste streams. A large contributor to this cost is also the controlled removal and waste management of toxic chromates. Due to tightening regulatory requirements, economic significance of identification and implementation of chrome-free non-toxic alternatives is expected. Development of chrome-free treatments (including chrome free primers), which can protect metal surfaces as well as their chromated counterparts, would be more safe and compliant, resulting in dramatic cost reductions. Further implementation of these safe protective coating systems in industrial settings would then allow cost savings to be passed on to private and commercial sectors [Morris et al., 2007].

Concerning passivation of galvanized steel sheets that may use dichromium tris(chromate) in the steel industry, the substitution of applications in Western Europe is effective and may apply to dichromium tris(chromate) too. There are still difficulties in some countries of Eastern Europe and for exportation for economical reasons [FFA, 2011].

8.4 Alternatives with other chromate compounds, grouping issue

Other chromate compounds (sodium (di)chromate, ammonium (di)chromate, potassium (di)chromate, etc.) also provide anti-corrosion properties through different processes (such as chromate conversion coating, chromic anodizing, etc.) or by direct application of paints/primers or coatings on metal surfaces (zinc chromates, strontium chromate, calcium chromate….).

Regarding the use as anticorrosive agent in preparations (coatings and primers), especially in the steel industry where uses are not sufficiently described, it is assumed that dichromium tris(chromate), strontium chromate (CAS n°7789-06-2) and to a lesser extent potassium hydroxyoctaoxodizincatedichromate(1-) (zinc potassium chromate - CAS n°11103-86-9) and pentazinc chromate octahydroxide (CAS n°49663-84-5) may be substituted by each other. Indeed such substances may exhibit the same mechanism of action and similar physicochemical properties, even if each process/application is yet linked to one specific substance. Please refer to the relevant annex XV dossiers for each substance. The substitution within the aerospace industry (specific touch up of aircraft parts) is not known but it is theoretically possible.

The use of dichromium tris(chromate) in chromate conversion coating and chromic anodizing is assumed, given similar mechanism of action (cf. chapter 7.4). Dichromium tris(chromate), sodium (di)chromate and potassium (di)chromate could be substituted by each other for specific applications. For potassium dichromate this can be supported by a similar solubility range (cf. table 8). The possibility to substitute dichromium tris(chromate) and chromium trioxide (and acids generated from chromium trioxide and their oligomers) is not known but may be assumed for specific applications too.

Table 8: Solubility of main chromate compounds in water

Substance name	CAS number	Solubility (g/L)
Lead chromate	7758-97-6	0.0002
Barium chromate	10294-40-3	0.0027
Pentazinc chromate octahydroxide	49663-84-5	0.02
Zinc potassium chromate	11103-86-9	0.5 to 1.5
Strontium chromate	7789-06-2	1
Dichromium tris(chromate)	24613-89-6	96.6
Potassium dichromate	7778-50-9	45
Ammonium dichromate	7789-09-5	360
Sodium chromate	7775-11-13	530
Potassium chromate	7789-00-6	629
Chromium trioxide	1333-82-0	1667
Sodium dichromate	7789-12-0	2355

9. RISK-RELATED INFORMATION

9.1 Risk assessment of Cr(VI) compounds from the EU risk assessment report

Dichromium tris(chromate) is not covered by the Risk Assessment Report (RAR) published in 2005 (E.C., 2005) which focuses on the most used Cr(VI) substances that are chromium trioxide, sodium chromate, sodium dichromate, potassium dichromate and ammonium dichromate. Therefore risk related to the use of dichromium tris(chromate) has not been assessed yet. However, it belongs to the Cr(VI) compounds family, with a lower hazard concern than other Cr(VI)compounds such as dichromates which combine carcinogenic, mutagenic and reprotoxic properties. RAR draws the conclusion that there is a need for limiting the risks, in particular for workers, and that risk reduction measures which are already being applied shall be taken into account. In view of the carcinogenic and genotoxic properties of Cr(VI) the report concludes that there are concerns for all exposure scenarios. Cr(VI) compounds, including strontium chromate, are indeed considered as non threshold CMR because of the carcinogenic property of the hexavalent oxidative status of chrome. Even if the classification and labelling of Cr(VI) compounds may change case by case, they all get the common Carc. property (1A or 1B according to the case).

In addition, there are concerns for acute toxicity as a result of short-term peak exposures, for skin and eye irritation, respiratory tract sensory irritation, skin sensitisation, occupational asthma and reproductive toxicity (fertility and developmental). These concerns are deemed relevant for all chromates as well.

9.2 Risk assessment from scientific committees on occupational exposure limits

The Scientific Committee on Occupational Exposure Limits (SCOEL) published in December 2004 a report where the carcinogenic effect is considered as the critical effect for hexavalent chromium compounds. In the current state of knowledge no threshold can indeed be identified regarding the proven human carcinogenicity of chromates. SCOEL recommendation has been newly reviewed by the French agency for food, environmental and occupational health safety (Anses) which considers that SCOEL current OEL of 50 µg of Cr(VI) / m^3 does not adequately protect workers from risk of lung cancer (Anses, 2010). Anses recommends to implement the lowest feasible OEL value for uses which cannot be substituted yet, supporting the "as low as reasonably achievable" principle. This OEL-8h for hexavalent chromium as been proposed at 1 µg of Cr(VI) / m^3 and corresponds to an individual excess risk of lung cancer estimated at $1\ 10^{-2}$ (10 additional lung cancer cases in a population of 1000 workers). It is 5 times lower than the lowest current OEL implemented in Europe (Danish OEL).

Anses study has been carried out on the basis of exposure data to all Cr(VI) compounds. Specific data on exposure to dichromium tris(chromate) are unfortunately not available. But we may however consider exposure data collected in this study from the "metal treatment and surface finishing" sector which uses dichromium tris(chromate). In such hypothetic context where exposure to this compound is assumed equivalent to exposure to any of Cr(VI) compounds, we may consider that exposure (cf. arithmetic mean) may exceed the OEL of 1 µg of Cr(VI)/m^3 and for some cases (cf. range) largely exceed it and other worldwide implemented OEL (see table 10).

Table 10: Results of exposure measurements 8 hours to Cr(VI) compounds (expressed in µg CrVI/m^3) per type of metal working branches (Anses, 2010)

Groups	**Number of samples**	**Arithm Mean**	**Geom Mean**	**Median**	**Range**	25th perc.	75th perc.	90th perc.
All groups	458	7,26	0,93	0,603	0,01 - 367	0,453	3	10,3
Metal treatment and surface finishing	162	2,15	0,65	0,5	0,01 - 70	0,5	1	3
Ships and floating structures construction	26	9,41	0,60	0,75	0,01 – 140,1	0,15	2	2,5
Installation of metal structures and tubing	31	0,35	0,06	0,06	0,01 – 1,5	0,01	0,5	1,05
Manufacturing of ventilating and industrial refrigeration equipments	26	6,15	1,70	1,2	0,14 – 50,7	0,52	5,8	21,20

According to an occupational survey from the US department of the air force in 2000 (DoD, 2000), exposure may occur during the scuff sanding of aircrafts. Scuff sanding of epoxy primers releases particulates that contain chromates from previous surface priming procedures. The particulates can be transported into the workers breathing zones and results in chromate exposure. The current very restricting US Air Force OEL for chromate compounds is 0,5 µg of Cr(VI) / m^3, twice lower than the new French proposal of OEL set at 1 µg of Cr(VI) / m^3. Regarding strontium chromate, air sampling results show that 8 hours TWA exposures were greatly in excess of this OEL, with a maximum of exposure around 20 µg of Cr(VI)/m^3. These results may apply for dichromium tris(chromate) as well within the EU where zinc chromates are still used, given the same uses and the same methods of aircraft maintenance and painting.

According to the UK Health and Safety Executive (HSE information sheet, engineering sheet n°32), exposure to chromate compounds in primers paints relates to inhalation of dust, mist, spray, fume or contact with the skin and eyes. The actual risks arising from use of primer paints containing chromium VI may not be as high as those described in the EU risk assessment report for other chromates. As well as those directly handling and applying the paints, anyone in the vicinity is at risk of exposure. They may inhale dust, mist, spray given off during application and/or come into direct skin or eye contact with the paints. Those at risk of exposure also include people working on articles previously coated with such paints, eg rubbing down or sanding painted articles, or doing “hot work” on them such as cutting, welding and brazing. People maintaining or cleaning plant and equipment used to apply or contain such paints may be at risk too.

In conclusion on risks, the European risk assessment report concludes that there are concerns for all exposure scenarios exposure to chromium(VI) compounds given their non threshold CMR status. Several European and International occupational studies and several health institutes point out exposure of workers to chromates that are used in coatings in the aerospace sector (including zinc chromates and strontium chromate). Data from the automotive refinish sector (non individual cars) are not shared by Industry but identical scenarios are expected as well, given similar uses in coatings and similar methods of maintenance and painting. Occupational exposure may exceed usual OELs and greatly exceed the proposed new French OEL of 1 µg of Cr(VI)/m^3 that may not be fulfilled by current implemented protection measures and equipments. The number of European workers concerned is however not known.

REFERENCES

Bastarache E. (2010). Information taken from the Ceramicstoday website on January 2010 - link: http://www.ceramicstoday.com/articles/chrome_english.htm

Cross H.J., Faux S.P., Sadhra S. *et al.* (1997). Criteria Document for Hexavalent Chromium Commissioned by International Chromium Development Association (ICDA), Paris, France.

CRAMIF, 2010. DTE 220 - Traitement de surface - Substituer ou à défaut, réduire et maîtriser l'exposition au chrome hexavalent, 45p..

EC (2000). EU-Directive 2000/53/EC on end-of life vehicles.

E.C. (2005). European Union Risk Assessment Report - Chromium trioxide (CAS-No: 1333-82-0), sodium chromate (CAS-No: 7775-11-3), sodium dichromate (CAS-No: 10588-01-9), ammonium dichromate (CAS-No: 7789-09-5) and potassium dichromate (CAS-No: 7778-50-9) Risk Assessment. 415 p. (EUR 21508 EN - Volume: 53).

Elbetieha A., Al-Hamood M.H. (1997). Long-term exposure of male and female mice to trivalent and hexavalent chromium compounds: effect on fertility. *Toxicology;* 116(1-3):39-47Eybel R., Viola A. (2011). Meeting the Challenge of Environmental Regulations in Europe and North America (Communication), ASETS Conference 2011.

Fairthurst, S. and Minty, C.A. (1989). The toxicity of chromium and inorganic chromium compounds. 243 p. HMSO London. ISBN 0118855212.

FFA (French Steel Federation), 2011. Response to the consultation of the French Ministry of Ecology, Sustainable Development, Transport and Housing. 15th March of 2011.

Galvanotechnik (2005). Korrosionsschutz ohne Chrom(VI) Nur noch 739 Tage Chromatierung – und dann?, Bericht über die Informationstagung der DGO am 21. Juni 2005 in Velbert, Galvanotechnik 11/2005, Eugen G. Leuze Verlag, D - 88348 Bad Saulgau.

HSDB (2011). Hazardous Substances Data Bank. Chromic acid, chromium(3+) salt. http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~6I8Wf1:1

HSE (2007) Human health risk reduction strategy for chromates. Prepared by Health and Safety Executive (UK).

INERIS (2009). Inclusion de substances à l’annexe XIV du Règlement Reach : avis technique sur des composés du chrome hexavalent, 2009. (Technical review of hexavalent chromium compounds), *confidential.*

INERIS (2010). Données technico-économiques sur les substances chimiques en France : Chrome et ses composés, 99 p.

Junaid M., Murthy C.M., Saxena D.K. (1996a). Embryotoxicity of orally administered chromium in mice: Exposure during the period of organogenesis. *Toxicology Letters;* 84(3):143-148.

Junaid M., Murthy R.C., Saxena D.K. (1996b). Embryo- and fetotoxicity of chromium in pregestationally exposed mice. *Bull. Environ. Contam. Toxicol.;* 57(3):327-334.

KEMI (2011) Swedish Chemicals Agency (KEMI), SPIN Database. 3 June 2011.

Mairhöfer, K. (2008). Günstiger Ersatz für die galvanische Verchromung - Serienstart für hochwertige Chrom-Optik, JOT. 8.2008, p.34.

Morris, E., Ray, C., Albers, R, McLaughlin, J., Bean, S., DeAntoni, J., Patel, R. (2007). Using chrome-free primer technology to develop a chrome-free pretreatment. Department of Defense Tri-service Corrosion conference 2007.

https://www.corrdefense.org/Technical%20Papers/Using%20Chrome-Free%20Primer%20Technology%20to%20Develop%20a%20Chrome-Free%20Pretreatment.pdf

Prosurf (2008). Prosurf project (Promotion and Support of SME Research and Innovation in the Surface Finishing and Printed Circuit Manufacturing Sectors), D3 - Economic intelligence document detailing analysis of market trends and opportunities, 2008, p. 17.

http://www.prosurf-online.eu/

Rybka, E. (2008). 6. Fachtagung "Chrom VI-freie Alternativen in der Industrie", 14. - 15. April 2008, Stuttgart, presentation "ChromVI-freie Neuentwicklungen", p. 8, Magni Europe

Trivedi B., Saxena D.K., Murthy R.C. *et al.* (1989). Embryotoxicity and fetotoxicity of orally administered hexavalent chromium in mice. *Reproductive Toxicology;* 3(5):275-278.

TURI (2006). Toxics Use Reduction Institute (TURI), University of Massachusetts Lowell, Five Chemicals Study, Chapter 6: Hexavalent Chromium, 2006.

www.turi.org/library/turi_publications/five_chemicals_study/final_report/chapter_6_hexavalent_chromium

UBA (2007) Umweltforschungsplan FKZ 205 67 462/02. Abschlussbericht zum Forschungsvorhaben Reach - Umsetzungshilfen (RUH), Umsetzunghilfen für ein erfolgreiches Risikomanagement im Rahmen von REACH, 28. Februar 2007 , hier: Anhang 1 -Branchenanlyse der deutschen Galvano- und Oberflächentechnik-;

US-EPA. (2000). Hazard summary on Chromium compounds on the US-EPA website - link: http://www.epa.gov/ttn/atw/hlthef/chromium.html

ANNEXES

Annex I: common background description of chromium and chromate compounds

Chromium is a member of the transition metals, in group 6. Chromium(0) is the metallic form (metallic chromium Cr) and is essentially inert. Chromium exhibits a wide range of possible oxidation states. The most common oxidation states of chromium are (+2), (+3), and (+6). Chromium (II) is the divalent form (oxidation state (+2)): such chromous compounds include chromous chloride ($CrCl_2$) and chromous sulfate ($CrSO_4$).

Chromium (III) is the trivalent form (oxidation state (+3)) which is the most stable. Chromium (VI) is the hexavalent form which refers to chemical compounds that contain the element chromium in the (+6) oxidation state.

Chromium (VI) (or Cr (VI)) is most commonly encountered as oxospecies in the (mono)chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions which are strong oxidising agents at low pH. Their oxidative property is widely used in organic chemistry. Chromates and dichromates are salts of chromic acid and dichromic acid, respectively. Chromic acid, which is an oxacid has the hypothetical structure H_2CrO_4. By losing two protons (H^+), chromic acid and dichromic acid form chromate ion and dichromate ion respectively. Neither chromic nor dichromic acid can be isolated, but their anions are found in a variety of compounds: the chromates and dichromates. The dark red chromium (VI) oxide CrO_3 (chromium trioxide) is the acid anhydride of chromic acid and it is sold industrially as “chromic acid”.

Chromate salts contain the chromate anion CrO_4^{2-} and usually have an intense yellow color. Dichromate salts contain the dichromate anion $Cr_2O_7^{2-}$ and usually have an intense orange color. By comparison, the chromates and dichromates of heavy metals (such as silver and lead) often have a red color.

In aqueous solution, hexavalent chromium exists as hydrochromate $HCrO_4^-$, chromate CrO_4^{2-}, and dichromate $Cr_2O_7^{2-}$ ionic species. Chromate anion tends to dimerize in dichromate. The proportion of each ion in solution is pH dependent. In basic and neutral pH, the chromate form predominates. As the pH is lowered (6.0 to 6.2), the hydrochromate concentration increases. At very low pH, the dichromate species predominate (US-EPA, 2000). Under particular conditions, a polymerisation can occur leading to the production of polychromates with the following formula $Cr_nO_{3n+1}^{2-}$.

Main chromium forms are the following according to their oxidation state:

Chromium metals and alloys (Cr (0)):

Chromium metal

Stainless steel

Other chromium containing alloys

Divalent (Cr (2+)):

Chromous chloride	$CrCl_2$
Chromous sulfate	$CrSO_4$

Trivalent (Cr (3+)):

Chromic oxide	Cr_2O_3
Chromic chloride	$CrCl_3$
Chromic sulfate	$Cr_2(SO_4)^3$
Chromic potassium sulphate	$KCr(SO_4)^2$
Chromite ore	$FeO.Cr_2O_3$

Hexavalent (Cr (6+)) chromate :

Chromium trioxide	CrO_3
Chromic acid	H_2CrO_4
Sodium chromate	Na_2CrO_4
Potassium chromate	K_2CrO_4
Zinc chromate	$ZnCrO_4$
Strontium chromate	$SrCrO_4$

Hexavalent (Cr (6+)) dichromate :

Sodium dichromate	$Na_2Cr_2O_7$
Potassium dichromate	$K_2Cr_2O_7$
Ammonium dichromate	$(NH4)_2Cr_2O_7$
Zinc dichromate	$ZnCr_2O_7$

Annex II: List of chromate compounds (Kemi, 2002)

Name	**Molecular formula**	**CAS no**
Ammonium dichromate	Cr2H2O7.2H3N	7789-09-5
Ammonium chromate	CrH2O42H3N	7788-98-9
Barium chromate	Ba.CrH2O4	10294-40-3
Basic lead silicochromate (pigment)	PbCrO4.SiO2	11113-70-5
Calcium dichromate	Ca.Cr2H2O7	14307-33-6
Calcium chromate	Ca.CrH2O4	13765-19-0
Sulphuric acid, chromium(III) potassium salt	Cr.2H2O4S.12H2O.K	7788-99-0
Chrome yellow, Lead chromium sulphate (pigment)	PbCrO4+PbSO4	1344-37-2
Chromic(VI) acid-chromic salt	CrH2O4 (?)	41261-95-4
Chromic(VI) acid-chromic salt	CrH2O4 (3+)	24613-89-6
Chromic(VI) acide	CrH2O4	7738-94-5
Chromic acid, magnesium salt	CrH2O4.Mg	13423-61-5
Chromic acid, zinc salt	CrH2O4.Zn	13530-65-9
Chromite	FeO.Cr2O3	1308-31-2
Chromium carbide	C2Cr3	12012-35-0
Chromium(III) chloride	Cl3Cr	10025-73-7
Chromium cupper iron oxide	Cr2CuFe2O7	55353-02-1
Chromium fluoride	CrF3	7788-97-8
Chromium hydroxide sulphate	CrHO5S	12336-95-7
Chromium hydroxide sulphate	Cr4H2O22S5	85251-54-3
Chromium(III) nitrate	Cr.3HNO3	13548-38-4
Chromium(III) trihydroxide	CrH3O3	1308-14-1
Chromium(III) oxide	Cr2O3	308-38-9
Chromium oxide green (pigment)	Cr2O3	308-38-9
Chromium(III) sulphate	Cr.3/2H2O4S	10101-53-8
Chromium(IV) oxide	CrO2	12018-01-8
Chromium(VI) trioxide	CrO3	1333-82-0
Guignet´s green (pigment mixture)	Cr2O3xH2O (x = about 2)	12001-99-9
Lead chromate, basic lead chromate orange (pigment)	PbCrO4.PbO	1344-38-3
Lead chromate, Chrome green	CrH2O4.Pb	7758-97-6
Lead chromate oxide	CrH4O5.2Pb	18454-12-1
Lead chromium molybdate sulphate (pigment)	PbCrO4, PbMoO4, PbSO4	12656-85-8
Lithium chromate	CrH2O4.2Li	14307-35-8
Magnesium chromate	CrO2.1/2Mg	12053-26-8
Potassium chromate	CrH2O4.2K	7789-00-6

Potassium dichromate	Cr2H2O7.2K	7778-50-9
Potassium tetrachromate	K2Cr4O1312422-53-6	
Potassium zinc chromate oxide	K2O.ZnO.4CrO3.3H2O	12433-50-0
Sodium chromate	CrH2O4.2Na	7775-11-3
Sodium dichromate	Cr2H2O7.2Na	10588-01-9
Strontium chromate	CrH2O4.Sr	7789-06-2
Zinc chromate hydroxide	CrH8O12Zn5	49663-84-5
Zinc chromate oxide	CrO5Zn2.H2O	15930-94-6
Zinc potassium chromate	Cr2HO9Zn2.K	11103-86-9
Zinc potassium chromate, Zinc yellow (mixture)	ZnO, K2O, CrO4, H2O	37300-23-5

Source: http://apps.kemi.se/flodessok/floden/kemamne_eng/oorganiska_kromsalter_eng.htm

Annex III: Human health hazard assessment

This Annex is given for information only. An Annex XV report on SVHC identification is indeed not the place to discuss the already agreed classification of dichromium (tris)chromate. Its content is however a useful background in support to part II of this report.

Most of the following information are taken from the Risk Assessment Report on chromium compounds (chromium trioxide, sodium dichromate, sodium chromate, ammonium dichromate and potassium dichromate), published by the ECB in 2005 (E.C., 2005).

Considering that all chromate/dichromate ions produced from Cr (VI) compounds will behave similarly in biological tissues, other than the additional property of acidity and its potential influence on toxicity for chromium (VI) trioxide, it has been assumed that all the Cr (VI) compounds can be treated as a common group.

According to the hazard summary from the US EPA (US-EPA, 2000), the respiratory tract is the major target organ for chromium (VI) toxicity, for acute (short-term) and chronic (long-term) inhalation exposures. Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. Epidemiological studies raise concerns for the carcinogenic potential of the Cr (VI) compounds. Animal studies have shown chromium (VI) to cause lung tumors via inhalation exposure.

Toxicokinetics (absorption, metabolism, distribution and elimination)

There is a reasonably good database available on the toxicokinetics of the Cr (VI) compounds under review, although there are relatively few human data. The available data indicate that generally Cr (VI) compounds are likely to behave in a similar manner in respect of toxicokinetics, and that the kinetic behaviour of these substances would be similar in those species studied, including humans.

Following inhalation exposure, animal studies have shown that 20-30% of the administered Cr (VI) is absorbed via the respiratory tract. Highly water-soluble Cr (VI) is poorly absorbed via the gastrointestinal tract (only 2-9% of the dose was absorbed in human studies) due to reduction to the relatively poorly absorbed Cr (III). Only limited dermal absorption takes place through intact skin, with 1-4% Cr (VI) from an aqueous solution crossing the skin in guinea pig studies.

According to results of animal testing, chromium species derived from these compounds can remain in the lungs for several weeks after inhalation exposure and also becomes bound to hemoglobin in erythrocytes for the lifespan of the cells. Part of Cr (VI) becomes reduced to Cr (III) after entering the body due to the influence of reducing agents, for example glutathione. Distribution is widespread even after a single dose and includes transfer of absorbed Cr (VI) across the placenta. Excretion occurs in urine and faeces. Repeated exposure leads to accumulation of chromium in several tissues, particularly the spleen because of uptake of senescent erythrocytes.

Acute toxicity

Highly water-soluble Cr (VI) compounds are very toxic by inhalation and toxic by ingestion. The respiratory tract and the kidney are damaged by these compounds following inhalation and oral exposure respectively. Although acutely harmful or toxic by the dermal route, more severe responses may be observed due to greater uptake via the skin if there is any prior or simultaneous damage to the skin. Depending upon the pH of the Cr (VI) solution, corrosive effects can occur on contact (see section 1.4 on corrosivity).

Irritation

Single application of a low concentration of highly water-soluble Cr (VI) in solution to undamaged human skin resulted in only a mild irritant response around the hair follicles. Animal data indicate that irritation occurs following single application to the skin for 4 hours. It is not possible to determine a clear concentration-response relationship for human skin irritation from the single-exposure animal or occupational data available. Repeated-exposure skin responses are considered under corrosivity (see section 1.4 on corrosivity).

Significant damage to the eye can occur upon accidental exposure to highly water-soluble Cr (VI) compounds. Severe and persistent effects occur when there is contact with the low pH aqueous chromium (VI) trioxide or Cr (VI) solutions at high temperature. A number of case reports have detailed both inflammation of the cornea and conjunctivae and in more severe cases, corneal erosion and ulceration. The severity of response is increased by low pH or high temperature. Accidental eye contact with the corrosive aqueous chromium (VI) trioxide results in conjunctival congestion and necrosis and corneal oedema and opacity. It is not possible to determine a clear concentration-response relationship from the data available.

In a very poorly-reported volunteer study, 10 subjects were apparently exposed to chromium (VI) trioxide at concentrations of 10-24 mg/m^3 (5-12 mg Cr (VI)/m^3) for “brief periods of time”. It was claimed that this exposure caused nasal irritation. According to the authors, exposure to lower but unspecified concentrations produced slight if any irritation of the upper respiratory tract. Given the poor reporting in this study the results cannot be considered to be reliable.

Symptoms of sensory irritation of the respiratory tract are known to occur among chrome plating workers exposed to a mist of aqueous chromium (VI) trioxide. Since this is corrosive, such symptoms are to be expected. No quantitative data on such irritation are available from studies of workers. No studies reporting symptoms of sensory irritation are available for the other Cr (VI) compounds. Overall, it is not possible to determine a reliable concentration-response relationship for respiratory tract irritation using the available data.

Corrosivity

Highly water-soluble Cr (VI) compounds can cause very severe skin effects under certain conditions. In workers repeatedly exposed to highly water-soluble Cr (VI), where there is some slight initial damage to the skin, ulcers can develop which constitute a serious and persistent effect. Animal data are consistent with the observations made in humans. It is not possible to determine a clear concentration-response relationship for repeated-exposure human skin effects from the occupational data available and quantitative data could be misleading given the potential for severe effects resulting from repeated contamination of slightly damaged skin. Overall, highly water-soluble Cr (VI) compounds should be regarded as corrosive.

Sensitisation

Skin sensitisation resulting from contact with Cr (VI) is relatively common in humans working with the compounds. This has been demonstrated in patch testing of contact dermatitis patients and in investigations of various occupational groups. In addition, skin sensitisation potential has been clearly demonstrated in standard and modified guinea pig maximisation tests and in the mouse ear swelling test.

Current understanding of the mechanism involved in the sensitisation indicates that Cr (III) is the ultimate hapten. Skin contact with Cr (VI) leads to penetration of Cr (VI) into the skin where it is reduced to Cr (III). There is some evidence for cross-reactivity between Cr (III) and Cr (VI); Cr (VI)-sensitised subjects may also react to Cr (III). Overall, it is not possible to reliably determine a threshold for either induction or challenge in an exposed population using the available data.

According to Ceramicstoday (Bastarache E., 2010), hexavalent chromium can penetrate the skin where it is reduced to trivalent chromium which plays the role of an hapten; when fixed on a protein, it becomes a complete antigen. Chromate sensivity has proved fairly persistent once developed. Contact with textiles colored with chromate-based pigments can be sufficient to exacerbate the dermatitis. The wearing of leather shoes tanned with chromates can produce dermatitis of the feet if these are allowed to remain sweaty. In sensitized individuals, the absorption of chromium by pulmonary and/or oral way could cause an exzematous reaction. After cutaneous exposure to chromic acid, erosions of the skin may occur. These « chrome holes » initially appear as papular lesions, either singly or grouped, with central ulceration.

The available case reports and evidence from well-conducted bronchial challenge tests, show that inhalation of Cr (VI) compounds can cause occupational asthma. As with skin, Cr (VI) - sensitised subjects may react to Cr (III). It is not possible to determine a no-effect level or exposure-response relationship for induction or elicitation of occupational asthma.

Repeated dose toxicity

Please refer to sections 1.4 and 1.5.

Mutagenicity

In vitro data

There is a very large body of evidence indicating that the Cr (VI) ion in solution is directly mutagenic in *in vitro* systems. Extensive *in vitro* testing of highly water-soluble Cr (VI) compounds has produced positive results for point mutations and DNA damage in bacteria, point mutations, mitotic crossing-over, gene conversion, disomy and diploid in yeasts, and gene mutation, DNA damage, chromosome aberrations, sister chromatid exchanges and unscheduled DNA synthesis in mammalian cells.

The *in vitro* genotoxicity of Cr (VI) was diminished considerably by the presence of reducing agents, in the form of tissue S9 or S12 fractions, gastric juice or reducing agents such as glutathione, ascorbate or sulphite. These all serve to reduce Cr (VI) to Cr (III) outside the cell therefore greatly reducing entry of chromium into the cell.

In vivo data

The genotoxicity of Cr (VI) compounds *in vivo* has been less extensively studied. Parenteral administration of sodium or potassium dichromate or potassium chromate to rats or mice resulted in significant increases in chromosome aberrations and micronucleated cells in the bone marrow and DNA single-strand breaks, interstrand cross-links and DNA-protein cross-links in the liver, kidneys and lung. A mouse spot test involving intraperitoneal injection of potassium chromate gave positive results. Oral studies have been negative but these employed lower dose levels and absorption is known to be poor by the oral route. Overall, water soluble Cr (VI) compounds are *in vivo* somatic cell mutagens in animal studies.

A significant increase in post implantation deaths in a dominant lethal assay was reported in mice following intraperitoneal injection of potassium dichromate. Toxicokinetic data for water-soluble Cr (VI) compounds indicate that chromium will reach the germ cells following inhalation exposure (i.e. a relevant route of exposure for humans). Therefore taking these two observations together, it can be concluded that water-soluble Cr (VI) compounds have the potential to produce germ cell mutagenicity.

Human data

A few studies have been conducted in which circulating lymphocytes have been isolated from chromium-exposed workers and examined for chromosome aberrations, micronuclei, sister chromatid exchanges (SCE) and changes in chromosome numbers. In general, the results from better-conducted and reported studies including chromium plating workers in Japan and SS-MMA (manual metal arc on stainless steel) welders in Scandinavia have been negative.

Evidence of genotoxicity has been reported in several other studies of chromate production workers in Eastern Europe and chromium plating workers in Italy. However the manner in which these were conducted and reported precludes full assessment of the significance of the findings.

Summary and discussion of mutagenicity

Few studies of genotoxic potential in humans are available. No evidence of genotoxic activity has been found in adequately-conducted studies in circulating lymphocytes from chromium exposed workers. In contrast, there is a vast array of genotoxicity data *in vitro* and less extensive testing in animals available. The evidence clearly indicates that highly water-soluble Cr (VI) compounds can produce significant mutagenic activity *in vitro* and *in vivo*. The Cr (VI) compound under consideration is therefore regarded as *in vivo* somatic cell mutagen. In addition, toxicokinetic and dominant lethal data suggest that water-soluble Cr (VI) has the potential to be an *in vivo* germ cell mutagen. For information and according to the American Conference of Governmental Industrial Hygienists (ACGIH) (Bastarache E., 2010), water-soluble hexavalent chromium compounds include: chromic acid, chromic acid anhydrides, monochromates and dichromates of sodium, of potassium, of ammonium, of lithium, of cesium, of rubidium. Water-insoluble hexavalent chromium compounds include: zinc chromate, calcium chromate, lead chromate, barium chromate, strontium chromate and sintered chromium trioxide.

Carcinogenicity

Carcinogenicity: oral

No data available.

Carcinogenicity: inhalation

A few animal carcinogenicity studies were available. Results indicated that sodium dichromate was clearly carcinogenic, producing lung tumours when administered to rats by continuous inhalation of aqueous aerosol or long-term repeated intratracheal instillation in saline. Also, there was a single incidence of a squamous cell carcinoma of the pharynx after inhalation of sodium dichromate aerosol in rats.

In rats and mice, inhalation studies using an aerosol or mist of chromium (VI) trioxide produced 1-2 test group animals with lung tumours where such were mainly absent among corresponding controls. These studies suffered from some deficiencies in design such as small group size or inadequate dosing regimes. In two intrabronchial implantation studies in the rat, 1-2 animals with carcinomas of the respiratory tract were found in chromium (VI) trioxide-treated groups. No respiratory tract tumours were observed in controls in these studies.

Carcinogenicity: dermal

No data available.

Carcinogenicity: human data

forms of Cr (III) and Cr (VI). Unfortunately, detailed analysis of smoking habits is almost invariably absent. In chromate production, workers are exposed to Cr (III) during the production of Cr (VI) in water-soluble form e.g. sodium chromate. Although studies of chromate production have clearly established that there is an increase in lung cancer mortality, it is not clear precisely which Cr (VI) compound(s) produced the effect. An excess risk of lung cancer mortality has also been reported for workers in the chromate pigment production industry. However, this industry involves exposure to sparingly soluble or poorly soluble zinc or lead chromates as well as the sodium dichromate.

Overall, it was concluded that chromium (VI) trioxide in solution is a human carcinogen but only limited information is available for the other Cr (VI) compounds.

Summary and discussion of carcinogenicity

Epidemiology data from chromate production, chromium pigment manufacture and other chromium-exposed groups showing clear increases in lung cancers cannot be specifically related to exposure to Cr (VI) compounds. However, it is highly probable that Cr (VI) ions in solution were the ultimate carcinogenic entity in these situations. Hence these epidemiological studies raise concerns for the carcinogenic potential of the Cr (VI) compounds.

In animal carcinogenicity studies, sodium dichromate was carcinogenic in rats, causing lung tumour production, when given by repeated long term inhalation or intratracheal instillation. In rats and mice, inhalation or intrabronchial implantation studies using chromium (VI) trioxide produced 1-2 test group animals with lung tumours where such were mainly absent among corresponding controls. Thus, in animal studies there is some evidence of respiratory tract carcinogenic activity for sodium dichromate and chromium (VI) trioxide. Similar studies in rats using other Cr (VI) compounds, able to produce Cr (VI) in solution, produced carcinogenicity in the lung. Hence there is good reason from animal studies to be concerned about the carcinogenic potential of the Cr (VI) compounds, in terms of the inhalation route and the respiratory tract as a site of action. Data for the oral and dermal routes and carcinogenicity studies on the Cr (VI) compounds are not available. Chromium (VI) compounds might be expected to have potential to cause cancer on repeated oral or dermal exposure. In the case of the oral route, any systemic carcinogenic potential could be limited by poor absorption of Cr (VI), and reduction to Cr (III) within the gastrointestinal tract although site of contact activity would remain an issue. Similar considerations apply to the skin.

Overall, therefore, the Cr (VI) compounds are considered to have proven or suspect carcinogenic potential. From the available information, and taking into account the genotoxic potential of these substances, it is not possible to identify any dose-response relationship or thresholds for this effect.

Toxicity for reproduction

Effects on fertility

The effects of potassium dichromate on male and female fertility were investigated in sexually mature (7 weeks old) Swiss mice administered this hexavalent chromium compound in drinking water (Elbetieha A. and Al-Hamood M.H., 1997). Groups of 9-20 males were administered 0, 1,000, 2,000, 4,000 or 5,000 mg/L potassium dichromate equivalent to doses of approximately 0, 166, 333, 666, 833 mg/kg/day (0, 60, 120, 235, 290 mg Cr (VI)/kg/day) for 12 weeks and then mated for ten days, 1 male to 2 untreated females. The exposed males were then removed and 1 week later the females were terminated. Similarly, groups of 11-18 females were administered 0, 2,000 or 5,000 mg/L potassium dichromate equivalent to doses of approximately 0, 400, 1,000 mg/kg/day (0, 140, 350 mg Cr (VI)/kg/day) for 12 weeks and then mated for ten days, 3 females to 1 untreated male. One week after the removal of the males, the females were terminated. Number of pregnant females, total implantations, viable fetuses and resorptions were recorded. In addition, satellite groups of 10-13 males and 8-10 females administered 0, 2,000 (males only) or 5,000 mg/L potassium dichromate for 12 weeks were sacrificed at the end of the treatment. Body and reproductive organ weights were recorded in these animals. No explanation is provided in the study report concerning the variability in group size. Also, it is unclear how dose levels were selected.

At higher concentrations, the treated animals consumed less water per day compared to the control group (no more details provided). It is unclear whether or not the dose was adjusted for the reduced water consumption or if these animals received a lower dose. There were no deaths or clinical signs of toxicity in any group of male or female mice exposed. Compared to the control group, a statistically significant reduction in absolute body weight of 10% and 12% was seen in satellite group males at 2,000 and 5,000 mg/L (the only two dose levels at which body weight was recorded), respectively. Body weight of satellite group females administered 5,000 mg/L potassium dichromate (the only dose at which body weight was recorded) was unaffected. Relative testes weights were statistically significantly increased at 2,000 (by 17.5%) and 5,000 mg/L (by 21.5%). Relative seminal vesicles and preputial gland weights were statistically significantly reduced at

5,000 mg/L only (by 27% and 34%, respectively). A statistically significant increase in relative ovarian weight (by 50%) was reported at 5,000 mg/L. It is noted that in the absence of information on the absolute organ weights, the increase seen in relative testis weight could be accounted for by the reduction in absolute body weight observed in males. It is also noted that, in the absence of histopathological examinations, it is difficult to interpret the toxicological significance of these organ weight changes.

Compared to the control groups, the percentage of pregnant unexposed females mated with treated males and of pregnant exposed females mated with untreated males was unaffected by the treatment. The mean number of implantation sites was statistically significantly reduced in females impregnated by males treated with 2,000 (6.33 versus 8.18 in the control group) and 4,000 mg/L potassium dichromate (6.86 versus 8.18), but not with the highest dose (7.84 versus 8.18). Given the absence of a dose-response relationship, the toxicological significance of this finding is uncertain. However, it is possible that at higher concentrations, the actual doses the animals received were lower than the nominal doses, due to the reduced water consumption. There were no resorptions and dead fetuses in the control group and in the females impregnated by males treated with 2,000 or 4,000 mg/L potassium dichromate. However, 3 resorptions were noted in the females impregnated by males treated with the lowest dose (1,000 mg/L). Given the absence of a clear dose-response relationship and that it is not clearly reported whether these findings occurred in one single litter or in different litters, the 3 resorptions seen at 1,000 mg/L are regarded as being incidental. A total number of 6 resorptions and of 6 dead fetuses was also observed in the females impregnated by males treated with the highest dose (5,000 mg/L). Although it is not reported whether these findings occurred in one single litter or in different litters, given the incidence, it is unlikely they occurred in one isolated litter. Hence, the fetolethality reported at this dose level (5,000 mg/L) is regarded as being treatment-related. The mean number of implantations and of viable fetuses was also statistically significantly reduced in females treated with 2,000 mg/L (7.35 versus 9.00 and 6.55 versus 8.76, respectively) and 5,000 mg/L potassium dichromate (7.44 versus 9.00 and 5.88 versus 8.76, respectively). There was also a statistically significant increase in the number of pregnant females with resorptions at 2,000 (53% versus 11%) and at 5,000 mg/L (63% versus 11%). Similarly, a total number of 37 and 14 resorptions (versus 4 in the control group) were observed at 2,000 and 5,000 mg/L, respectively.

Overall, the results of this study indicate that oral administration of potassium dichromate to mice for 12 weeks produced adverse effects on male and female fertility (reduced number of implantations) at 2,000 mg/L (333 mg/kg/day (120 mg Cr (VI)/kg/day) and 400 mg/kg/day (140 mg Cr (VI)/kg/day) in males and females, respectively) and above. These effects occurred, for the males, at dose levels at which a significant reduction in absolute body weight was noted. In the females, no effects on body weight were noted, but at the highest dose of 1,000 mg/kg/day (350 mg Cr (VI)/kg/day) there was a significant increase in relative ovarian weight. A NOAEL for these fertility effects of 1,000 mg/L (equivalent to 166 mg/kg/day potassium dichromate or 60 mg Cr (VI)/kg/day) was identified in males from this study. No NOAEL value was determined for the females as these fertility effects (reduced number of implantations) were reported even at the lowest dose tested of 2,000 mg/L (equivalent to 400 mg/kg/day potassium dichromate or 140 mg Cr (VI)/kg/day). A reduced number of viable fetuses and an increased number of resorptions were observed in females treated with 2,000 and 5,000 mg/L (400 and1,000 mg/kg/day (140 and 350 mg Cr (VI)/kg/day)). In addition, an increased number of resorptions and dead fetuses were seen in untreated females impregnated by males given the highest dose of 5,000 mg/L (833 mg/kg/day (290 mg Cr (VI)/kg/day).

Developmental toxicity

In a developmental toxicity study (Trivedi B. *et al.*, 1989), groups of 10, 13, 12 and 10 pregnant female ITRC-bred albino mice were administered daily 0, 250, 500 and 1,000 ppm of potassium dichromate (equivalent to doses of approximately 0, 60, 120 and 230 mg/kg/day (0, 20, 40 and 80 mg Cr (VI)/kg/day)) in drinking water during gestation from day 0 (vaginal plug identified) to day 19 when dams were sacrificed. At sacrifice, fetuses were subjected to routine external, visceral and skeletal examination, and levels of total chromium in the maternal blood, in the placenta and in the fetuses were measured.

No deaths or clinical signs of toxicity were observed in any of the treated dams. Compared to controls, a statistically significant reduction in maternal body weight gain of 21% was seen at 500 ppm, while at 1,000 ppm, a body weight loss of 4% was recorded. Body weight gain was also reduced by 18% at 250 ppm, although it did not attain statistical significance. No litters were produced at the top dose. Also, 3 females of the low-dose group and 2 females of the middose group did not have any litters. A dose-related (statistically significant in the mid-and highdose groups) increase in pre-implantation loss was seen across treated groups. There were no implantations (100% pre-implantation loss) in the dams treated with 1,000 ppm. Statistically significantly increased incidences of post-implantation losses and resorptions were observed at 250 and 500 ppm. There was also a dose-related (statistically significant in the mid-dose group) reduction in litter size at 250 and 500 ppm. Fetal weight and crown-rump length were statistically significantly reduced in the low- and mid-dose groups. No malformations or major skeletal abnormalities were observed. A statistically significant increased incidence of kinky tail and subdermal hemorrhagic patches and/or streaks on the snout, limbs, back, neck and tail was seen at 500 ppm. A statistically significantly reduced ossification in the phalangeal, sternebral, cranial, thoracic and caudal bones was observed in fetuses of dams treated with 500 ppm. Fetal cranial ossification was also significantly reduced at 250 ppm. No significant abnormalities were seen during soft tissue examinations in any of the treated groups. Total chromium levels were significantly increased above levels in the control group for the maternal blood at 500 and 1,000 ppm, for the placenta at 250 and 500 ppm and for the fetal tissues at 500 ppm.

The complete absence of implantations seen at 1,000 ppm was associated with marked maternal toxicity (body weight loss). A range of adverse effects on development was noted at 500 ppm. These effects occurred at a dose level at which there was a maternal body weight gain reduction of 21%. However, since this reduction in body weight gain can be explained by the reduced litter size and the reduced fetal weight reported at this dose level, these findings may represent a direct effect of potassium dichromate on development. At 250 ppm, adverse effects on development (increased incidence of post-implantation losses and resorptions, reduced fetal weight, decreased crown-rump length and delayed cranial ossification) were observed in the absence of significant maternal toxicity and in association with significant placental levels of total chromium. It can be concluded from the results of this study that oral administration of potassium dichromate through drinking water to pregnant mice caused fetotoxic effects even at dose levels (250 and possibly 500 ppm) at which no maternal toxicity was observed. Thus, a NOAEL value of 120 mg/kg/day (40 mg Cr (VI)/kg/day) for maternal toxicity can be identified from this study, but no NOAEL can be identified for developmental effects as adverse effects were reported even at the lowest dose tested of 60 mg/kg/day (20 mg Cr (VI)/kg/day).

Junaid *et al.* (Junaid M. *et al.*, 1996a) exposed pregnant Swiss albino mice (10 per group) to 0, 250, 500 or 750 ppm potassium dichromate in drinking water during days 6-14 of gestation. Dams were subject to caesarean section on day 19 and fetuses examined. Based on average daily water intakes, Cr levels received were and 2.00, 3.75 and 5.47 mg/mouse/day. Based on a bodyweight of 30 g, the estimated intake of potassium dichromate was 190, 350 and 520 mg/kg/day (70, 125 and 180 mg Cr

(VI)/kg/day). There were no maternal deaths or clinical signs of toxicity but weight gain was decreased at 350 and 520 mg/kg/day (125 and 180 mg Cr (VI)/kg/day) (reductions of 8.2 and 24% respectively). The number of fetuses per litter was statistically significantly decreased by 20 and 18%, fetal weight was decreased (by 13 and 20% respectively compared to controls) and the number of dead fetuses increased (3 in 2 litters, 12 in 7 litters respectively) at 350 and 520 mg/kg/day (125 and 180 mg Cr (VI)/kg/day). Post implantation loss increased to statistically significant levels of 22 and 34% at 350 and 520 mg/kg/day (125 and 180 mg Cr (VI)/kg/day). Reduced ossification, incidence of dropped wrist and subdermal haemorrhagic patches were increased at these dose levels. Overall, chromium (VI) caused fetotoxicity but not malformations at 350 mg/kg/day (125 mg Cr (VI)/kg/day), a dose level which did not produce overt signs of maternal toxicity but caused a small decrease in bodyweight gain. The NOAEL for fetal effects was 190 mg/kg/day (70 mg Cr (VI)/kg/day).

Other studies

In a study (Junaid M. *et al.*, 1996b) specifically performed to assess the effect of pregestational exposure to chromium on development, groups of 15 female Swiss albino mice of proven fertility were administered daily 0, 250, 500 or 750 ppm potassium dichromate (equivalent to doses of approximately 0, 63, 119 and 174 mg/kg/day (0, 20, 40 and 60 mg Cr (VI)/kg/day) in drinking water for 20 days. The animals were then immediately mated for 24 hours with untreated males, and, subsequently, 10 pregnant females were randomly selected from each group and sacrificed on day 19 of gestation. Both ovaries were removed from the dams to determine the number of corpora lutea. Numbers of implantations and resorptions were recorded and the fetuses were subjected to routine external, visceral and skeletal examination. In addition, at sacrifice, levels of total chromium in the maternal blood, in the placenta and in the fetal tissues were measured.

No clinical signs of toxicity were observed in any of the treated females. Mortality (3/15) was noted at the top dose. Although autopsy of these animals could not establish the cause of death, given the number of deaths and the fact that they occurred at the highest dose, they are likely to be treatment-related. Body weight gain was unaffected during the treatment. However, during gestation, almost no body weight gain was seen in the top-dose dams, and a reduction in body weight gain of 14% was observed in the mid-dose dams. Compared to controls, a statistically significant reduction in the number of corpora lutea of 44% was noted at 750 ppm. Also, no implantations were seen in this group. The number of implantations was also statistically significantly reduced (by 29% of the control value) in the dams pregestationally treated with 500 ppm potassium dichromate. A dose-related (statistically significant in the mid-dose group) increase in pre-implantation loss was seen at 250 and 500 ppm. Statistically significantly increased incidences of post-implantation losses were observed at 250 and 500 ppm, and of resorptions at 500 ppm. Fetal weight and crown-rump length were statistically significantly reduced in the low- and mid-dose groups. There was also a dose-related (statistically significantin the mid-dose group) reduction in litter size at 250 and 500 ppm. No malformations or major skeletal abnormalities were observed. A statistically significant increased incidence of kinky tail, short tail and subdermal hemorrhagic patches was seen at 500 ppm. A statistically significant reduced ossification in the parietal, interparietal and caudal bones was observed in fetuses of dams pregestationally treated with 500 ppm. Fetal caudal ossification was also significantly reduced at 250 ppm. No significant abnormalities were seen during soft tissue examinations in any of the treated groups. Total chromium levels were significantly increased above levels in the control group for the maternal blood in all the treated groups, for the placenta at 250 and 500 ppm and for the fetal tissues at 500 ppm.

Overall, the results of this study indicate that pregestational oral administration through drinking water of potassium dichromate for 20 days to female mice produced adverse effects on female fertility (reduced number of corpora lutea and/or increased pre-implantation loss) at 500 ppm (119 mg/kg/day (40 mg Cr (VI)/kg/day)) and above. Fetotoxic effects were also seen starting from the lowest dose level tested, 250 ppm (63 mg/kg/day (20 mg Cr(VI)/kg/day)). Significant maternal toxicity (mortality) was observed at 750 ppm. Body weight gain was also dramatically reduced at this dose level. However, it is noted that this reduction was mainly due to the complete absence of implantations. No significant maternal toxicity was seen at the low and middose levels. Although there was a reduction in body weight gain of 14% at 500 ppm, this was accounted for by the reduced litter size and the reduced fetal weight. It is finally noted that significant levels of total chromium were found in all treated animals at sacrifice, i.e. at around 21 days after the end of the treatment. NOAEL values of 119 mg/kg/day (40 mg Cr (VI)/kg/day) and 63 mg/kg/day (20 mg Cr (VI)/kg/day) can be identified from this study for maternal toxicity and fertility effects respectively. No NOAEL can be identified for developmental effects. Developmental toxicity including increased post-implantation losses and resorptions, reduced litter size, fetal weight and crown-rump length, increased incidence of kinky tail, short tail and subdermal hemorrhagic patches, and delayed ossification of the parietal, interparietal and caudal bones, occurred even in the absence of maternal toxicity.

Human data

A poorly reported study of the course of pregnancy and childbirth in a group of women employed in a chromate production plant produced inconclusive results. Another study claimed that a group of women engaged in the production of “chromium compounds” showed a much greater incidence of pregnancy complications in comparison with a control group without occupational exposure to chromium. The type of exposure to chromium was not specified and the study is of poor quality. No conclusions can be drawn regarding any potential effects of chromium on reproduction in humans due to the poor quality of the investigations conducted.

Summary and discussion of reproductive toxicity

Human data relating to effects on reproduction are limited to poorly reported studies of female workers from which no conclusions can be drawn. There are three animal studies available which focus on fertility. Adverse effects were produced in mice receiving potassium dichromate for 12 weeks in drinking water at 333 mg/kg/day (120 mg Cr (VI)/kg/day) and 400 mg/kg/day (140 mg Cr (VI)/kg/day) and above in males and females respectively. A NOAEL of 166 mg/kg/day (60 mg Cr (VI)/kg/day) was identified in males but no NOAEL was found for females as 400 mg/kg/day was the lowest dose level tested. An increase in resorptions following treatment of males and a decrease in implantations in treated females were among the findings in this study. In another study, pregestational oral administration of potassium dichromate in drinking water to female mice produced adverse effects on fertility (reduced number of corpora lutea and increased pre-implantation loss) at 500 ppm (119 mg/kg/day (40 mg Cr (VI)/kg/day)) and above. NOAEL values of 119 mg/kg/day (40 mg Cr (VI)/kg/day) and 63 mg/kg/day (20 mg Cr (VI)/kg/day) can be identified from this study for maternal toxicity and fertility effects respectively. In a third study, fetotoxicity, including post-implantation losses, has been observed in the mouse following administration of potassium dichromate in drinking water during gestation (days 0-19). Significant developmental effects occurred at the lowest dose level tested, 60 mg/kg/day (20 mg Cr (VI)/kg/day) in the absence of maternal toxicity. Therefore no developmental NOAEL was determined. Qualitatively similar results were obtained in another study in which (350 mg/kg) potassium dichromate (125 mg Cr (VI)/kg) was administered for a shorter period, on days 6-14 of gestation.

Overall, highly water-soluble chromium (VI) compounds should be considered to be developmental toxicants in the mouse. These findings can be regarded as relevant to humans.

It is noted that some of the adverse effects on reproduction observed in animal studies may be related to the germ cell mutagenicity of these chromium (VI) compounds (see Mutagenicity section).

No reproductive toxicity studies are available using the inhalation or dermal routes of exposure.

Annex IV: Treatment and coating of metals, metal finishing processes using chromium (VI) compounds

The main process which involves chromium is electroplating (chrome plating), but other uses are in conversion coatings (passivating and anodising) (E.C., 2005). The electroplating sector constitutes approximately 43% of the total number of companies with metal finishing activities.

According to the industry (French consultation, 2010), main activities of the metal finishing sector using chromate compounds are anodising application, chemical and electrolytic coatings and paints, which represent respectively 5%, 24% and 32% of the total metal finishing activity. Main purposes of metal treatments are appearance improving (12%), resistance to corrosion (46%), wear resistance (24%) and others (electrical conductivity, etc.).

Formulation of metal treatment products

There are many different companies throughout the EU who make formulations for use in metal treatment (E.C., 2005). The formulations are usually confidential. However, the same two basic mixing processes are used to manufacture them: dry mixes or liquid mixes. The process is essentially one of mixing components together into a product and then packaging.

Conversion coating (usually called chromate conversion coating – CCC) or chromating

Conversion coatings are produced by the chemical treatment of metallic surfaces to give a barrier layer of complex chromium compounds on the metal surface, to protect the base metal from corrosion (E.C., 2005). It can also provide a good base for subsequent painting, give a chemical polish and/or colour the metal.

There is a range of processes which fit under this heading; the two involving chromium compounds are **passivating** and **anodising**. Passivating is a chemical treatment applied to a metal product to enhance corrosion resistance whereas anodising is an electrolytic process designed to produce an oxide film integral with the surface of the metal. The compositions of the treatment baths are proprietary and can vary greatly and may contain either chrome (VI) or chrome (III). The coatings can be applied either by immersion or electrolytically (E.C., 2005).

Chromate conversion coating is a type of conversion coating applied to passivate aluminium, zinc, cadmium, copper, silver, magnesium, tin and their alloys to slow corrosion and to make metal-plated parts more durable. The strong oxidative properties of chromates are used to deposit a protective oxide layer of complex chromium compounds on metallic surfaces to protect the base metal from corrosion. This passivation and the self healing properties by the chromate stored in the chromate conversion coating, which is capable to migrate to local defects, are the benefits of this coating method. It can also provide a good base for subsequent painting, give a chemical polish and/or colour the metal.

The chromate coating acts like a paint, protecting the zinc from white corrosion, this can make the part several times more durable depending on chromate layer thickness. It cannot be applied directly to steel or iron, and does not enhance zinc's cathodic protection of the underlying steel from brown corrosion. It is also commonly used on aluminium alloy parts in the aircraft industry where it is often called chemical film, or the well known brand name Alodine. It has additional value as a primer for subsequent organic coatings, as untreated metal, especially aluminium, is difficult to paint or glue. Chromated parts retain their electrical conductivity to varying degrees, depending on coating thickness. The process may be used to add color for decorative or identification purposes. Coating thickness vary from a few nanometers to a few micrometers thick.

The protective effect of chromate coatings on zinc is indicated by color, progressing from clear/blue to yellow, gold, olive drab and black. Darker coatings generally provide more corrosion resistance. Chromate conversion coatings are common on everyday items such as hardware and tools and usually have a distinctive yellow color.

The composition of chromate conversion solutions varies widely depending on the material to be coated and the desired effect. Most solution compositions are proprietary. The widely used Cronak process for zinc and cadmium consists of 5–10 seconds of immersion at room temperature in a solution of 182 g/L sodium dichromate crystals ($Na_2Cr_2O_72H_2O$) and 6 mL/L concentrated sulfuric acid.

Anodising of aluminium is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. Anodising increases corrosion resistance and wear resistance, and provides better adhesion for paint primers and glues than bare metal. The most widely used anodising specification, MIL-A-8625, defines three types of aluminium anodisation: Type I is **chromic acid anodisation**, Type II is sulfuric acid anodisation and Type III is sulfuric acid hardcoat anodisation. The oldest anodising process uses chromic acid which does not lead to the deposition of chromium but uses chromic acid as electrolyte in the solutionhttp://en.wikipedia.org/wiki/Chromic_acid. It is widely known as the Bengough-Stuart process. In the UK it is normally specified as Def Stan 03/24 and used in areas that are prone to come into contact with propellants etc. There are also Boeing and Airbus standards. Chromic acid produces thinner, 0.5 µm to 18 µm more opaque films that are softer, ductile, and to a degree self-healing. They are harder to dye and may be applied as a pretreatment before painting. A sealing is usual needed after anodising and uses different processes, particularly potassium dichromate salt (please see *infra*).

Sealing after anodising

Acidic anodising solutions produce pores in the anodised coating. These pores can absorb dyes and retain lubricants, but are also an avenue for corrosion. When lubrication properties are not critical, they are usually sealed after dyeing to increase corrosion resistance and dye retention. Different types of sealing exist. Teflon, nickel acetate, cobalt acetate, and hot sodium or potassium dichromate seals are commonly used.

Chrome (electro)plating or chrome dipping or chroming

Chrome plating, often referred to simply as chrome, is a technique of electroplating a thin layer of chromium onto a metal object. Chrome is only applied by electroplating. Chromium plating is mainly done either to increase resistance to rust and corrosion, to facilitate cleaning procedures, to increase surface hardness and resistance to wear and tear (hard chrome plating) or for decoration and aesthetic reasons, in order to achieve a shining surface (decorative chrome plating). The surface thickness for the former is typically 10 to 1000 µm, for the latter, between 0.25 and 1.0 µm.

Chrome plating methods

There are two types of industrial chrome plating solutions:

1. Hexavalent chromium baths which main ingredient is chromic anhydre. When mixed with acid, chromate ions CrO_4^{2-}, first form dichromate ions $Cr_2O_7^{2-}$, then chromic acid H_2CrO_4. Solutions containing chromic acid are powerfully oxidizing and highly corrosive.
2. Trivalent chromium baths whose main ingredient is chromium sulfate or chromium chloride

The component will generally go through these different stages.

- Degreasing to remove heavy soiling.
- Manual cleaning to remove all residual traces of dirt and surface impurities.
- Various pretreatments depending on the substrate.
- Placed into the chrome plating vat and allowed to warm to solution temperature.
- Plating current applied and component is left for the required time to attain thickness.

There are four methods of chromium plating: barrel; manual; semi-automatic and automatic (E.C., 2005):

Barrel plating is used for plating small parts at low cost. Either the parts and solution are rotated together in an open-ended barrel or parts are enclosed in a cage and transferred manually or automatically from one plating solution to another. The advantages of using barrel plating are low cost and a more enclosed process, so reducing exposure to the plating solutions.

Manual plating is a series of tanks that contain the appropriate plating and cleaning solutions. Parts are placed on racks or hangers and manually transferred from tank to tank. This type of plating process is labour intensive and, as platers spend a larger proportion of their working time at the tanks, there is a relatively higher risk of exposure. However, the use of this method is declining because of the high costs associated with labour intensive processes.

In semi-automatic plating, parts are manually loaded on to jigs and then the operator moves the jigs between the baths using an overhead hoist in a predetermined sequence. The operator usually stands on a platform by the side of the plating line. This method usually results in lower exposure than manual plating as the operators can distance themselves from the plating solutions for large amounts of time.

The main difference between automatic and semi-automatic plating is that the movement of the jigs is controlled electronically in automatic plating and therefore the operator spends very little time near the plating solutions, except when there is a problem with the process.

Chrome plating processes

There are two main distinct types of chromium plating processes; decorative and hard chrome plating. It is possible to use chromium (III) salts for decorative chrome plating and there has been an increase in chromium (III) decorative plating in recent years at the expense of chromium (VI) decorative plating (E.C., 2005).

Hard chrome plating is chrome plating that has been applied as a fairly heavy coating (usually measured in thousandths of an inch) for wear resistance, lubricity, oil retention, and other 'wear' purposes. Some examples would be hydraulic cylinder rods, rollers, piston rings, mold surfaces, thread guides, gun bores, etc. 'Hard chrome' is not really harder than other chrome plating, it is called hard chromium because it is thick enough that a hardness measurement can be performed on it, whereas decorative chrome plating is only millionths of an inch thick and will break if a hardness test is conducted, so its hardness cannot really be measured directly.

Decorative chrome plating is sometimes called nickel-chrome plating because it always involves electroplating nickel onto the object before plating the chrome (it sometimes also involves electroplating copper onto the object before the nickel, too). The nickel plating provides the smoothness, much of the corrosion resistance, and most of the reflectivity. The chrome plating is exceptionally thin, measured in millionths of an inch rather than in thousandths. Nickel plating is the main touch of a decorative chrome plated surface (such as a chrome plated wheel or truck bumper). The chrome adds a bluish cast (compared to the somewhat yellowish cast of nickel), protects the nickel against tarnish, minimizes scratching, and symbiotically contributes to corrosion resistance. Without such nickel undercoating no reflective and decorative surface is possible.

The most important issue for durable chrome plating for outdoor exposure such as on a vehicle is that at least two layers of nickel plating are needed before the chrome layer called "duplex nickel plating": semi-bright nickel followed by bright nickel. The reason for this involves galvanic corrosion issues. The bright nickel is anodic to the semi-bright nickel, and sacrificially protects it, spreading the corrosion forces laterally instead of allowing them to penetrate through to the steel.

Electrolytic chromium/chromium oxide coated steel (E.C., 2005)

Steels used in packaging, e.g. cans, are non-alloyed steel flat products and are used for drinks or food products. Depending on the application, the steel can be covered with a metal coating (tin or chromium) or with an additional organic coating. The two main steels used for packaging products are tinplate and electrolytic chromium coated steel (ECCS). Their technical specifications are described in EN10202. They are both certified for food contact materials. After tinning, tinplate is subject to a passivation treatment in which chromium and chromium oxides are deposited on to the surface, to improve resistance to oxidation and improve suitability for lacquering and printing. The most widely used passivation process for tinplate is a cathodic treatment in a solution of sodium dichromate (3.5 to 9 mg/m^2). ECCS is always used lacquered. On the surface of the strip a coating mass between 50 and 140 mg/m^2 (total chromium) is applied. Chromium (VI) is used in both processes, but is reduced to chromium metal and chromium (III) on the final product. Consumer exposure to chromium (VI) is therefore likely to be negligible from this source.