

## **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: Pentazinc chromate octahydroxide**

**EC Number(s): 256-418-0**

**CAS Number(s): 49663-84-5**

**Submitted by: FRANCE<sup>1</sup>**

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<sup>1</sup> 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: Pentazinc chromate octahydroxide**

**EC Number(s): 256-418-0**

**CAS Number(s): 49663-84-5**

- 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 1A<sup>2</sup> which corresponds to classification as carcinogen category 1<sup>3</sup>

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

Pentazinc chromate octahydroxide is covered by index number 024-007-00-3<sup>4</sup> 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. 1A (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. 1 (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 dossier of the substance submitted: yes**

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<sup>2</sup> 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.

<sup>3</sup> 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).

<sup>4</sup> International chemical identification: zinc chromates including zinc potassium chromate.

## PART I

### JUSTIFICATION

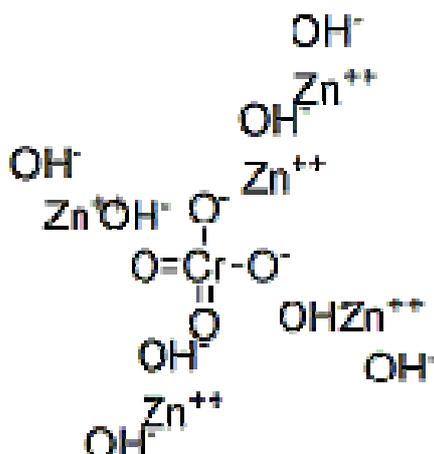
#### 1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

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

##### 1.1 Name and other identifiers of the substance

Table 1: Substance identity

<b>EC number:</b>	256-418-0
<b>EC name:</b>	Pentazinc chromate octahydroxide
<b>CAS number (EC inventory):</b>	49663-84-5
<b>CAS name:</b>	Zinc chromate hydroxide (Zn <sub>5</sub> (CrO <sub>4</sub> )(OH) <sub>8</sub> )
<b>IUPAC name:</b>	Pentazinc chromate octahydroxide
<b>Annex I index number:</b>	024-007-00-3
<b>Molecular formula:</b>	CrH <sub>8</sub> O <sub>12</sub> Zn <sub>5</sub>
<b>Molecular weight:</b>	579
<b>Synonyms</b>	Zinc tetraoxochromate, Zinc tetroxy chromate, Zinc chromate hydroxide, Basic zinc chromate, Zinc chromate, Trizinc dioxido(dioxo)chromium dihydroxide
<b>Main trade names</b>	Micronised zinc tetroxy chromate - ZTC, Zinc chromate – ZTO, Habicor ZTC, Zinc tetraoxochromate TC20

**Structural formula:****1.2 Composition of the substance**

**Name:** Pentazinc chromate octahydroxide

**Description:** The substance Pentazinc chromate octahydroxide is a mono constituent inorganic substance having the following characteristics and physical-chemical properties.

**Degree of purity:** Confidential data

Table 2: Constituents

Constituent	Typical concentration	Concentration range	Remarks
Pentazinc chromate octahydroxide EC n°: 256-418-0			Confidential data

Table 3: Impurities (depending on the manufacturers or importers)

Impurities	Typical concentration	Concentration range	Remarks

Table 4: Additives

Additives	Typical concentration	Concentration range	Remarks
<i>none</i>	/	/	/

### 1.3 Physico-chemical properties

Table 5: Overview of physicochemical properties

Property	Value	Remarks
Physical state at 20°C and 101.3 kPa	Light yellow powder, odourless.	
Melting/freezing point	The substance doesn't melt but decomposes above 300 °C	
Boiling point	n/a	
Vapour pressure	n/a	
Relative density	3.4 g/cm <sup>3</sup> at 20 °C	
Water solubility	< 0.02 g/L at 20°C	
Partition coefficient n-octanol/water (log value)	n/a inorganic compound	
Dissociation constant	n/a	
Oxidising properties	Not oxidising according to the CLP.	Conclusive study on oxidising properties but not sufficient for classification.
Granulometry	Particle size mass median diameter is 4.83 µm	

## 2 HARMONISED CLASSIFICATION AND LABELLING

Pentazinc chromate octahydroxide is covered by index number 024-007-00-3 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)		
Carc. 1A	H350	GHS08	H350		A
Acute Tox. 4 *	H302	GHS07	H302		
Skin Sens. 1	H317	GHS09	H317		
Aquatic Acute 1	H400	Dgr	H410		
Aquatic Chronic 1	H410				
<p><b>Key:</b>  Carc. 1 A: Carcinogenicity  Acute Tox. 2, Tox. 3, Tox. 4: Acute toxicity  Skin Sens.1: Skin sensitization  Aquatic Acute 1, Aquatic Chronic 1: Hazardous to the aquatic environment  H302: Harmful if swallowed  H317: May cause an allergic skin reaction  H350: May cause cancer  H400: Very toxic to aquatic life  H410: Very toxic to aquatic life with long lasting effects  GHS08: Health hazard  GHS07: Exclamation mark  GHS09: Environment  Dgr: Danger</p> <p><b>Note A :</b>  Without prejudice to Article 17(2) of Regulation (EC) No 1272/2008, the name of the substance must appear on the label in the form of one of the designations given in Part 3 of Annex VI to that Regulation.  In that Part, use is sometimes made of a general description such as "... compounds" or "... salts". In this case, the supplier who places such a substance on the market is required to state on the label the correct name, due account being taken of Section 1.1.1.4 of Annex VI to Regulation (EC) No 1272/2008.  In accordance with Regulation (EC) No 1272/2008, where a substance is included in Part 3 of Annex VI to that Regulation, the labelling elements relevant for each specific classification covered by the entry in that Part shall be included in the label, together with the applicable label elements for any other classification not covered by that entry, and any other applicable label elements in accordance with Article 17 of that Regulation.  For substances belonging to one particular group of substances included in Part 3 of Annex VI to Regulation (EC) No 1272/2008, the labelling elements relevant for each specific classification covered by the entry in that Part shall be included in the label, together with the applicable label elements for any other classification not covered by that entry, and any other applicable label elements in accordance with Article 17 of that Regulation.  For substances belonging to more than one group of substances included in Part 3 of Annex VI to Regulation (EC) No 1272/2008, the labelling elements relevant for each specific classification covered by both entries in that Part shall be included in the label, together with the applicable label elements for any other classification not covered by that entry, and any other applicable label elements in accordance with Article 17 of that Regulation. In cases where two different classifications are given in the two entries for the same hazard class or differentiation, the classification reflecting the more severe classification shall be used.'</p>					

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
Carc. Cat. 1; R45 Xn; R22 R43 N; R50-53	T; N R: 45-22-43-50/53 S: 53-45-60-61		AE
<p><u>Key:</u>                      Carc.: Carcinogenic                      Xn: Harmful                      N: Dangerous for the environment                      R22: Harmful if swallowed                      R43: May cause sensitization skin contact                      R45: May cause cancer                      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</p> <p>Note A:                      The name of the substance must appear on the label in the form of one of the designations given in Annex I (see Article 23(2)(a)). In Annex I, use is sometimes made of a general description such as "... compounds" or "... salts". In this case, the manufacturer or any other person who markets such a substance is required to state on the label the correct name, due account being taken of the chapter entitled "Nomenclature" of the Foreword: Example: for BeCl<sub>2</sub> (Einecs No 232-116-4): beryllium chloride.                      The Directive also requires that the symbols, indications of danger, R- and S-phrases to be used for each substance shall be those shown in Annex I (Article 23(2)(c), (d) and (e)). For substances belonging to one particular group of substances included in Annex I, the symbols, indications of danger, R and S-phrases to be used for each substance shall be those shown in the appropriate entry in Annex I. For substances belonging to more than one group of substances included in Annex I, the symbols, indications of danger, R and S-phrases to be used for each substance shall be those shown in both the appropriate entries given in Annex I. In cases where two different classifications are given in the two entries for the same hazard, the classification reflecting the more severe hazard classification is used.</p> <p>Note E : Substances with specific effects on human health that are classified as carcinogenic, mutagenic and/or toxic for reproduction in categories 1 or 2 are ascribed Note E if they are also classified as very toxic (T+), toxic (T) or harmful (Xn). For these substances, the risk phrases R20, R21, R22, R23, R24, R25, R26, R27, R28, R39, R68 (harmful), R48 and R65 and all combinations of these risk phrases shall be preceded by the word 'Also'.</p>			

### **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) pentazine chromate octahydroxide 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**

Pentazinc chromate octahydroxide is covered by index number 024-007-00-3 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. 1A (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. 1 (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) pentazinc chromate octahydroxide (also called basic zinc 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 that shares useful data on uses, exposure, etc.

Information reported in this chapter is collected from a review of the literature and from registration dossiers for this substance but remains very limited. Indeed the content of the registration dossiers is succinct and a consultation of French stakeholders performed early 2011 failed to recover useful data on use, exposure, alternative and risks.

However, the chemical properties, uses and sectors of use of pentazinc chromate octahydroxide are very similar to those of strontium chromate. Pentazinc chromate octahydroxide is thus closely related to strontium chromate for which an annex XV-SVHC dossier has already been submitted and built on a fruitful information. Present dossier reuses the background content of strontium chromate (sector of uses, etc.) and updates it with data, when available, from the registration dossiers and literature.

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

#### 7.1 Zinc chromate substances family

General entry Index n°024-007-00-3 of Regulation (EC) No 1272/2008 refers to the family of zinc chromate compounds (zinc chromates) which includes substances referred in table 8.

Table 8: Zinc chromate compounds family; registration status under REACH regulation.

Substance name	Molecular formula	CAS number	Pre-registered	Registered
Pentazinc chromate octahydroxide	CrH8O12Zn5	49663-84-5	yes	yes
Basic zinc chromate (Chromic acid, zinc salt)	CrO4Zn CrH2O4.Zn	13530-65-9	no	no
Zinc chromate oxide monohydrate (zinc chromate hydroxide)	Zn2(CrO4)O	15930-94-6	no	no
Zinc chromate yellow (C.I. Pigment yellow 36)	CrKO4Zn	37300-23-5	no	no
Potassium hydroxyoctaoxidizincatedichromate(1-) (zinc potassium chromate)	Cr2HO9Zn2.K	11103-86-9	yes	yes

Note that the following CAS numbers also refer to the basic zinc chromate with the same molecular formula CrO4Zn: 1308-13-0; 12705-38-3; 1328-67-2; 14675-41-3; 37224-56-9; 53809-63-5; 57790-30-4. None of them are registered neither preregistered. Confusion between zinc chromates is observed in the literature where zinc chromate or zinc basic chromate often refer to several substances with several CAS numbers.

“Zinc chromates” refer hereafter to both zinc potassium chromate and pentazinc chromate octahydroxide, that are to date the only two substances registered under REACH amongst the whole zinc chromates family.

## 7.2 Manufacturers

Pentazinc chromate octahydroxide is produced/distributed within Europe by at least three companies<sup>5</sup> that are located in Austria (Habich GmbH) and France (SNCZ).

## 7.3 Manufacturing process

According to a review of the literature, pentazinc chromate octahydroxide is reacted under controlled conditions by precipitation in a wet chemical process with water-soluble chromate solution and zinc salts. The product is then dehydrated, dried and grinded. Final product is a low dust yellow finely micronized powder.

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

<sup>5</sup> According to their internet website (list of manufactured products).

## **7.4 Quantities manufactured, import and export**

The worldwide production and consumption of pentazinc chromate octahydroxide is not known. Data from the registration are confidential.

However 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). This takes into account the general trend observed over the last years.

Other manufacturers are located mainly in Asia and USA.

## **7.5 Functions of the substance according to its properties; mechanism of action**

### **7.5.1 Functions**

Zinc chromates are known to be yellow rust-inhibiting pigments which provide excellent corrosion protection to metal substrates (iron, steel, galvanized steel, zinc, aluminum and aluminum alloys) by passivation (e.g. anodic passivation) and effective at relatively low loading levels.

According to the literature, pentazinc chromate octahydroxide is used as

- anti-corrosive agent for the formulation of wash primers/etch primers and shop primers, particularly two pack primers (poly(vinyl butyryl) PVB wash primers) which consist of phosphoric acid and zinc tetraoxochromate dispersed in an alcoholic poly(vinylbutyral) solution,
- colouring and hiding agent in paints and coatings (if used in high thickness layers),
- anti-scaling agent in paints and coatings.

Wash primers (also called etch primers) are thin and cross linked coatings applied directly to the substrate (aluminum, steel or anodized aluminum) that

- provide long term protection from filiform corrosion by passivating metals and building up a surface bonded protective metal oxide layer (anodic passivation) before applying a full bodied primer or topcoat,
- promote adhesion of subsequent paint layers by etching the metal surface and precipitating metal phosphates.

Shop primers are thin coatings applied to metal surfaces to provide only temporary corrosion protection during transportation, storage and production.

### **7.5.2 Mechanism of action in paint primers**

The anticorrosion mechanism of action is the following. In protective coatings containing chromate compounds as the inhibitive pigment, chromate species are present and may leach and react at the metal/coating interface. Galvanic couple corrosion is a chemical reaction that consists in an exchange of electrons between different metals (noble metal and less noble metal, like an anode and a cathode) and results in corrosion (for instance, the combination between stainless steel screws or bolts on an aluminum part provides a high potential of electrons transfer). Even at very low

concentration, chromate compounds have the unusual and unique property of affording corrosion protection when the support is scratched or damaged in that it actively suppresses both the cathodic and anodic sites between two different metallic parts which induce this galvanic couple reaction.

Active protection against rust relies on inhibitors once barrier properties breached. Inhibitors require water to dissolve and must easily migrate to exposed substrates. Their effectiveness depends on the solubility of the chromate inhibitor: if too soluble, they may flush out or cause osmotic blistering; if less soluble they are not active enough. Water permeability and inhibitor ion mobility performance is thus dependent upon the coating system (primer and topcoat). According to literature strontium chromate shows the ideal solubility (1.06 g/L); zinc potassium chromate has a similar solubility (0.5 to 1.5 g/L) and may thus be as effective. An illustration of the mechanism of action is available at [http://www.hazmat-alternatives.com/Alt\\_tech-Chromates.php](http://www.hazmat-alternatives.com/Alt_tech-Chromates.php). No single non-chrome inhibitor tested yet functions in this manner; if there is lots of room for error and approximation with chromate compounds, this is not the case for non-Cr(VI) substitutes.

### 7.5.3 Main active substances

There are a variety of inhibiting pigments for use in primers on metal substrate (Weldon, 2009). These include chromates (strontium chromate, barium chromate, etc.), lead-based pigments (including lead chromate), zinc phosphate, zinc hydroxyl phosphate, calcium borosilicate, barium metaborate and various molybdate pigments. Three of the more common chromate based inhibitive pigments include zinc potassium chromate, zinc tetraoxochromate and strontium chromate.

## 7.6 Types of uses

According to the literature and public data from the registration dossiers, pentazinc chromate octahydroxide is used by four industrial activity sectors:

- formulation of liquid mixtures (coatings such as primer paints and wash primers, thinners, paint removers, etc.),
- industrial use of mixtures in the aeronautic/aerospace sector,
- industrial use of mixtures in the vehicle coating sector,
- laboratory uses (analysis, R&D, etc.) in very small quantities, no more developed hereafter.

Note that tonnages used by each application and number of sites concerned are not known, except for the formulation sector for which some estimations are proposed.

The largest chromates amount used in Sweden is for paint production mainly as corrosion inhibitor and as pigments (e.g. zinc chromate and strontium chromate)<sup>6</sup>.

Some doubtful uses of pentazinc chromate octahydroxide are also reported in the literature, for which no information is available:

- formulation of coating powders that are mixtures of pigments, resins, curing agents and other additives; they give durable finish and are used to coat metal window frames, many car components and most “white goods” such as fridge freezers and washing machines. Coating powders are sprayed by an electrostatic process that gives a fairly uniform thickness of coating,

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<sup>6</sup> [http://apps.kemi.se/flodessok/floden/kemamne\\_eng/oorganiska\\_kromsalter\\_eng.htm](http://apps.kemi.se/flodessok/floden/kemamne_eng/oorganiska_kromsalter_eng.htm)

- coloring and hiding power because of its structure and its tinting strength,
- anti-scaling agent, that may be related to the anti-corrosive function,
- plastic formulation and fireworks (from Industry sources : ICDA, 2007)

No use under research and development or product and process oriented research and development is expected.

#### **7.6.1 Formulation of pentazinc chromate octahydroxide containing mixtures/preparations**

According to the registration dossiers, pentazinc chromate octahydroxide is used to formulate liquid mixtures such as coatings (primer paints and wash/shop primers). It is assumed that the total tonnage of pentazinc chromate octahydroxide manufactured within the EU (tonnage band 10-100 tons/year) is used for this purpose. Even if the market “sector by type of chemical product” (generic description item in the registration dossiers) refers also to thinners and paint removers in the registration dossiers, such mixtures are not expected to be formulated from pentazinc chromate octahydroxide.

Final concentration of pentazinc chromate octahydroxide in ready for use primer paints is not known. As for strontium chromate, it is assumed that this concentration may usually be from less than 1% up to 25% w/w depending of the desired performances. High anticorrosive effectiveness requires the highest concentration.

According to one formulator, the manufacture of paste mixtures (as sealants) is stopping because of continuously decreased sales over the last years: last chromate containing sealants are now formulated with strontium chromate, barium chromate and for some with zinc potassium chromate. However, the Habich company still manufactures and distributes two pastes containing 60% of pentazinc chromate octahydroxide (Xylene - paste n°4 and Solvent Naphta light – paste n°18)<sup>7</sup>.

The Nordic product register has inventoried in 2009 up to 12 different preparations containing pentazinc chromate octahydroxide in Sweden (paints, lacquers and varnishes, colouring agents). This represents 2 tons/year of this substance. These preparations are related to the following industrial uses: bodywork repair, maintenance and repair of motor vehicle, motor vehicle painters.

Based on the strontium chromate dossier (for which 10 formulators were estimated) because of similar uses and sector of uses and considering the lower market of pentazinc chromate octahydroxide, it is assumed that less than 5 formulators may use it in Europe. The number of sites is not known. Preparations are then 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 and part of vehicles) and waste stages.

Anticorrosive preparations usually contain strontium chromate and/or barium chromate and/or zinc chromates (including pentazinc chromate octahydroxide) as they exhibit similar properties.

Formulation of coatings usually encloses the following steps which may be responsible for occupational exposure to strontium chromate: receipt and storage of raw materials packaged in bags (here powders), charging / mixing / dispersing in liquids all raw materials in batches, filtering, filling / packaging of the formulation (mixture) and cleaning of the equipments.

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<sup>7</sup> <http://www.habich.com/en/produkte.htm>

### 7.6.2 Use in the aerospace sector

Use in the aerospace sector is not reported in the registration dossiers.

However data collected from literature and from French consultations confirm it. According to Gifas – French aerospace industries association (French consultation, 2011), pentazinc chromate octahydroxide is used in wash primers and jointing compounds (sealants) for aluminum, steel or anodized aluminum substrates. From the consultation conducted in 2010, zinc chromates may also be used in topcoats.

According to Kutz (2005), aircraft coating systems applied on exterior surfaces normally consist of a chromate conversion coating or anodized coating foundation layer (using most commonly dichromate compounds), a corrosion inhibiting primer layer (containing chromate pigments such as zinc chromates or strontium chromate) and a top coat. Isocyanate-cured polyester and acrylic resins containing pigments are most commonly used as topcoats (50-75 µm thickness). Coating systems on interior surfaces usually do not have a top coat applied.

Uses of primers are always framed by specifications and conform to aviation requirements from programs of civil and military aviation of several aerospace companies. In the majority of cases, all primers qualify to standards (for aerospace, defense or general industrial purposes). According to the technical literature of the aerospace sector, these primers are based on the use of zinc chromate, barium chromate, zinc tetroxochromate, strontium chromate or even blends of them as the anti-corrosive pigment. Top coats may also contain zinc chromate and/or barium chromate and/or strontium chromate.

As for strontium chromate, the industrial use of primer paints applied on metal parts usually encloses the following steps which may be responsible for occupational exposure: receipt and storage of the mixtures, preparation if not ready to use regarding the equipment used (mixing, diluting), application on the support by brush and spray, cleaning of the equipments. Note that spraying generates aerosols and is always technically preferred. Preliminary preparation of the support is usually manual and encloses the following steps: stripping of previous coatings (usually the same as the one applied when the process is under specification) by sanding, scrapping and deburring and removing the dust before cleaning.

Alike, the industrial use of sealants applied on metal parts usually encloses the following steps which may be responsible for occupational exposure: receipt and storage of the mixtures, preparation if not ready to use, application on the support by spreader or by hand, cleaning of the equipments. Preliminary preparation of the support may enclose the removing of the previous sealant (usually the same as the one applied when the process is under specification) by sanding, scrapping and deburring and removing the dust before cleaning.

Due to same uses between both substances, exposure to zinc chromates and strontium chromate are deemed similar. According to AsetsDefense<sup>8</sup>, exposure to strontium chromate primers of personnel at the original equipment manufacturer level occurs during depot overhaul, repaint (painting operations) and operational level touch-up and repair. Maintainers are exposed in scuff sand and paint operations. Scuff sanding of aircraft epoxy primer containing strontium chromate releases particulates that contain chromates from previous surface priming procedures. These particulates can be transported into the workers' breathing zones and result in chromate exposures. Exposure to strontium chromate sealants of personnel at the original equipment manufacturer level occurs

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<sup>8</sup> <http://www.asetdefense.org/>

during overhaul and repaint and during operational level removal of access panels for inspection and repair.

According to AsetsDefense, removing of chromated sealants is an additional potential Cr(VI) exposure source. Because sealants are usually well hidden, they do not present a significant source of exposure to users during service, but operational and depot maintainers will be exposed when removing panels, windshields, fasteners, etc. that may be sealed with chromated sealants.

### **7.6.3 Use in the transportation vehicle sector**

Use in the automotive sector is the single industrial application reported in the registration dossiers.

Some zinc chromates containing wash primers are specially formulated and sold for use in the automotive refinish market. Because of European regulations (End of Life Vehicles Directive and RoHS Directive) the use of chromate compounds is restricted to only applications where requirements for sustainability and security are strong. Zinc chromates are used in primers anti-corrosive paints, fillers and sealants for the construction and maintenance of fleet and commercial vehicles, heavy duty vehicles and trucks, military vehicles, agricultural equipments, excluding personal vehicles.

Annual tonnages and the number of sites (sites of use) involved are not known. Information is very limited.

All military transportation sectors (air, terrestrial, naval) are covered by specifications. Other sectors of use (public uses) are also covered by European and international public standards (ISO 2040 as an example).

Due to same uses between both substances, exposure to zinc chromates and strontium chromate is expected similar. This is confirmed by the exposure scenarios described in the registration dossiers.

The industrial use of coatings (paints) applied on vehicle metal parts usually encloses the following steps which may be responsible for occupational exposure: receipt and storage of the mixtures, preparation if not ready to use regarding the equipment used (mixing, diluting), application on the support by industrial spraying except for maintenance in some areas (manual operation), cleaning of the equipments. Note that spraying generates aerosols. Preliminary preparation of the support is usually manual and encloses the following steps: stripping of previous coatings from coated vehicles (usually the same as the one applied when the process is under specification) by sanding, scrapping and deburring and removing the dust before cleaning.

## **7.7 Description of the supply chain**

Due to same uses, the supply chain of zinc chromates is expected to be similar to strontium chromate. The following information initially described for strontium chromate (French consultation conducted in 2010) may thus apply to zinc chromates as well. Europe benefits from a complete high performance anticorrosion supply chain:

- manufacturing/import of chromate pigments,
- manufacturing of industrial chromate containing formulations,

- industrial applications of such formulations in the three sectors previously described, involving many users, suppliers, etc... for which a clear picture is however not available neither for the aerospace sector neither for the automotive sector.

As stated in the strontium chromate dossier, the market for surface treatment activities supplying the aerospace sector consists in a very large number of industries. All these sub-sectors may give the impression of a limited market, but added together, they represent a significant market for formulators. The manufacturing of aircraft parts coated with chromate compounds involve many suppliers worldwide (usually small and medium companies) which are located near the sites where those pieces are assembled (assembly lines). The same picture may apply for the automotive sector. But the number of downstream users / decision makers which enforce specifications is limited in both sectors of aerospace and automotive industry.

## **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 within the EU is low and no data has been shared by Industry regarding the substitution of zinc chromates. Following information is from available literature. Main available/public information comes from the USA where R&D on chrome-free alternatives has been launched long, under the leadership of the US DoD (United States Department of Defense) in order to provide the military with chromium(VI) alternatives.

### **8.1 Alternatives researches for United States military uses regarding Cr(VI) compounds**

US DoD 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.asetdefense.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 failures such as 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. If laboratory tests are easily implemented, service life assessment takes time.

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). Perhaps the most important point for any decision maker to be aware of is that there is not any single drop-in substitute for all uses of hexavalent chrome. Further a substitute may work for one use but not for another. Substitution can affect other maintenance practices - so it can take some time to implement.

According to AsetsDefense, primary alternatives to chromate primers are barium chromate and non-chrome products. Barium chromate is considered to be less toxic than other chromates used in primers and not classified as a CMR substance. Non-chrome primers contain alternative inhibitors such as rare earth metals. Zn-rich primers have long been used for steel infrastructure, and new Mg-rich primers are under development and evaluation for DoD use. A number of alternatives are commercially available and some have been authorized and qualified to military specifications.

Note that the use of zinc chromate containing primers by the US army has been phased out 20-25 years ago, and primarily replaced by strontium chromate, considered less toxic at this time. Specific information on zinc chromate substitution is thus not available.

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

### **8.2.1 Technical alternatives and remaining difficulties: global picture**

Regarding the anti-corrosive properties of chromates used in paints (strontium chromate, barium chromate, zinc chromate, lead chromate), the most common alternatives discussed in the literature are zinc phosphate, calcium phosphate, magnesium phosphate, combined zinc-aluminum phosphates, barium metaborate, cerium molybdate, calcium silicate and many organic pigments (Baghni and Lyon, 2005). Alternative substances such as silica ions exchanger, polyphosphates, molybdates, etc. are also used in specific paints applications.

Since the decline in the use of lead and chromate containing anti-corrosive pigments on toxicological and ecological grounds, the importance of phosphate containing pigments has grown. As they still cannot replace the traditional anti-corrosive pigments in every respect, efforts are being made to improve both their effectiveness, 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 orthophosphates and polyphosphates, zinc phosphate, chromium phosphate, aluminum triphosphate, barium phosphate and aluminum zinc phosphate. According to some formulators internet websites, high performance polyphosphates are amongst the technically most sophisticated Cr(VI) free anticorrosive inhibitors in today's market especially when ultimate protection is required. Wide spectrum anticorrosive non chrome pigments are also available for universal uses.

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.

Note that neither the hazards nor the risks related to the use these alternatives are here assessed.

The general impression 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 Cr(VI) 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.

### 8.2.2 Economic issue

Development of alternatives is costly. But on the other hand new chemical regulations and severe rules on occupational exposure to Cr(VI) 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. Cr(VI) 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, in the near future, are expected to protect metal surfaces as well as their chromated counterparts, would be safer and more compliant, resulting in significant 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).

### 8.2.3 Alternatives in the aerospace sector

According to Gifas (French consultation, 2011), a substitution program to the use of pentazine chromate octahydroxide in wash primers and sealants is running on and may be agreed soon. The deadline is not however specified, but the general timeframe stated by the aerospace Industry for other chromate compounds (including strontium chromate) may apply as well (i.e. 5 to 7 years). Given that zinc chromates were used for a long time and for some applications already replaced by strontium chromate, complete substitution may be available earlier.

Substitution needs time, due to the necessary commitments to safety in the aerospace sector (civil and military) which involve that:

- all materials, processes and suppliers are qualified,
- no change are thus tolerated even minor without a complete check, re-qualification or re-certification if necessary,
- there is a need to maintain the technologies and products throughout their entire life cycle (30 years for an aircraft).

Further detailed data have not been shared by the industry but literature information regarding specific aerospace applications is reported hereafter.

According to the US Army Research Laboratory (ARL 2004) some of the tested alternatives offer a similar level of performance to the control chromate containing wash primers under specification DOD-P-15328D and the results were deemed “very promising”. However it was stated that no single laboratory test can warrant the same protection over the entire aircraft life cycle. In 2004 military specification was running on and the replacing of DoD (department of defense) material with one of the alternative systems was imminent.

Many paints manufacturers provide on their internet website lead and chromate free epoxy primers for commercial, civil and also military aerospace, designed for use on the exterior and interior of

aircraft. Such primers utilize a corrosion inhibitive package. They are designed for use with topcoats, pastes and adhesives. Some of them are already approved to BOEING BMS specifications.

Classical phosphate anticorrosive pigments show acceptable corrosion resistance, but the performance do not approach the requirements of most aero engine specifications, and especially not airframe in the field of aerospace and defense applications. New phosphate anticorrosive pigment technologies are being produced that are approved by several European aero engine and aerospace manufacturers, meaning that their effectiveness has already been agreed. For instance polyphosphate and orthophosphate are specially formulated for the aerospace industry: aircraft primers / wash and shop primers.

Note that barriers to substitution in this sector have been raised by several end-users on strontium chromate that may apply to zinc chromates too. The practicality, implementation and effectiveness of substitutes that are available on the market are still subjected to debate. Effectiveness is yet assessed solely on the basis of laboratory tests that do not reflect the real long term exposure to hard weathering conditions during the all aircraft service life. Manufacturers that supply the aerospace industry with products containing chromates include many small companies that may not have the resources to engage a long term R&D to develop viable Cr(VI)-free alternatives. Where there are validated alternatives in some applications, they are however not applicable for all uses and for all aluminum alloys. Validation of Cr(VI)-free bond primers (promoting adhesion) are even less successful than for other primers. According to the US aerospace industries association (AIA), over all the substitution candidates tested, alternatives have not yet been developed that provide equivalent corrosion protection for all product applications. But note that it is already agreed that substitution solutions are not universal and shall be developed on a case by case basis. According to Gifas, industry is unable to find a suitable alternative meeting all the safety aerospace requirements and extensive R&D shall be continued until qualification of alternatives is effective; however no time schedule is shared on this topic. Moreover, Industry may claim the full availability of the substances (strontium chromate and zinc chromates) over the life cycle of the current programs (> 25 years) in order to maintain them in operational conditions.

### **8.2.4 Alternatives in the automotive sector**

According to some formulators that manufactured or still manufacture zinc chromate containing wash primers designed for the automotive sector, efficient substitutes are already on the market. However further information is not available.

It is expected that free-chromate primers that are developed for the aerospace market, in the frame of severe specifications due to security reasons, will also match those of the automotive sector.

Potential barriers to substitution in this sector are not known.

### **8.2.5 Alternatives with other chromate compounds, grouping issue**

Because of their special properties described in chapter 7.5, various chromate pigments are used as high performances and cost effective anticorrosive agent in primer paints. These include zinc chromates including alkali chromates, pentazinc chromate octahydroxide (CAS n°49663-84-5), zinc potassium chromate (CAS n°11103-86-9), strontium chromate (CAS n°7789-06-2) and calcium chromate (CAS n° 13765-19-0). Strontium chromate and to a lesser extent zinc chromates are the most commonly used in primer paints. The use of calcium chromate in paints is now rare and it may

only be available as an imported material. Lead chromate is primarily used in topcoat paints but they may also be added to primer paints to provide coloring. No registration dossier has been submitted to ECHA for both lead chromate and calcium chromate.

Given the similarity of their uses and mechanism of action as anticorrosive agents (cf. chapter 7.5.2), it is assumed that strontium chromate and zinc chromates (zinc potassium chromate and pentazinc tetroxychromate) can be substituted by each other. This is confirmed by a similar solubility range (cf. table 9). Note that the effectiveness of pentazinc chromate octahydroxide may be lower, given its lower solubility. A grouping approach is thus justified between those 3 chromium salts.

Potential substitution with lead chromate may be assumed but regarding the hiding power only; note that zinc chromate and strontium chromates are not used for this purpose. Because of its very low solubility (cf. table 9), lead chromate may have poor anticorrosive effectiveness if used in primers. An efficient substitution between strontium/zinc chromates and lead chromate in anticorrosive applications may still be subjected to debate.

Table 9: 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

Other Cr(VI) compounds (sodium (di)chromate, ammonium (di)chromate, potassium (di)chromate, etc.) also provide anti-corrosion properties but through different processes (such as chromate conversion coating, chromic anodizing, etc.) than direct application of paints/primers or coatings on metal surfaces. Direct substitution between dichromates and strontium/zinc chromates within the same process is thus unexpected, except if strontium/zinc chromates are used to produce chromic acids in solution (that is achievable in theory).

In conclusion on alternatives, available information concerns only the aerospace sector. Substitution of Cr(VI) compounds is under development but well engaged. Some substitutes/alternatives are already available for certain applications according to formulators and already approved by decision makers. Their implementation and effectiveness are however still debated and questioned by US and EU end-users. Contrary to the wide effectiveness of some chromate compounds in many various applications, there is no single drop-in substitute for all uses of hexavalent chrome: substitution has to be developed on a case by case basis. Hazards and risks of available alternatives are not assessed and may be of interest given that some of them are based on rare earth elements: note that some end-users implement substitutes based on cadmium and/or nickel salts that raise similar health hazard issues as chromium salts. Estimated delays for substitution are not yet agreed between actors but are expected within 5 to 7 years according to the main sources in Europe. Remaining issues are linked to specification requirements, safety commitments and difficulties for SMEs to engage R&D investments and to bear such competition. Use of chromates is deemed required by Industry over the life cycle of the current programs (> 25 years).

## **9 RISK-RELATED INFORMATION**

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

Pentazinc chromate octahydroxide 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 pentazinc chromate octahydroxide 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<sup>3</sup> 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  $1 \mu\text{g}$  of Cr(VI) /  $\text{m}^3$  and corresponds to an individual excess risk of lung cancer estimated at  $1 \cdot 10^{-2}$  (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 pentazinc chromate octahydroxide 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 pentazinc chromate octahydroxide. In such hypothetical 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  $1 \mu\text{g}$  of Cr(VI)/ $\text{m}^3$  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  $\mu\text{g}$  CrVI/ $\text{m}^3$ ) per type of metal working branches (Anses, 2010)

Groups	Number of samples	Arithm Mean	Geom Mean	Median	Range	25 <sup>th</sup> perc.	75 <sup>th</sup> perc.	90 <sup>th</sup> perc.
All groups	458	7,26	0,93	0,603	0,01 - 367	0,45 3	3	10,3
<b>Metal treatment and surface finishing</b>	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  $0,5 \mu\text{g}$  of Cr(VI) /  $\text{m}^3$ , twice lower than the new French proposal of OEL set at  $1 \mu\text{g}$  of Cr(VI) /  $\text{m}^3$ . 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  $20 \mu\text{g}$  of Cr(VI)/ $\text{m}^3$ . These results may apply for pentazinc chromate octahydroxide 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  $1 \mu\text{g}$  of Cr(VI)/ $\text{m}^3$  that may not be fulfilled by current implemented protection measures and equipments. The number of European workers concerned is however not known.

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**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<sub>2</sub>) and chromous sulfate (CrSO<sub>4</sub>).

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<sub>4</sub><sup>2-</sup>) and dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) 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<sub>2</sub>CrO<sub>4</sub>. By losing two protons (H<sup>+</sup>), 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<sub>3</sub> (chromium trioxide) is the acid anhydride of chromic acid and it is sold industrially as “chromic acid”.

Chromate salts contain the chromate anion CrO<sub>4</sub><sup>2-</sup> and usually have an intense yellow color. Dichromate salts contain the dichromate anion Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> 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<sub>4</sub><sup>-</sup>, chromate CrO<sub>4</sub><sup>2-</sup>, and dichromate Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> 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<sub>n</sub>O<sub>3n+1</sub><sup>2-</sup>.

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	$\text{CrCl}_2$
Chromous sulfate	$\text{CrSO}_4$

## Trivalent (Cr (3+)):

Chromic oxide	$\text{Cr}_2\text{O}_3$
Chromic chloride	$\text{CrCl}_3$
Chromic sulfate	$\text{Cr}_2(\text{SO}_4)_3$
Chromic potassium sulphate	$\text{KCr}(\text{SO}_4)_2$
Chromite ore	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$

## Hexavalent (Cr (6+)) chromate :

Chromium trioxide	$\text{CrO}_3$
Chromic acid	$\text{H}_2\text{CrO}_4$
Sodium chromate	$\text{Na}_2\text{CrO}_4$
Potassium chromate	$\text{K}_2\text{CrO}_4$
Zinc chromate	$\text{ZnCrO}_4$
Strontium chromate	$\text{SrCrO}_4$

## Hexavalent (Cr (6+)) dichromate :

Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7$
Potassium dichromate	$\text{K}_2\text{Cr}_2\text{O}_7$
Ammonium dichromate	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
Zinc dichromate	$\text{ZnCr}_2\text{O}_7$

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

<b>Name</b>	<b>Molecular formula</b>	<b>CAS no</b>
Ammonium dichromate	Cr <sub>2</sub> H <sub>2</sub> O <sub>7</sub> .2H <sub>3</sub> N	7789-09-5
Ammonium chromate	CrH <sub>2</sub> O <sub>4</sub> 2H <sub>3</sub> N	7788-98-9
Barium chromate	Ba.CrH <sub>2</sub> O <sub>4</sub>	10294-40-3
Basic lead silicochromate (pigment)	PbCrO <sub>4</sub> .SiO <sub>2</sub>	11113-70-5
Calcium dichromate	Ca.Cr <sub>2</sub> H <sub>2</sub> O <sub>7</sub>	14307-33-6
Calcium chromate	Ca.CrH <sub>2</sub> O <sub>4</sub>	13765-19-0
Sulphuric acid, chromium(III) potassium salt	Cr.2H <sub>2</sub> O <sub>4</sub> S.12H <sub>2</sub> O.K	7788-99-0
Chrome yellow, Lead chromium sulphate (pigment)	PbCrO <sub>4</sub> +PbSO <sub>4</sub>	1344-37-2
Chromic(VI) acid-chromic salt	CrH <sub>2</sub> O <sub>4</sub> (?)	41261-95-4
Chromic(VI) acid-chromic salt	CrH <sub>2</sub> O <sub>4</sub> (3+)	24613-89-6
Chromic(VI) acide	CrH <sub>2</sub> O <sub>4</sub>	7738-94-5
Chromic acid, magnesium salt	CrH <sub>2</sub> O <sub>4</sub> .Mg	13423-61-5
Chromic acid, zinc salt	CrH <sub>2</sub> O <sub>4</sub> .Zn	13530-65-9
Chromite	FeO.Cr <sub>2</sub> O <sub>3</sub>	1308-31-2
Chromium carbide	C <sub>2</sub> Cr <sub>3</sub>	12012-35-0
Chromium(III) chloride	Cl <sub>3</sub> Cr	10025-73-7
Chromium copper iron oxide	Cr <sub>2</sub> CuFe <sub>2</sub> O <sub>7</sub>	55353-02-1
Chromium fluoride	CrF <sub>3</sub>	7788-97-8
Chromium hydroxide sulphate	CrHO <sub>5</sub> S	12336-95-7
Chromium hydroxide sulphate	Cr <sub>4</sub> H <sub>2</sub> O <sub>22</sub> S <sub>5</sub>	85251-54-3
Chromium(III) nitrate	Cr.3HNO <sub>3</sub>	13548-38-4
Chromium(III) trihydroxide	CrH <sub>3</sub> O <sub>3</sub>	1308-14-1
Chromium(III) oxide	Cr <sub>2</sub> O <sub>3</sub>	308-38-9
Chromium oxide green (pigment)	Cr <sub>2</sub> O <sub>3</sub>	308-38-9
Chromium(III) sulphate	Cr.3/2H <sub>2</sub> O <sub>4</sub> S	10101-53-8
Chromium(IV) oxide	CrO <sub>2</sub>	12018-01-8
Chromium(VI) trioxide	CrO <sub>3</sub>	1333-82-0
Guignet's green (pigment mixture)	Cr <sub>2</sub> O <sub>3</sub> xH <sub>2</sub> O (x = about 2)	12001-99-9
Lead chromate, basic lead chromate orange (pigment)	PbCrO <sub>4</sub> .PbO	1344-38-3
Lead chromate, Chrome green	CrH <sub>2</sub> O <sub>4</sub> .Pb	7758-97-6
Lead chromate oxide	CrH <sub>4</sub> O <sub>5</sub> .2Pb	18454-12-1
Lead chromium molybdate sulphate (pigment)	PbCrO <sub>4</sub> , PbMoO <sub>4</sub> , PbSO <sub>4</sub>	12656-85-8
Lithium chromate	CrH <sub>2</sub> O <sub>4</sub> .2Li	14307-35-8
Magnesium chromate	CrO <sub>2</sub> .1/2Mg	12053-26-8
Potassium chromate	CrH <sub>2</sub> O <sub>4</sub> .2K	7789-00-6

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Potassium dichromate	Cr <sub>2</sub> H <sub>2</sub> O <sub>7</sub> .2K	7778-50-9
Potassium tetrachromate	K <sub>2</sub> Cr <sub>4</sub> O <sub>13</sub> 12422-53-6	
Potassium zinc chromate oxide	K <sub>2</sub> O.ZnO.4CrO <sub>3</sub> .3H <sub>2</sub> O	12433-50-0
Sodium chromate	CrH <sub>2</sub> O <sub>4</sub> .2Na	7775-11-3
Sodium dichromate	Cr <sub>2</sub> H <sub>2</sub> O <sub>7</sub> .2Na	10588-01-9
Strontium chromate	CrH <sub>2</sub> O <sub>4</sub> .Sr	7789-06-2
Zinc chromate hydroxide	CrH <sub>8</sub> O <sub>12</sub> Zn <sub>5</sub>	49663-84-5
Zinc chromate oxide	CrO <sub>5</sub> Zn <sub>2</sub> .H <sub>2</sub> O	15930-94-6
Zinc potassium chromate	Cr <sub>2</sub> HO <sub>9</sub> Zn <sub>2</sub> .K	11103-86-9
Zinc potassium chromate, Zinc yellow (mixture)	ZnO, K <sub>2</sub> O, CrO <sub>4</sub> , H <sub>2</sub> O	37300-23-5

Source: [http://apps.kemi.se/flodessok/floden/kemamne\\_eng/oorganiska\\_kromsalter\\_eng.htm](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 pentazinc chromate octahydroxide. 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<sup>3</sup> (5-12 mg Cr (VI)/m<sup>3</sup>) 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 sensitivity 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 and 1,000 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 high-dose 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 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 significant in 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.