Annex XV dossier

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE AS A CMR CAT 1 OR 2, PBT, vPvB OR A SUBSTANCE OF AN EQUIVALENT LEVEL OF CONCERN

Substance Name: Sodium chromate

EC Number: 231-889-5

CAS Number: 7775-11-3

- *It is proposed to identify the substance as a carcinogenic, mutagenic and toxic for reproduction substance according to Article 57 (a), (b) and (c).*

Submitted by: France

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Summary of how the substance meets the CMR (Cat 1 or 2), PBT or vPvB criteria, or is considered to be a substance of an equivalent level of concern

According to Article 57 of Regulation 1907/2006 (the REACH Regulation), substances meeting the criteria for classification as carcinogenic (category 1 or 2), as mutagenic (category 1 or 2) or as toxic for reproduction (category 1 or 2) in accordance with Council Directive 67/548/EEC may be included in Annex XIV.

Sodium chromate has been classified as a carcinogenic (Carc. Cat. 2), as a mutagenic (Muta. Cat. 2) and as a reprotoxic (Repr. Cat. 2) according to Commission Directive 2004/73/EC of 29 April 2004 adapting to technical progress for the twenty-ninth time Council Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. The corresponding classification in Annex VI of Regulation (EC) No 1272/2008 adopted on 10 August 2009 is Carc. 1B, Muta. 1B and Repr. 1B. Consequently, sodium chromate has to be considered as a substance meeting the criteria of Article 57 (a), of Article 57 (b) and of Article 57 (c) of the REACH Regulation.

Registration number(s) of the substance or of substances containing the substance: not available

PART I: JUSTIFICATION

This report covers only sodium chromate. The risk related to chromium (VI) compounds has already been assessed in the Risk Assessment Report (RAR) published in 2005 (E.C., 2005) and which focused on chromium trioxide, sodium chromate, sodium dichromate, potassium dichromate and ammonium dichromate. Sodium dichromate is already included in the candidate list.

Three other Annex XV reports are submitted jointly and concern potassium dichromate, potassium chromate and ammonium dichromate. Part I of each report is similar (except for potassium chromate which is not classified as toxic for reproduction) since information comes from the Risk Assessment Report.

Common background description of chromium, chromate and dichromate compounds

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

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

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

In aqueous solution, hexavalent chromium exists as hydrochromate $HCrO_4^-$, chromate CrO_4^{2-}, and dichromate $Cr_2O_7^{2-}$ ionic species. Chromate anion tends to dimerize in dichromate. The proportion of each ion in solution is pH dependent. In basic and neutral pH, the chromate form predominates. As the pH is lowered (6.0 to 6.2), the hydrochromate concentration increases. At very low pH, the dichromate species predominate (US-EPA, 1998). Under particular conditions, a polymerisation can occur leading to the production of polychromates with the following formula $Cr_nO_{3n+1}^{2-}$.

Main chromium forms are the following according to their oxidation state:
Chromium metals and alloys (Cr (0)):

- Chromium metal
- Stainless steel
- Other chromium containing alloys

Divalent (Cr (2+)):

Chromous chloride	$CrCl_2$
Chromous sulfate	$CrSO_4$

Trivalent (Cr (3+)):

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

Hexavalent (Cr (6+)) chromate :

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

Hexavalent (Cr (6+)) dichromate :

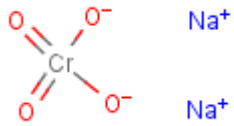
Sodium dichromate	$Na_2Cr_2O_7$
Potassium dichromate	$K_2Cr_2O_7$
Ammonium dichromate	$(NH4)_2Cr_2O_7$
Zinc dichromate	$ZnCr_2O_7$

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Chemical Name:	Sodium chromate
EC Number:	231-889-5
CAS Number:	7775-11-3
IUPAC Name:	Disodium chromate
Synonyms:	Sodium monochromate, Disodium chromium tetraoxide

1.2 Composition of the substance

Chemical Name:	Sodium chromate
EC Number:	231-889-5
CAS Number:	7775-11-3
IUPAC Name:	Disodium chromate
Molecular Formula (Hill)	Na_2CrO_4
Molecular Formula (CAS):	$CrH_2O_4.2Na$
Structural Formula:	
Molecular Weight:	161.99 g/mol
Typical concentration (% w/w):	99 % (typical impurities: none stated)

Impurities are not known.

1.3 Physico-chemical properties

The following information on physico-chemical properties was taken from the Risk Assessment Report on chromium compounds, published by the ECB in 2005 (E.C., 2005).

Physico-chemical parameters such as boiling point, octanol-water partition coefficient and vapour pressure have little meaning for solid ionic inorganic compounds.

Table 1: Summary of physico-chemical properties

REACH ref Annex, §	**Property**	**Value**
VII, 7.1	Physical state at 20°C and 101.3 kPa	Slightly deliquescent yellow crystals in hydrated form (usually tetra or deca hydrated)
VII, 7.2	Melting/freezing point (°C)	Decahydrate loses H_2O and melts at ~20°C; anhydrous salt melts at ~762°C
VII, 7.3	Boiling point	n/a: inorganic ionic compound
VII, 7.4	Relative density	~2.4 - 2.7
VII, 7.5	Vapour pressure	n/a: inorganic ionic compound
VII, 7.7	Water solubility at 20°C (g/L)	~530 (the aqueous solution is alkaline (pH 9))
VII, 7.8	Partition coefficient n-octanol/water (log value)	n/a: inorganic ionic compound

2 MANUFACTURE AND USES

Information on manufacture and uses may be useful for prioritisation of substances for inclusion in Annex XIV but this should be summarised under section 1 of the second part of this report.

3 CLASSIFICATION AND LABELLING

According to Article 57 of Regulation 1907/2006 (the REACH Regulation), substances meeting the criteria for classification as carcinogenic (category 1 or 2), as mutagenic (category 1 or 2) or as toxic for reproduction (category 1 or 2) in accordance with Council Directive 67/548/EEC may be included in Annex XIV.

Sodium chromate has index number 024-018-00-3 in Annex VI, part 3, Tables 3.1 and 3.2 of Regulation (EC) No 1272/2008.

Sodium chromate is classified in Annex VI (part 3, Tables 3.1 and 3.2) of Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

Its 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 is:

Classification	Labelling	Concentration Limits	Notes
Carc. Cat. 2; R45 Muta. Cat. 2; R46 Repr. Cat. 2; R60-61 T+; R26 T; R25-48/23 Xn; R21 C; R34 R42/43 N; R50-53	T+; N R: 45-46-60-61-21-25-26-34-42/43-48/23-50/53 S: 53-45-60-61	R42/43: C ≥ 0.2 %	E 3

Key:
Carc.: Carcinogenic; Muta: Mutagenic; Repr.: Toxic for reproduction
R21: Harmful in contact with skin
R25: Toxic if swallowed
R26: Very toxic by inhalation
R34: Causes burns
R42/43: May cause sensitization by inhalation and skin contact
R45: May cause cancer
R46: May cause heritable genetic damage
R48/23: Toxic: danger of serious damage to health by prolonged exposure through inhalation
R50-53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R60: May impair fertility
R61: May cause harm to the unborn child
T+: Very toxic
T: Toxic
Xn: Harmful
C: Corrosive
N: Dangerous for the 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
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’.
Note 3 : The concentration stated is the percentage by weight of chromate ions dissolved in water calculated with reference to the total weight of the mixture

Its harmonised classification according to part 3 of Annex VI, Table 3.1 of Regulation (EC) No 1272/2008 is:

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. 1B Muta. 1B Repr. 1B Acute Tox. 2 * Acute Tox. 3 * STOT RE 1 Acute Tox. 4 * Skin Corr. 1B Resp. Sens. 1 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350 H340 H360-FD H330 H301 H372** H312 H314 H334 H317 H400 H410	GHS06 GHS08 GHS05 GHS09 Dgr	H350 H340 H360FD H330 H301 H372 ** H312 H314 H334 H317 H410	Resp. Sens.; H334: C ≥ 0.2 % Skin Sens.; H317: C ≥ 0.2 %	3

Key:
Carc. 1 B: Carcinogenicity; Muta. 1B: Germ cell mutagenicity; Repr. 1B: Reproductive toxicity; Acute Tox. 2, Tox. 3, Tox. 4: Acute toxicity ; STOT RE 1 : Specific target organ toxicity — repeated exposure; Skin Corr. 1B: Skin corrosion/irritation; Resp. Sens. 1 : Respiratory/skin sensitization ; Skin Sens. 1: Respiratory/skin sensitization
Aquatic Acute 1, Aquatic Chronic 1: Hazardous to the aquatic environment
H301: Toxic if swallowed
H312: Harmful in contact with skin
H314: Causes severe skin burns and eye damage
H317: May cause an allergic skin reaction
H330: Fatal if inhaled
H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled
H350: May cause cancer
H340: May cause genetic defects
H360-FD: May damage fertility. May damage the unborn child
H372**: Causes damage to organs through prolonged or repeated exposure
H400: Very toxic to aquatic life
H410: Very toxic to aquatic life with long lasting effects
GHS05: Corrosion
GHS06: skull and crossbones
GHS08: Health hazard
GHS09: Environment
Dgr: Danger
Note 3: The concentration stated is the percentage by weight of chromate ions dissolved in water calculated with reference to the total weight of the mixture
An asterisk (*) indicates: Minimum classification for a category
Asterisks (**) indicate: Route of exposure cannot be excluded

4 ENVIRONMENTAL FATE PROPERTIES

Not relevant for this dossier.

5 HUMAN HEALTH HAZARD ASSESSMENT

Please refer to Annex I to get an informal overview of the human health hazard assessment on chromium compounds (chromium trioxide, sodium dichromate, sodium chromate, ammonium

dichromate and potassium dichromate) from the Risk Assessment Report (E.C., 2005) and from other sources regarding the irritation, corrosion and sensitisation effects.

6 HUMAN HEALTH HAZARD ASSESSMENT OF PHYSICO-CHEMICAL PROPERTIES

Not relevant for this dossier.

7 ENVIRONMENTAL HAZARD ASSESSMENT

Not relevant for this dossier.

8 PBT, VPVB AND EQUIVALENT LEVEL OF CONCERN ASSESSMENT

Not relevant for this dossier.

PART II: INFORMATION ON USE, EXPOSURE, ALTERNATIVES AND RISKS

1 INFORMATION ON MANUFACTURE AND USES

A global overview of chromium and chromium compounds manufacturing and uses is given in Annex II.

Following information concerns specifically sodium chromate (or other chromates when data on sodium chromate are not available).

Sodium chromate is the first chemical produced from chromite ore in the manufacture of chromate chemicals. The ore, containing approximately 30% chromium, is first dried, crushed and ground in ball mills. Sodium chromate is made by alkaline (sodium carbonate) oxidation in kilns at temperatures in the range of 1,000-1,200°C. After about 4 hours the reacted material leaving the kilns is either crushed and cooled before extraction of the water soluble components or quenched directly to form slurry containing sodium chromate, aluminate and vanadate in the aqueous phase. The slurry is conditioned to precipitate soluble alumina before separating the unreacted mineral residue, some of which is recycled to the kiln process after drying to aid extraction efficiency. The chromate solution is passed through other conditioning stages to remove soluble impurities. For example, sodium hydroxide and calcium hydroxide are used to precipitate soluble vanadium impurities as calcium vanadate. The latter is removed by pressure filtration and excess calcium is precipitated as the carbonate by treatment with sodium carbonate. At this stage, the partially purified solution contains around 35% sodium chromate (E.C., 2005).

According to the Risk Assessment Report (E.C., 2005), global world production capacities for sodium chromate have been estimated by the industry at 910 kT/year.

EU production (without import) of sodium chromate was estimated in 1997 around 103,000 tons per year (E.C., 2005). No more detailed and aggregated information on volumes imported and used in Europe is available.

The annual importation of chromate, dichromate and peroxochromate (excluded: zinc or lead chromate and sodium dichromate) in France was estimated at 1286 tons and the annual exportation was estimated at 7 tons in 2005 (INRS, 2005). According to INRS, sodium chromate is no more used in France.

In the Risk Assessment Report it is mentioned that sodium chromate is mainly used in manufacture of other chromium compounds (E.C., 2005) (see Figure A1 in Annex II). According to the Industry (French consultation, 2010), sodium chromate is used as an analytical reagent in laboratories; however, this use is limited.

The US Department of Defense (ASETSDefense, 2010) mentioned that sodium chromate is used in conversion coatings and as a corrosion inhibitor in cooling systems. These uses have not been checked currently at the European level. For more information on treatment and coating of metals, metal finishing processes using chromium (VI) compounds, please refer to Annex III.

Other potential uses referenced in literature (HSDB, 2005) are the following:

- chemical intermediate for pigments and catalysts,
- corrosion inhibitor (sealed water in cooling systems, oil-well drilling muds, protection of iron),
- mordant for dyes, dying paint pigment (in manufacture of pigments/inks),

- drilling mud additive,
- component of cells for chlorate manufacture,
- leather tanning,
- by making use of Cr-51 isotope, sterile sodium chromate (VI) solution is used in pharmaceuticals for the determination of circulatory red cell volume, cell survival time and evaluation of blood lose.
- aluminium etchant ingredient.

All these referenced uses have not been checked currently at the European level.

According to Industry, sodium chromate was removed from paint stripper and cutting fluid in the aeronautic sector (French consultation, 2010).

This Annex XV report focused on the potential use of sodium chromate as an analytical reagent in laboratories and as an intermediate in manufacture of other chromium compounds as it has not been possible to check the other uses at the European level.

2 INFORMATION ON EXPOSURE

From 2007, coatings containing hexavalent chromium will no longer be permitted under the End of Life Vehicles Directive (Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles) and the Waste Electrical and Electronic Equipment Directive (Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment). This will impact on some of the passivation applications where Cr (VI) is present in the finished articles and substitution will become a necessity.

In addition, Migration limits have been established within Council Directive 2009/48/EC, for the presence of chromium (VI) in children's toys.

Considering that chromium compounds are no more manufactured in Europe (cf. section 2.1 in Annex II), workers exposure related to the manufacturing of chromium (VI) compounds is not expected.

2.1 Exposure of workers

2.1.1 Global overview of workers exposure to chromium (VI) compounds in Europe

Several million workers worldwide are exposed to airborne fumes, mists and dust containing chromium or its compounds. Of the occupational situations in which exposure to chromium occurs, highest exposures to chromium (VI) may occur during chromate production, welding, chrome pigment manufacture, chrome plating and spray painting. Highest exposures to other forms of chromium occur during mining, ferrochromium and steel production, welding and cutting and grinding of chromium alloys (IARC, 1997).
Data on exposure levels are available for several specific industries and job categories covering several decades. In the past, exposures to chromium (VI) in excess of 1 mg/m^3 were found repeatedly in some processes, including chromium plating, chromate production and certain welding operations; exposures to total chromium have been even higher. Modern control technologies have markedly reduced exposures in some processes, such as electroplating, in recent years (IARC, 1997).

In epidemiological studies on cancer in humans, clearly and consistently elevated lung cancer risks have been observed in chromate production (exposure mainly to trivalent and water-soluble hexavalent chromium compounds), in chromate pigment production (exposure mainly to water-soluble and water-insoluble chromates) and also in chromium plating using chromic acid (ICDA, 2001).

A recent recommendation from the Scientific Committee on Occupational Exposure Limits (SCOEL) concluded that lung cancer was the critical effect of concern for occupational exposure, such that controls aimed at reducing lung cancer should also reduce the risk of other effects (SCOEL, 2004). In view of the genotoxicity of Cr (VI) compounds, it is not possible to identify a clear threshold below which there would be no increased risk of lung cancer. Consequently, no conclusions were reached concerning the magnitude of the cancer risk in workers. However, the recommendation from SCOEL has been published containing quantitative risk estimates for lung cancer. Table 2 shows the quantitative risk estimates for lung cancer as presented in the SCOEL/SUM/86 final document (SCOEL, 2004).

Table 2: Risk Assessment for Lung Cancer

Excess lung cancer cases per 1000 male workers	**Exposure (Working Lifetime to a range of Cr (VI) compounds)**
5-28	0.05 mg/m^3
2-14	0.025 mg/m^3
1-6	0.01 mg/m^3
0.5-3	0.005 mg/m^3
0.1-0.6	0.001 mg/m^3

The values in the Table 2 are based on an analysis of 10 epidemiological studies and were derived using a linear no-threshold model. SCOEL agreed that such a linear extrapolation approach was appropriate given that the Cr (VI) compounds are comprehensively genotoxic. It is important to note that the SCOEL report draws attention to areas of uncertainty associated with these risk estimates. For example, SCOEL felt that the irritant and inflammatory properties of the Cr (VI) compounds might contribute to the carcinogenic process. Such effects are likely to have dose thresholds, and hence the modelled risk values may be over-estimated at low exposures. In addition, SCOEL noted that at low exposures to Cr (VI) compounds, there are physiological defence mechanisms in the lungs that can convert Cr (VI) to the less harmful trivalent forms of chromium. This again suggests that a linear model may overestimate risks at low exposures. In essence, the SCOEL report presents risk estimates derived using a linear no-threshold model, but on the other hand, also includes toxicological reasons why the model could lead to an overestimation of lung cancer risk at low levels of exposure. Therefore, although the risk estimates are presented here for information, the uncertainties surrounding them must not be overlooked.

Overall, the SCOEL SUM recommends that for the soluble chromates (VI), consideration could be given to setting an occupational exposure limit at either 0.01 mg/m^3 or 0.025 mg/m^3 (8-hour TWA).

There are a number of countries with exposure limits for chromates and these have been tabulated below (E.C., 2005). These limits are provided for information and not as an indication of the level of control of exposure achieved in practice in workplaces in these countries.

Table 3: Occupational Exposure Limits

Country	**Compound**	**Limit (mg/m^3 as Cr)**	**Type of Limit**
UK	Cr (VI) compounds	0.05	8-hour TWA (MEL)
Germany	Production of soluble Cr (VI) compounds Other Cr (VI) compounds	0.1 0.05	8-hour TWA (TRK)
USA ACGIH	Water soluble Cr (VI) compounds	0.05	8-hour TWA (TLV)
USA OSHA	Cr (VI) compounds	0.1 (as CrO_3)	STEL/ceiling (PEL)
USA NIOSH	Cr (VI) compounds	0.001	TWA (REL) 10-hour workday 40-hour workweek
Netherlands	Soluble Cr (VI) compounds	0.025 0.05	8-hour TWA STEL
Sweden	Chromates and chromic acid	0.02 0.06	8-hour TWA STEL
Finland	Cr (VI) compounds	0.05	TWA
Japan	Cr (VI) compounds – carcinogenic forms Cr (VI) compounds	0.01 0.05	8-hour TWA 8-hour TWA
France	Cr (VI) compounds	0.05 0.1	8-hour TWA STEL

Key:
MEL: Maximum exposure limit
NIOSH: National Institute for Occupational Safety and Health
PEL: Permissible exposure limit
OSHA: Occupational Safety and Health Administration
REL: Recommended exposure limit
STEL: Short term exposure limit
TLV: Threshold limit value
TRK : Technical exposure limit
TWA: Time weighted average

For information, the Occupational Safety and Health Administration (OSHA) proposed to tighten the standard for hexavalent chromium occupational exposure with a permissible exposure limit (PEL) value for chromium (VI) of 0.005 mg/m^3 (calculated as an 8-hour time-weighted average (TWA)) (OSHA, 2008).

Values of Occupational exposure limits (OELs) are broadly similar across the EU. However there may be differences across Member States in relation to the legal or advisory framework associated with OELs affecting the way OELs are interpreted and complied with. These proposed occupational exposure limits only relate to inhalation exposure. Occupational exposure limits are not usually set for dermal exposure.

As the bronchial tree is the primary target organ for carcinogenic effects of Cr (VI), inhalation of chromium-containing aerosols is therefore a major concern with respect to exposure to chromium compounds. The Risk Assessment Report on chromium compounds provides inhalation exposure data for Cr (VI) compounds for different industry sector (E.C., 2005). These data are summarised in the Table 4. Reasonable worst-case (RWC) inhalation exposures are based on the 90th percentile of available measured data with professional judgment used where limited data were available.

Table 4: Summary of occupational inhalation exposure data from the Risk Assessment Report

Industry	**Number of samples**	**Range of exposures (mg/m^3)**	**Geometric mean (mg/m^3)**	**Reasonable worst case (RWC) (mg/m^3)**	**Source**
Manufacture of the five chromates	1,889	nd-0.78	0.004	0.02	measured data
Manufacture of other Cr containing chemicals					
- dyestuffs	39	nd-1.4	0.02	0.5 (8 hours) 1.5 (short term)	measured data judgement
- chrome tan	115	0.00001 - 0.025	0.002	0.007	measured data

Inhalation exposure data on manufacturing process are given only for information as chromium compounds are no more manufactured in Europe (see Annex II).

The manufacturing process for the five chromates is largely enclosed with breaching for bagging of product and some maintenance activities. The measured exposure data indicate that inhalation exposures for operators are usually very low, with those for maintenance staff and packers slightly higher. Exposures during the manufacture of the five chromates range from none detected to 0.78 mg/m^3. A reasonable worst-case exposure is 0.02 mg/m^3, based on the 90th percentile of the industry data for 1994-1997 for Company 1 (see the Risk Assessment Report for more information).

There are two types of chromium pigments: those that remain as chromium (VI) and those which are reduced to chromium (III). For both types, exposures usually occur during weighing and mixing of ingredients. Once they have been mixed and reacted then there is no further exposure. The range of exposures is quite large, from none detected to 1.4 mg/m^3. It seems likely that the high exposures were obtained when local exhaust ventilation (LEV) was not in use. A reasonable worst-case exposure of 0.5 mg/m^3 was agreed. For short term exposures a RWC is 1.5 mg/m^3 (E.C., 2005). In manufacture of pigments and dyes, although there are a number of companies in the EU, the exact number of workers involved is unknown.

For few plants which continue to use Cr (VI) compounds for tanning use, chrome salts are made either by reacting sodium dichromate with sulphur gas in an enclosed process or by reacting sodium dichromate and sodium chromate with a reducing sugar. In both cases liquid chromates are used and exposures will be low as there is little potential for exposure except when liquid chromate is discharged from a road tanker into a storage vessel. The production process itself takes place in an enclosed system. The range of exposures is 0.00001 - 0.025 mg/m^3. A reasonable worst-case exposure is 0.007 mg/m^3, based on the 90th percentile of the available data (E.C., 2005). The exact numbers of workers involved in the manufacture of chromium (VI) tanning agents is unknown but expected to be low since chromium (III) sulphate is now commonly used for this purpose.

The Risk Assessment Report on chromium compounds also provides dermal exposure data for Cr (VI) compounds for different industry sector (E.C., 2005). These data are summarised in the Table 5. The EASE (Estimation and Assessment of Substance Exposure) model was used to predict dermal exposures during the manufacture of chromates.

Table 5: Summary of occupational dermal exposure data from the Risk Assessment Report

Industry	**Range of exposures ($mg/cm^2/day$)**	**Source**
Manufacture of the 5 chromates	0 - 0.1	EASE
Manufacture of other Cr containing chemicals		
- dyestuffs	0.1 - 1	EASE
- chrome tan	0 - 0.1	EASE

Dermal exposure data on manufacturing process are given only for information as chromium compounds are no more manufactured in Europe (see Annex II).

In the manufacture of the five chromate compounds dermal exposures were predicted to be 0 to 0.1 $mg/cm^2/day$ during packing operations. It was not possible to predict dermal exposures during maintenance operations because of lack of information. Personal Protective Equipment (PPE) is worn during all manufacturing stages. PPE, properly selected and worn will significantly reduce exposure.

In the manufacture of other chromium-containing chemicals dermal exposures most often occur during weighing and charging of reactants to vessels. In the manufacture of dyestuffs dermal exposure is predicted to be 0.1-1 $mg/cm^2/day$. In chrome tan manufacture dermal exposures are predicted to be 0-0.1 $mg/cm^2/day$ (E.C., 2005).

2.1.2 Workers exposure to sodium chromate specifically in Europe

No information available.

2.2 Exposure of the general population via consumer products

Chromium (VI) compounds are not known to be present in greater than residual concentrations in products available directly to the consumer (E.C., 2005).

2.2.1 Dyestuffs

According to the Italian Textile and Health Association (Associazione Tessile e Salute, 2009) hexavalent chromium can be present in textiles which are dyed with post-chromating dyes when chromating conditions are not properly checked. Today, it is object of investigation in textiles, but the overall analyses made showed that it has been detected in very rare cases. Moreover, the Italian production, through the addition of a reduction after dyeing, ensures the absence of Cr (VI) in the textile product (see Annex IV for more information on the textile dyeing process using chromates).

2.2.2 Leather goods

Concerning leather goods, most of the tanning within the EU is carried out using basic trivalent chromium (III) sulphate. Basic trivalent chromium sulphate manufactured within the EU contains no measurable Cr (VI) (Cross H.J. *et al.*, 1997). Consequently, consumer exposure to Cr (VI) from leather goods based on leather tanned within the EU is expected to be insignificant.
A French study (Martinetti R., 1994) has demonstrated that under specific conditions of humidity, ultraviolet-C light and pH, there is a possibility of transforming chromium (III) compounds into chromium (VI) compounds which could migrate from the leather. However research is still needed to better understand the transformation mechanism of chromium (III) to chromium (VI) in finished leather as well as the potential toxic effects to man at this very low range of values.
Considering that health problems with chromium are mostly related to leather products (chromium is also found in textile products like dyed wool and silk), the German enforcement authorities strongly advise all those marketing leather products in Germany to ensure that the Cr (VI) content of the leather does not exceed 3 ppm which is the detection limit (CBI, 2008).

2.3 Exposure of the general population via the environment

Nonoccupational sources of exposure to chromium include food, air and water, but the levels are usually several orders of magnitude lower than those typically encountered in occupational situations (IARC, 1997).

Releases of chromium (VI) from any sources are expected to be reduced to chromium (III) in most situations in the environment. The impact of chromium (VI) as such is therefore likely to be limited to the area around the source (E.C., 2005).

2.3.1 Exposure via drinking water

The concentration of chromium in water varies according to the type of the surrounding industrial sources and the nature of the underlying soils (WHO, 2000). For example, in the Netherlands, the chromium concentration of 76% of the supplies was below 1 µg/L and of 98% below 2 µg/L (WHO, 2003). As far as drinking water quality and consumer protection is concerned WHO and the European Union (under the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption) have established a guideline value of 50 µg/L for total chromium in drinking water (WHO, 2003).

2.3.2 Exposure via food

Food contains chromium at concentrations ranging from <10 to 1300 µg/kg. Highest concentrations have been found in meat, fish, fruit, and vegetables. Utensils used in the preparation of food may contribute to chromium levels (WHO, 2003).

2.3.3 Exposure via ambient air

Hexavalent chromium substances are of low volatility and so emissions to air are unlikely from most processes. Specific information provided by manufacturers and users indicates that there are some releases to air from production and from some use steps; these are expected to be in particulate form (E.C, 2005).

Ranges of chromium levels in Member States of the European Union were given as follows: remote areas: 0-3 ng/m^3, urban areas: 4-70 ng/m^3 and industrial areas: 5-200 ng/m^3, e.g. the mean concentration of total chromium in air in the Netherlands varied from 2 to 5 ng/m^3 (WHO, 2003). Mass median diameters of chromium-containing particulates in ambient air have been reported to be in the range 1.5–1.9 μm (WHO, 2000). According to the EPA (US-EPA, 1998), chromium particles of small aerodynamic diameter (< 10 μm) will remain airborne for a long period. Consequently, population may be exposed to chromium through inhalation of ambient air.

The retention of chromium compounds from inhalation, based on a 24-hour respiratory volume of 20 m^3 in urban areas with an average chromium concentration of 50 ng/m^3, is about 3–400 ng. Individual uptake may vary depending on concomitant exposure to other relevant factors, e.g. tobacco smoking, and on the distribution of the particle sizes in the inhaled aerosol (WHO, 2000).

Mean chromium intakes (estimated total exposure) from food and water range from 52 to 943 μg/day (WHO, 2003). The estimated total intake of chromium from air, water, and food by the general population in the United Kingdom is in the range 78–106 μg/day. Food contributed 93–98% of the total intake and water 1.9–7%. The contribution from air was negligible. In the Netherlands, the estimated mean daily chromium intake is 100 μg, with a range of 50–200 μg. In general, food appears to be the major source of intake. Drinking-water intake can, however, contribute substantially when total chromium levels are above 25 μg/L.

2.3.4 Exposure via the environment (water, sediment, soil and food chain)

The following information on exposure via the environment was taken from the Risk Assessment Report on chromium compounds, published by the ECB in 2005 (E.C., 2005).

They are potential releases to water as some of the processes take place in water. Then released, the behaviour of chromium species in the environment can be influenced by environmental factors, such as pH and water hardness.

In the Risk Assessment Report on chromium compounds, it was assumed that for acidic (or neutral, where high concentrations of reductants for chromium (VI) exist) soils, sediments and waters, chromium (VI) will be rapidly reduced to chromium (III) and that 3% of the chromium (III) formed will be oxidised back to chromium (VI). The net result of this is that of the estimated chromium (VI) release to the environment, 3% will remain as chromium (VI) and 97% will be converted to chromium (III). Consequently, exposure to chromium (VI) in the environment is expected to be reduced by the formation of chromium (III).
Under less favourable conditions, e.g. alkaline conditions (~pH>8) and/or neutral conditions, where low concentrations of reductants for chromium (VI) exist, it will be assumed that the rate of reduction of chromium (VI) to chromium (III) is slow, with a long half-life of around 1 year. Such conditions are found in seawater, where a pH of around 8 is typical.

In addition, chromium (VI) exists mainly as highly soluble oxoanions in the environment and is expected to be mobile in soils and sediments although its adsorption is pH dependent. As a consequence, exposures through soils and sediments are not likely to be significant.

Moreover, there are no direct emissions to land, although the particulate emissions to air are likely to be deposited to land. Sludge application is another potential route to land; however, from comments from producers and users it is more usual for solid waste and sludges to be disposed of to landfill.

Chromium (VI) has been shown to be taken up by a wide range of organisms from water, sediment and soil. For fish, although uptake does occur, the bioconcentration factors for chromium (VI) are usually very low (~1 L/kg). However, the uptake of chromium by other organisms appears to be higher than seen for fish, although few of the experiments distinguish between chromium (VI) and chromium (III) concentrations in the organisms. Similar to the situation for fish, it is possible that once taken up by the organism, chromium (VI) is reduced to chromium (III) in the tissues, resulting in a build up of chromium (III) and hence an overestimate for the true bioconcentration factor for chromium (VI). BCFs of up to around 9,100 L/kg (on a mussel dry weight basis) for chromium (VI) and 2,800 L/kg (on a mussel dry weight basis) for chromium (III) have been determined in mussels, and BCFs of around 500 L/kg (on a cell dry weight basis) for chromium (VI) and 12,000-130,000 L/kg (on a cell dry weight basis) for chromium (III) have been determined in algae. Transfer of chromium via the alga to bivalve, and sediment to bivalve food chains appears to be relatively low. However, in the Risk Assessment Report on chromium compounds, it was concluded that further work could be done to test whether the mussel-based food chain is of concern.

3 INFORMATION ON ALTERNATIVES

No data available

4 RISK-RELATED INFORMATION

In relation to human health related with chromium (VI) compounds, the Risk Assessment Report conducted in 2005 (E.C., 2005) concluded that further measures were needed to limit the risks for workers, consumers and humans via the environment, and that risk reduction measures which are already being applied shall be taken into account.
In view of the genotoxic and carcinogenic properties of chromium (VI) the report concludes that there are concerns for all exposure scenarios. 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 toxicity). Therefore, these concerns are relevant for all chromates as well.

Applying the existing workplace health and safety legislation can lead to adequate control of the inhalation risks of exposure to chromium (VI) compounds, assuming that the adequate control is defined as reducing the exposure to below 0.01 $mg/m^{3.}$. Even if it seems possible to reduce inhalation exposure below 0.01 mg/m^3, this exposure average can however not be technically consistently maintained. Furthermore, some exposures (dermal route in particular) remain insufficiently monitored. At last, other concerns remain for health risks at this level of exposure.

OTHER INFORMATION

Consultation of the industry

A closed consultation focused on sodium chromate has been conducted at both the French and the European levels from the 18th December 2009 to the 15th January 2010, which has completed a previous French consultation on all chromium (VI) compounds.

Comments and technical contributions have been received from the following industrial sectors:

- chemical companies federation (UIC),
- reagents and chemicals manufacturing (Carlo Erba Reactifs, Daiichi-sankyo),
- pharmaceutical industry (Valdepharm),
- metal production (French ores, industrial minerals and non ferrous metals Federation; French steel Federation),
- mechanical industry (Technical centre for mechanical industry),
- civil and military aircraft manufacturing (French aerospace industries association, Airbus industry, Eurocopter-EADS),
- metal finishing (French metal finishing trade union),
- nuclear power industry,
- wood production for construction (OBBIA, CEI-Bois),
- building materials manufacturing (Delachaux),
- textile manufacturing and finishing (Italian Textile and Health Association),
- etc.

Grouping approach of chromium (VI) compounds

Regarding the potential inclusion of several chromium (VI) compounds in the Annex XIV of REACH ("authorization list") and according ECHA's approach on substances prioritisation[1], a grouping approach seems justified in order to prevent simple replacement of a substance that will be subjected to authorisation by another form of the substance which will not.
Indeed, some shared uses have been identified amongst chromium (VI) compounds (especially in the metal finishing sector) and it appears possible within the same process to easily replace one compound by another of the same family (sodium dichromate and potassium dichromate for instance). Moreover it appears possible to produce on-site a compound which may be subjected to authorisation from another one, by relevant chemical processes.

[1] General Approach for Prioritisation of Substances of Very High Concern (SVHCs) for Inclusion in the List of Substances Subject to Autorisation. Document developed in the context of ECHA's first Recommendation for the inclusion of substances in Annex XIV - 1 June 2009.

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ANNEXES

1 Annex I: 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 sodium chromate. Its content is however a useful background in support to part II of this report.

Most of the following information are taken from the Risk Assessment Report on chromium compounds (chromium trioxide, sodium dichromate, sodium chromate, ammonium dichromate and potassium dichromate), published by the ECB in 2005 (E.C., 2005). Please refer to the original document for more detailed information. It is likely that potassium chromate has not been prioritised for this risk assessment either because of a different hazard classification (considering that this substance is not classified reprotoxic contrary to the five other chromates) either because of less significant volumes and uses.

However, 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 is 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.

1.1 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.

1.2 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).

1.3 Irritation

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

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

In a very poorly-reported volunteer study, 10 subjects were apparently exposed to chromium (VI) trioxide at concentrations of 10-24 mg/m^3 (5-12 mg Cr (VI)/m^3) for “brief periods of time”. It was claimed that this exposure caused nasal irritation. According to the authors, exposure to lower but unspecified concentrations produced slight if any irritation of the upper respiratory tract. Given the poor reporting in this study the results cannot be considered to be reliable.
Symptoms of sensory irritation of the respiratory tract are known to occur among chrome plating workers exposed to a mist of aqueous chromium (VI) trioxide. Since this is corrosive, such symptoms are to be expected. No quantitative data on such irritation are available from studies of workers. No studies reporting symptoms of sensory irritation are available for the other Cr (VI) compounds. Overall, it is not possible to determine a reliable concentration-response relationship for respiratory tract irritation using the available data.

1.4 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.

1.5 Sensitisation

Skin sensitisation resulting from contact with Cr (VI) is relatively common in humans working with the compounds. This has been demonstrated in patch testing of contact dermatitis patients and in investigations of various occupational groups. In addition, skin sensitisation potential has been clearly demonstrated in standard and modified guinea pig maximisation tests and in the mouse ear swelling test.
Current understanding of the mechanism involved in the sensitisation indicates that Cr (III) is the ultimate hapten. Skin contact with Cr (VI) leads to penetration of Cr (VI) into the skin where it is reduced to Cr (III). There is some evidence for cross-reactivity between Cr (III) and Cr (VI); Cr (VI)-sensitised subjects may also react to Cr (III). Overall, it is not possible to reliably determine a threshold for either induction or challenge in an exposed population using the available data.

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

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

1.6 Repeated dose toxicity

Please refer to sections 1.4 and 1.5.

1.7 Mutagenicity

1.7.1 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.

1.7.2 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.

1.7.3 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.

1.7.4 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.

1.8 Carcinogenicity

1.8.1 Carcinogenicity: oral

No data available.

1.8.2 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.

1.8.3 Carcinogenicity: dermal

No data available.

1.8.4 Carcinogenicity: human data

A number of epidemiology studies investigated cancer risks among workers exposed to various 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.

1.8.5 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.

1.9 Toxicity for reproduction

1.9.1 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).

1.9.2 Developmental toxicity

In a developmental toxicity study (Trivedi B. *et al.*, 1989), groups of 10, 13, 12 and 10 pregnant female ITRC-bred albino mice were administered daily 0, 250, 500 and 1,000 ppm of potassium

dichromate (equivalent to doses of approximately 0, 60, 120 and 230 mg/kg/day (0, 20, 40 and 80 mg Cr (VI)/kg/day)) in drinking water during gestation from day 0 (vaginal plug identified) to day 19 when dams were sacrificed. At sacrifice, fetuses were subjected to routine external, visceral and skeletal examination, and levels of total chromium in the maternal blood, in the placenta and in the fetuses were measured.

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

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

Junaid *et al.* (Junaid M. *et al.*, 1996a) exposed pregnant Swiss albino mice (10 per group) to 0, 250, 500 or 750 ppm potassium dichromate in drinking water during days 6-14 of gestation. Dams were subject to caesarean section on day 19 and fetuses examined. Based on average daily water intakes, chromium levels received were and 2.00, 3.75 and 5.47 mg/mouse/day. Based on a bodyweight of 30 g, the estimated intake of potassium dichromate was 190, 350 and 520 mg/kg/day (70, 125 and 180 mg Cr (VI)/kg/day). There were no maternal deaths or clinical signs of toxicity but weight gain was decreased at 350 and 520 mg/kg/day (125 and 180 mg Cr (VI)/kg/day) (reductions of 8.2 and

24% respectively). The number of fetuses per litter was statistically significantly decreased by 20 and 18%, fetal weight was decreased (by 13 and 20% respectively compared to controls) and the number of dead fetuses increased (3 in 2 litters, 12 in 7 litters respectively) at 350 and 520 mg/kg/day (125 and 180 mg Cr (VI)/kg/day). Post implantation loss increased to statistically significant levels of 22 and 34% at 350 and 520 mg/kg/day (125 and 180 mg Cr (VI)/kg/day). Reduced ossification, incidence of dropped wrist and subdermal haemorrhagic patches were increased at these dose levels. Overall, chromium (VI) caused fetotoxicity but not malformations at 350 mg/kg/day (125 mg Cr (VI)/kg/day), a dose level which did not produce overt signs of maternal toxicity but caused a small decrease in bodyweight gain. The NOAEL for fetal effects was 190 mg/kg/day (70 mg Cr (VI)/kg/day).

Other studies

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

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

Overall, the results of this study indicate that pregestational oral administration through drinking water of potassium dichromate for 20 days to female mice produced adverse effects on female fertility (reduced number of corpora lutea and/or increased pre-implantation loss) at 500 ppm (119 mg/kg/day (40 mg Cr (VI)/kg/day)) and above. Fetotoxic effects were also seen starting from the lowest dose level tested, 250 ppm (63 mg/kg/day (20 mg Cr(VI)/kg/day)). Significant maternal

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

1.9.3 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.

1.9.4 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 and developmental effects. 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.

1.10 Other effects

Not relevant for this dossier.

1.11 Derivation of DNEL(s) or other quantitative or qualitative measure for dose response

Not relevant for this dossier.

2 Annex II : Overall description of chromium manufacturing and chromium uses

Following information has been compiled and summarized from HSDB (HSDB, 2005) (general entry for chromium ions and inorganic and organic chromium compounds), the European Risk Assessment Report (E.C., 2005) and from the following industrial websites:

- http://www.elementischromium.com/products/manufacturing.htm

- http://www.icdachromium.com/home.php#

2.1 Manufacture

Chromium is mined outside of the EU as chromite ($FeCr_2O_4$) ore which contains trivalent chromic oxide and this is oxidised to sodium chromate during kiln roasting in the chromate-producing industry (SCOEL, 2004). Chromite ore and soda ash (sodium carbonate) and sometimes ground lime, limestone or dolomite are the principal raw materials in the manufacture of chromium chemicals. These compounds are subjected to a high temperature calcination process to produce sodium chromate. The vast majority of sodium chromate produced is then reacted with sulphuric acid to produce sodium dichromate liquor with sodium sulphate as a co-product. The sodium dichromate is used as the derivative to manufacture the whole range of chromium based chemicals. Process of manufacturing is illustrated in Figure A1. Hexavalent compounds, with the exception of some small amounts in minerals, do not occur naturally in the environment but are formed from trivalent chromium during chromate-production processes.

Only one EU producer has been listed since 2004 in UK and only manufactured sodium dichromate. This plant has closed down in 2009. Main manufacturers are now located in South Africa and main EU importers are located in UK. Companies wishing to use chromate compounds must use imported sources.

2.2 Main applications and uses of chromium and chromium compounds referenced in literature

Three main sectors of activity using chromium compounds can be distinguished.

2.2.1 Alloy and chromium metal production

Of the world's total production of chromite, approximately 95% is smelted into ferrochromium alloys. These are for subsequent use in the stainless steel, steel and other alloy industries. Chromium metal, composed of nearly 100% chromium, is produced by the aluminothermic or electrolytic process. It is mainly used for specialty alloys.

Main uses referenced by HSDB (HSDB, 2005) are fabrication of alloys, preparation of alloy steels to enhance corrosion and heat resistance and production of non-ferrous alloys to impart special qualities to the alloys.

2.2.2 Refractory applications

Production of chromite for refractory use and foundry sands is about 3% of world production of chromite. Refractory chromite is used in sectors of ferrous and non-ferrous metallurgy, in cement

kilns and in the glass industry. Pure chromium oxide is used alone or together with alumina, zirconia and silica for high temperature and attack resistant refractories.

2.2.3 Chromium chemicals manufacturing and related uses

2% of the world's production of chromite was used in 2008 for manufacturing a variety of chromium chemicals (including chromium (VI) compounds) from conversion of sodium chromate (sodium dichromate, ammonium and potassium dichromate, chromic acid, chromic oxide and basic chromium sulphate, etc.).

The earliest use of chromium chemicals was during or before the 19th century for colour and pigment applications, due to their very bright colours in clear yellow, orange, green, turquoise and blue. Main uses referenced by HSDB are manufacturing of coloured pigments used in dyes, paints and plastics, ceramics, cements, papers, rubbers, composition floor covering, surface finishes and other materials.

The second largest use of chromium chemicals is in the metal finishing industry. Chromium is actually known for its luster when polished and its protection when coated on metal surfaces. It is used as a protective, decorative and increased wear resistance by coating in the sector of metal finishing on vehicles parts, plumbing fixtures, furniture parts and many other items, usually applied by electroplating.

Chromium is also regarded with great interest because of its high corrosion resistance and hardness. A major development was actually the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium and nickel to form stainless steel and special high chromium content super-alloys used in gas turbine engines. Besides decorative plating, hard chromium plating is applied extensively to corrosion and wear resistant engineering surfaces and to pickling of plastics. Chromium plating is usually made from chromic acid. Stainless steel manufacturing and chrome (electro)plating are currently the highest-volume uses of chromium. Primer paints containing hexavalent chromium is still widely used for aerospace and automobile fishing applications regarding the resistance to corrosion.

Other smaller uses are the following:

- mordant in textile industry in dyeing silk treating, printing, and moth proofing wool,
- tanning in leather industry,
- fixing baths in photographic,
- catalytic manufacture (catalysts for halogenation, alkylation, and catalytic cracking of hydrocarbons, etc.)
- fuel additives and propellant additives in ceramics,
- fabrication of magnetic tapes,
- use in cooling “fluids”,
- use in wood preservatives,
- use in medicine as astringents and antiseptics,
- etc.

This multiplicity of uses explains that chromium is commonly found in a wide range of articles such as aircrafts, motorcars, barrels, buses, cans, electrical appliances, flatware, hardware, lumber, pharmaceuticals, pigments and dyes, railroad equipment, ships, etc.

Specific application in wood preservation:

Potassium dichromate, sodium dichromate and chromium trioxide have been used in the formulation of water-borne wood preservatives for about a century (ICDA, 1998). They function as essential chemical fixatives for the copper and other fungicidal and insecticidal components in the widely used chromated-copper preservatives, of which the best known example is CCA (copper-chrome-arsenic mixture). Studies have shown that chromium in these preservatives has little or no direct action against decay fungi. However, stabilisation of the other preservative components achieved through valency state reduction of chromium makes them resistant to leaching and provides the treated wood with long-term durability against fungal and insect attack, even in high risk environments. It should be noted that chromium compounds have virtually no fungicidal (or insecticidal) activity in wood. Despite the long and successful history of use of chromate containing wood preservatives, a number of regulatory authorities have and are considering restrictions or bans on their use for certain products; interestingly, CCA preservatives are still permitted for timber for export and for local heavy duty applications.

Now, the use of potassium dichromate and sodium dichromate in the formulation of wood preservatives is not allowed in Europe following European Commission decision of the 5th of December 2007 on the basis of the 27th meeting of representatives of Member States Competent Authorities for the implementation of Directive 98/8/EC concerning the placing of biocidal products on the market ("Way forward on chromium"). The harmonized approach taken is the following: in order to ensure that chromic acid in wood preservatives has none or a negligible biocidal activity, chromium-containing wood preservatives meeting the following requirements on their composition and use shall be allowed to remain on the market. No other form than chromic acid (chromium trioxide) should be allowed in the product. Other chromium compounds, such as potassium dichromate or sodium dichromate should not be allowed, as no data have been provided to demonstrate that these compounds have no, or only a negligible, biocidal activity. This approach has however not been endorsed by several countries (UK, IE, LT and HU).

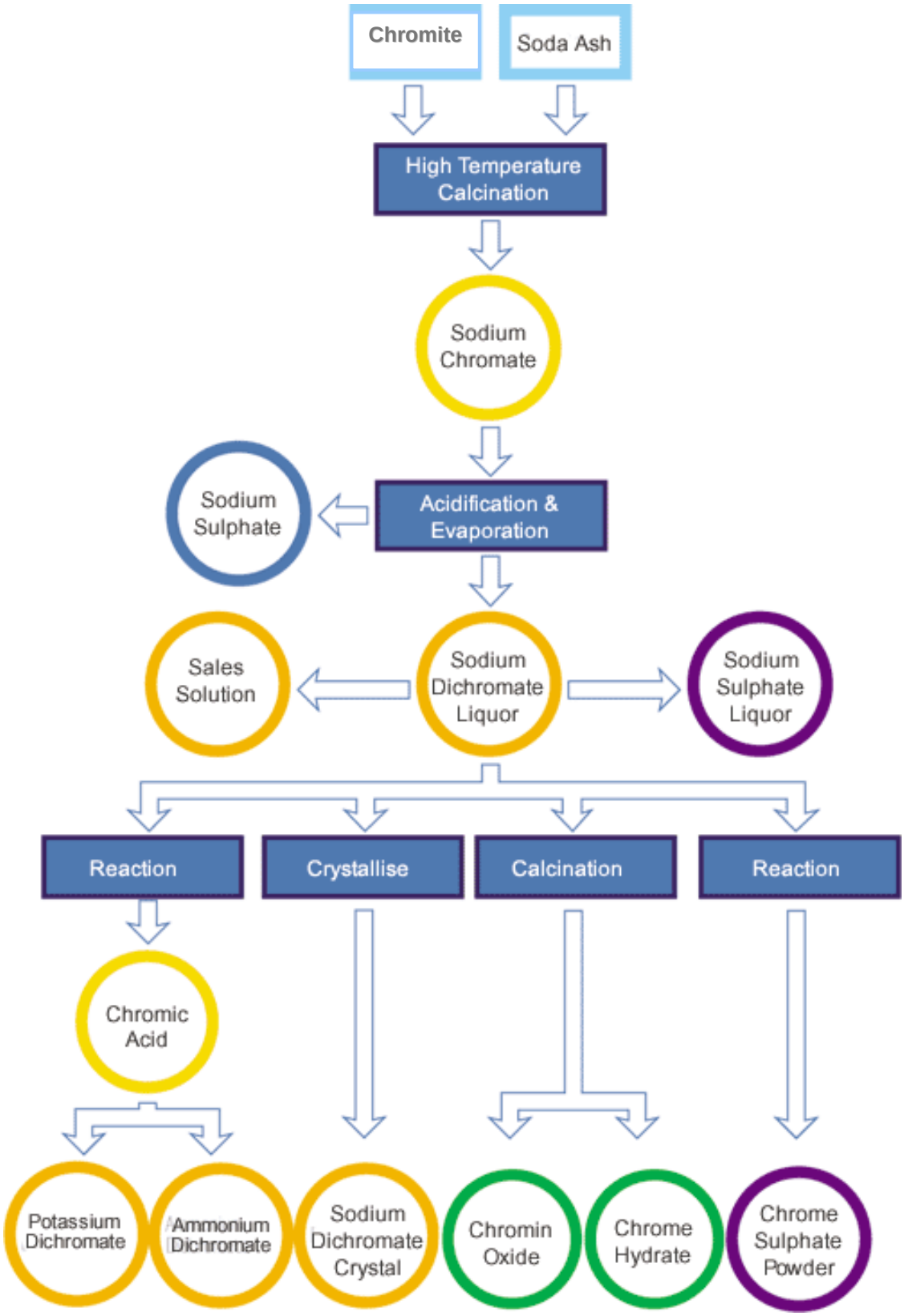

Figure A1: Example of chromium compounds manufacturing process (from ICDA website)

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

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

According to the industry (French consultation, 2010), main activities of the metal finishing sector using chromate compounds are anodising application, chemical and electrolytic coatings and paints, which represent respectively 5%, 24% and 32% of the total metal finishing activity. Main purposes of metal treatments are appearance improving (12%), resistance to corrosion (46%), wear resistance (24%) and others (electrical conductivity, etc.).
The distribution of chromium (VI) compounds used by metal finishing workshops to prepare treatment baths (all merged processes) was in 2004 according to the French Metal Finishing Trade Union:

- chromium trioxide 64% (meaning that 64% of all metal treatment baths are prepared from chromium trioxide),
- potassium dichromate 17%,
- sodium dichromate 17%,
- ammonium dichromate 2%,
- potassium chromate 2%.

3.1 Formulation of metal treatment products

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

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

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

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

Chromate conversion coating is a type of conversion coating applied to passivate aluminium, zinc, cadmium, copper, silver, magnesium, tin and their alloys to slow corrosion and to make metal-plated parts more durable. The strong oxidative properties of chromates are used to deposit a protective oxide layer of complex chromium compounds on metallic surfaces to protect the base

metal from corrosion. This passivation and the self healing properties by the chromate stored in the chromate conversion coating, which is capable to migrate to local defects, are the benefits of this coating method. It can also provide a good base for subsequent painting, give a chemical polish and/or colour the metal.

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

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

The composition of chromate conversion solutions varies widely depending on the material to be coated and the desired effect. Most solution compositions are proprietary. The widely used Cronak process for zinc and cadmium consists of 5–10 seconds of immersion at room temperature in a solution of 182 g/L sodium dichromate crystals ($Na_2Cr_2O_7 2H_2O$) and 6 mL/L concentrated sulfuric acid.

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

3.3 Sealing after anodising

Acidic anodising solutions produce pores in the anodised coating. These pores can absorb dyes and retain lubricants, but are also an avenue for corrosion. When lubrication properties are not critical, they are usually sealed after dyeing to increase corrosion resistance and dye retention. Different types of sealing exist. Teflon, nickel acetate, cobalt acetate, and hot **sodium or potassium dichromate** seals are commonly used. Dichromate compounds are often used for this purpose in the aeronautic sectors which use aluminium alloys 2024 and 2019.

3.4 Chrome (electro)plating or chrome dipping or chroming

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

3.4.1 Chrome plating methods

There are two types of industrial chrome plating solutions:

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

The component will generally go through these different stages.

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

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

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

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

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

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

3.4.2 Chrome plating processes

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

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

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

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

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

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

3.4.3 Brightening

This process may be part of the surface preparation before a major process such as electroplating. Chromates are used only for copper, zinc and their alloys. Brightening basically involves dipping the substrate into a solution of chromium salts to remove scale, oxide films and tarnish. Chromate baths are not normally made up specifically for this purpose, but where a bath is already made up for plating or other use it may also be used for this purpose (E.C., 2005).

4 Annex IV: Uses of chromium (VI) salts in the textile sector (process)

This information is drawn from the Italian Textile and Health Association (Associazione Tessile e Salute, 2009). The entire document focuses on the use of sodium dichromate in dyeing of textile fibres (processes, control of human exposure - workers during the process and consumer through the articles-, control of environment exposure, waste management, etc.). This information is expected to be also valid for other Cr (VI) compounds used for the same purpose and process.

4.1 Dyeing of protein fibres

The use of sodium dichromate is based on a oxidation-reduction reaction which transforms the hexavalent chromium chemical into the corresponding trivalent chromium, with following creation of a stable complex between this and the dyeing molecule uniformly diffused and chemically bound inside the fibres.
Furthermore, hexavalent chromium added in the dyeing bath totally binds to the fibre as it does not exceed the material thanks to the stoichiometric dyeing method adopted.

The percentages to use according to the material weight vary between 0.1 and 3% of solution dichromate. The process is divided into three phases:

- First phase: ordinary dyeing with acid dyes
- Second phase: the called “chromating” process, which uses sodium dichromate, working at a temperature of 94-96°C for a variable time between 30 and 40 minutes
- Third phase: reduction (with thiosulphate and/or washing).

The dyeing and chromating processes are carried out in closed containers whereas the exhausted dyeing baths are drained through pipes which ensure their transport to the company’s and /or cooperative depuration system.
When applied to tops, the dyed material often undergoes further washing with ammonia and soap at a temperature between 30 and 40°C in continuous machines, called “backwashing machines”, which guarantee the fibre sliver to be deeper cleaned during the transport to the company’s or cooperative depuration plant.

The chemical agent is used as a solution and this strongly limits the risks for the operators; in fact the main risk is represented by inhalation and being the agent vapour tension in the form of metal ion practically void, its presence as aerosol in the working place is quite improbable.
Moreover, a deliberate exposure by skin contact or ingestion is absolutely to exclude because eating and/or drinking is strictly forbidden in the working place, also with regard to how the chemical agent is used in a closed system.

The closed circuit dosing system is equipped with a storage tank, into which the external supplier let the liquid chemical agent flow; this tank must be positioned in such a way so as to ensure conveyance of any accidental release to the depuration plant and to prevent its drying. The dosing system must also be equipped with highly precise volumetric weighing system and automatic distribution to the dying devices by means of a piping network.

In the rare event that the quantity of sodium dichromate to be used is so small that the automatic dosing system cannot be employed (dyeing of minimum quantities or lab tests), all the operations shall be carried out with the aid of personal protection devices like nitril gloves, glasses, mask.

Furthermore, it can be affirmed that at the end of the dyeing cycle, when the textile is still inside the dyeing apparatus and prior to sampling (when the colour compliance is checked), the whole quantity of hexavalent chromium has been already reduced to trivalent chromium as a security for the operators.

4.2 Chemical reaction with fibre and dyestuff

Cr (III) salt is not used as mordant since the treatment should take place in acid environment and at such conditions that wool with protonatized sites would not only bind with Cr^{3+} ions but on the contrary would tendentially repel them. This is the reason why Cr^{6+} as $Cr_2O_7^{--}$ anion is used.

Reacting with dichromate in acid environment, $Cr_2O_7^{--}$ anion is first fixed by ionic bond to the protonatized amino groups of the wool and then reduced by reaction with wool reducing groups, among which the -S-S- cystine group:

$Cr_2O_7^{--} + 6$ and$^- + 14\ H^+ \leftrightarrow 2\ Cr^{3+} + 7\ H_2O$

Now Cr^{3+} ion is already distributed inside the fibre and can bind with - COOH groups of the wool and form complexes with the dye, furthermore with a less acid pH it can also bind with the amino compounds of the fibre by means of coordinative linking.
In practice, there take place the simultaneous Cr^{6+} reduction and Cr^{3+} combination with the dye in the fibre.
In this way the Cr (III) ion works as linking species between fibre and dye, and this explains the high colour fastness levels obtained with these dyes.

4.3 Subsequent processes

The need to assess also the processes downstream the dyeing cycle is due to the assumption that should a residual part of hexavalent chromium be present inside the dyed material, this could cause exposure to inhalation by the operators in the downstream production areas because of the formation of fibrous particulate caused by mechanical operations, like for example the blending of top slivers.
Actually, the stoichiometric use of the chemical agent according to the type and quantity of the material to be processed and to the dye intensity implies the almost total absence of residual hexavalent chromium inside the dyed textile.