

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: Potassium chromate

EC Number: 232-140-5

CAS Number: 7789-00-6

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

Submitted by: France

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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: Potassium chromate

EC Number: 232-140-5

CAS number: 7789-00-6

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

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) or as mutagenic (category 1 or 2) in accordance with Council Directive 67/548/EEC may be included in Annex XIV.

Potassium chromate has been classified as a carcinogenic (Carc. Cat. 2) and as a mutagenic (Muta. Cat. 2) according to Commission Directive 96/54/EC of 30 July 1996 adapting to technical progress for the twenty-second 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 and Muta. 1B. Consequently, potassium chromate has to be considered as a substance meeting both the criteria of Article 57 (a) and of Article 57 (b) 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 potassium 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, sodium chromate and ammonium dichromate. Part I of each report is similar (except for this substance 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 ($\text{Cr}_2\text{O}_7^{2-}$) anions which are strong oxidising agents at low pH. Their oxidative property is widely used in organic chemistry. Chromates and dichromates are salts of chromic acid and dichromic acid, respectively. Chromic acid, which is an oxacid has the hypothetical structure H_2CrO_4 . By losing two protons (H^+), chromic acid and dichromic acid form chromate ion and dichromate ion respectively. Neither chromic nor dichromic acid can be isolated, but their anions are found in a variety of compounds: the chromates and dichromates. The dark red chromium (VI) oxide CrO_3 (chromium trioxide) is the acid anhydride of chromic acid and it is sold industrially as “chromic acid”.

Chromate salts contain the chromate anion CrO_4^{2-} and usually have an intense yellow color. Dichromate salts contain the dichromate anion $\text{Cr}_2\text{O}_7^{2-}$ 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 $\text{Cr}_2\text{O}_7^{2-}$ 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 $\text{Cr}_n\text{O}_{3n+1}^{2-}$.

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 ₂ O ₃
Chromic chloride	CrCl ₃
Chromic sulfate	Cr ₂ (SO ₄) ₃
Chromic potassium sulphate	KCr(SO ₄) ₂
Chromite ore	FeO.Cr ₂ O ₃

Hexavalent (Cr (6+)) chromate :

Chromium trioxide	CrO ₃
Chromic acid	H ₂ CrO ₄
Sodium chromate	Na ₂ CrO ₄
Potassium chromate	K ₂ CrO ₄
Zinc chromate	ZnCrO ₄
Strontium chromate	SrCrO ₄

Hexavalent (Cr (6+)) dichromate :

Sodium dichromate	Na ₂ Cr ₂ O ₇
Potassium dichromate	K ₂ Cr ₂ O ₇
Ammonium dichromate	(NH ₄) ₂ Cr ₂ O ₇
Zinc dichromate	ZnCr ₂ O ₇

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

Chemical Name: Potassium chromate

EC Number: 232-140-5

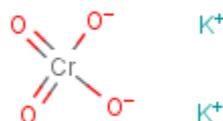
CAS Number: 7789-00-6

IUPAC Name: Dipotassium chromate

Synonyms: Dipotassium chromate, Bipotassium chromate, Dipotassium monochromate, Bipotassium monochromate, Neutral potassium chromate, Potassium chromate (VI), Chromate of potash (potass), Chromic acid dipotassium salt

1.2 Composition of the substance

Chemical Name:	Potassium chromate
EC Number:	232-140-5
CAS Number:	7789-00-6
IUPAC Name:	Dipotassium chromate
Molecular Formula (Hill):	K_2CrO_4
Molecular Formula (CAS):	$CrH_2O_4.2K$
Structural Formula:	



Molecular Weight:	194.19 g/mol
Typical concentration (% w/w):	99 to 99.9% (reagent, technical)

Impurities are not known.

1.3 Physico-chemical properties

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	Reference
VII, 7.1	Physical state at 20°C and 101.3 kPa	Yellow orthorhombic crystals (odorless)	(HSDB, 2005)
VII, 7.2	Melting/freezing point (°C)	975	(HSDB, 2005)
VII, 7.3	Boiling point	n/a: inorganic ionic compound	
VII, 7.4	Relative density at 18°C	2.73	(HSDB, 2005)
VII, 7.5	Vapour pressure	n/a: inorganic ionic compound	(E.C., 2005)
VII, 7.7	Water solubility at 20°C (g/L)	629	(HSDB, 2005)
VII, 7.8	Partition coefficient n-octanol/water (log value)	n/a: inorganic ionic compound	(E.C., 2005)

2 MANUFACTURE AND USES

Information on manufacture and uses may be useful for prioritisation of substances for inclusion in Annex XIV but this is 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) or as mutagenic (category 1 or 2) in accordance with Council Directive 67/548/EEC may be included in Annex XIV.

Potassium chromate has index number 024-006-00-8 in Annex VI, part 3, Tables 3.1 and 3.2 of Regulation (EC) No 1272/2008.

Potassium 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; R49 Muta. Cat. 2; R46 Xi; R36/37/38 R43 N; R50-53	T; N R: 49-46-36/37/38- 43-50/53 S: 53-45-60-61	R43: C ≥ 0.5 %	E 3
<p><u>Key:</u> Carc.: Carcinogenic; Muta.: Mutagenic R49: May cause cancer by inhalation R46: May cause heritable genetic damage R36/37/38: Irritating to eyes, respiratory system and skin R43: May cause sensitization by skin contact R50-53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment Xi: Irritant N: Dangerous for the environment T: Toxic 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</p>			

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 Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350i H340 H319 H335 H315 H317 H400 H410	GHS08 GHS07 GHS09 Dgr	H350i H340 H319 H335 H315 H317 H410	Skin Sens. 1; H317: C ≥ 0.5 %	3
<p><u>Key:</u> Carc. 1 B: Carcinogenicity; Muta. 1B: Germ cell mutagenicity; Eye Irrit.2: Serious eye damage/eye irritation; STOT SE 3: Specific target organ toxicity - single exposure; Skin Irrit. 2: Skin corrosion/irritation; Skin Sens. 1: Respiratory/skin sensitization Aquatic Acute 1, Aquatic Chronic 1: Hazardous to the aquatic environment H350i: May cause cancer by inhalation H340: May cause genetic defects H319: Causes serious eye irritation H335: May cause respiratory irritation H315: Causes skin irritation H317: May cause an allergic skin reaction H400: Very toxic to aquatic life H410: Very toxic to aquatic life with long lasting effects GHS08: Health hazard GHS07: Exclamation mark GHS09: Environment Dgr: Danger 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</p>					

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 potassium chromate (or other chromates when data on potassium chromate are not available).

Potassium chromate is manufactured (HSDB, 2005):

- either by roasting powdered chromite with potash and limestone, treating the cinder with hot potassium sulfate solution and leaching,
- either by the reaction of potassium dichromate and potassium hydroxide,
- either by roasting of chromite ore with potassium hydroxide.

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).

The annual consumption of potassium chromate in France was estimated around 1000 tons in 2005 (INRS, 2005). No more detailed information on volumes imported and used in Europe is available.

Potassium chromate is mainly used in:

- **Treatment and coating of metals:** potassium chromate is used as corrosion inhibitors for many applications including treatment of aluminium and steel surfaces for corrosion resistance (cf. chromate conversion coatings (CCC)) (ASETSDefense, 2010).
For more information on treatment and coating of metals, metal finishing processes using chromium (VI) compounds, please refer to Annex III.
- **Metallurgy of non-ferrous metals:** in France, the annual consumption of potassium chromate in production of non-ferrous metals was estimated around 0.2 tons in 2005 (INRS, 2005). Potassium chromate is used as an inhibitor coating for aluminium powder to prevent its contact with the water (in order to prevent the formation of hydrogen). Nowadays, this treatment is less used and is commonly replaced by a coating based on a fatty acid (isostearic acid).
In addition, in the manufacture of zinc, iron control (which is an impurity in the ore) can be done by measuring the redox potential with potassium chromate (INRS, 2005).
- **Manufacture of reagents and chemicals:** potassium chromate is used for manufacturing chromate containing reagents and chemicals used by many applications such as analysis (see *infra*) and routine checks, etc. (French consultation, 2010). One of the European producers uses around 0.1 ton per year of potassium chromate; around 21 workers of this plant are potentially exposed to potassium chromate (by sampling, packaging, formulating and manufacturing).

- **Manufacture of textile:** potassium chromate can be used in preparation and spinning of textile fibres, as a textile mordant (fixing agent) and as an oxidizing agent for dyes and as a component of stripping solution for wool dyeing (HSDB, 2005).

Potassium chromate is added to fix the dyes to the wool. The chromium (VI) in the reaction is reduced to chromium (III). The process can be operated in three ways. The chromium can be added to the bath first, to penetrate the fibres before addition of the dye - this is pre-chroming. The second method is to add the dye and the chromium together. The third method allows the dye to disperse through the fibres first before fixing it with the chromium. This latter method, known as after chroming, is the only process in significant use. In some cases other reducing agents are added to reduce the chromium (VI) in the bath (E.C., 2005). More information on the textile dyeing process using chromates (in particular sodium dichromate) is given in Annex IV.

In France, the annual consumption of potassium chromate in textile finishing in 2005 was estimated around 0.3 kg and around 50 kg in manufacture of artificial/synthetic fibres (INRS, 2005). In textile finishing, potassium chromate is specifically used as a textile mordant. In manufacture of artificial/synthetic fibres, potassium chromate is used for analysis in laboratory.

- **Colouring agent in ceramics:** potassium chromate is used in ceramics as colouring agents (Schwartz M.M., 2002) and in enamels. Actually, chromium salts are elements which contribute to the production of many ceramic colouring materials such as brown, yellows, greens, blacks, reds or purplish pinks, etc. The introduction of potassium chromate or dichromate in a low temperature plumbous glaze (maximum 900°C) leads according to firing conditions to chromium reds by formation of basic lead chromate (PbCrO_4 , PbO).

- **Tanning and dressing of leather:** tanning of leather is a chemical process in which chemicals like chromium are fixed into the fibres in order to stabilise the hide. The process of tanning is essentially a stabilisation of the collagen fibres in the leather by blocking reactive functions and by cross linking them within the leather. Chromium tanned leather can contain between 4 and 5% of chromium, which is tightly bound to the proteins. In the tanning process the chromium (III) is bonded to the leather, usually by bathing the leather in a bath containing brine and chromium (III) salts for 16 hours (E.C., 2005). Nowadays, all tanning within the EU (percentage unknown) is carried out using directly basic trivalent chromium (III) sulphate containing solutions. This procedure has thus replaced all the techniques based upon the use of chromium (VI) which, in the past, required the reduction to a valency of (III) in the tannery, before tanning (ICDA, 1997). However, INRS reported an estimated annual consumption of potassium chromate as mordant for printing leather in France around 800 tons in 2005 (INRS, 2005), considering that small isolated plants could still use Cr (VI) compounds in order to convert a commercial source of hexavalent chromium (usually sodium dichromate or potassium chromate) into a tanning salt *in situ*. This has however not been checked.

- **Manufacture of pigments/inks:** chromate pigments are used in paints and metal primers, and as colorants in rubber, paper and inks (E.C., 2005).

The Cr (VI) pigments are made from soluble sodium dichromate, which is pumped from storage tanks to the mixer to which the other reactants are also added. The resulting precipitate/slurry is then filtered, dried and bagged. They are often used in anti-corrosive primer paints and include strontium chromate, basic zinc chromate and lead chromate. Strontium chromates are the pigments most commonly used in primer paints, but many

variants do exist. Although primarily used in wet paints, Cr (VI) pigments may also be used in powder coating applications (according to a personal communication).

The “Exclusion list for printing inks and related products” (6th Revised Edition, replaces October 2007 edition) of EuPIA (European Printing Ink Association - European Printing Ink Group of CEPE¹) (EuPIA, 2009b) is a voluntary recommendation that excludes the use of CMR substances as raw materials (substances and preparations) for printing inks and related products. According to EuPIA, although it does not have legal obligation, this exclusion list has the full support of all printing ink manufacturer members in Europe. In addition, the “EuPIA Guideline on printing inks applied to the non-food contact surface of food packaging materials and articles” (September 2009) (EuPIA, 2009a) does not allow the use of CMR classified substances for ink manufacturing for food packaging. This guideline has been developed to support ink manufacturers in order to know how to formulate inks which comply with Regulation (EC) 1935/2003 of 27 October 2004 on materials and articles intended to come into contact with food, as this regulation does not specify any legislation concerning printing inks for food packaging.

- **Manufacture of paper and paperboard:** the annual consumption of potassium chromate in manufacture of paper and paperboard in France was estimated around 3 kg in 2005 (INRS, 2005). It is used in laboratory for testing the density and the whiteness of paper.
- **Laboratory:** potassium chromate is used as an analytical reagent (titrating agent) for the determination of chloride ions by the Mohr protocol, for the determination of chemical oxygen demand “COD” (French consultation, 2010) and in identification tests for H₂O₂ detection (HSDB, 2005).
- **Manufacture of pharmaceuticals:** potassium chromate is used for analytical tests (as a reagent) of the European pharmacopoeia (French consultation, 2010).
- **Pyrotechnics:** potassium chromate is used in pyrotechnics (French consultation, 2010).

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.

¹ European Council of producers and importers of paints, printing inks and artists’ colours

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/m³ 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 SUM 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 report recommends that for the soluble chromates (VI), consideration could be given to setting an occupational exposure limit at either 0.01 mg/m³ or 0.025 mg/m³ (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	0.1	8-hour TWA (TRK)
	Other Cr (VI) compounds	0.05	
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	8-hour TWA STEL
		0.05	
Sweden	Chromates and chromic acid	0.02	8-hour TWA STEL
		0.06	
Finland	Cr (VI) compounds	0.05	TWA
Japan	Cr (VI) compounds – carcinogenic forms	0.01	8-hour TWA
	Cr (VI) compounds	0.05	8-hour TWA
France	Cr (VI) compounds	0.05	8-hour TWA STEL
		0.1	

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/m³ (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 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
Use in metal treatment					
-electrolytic	315	<0.001 - 0.05	0.01	0.02	measured data
-passivation	42	<0.001		0.001	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).

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/m³. 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 $0.00001 - 0.025 \text{ mg/m}^3$. 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.

Occupational exposure to chromium (VI) during metal treatment can be from either electrolytic or passive processes. When electric current is used airborne chromium (VI) in the form of mist is generated. This mist is not generated with passive processes and so inhalation exposures during passive metal treatment will be very low. Exposure will also occur in both types of process when chromate solutions are made up and added to the treatment bath. Exposures for electrolytic metal treatment range from less than 0.001 to 0.05 mg/m^3 . A reasonable worst-case exposure is 0.02 mg/m^3 , based on the 90th percentile of available data (E.C., 2005).

In textiles industry where Cr (VI) compounds are used as fixing agents in dyeing process, inhalation and dermal exposure are likely to occur during weighing, mixing with water and during addition of the solution to the dyeing vat. Once in solution exposure is considerably reduced. According to the Italian Textile and Health Association (cf. Annex IV) (Associazione Tessile e Salute, 2009), all precaution are kept by their members in order to avoid the workers exposure to Cr (VI) (prevention of accidental release, closed automatic system, protection of trained operators by procedures and personal protection devices, use of chromate in solution in order to limit the exposure, etc.).

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 other Cr containing chemicals		
- dyestuffs	0.1 - 1	EASE
- chrome tan	0 - 0.1	EASE
Use in metal treatment		
-mixing of solutions	0 - 0.1	EASE
-adding to bath	0 - 0.1	
-drag out	1 - 5	
-re-threading steel strip	0.1 - 1	

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 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/cm²/day. In chrome tan manufacture dermal exposures are predicted to be 0-0.1 mg/cm²/day (E.C., 2005).

In metal treatment dermal exposures are likely to be similar for both electrolytic and passive processes. They can occur during making up of treatment solutions, adding the solution to the treatment bath, from drag out and splashing and when re-threading treated steel strips. EASE predicted dermal exposures to be 0 to 0.1 mg/cm²/day during mixing of solutions and adding to the treatment bath, 0.1 to 1 mg/cm²/day during re-threading of steel strips and 1 to 5 mg/cm²/day from drag out. Personal Protective Equipment (PPE) may be worn for these tasks. PPE, properly selected and worn will significantly reduce exposure (E.C., 2005).

2.1.2 Workers exposure to potassium chromate specifically in Europe

In France, the number of workers (primary users exclusively) potentially exposed to potassium chromate was estimated in 2005 from 950 to 1800. The table 6 resumes the number of workers exposed to potassium chromate per industry sector. The number of workers potentially exposed among downstream users is not known.

Table 6: Number of workers exposed to potassium chromate per industry sector in France (estimation in 2005)

Industry sector	Number of workers exposed to potassium chromate (estimation in 2005, France)
Manufacture of textile	150 – 500 (textile finishing) < 100 (manufacture of artificial/synthetic fibres)
Tanning and dressing of leather	500 - 1000
Manufacture of paper and paperboard	~ 100
Metallurgy of non-ferrous metals	< 100

One of the European producers uses around 0.1 ton per year of potassium chromate; around 21 workers of this plant are potentially exposed to potassium chromate (by sampling, packaging, formulating and manufacturing) (French consultation, 2010).

2.1.3 Prevention of workers exposure to chromium (VI) compounds in metal treatment

According to the International Chromium Development Association (ICDA) (ICDA, 2001), the most effective prevention of exposure is replacement of hexavalent chromium with trivalent, which has been shown to be feasible in some uses such as decorative chrome finishing. Where such a change to the process is not possible it is necessary to achieve adequate control by other means.

With some operations the emission of chromic acid (or other chromate) mist can be controlled by total enclosure of the process. Where this is not reasonably practicable, it is necessary to achieve adequate control by providing efficient exhaust ventilation and/or by treating the electrolyte (plating solution) with a mist suppressant to limit the emission of mist into the workplace atmosphere.

Even when the process can be completely enclosed, extract ventilation should still be provided at the enclosure. The extraction should be sufficient to ensure that there is movement of air into the enclosure when any access points in the enclosure are opened for purposes of process control, so preventing emission of mist into the workroom atmosphere. It is prudent to keep the exposure as low as is possible using best available techniques (E.C., 2006).

In the workplace, preventive steps such as engineering design containment, improved systems of work and hygiene measures minimise occupational exposure to hexavalent chromium compounds leading to a reduction in the experience of health effects. To measure and assist in the control of exposure at the workplace, ambient air monitoring is performed and the exposure levels compared to national occupational exposure standards. However, ambient air monitoring does not take into account all routes of exposure e.g. ingestion and through the skin and mucosa. Biological monitoring is therefore an added option for monitoring total exposure by analysis of the amounts of chromium in biological samples such as blood and urine. In addition, examination of exposed individuals are advised on a periodic basis through health surveillance and may allow an opportunity for early detection of health effects, which can then lead to appropriate preventive intervention to reverse, reduce or minimise such effects.

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 Chromated end products

Concerning chromated end products (after chromate conversion coating (CCC)), a layer of chromium oxide is formed on the metal surface. Cr₂O₃ is the main oxide, either colourless either from slightly yellow to brown depending on the treatment duration. This coating contains Cr (VI) and other chromium compounds with other valency. Cr (VI) content have been measured up to 15% of total chromium content (AFSSET, 2008).

2.2.2 Dyestuffs

Dyed wool garments are washed during and after treatment and the finished wool does not contain any Cr (VI). There is, therefore, no consumer exposure to Cr (VI) from wool garments (E.C., 2005). However, 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.

2.2.3 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).

2.2.4 Chromium pigments

Although some pigments can be manufactured from chromate the resulting pigments are Cr (III) based and any residual Cr (VI) is removed by washing during manufacture (E.C., 2005).

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/m³, urban areas: 4-70 ng/m³ and industrial areas: 5-200 ng/m³, e.g. the mean concentration of total chromium in air in the Netherlands varied from 2 to 5 ng/m³ (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 m³ in urban areas with an average chromium concentration of 50 ng/m³, 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

3.1 Alternative substances

The following information on chromate conversion coating are taken for most from a study on use and alternatives of chromium compounds identified as CMR substances. This study was performed

in 2008 by the AFSSET (French agency for environmental and occupational health safety) with the collaboration of ALCIMED (AFSSET, 2008).

According to the Industry (French consultation, 2010) and despite more than 10 years of research and development, substitution of chromium (VI) compounds commonly used in the aeronautic sector is not yet possible and will need 5 to 7 years more for performance specifications fulfilment (for instance security specifications, ensured efficiency over 30 years, etc.) before being agreed by decision makers.

Alternatives to the use of chromium (VI) compounds in metallurgy of non-ferrous metals, in textile manufacturing and in laboratory are also described below.

3.1.1 Chromate conversion coating

Chromate conversion coating which uses Cr (VI) compounds tends to be substituted by a process which uses trivalent chromium compounds or other corrosion inhibitors (molybdates, zirconates (or titanates), cerium, silanes and silicates). The substitution with trivalent chromium compounds is the most common alternative.

The different alternatives to chromate conversion coating (with Cr (VI)) are listed in the sections below.

3.1.1.1 Alternative based on molybdates

Two types of treatment based on molybdates are possible: one containing sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and the other based on a mixture of molybdate and phosphate.

Anti-corrosive performances of the treatment based on sodium molybdate are much lower than conversion coating which used chromium (VI) (72 h salt spray resistance to treatment with Mo, and 250 h resistance for the treatment with Cr (VI)).

Treatment based on a mixture of molybdate and phosphate formed a layer of oxide on the surface of the metal treated. This layer can provide corrosion resistance comparable to treatment with chromium (VI) for cyclic moisture/drying tests. By cons, it is less resistant to salt spray test. The filing of an organic layer can improve this feature. This type of treatment, protected by patents, is barely visible in the industry.

3.1.1.2 Alternative based on zirconates or titanates

The adhesion to paint is good and comparable to those obtained by treatment with hexavalent chromium. Moreover, these treatments can be in accordance with specifications very demanding in terms of corrosion if the metal part is covered with additional protective layers (paint or varnish). However, if, for aesthetic reasons or electrical conductivity, the metal should not be covered, the anti-corrosive properties do not seem sufficient to make these products viable substitutions.

3.1.1.3 Alternative based on vanadates and tungstates

Vanadates ions (VO_4^{3-}) and tungstate ions (WO_4^{2-}) can be used for processing metals. However, these ions do not have a good corrosion protection for the industry.

3.1.1.4 Alternative based on cerium

CeO_x protection systems are not inherently protective as Cr (VI) is, and the mechanism of Ce protection is not well understood. Surface cleaning and preparation are critical with Ce and it is essential for the coating to have the correct structure and thickness. Phosphating improves the protection by changing Ce (IV) to Ce (III) (Legg K.O., 2007). Treatment with cerium is protected by several patents and it is not used at the industrial scale.

3.1.1.5 Alternative based on silanes

For this type of treatment an appropriate cleaning/etching of the surface must precede the process of silane passivation. Once applied, it is necessary to apply heat treatment to obtain a dense layer of silane forming an effective barrier against corrosion.

Other organic systems are studied to improve the adhesion. For example, carboxylic acid groups and anhydrides. For these organic systems it is also necessary to perform a cleaning/etching of the surface prior to passivation. It should be noted that this treatment is expensive and has not been identified at the industry level.

3.1.1.6 Alternative based on trivalent chromium compounds

The chemical process is similar as conversion coating with Cr (VI).

The conversion coating based on Cr (III) presents anti-corrosion properties and self-healing less efficient than Cr (VI). This substitution is the most common in the industrial world, despite a cost ten times higher than traditional conversion coating process. However, the main problem of this alternative is the fact that chemical analysis testing shown that between 7% and 10% of the chromium on a trivalent passivated part oxidizes to hexavalent chromium (Winn D. and Dalton W., 2008). In addition, for trivalent chromate passivation systems to provide more than just minimal corrosion protection in ASTM B117 (The American Society of Testing and Materials test B117 on salt spray test specifications) accelerated corrosion testing, cobalt is required. Trivalent chromate systems use cobalt to improve performance, but cobalt is known to cause sensitization by inhalation and skin contact (it is classified R42/43 according to Annex I of Council Directive 67/548/EEC) (Winn D. and Dalton W., 2008) and some cobalt salts are classified Carc.2 and Repr.2.

3.1.1.7 Alternative based on silicates

An effective way of using silicates has been developed to replace hexavalent and trivalent chromate passivates. Through this patented process, a glass-like mineral layer is formed on the surface, replacing the surface oxide. This ceramic layer offers some excellent performance characteristics and advantages over chromate passivation. The ceramic system is a commercially available system that offers advantages over trivalent chromium passivate at a cost-competitive price and it has provided solutions in the trucking and automotive industries (Winn D. and Dalton W., 2008).

3.1.1.8 Conclusion on alternative substances for chromate conversion coating

Alternative substances to potassium chromate exists for conversion coating but most of them are more expensive and are protected by patents. They present anti-corrosive properties which do not seem sufficient however, for application in less corrosive environments these types of alternatives substances certainly have a place. Indeed, the implementation of these alternatives on the field showed positive results. Please refer to section 3.2 dedicated to alternatives developed in US military sectors.

3.1.2 Metallurgy of non-ferrous metals

The use of potassium chromate as an inhibitor coating for aluminum powder is commonly replaced by a coating with a fatty acid (isostearic acid) in order to prevent oxidation of aluminum powder (INRS, 2005).

3.1.3 Manufacture of textile

According to the Italian Textile and Health Association (Associazione Tessile e Salute, 2009) researches for an alternative to dyeing with chrome dyes as well as to replace this dye class with another one that does not require the use of this chemical agent have been conducted. Two types of alternatives to dyeing with chrome dyes exist, one using complex agents and the other one using reactive dyes.

3.1.3.1 Alternative based on complex agents

The replacement of the alkaline salts of hexavalent chromium with other complex agents like aluminium, iron, titanium or trivalent chromium salts combined with oxidizers has been in-depth searched without highlighting any practical applications. All the tests made highlight colour tones changing to red/bordeaux as well as the formation of a complex with instable textile material, which was confirmed also by decreased fastness in the textile product. According to textile industry, such reduced wet fastness, which also brings as a result to the total loss of the excellent fastness properties of chromium dyes, also reduces the safety level of the end user and at the same time creates ecological problems in terms of increased pollution of waste waters.

3.1.3.2 Alternative based on reactive dyes

Replacing the chrome dyes with reactive dyes is possible in few cases, mainly for light and medium shades with not specific requisites for high wet fastness. However, for some cases this is not practicable and technical difficulties have been observed as for example: shade, metamerism, crease-resistant treatment, decreased fastness, lower fixing percentage, higher consumption of water and chemicals, higher costs.

According to a personal communication alternative dyes, such as reactive and metal complex dyes have increasingly replaced chrome dyes for wool. The speed of replacement is relatively slow and it is estimated that, although the market for wool dyes will increase by 20-25% by 2008, chrome dye use is forecast to remain static or decrease.

3.1.4 Laboratory and manufacture of pharmaceuticals

Some of these uses cannot be substituted yet (French consultation, 2010). A standardized method using potassium permanganate is identified as substitute for the use as analytical reagent (titrating agent) for the determination the chemical oxygen demand “COD” in waste waters treatment (French standard NF T 90-101) (INRS, 2007).

There are no substitutes identified for analytical tests of the European pharmacopoeia (French consultation, 2010).

3.2 Chromate alternatives researches for United States military uses

United States Department of Defense has been developing and testing chromate alternatives for a number of years. On April 8, 2009 the Under Secretary of Defense for Acquisition Technology and Logistics issued a memo restricting the use of chromates in military systems. As a result of this memo the effort to develop, test and approve alternatives has been accelerated.

A number of alternatives are now available, or have been authorized, or implemented. More detailed information on the performance and implementation of alternatives is available on the searchable ASETSDefense database at: <http://db.asetdefense.org/Custom/customsearch.aspx>.

Searching the database for the document categories specification, authorization and implementation will produce various examples of these changes. Searching for other documents will provide reports showing the performance of various alternatives to chromated products.

However, the pace of substitution is necessarily quite slow because these substances are critical to the safe operation of military equipment, particularly aircraft. The costs of corrosion in general are very high, and corrosion can lead to catastrophic failures such as environmental embrittlement and stress corrosion cracking. Alternatives must be thoroughly laboratory-tested and then evaluated in service over a number of years to ensure that they will function safely and effectively in the range of operational environments experienced by defense equipment (ASETSDefense, 2010).

US Department of Defense has already made significant investments to find alternatives for a variety of its uses of hexavalent chromium. Some are approved and some are still undergoing necessary rigorous tests to prove their utility for military applications (which need to operate in extreme environments, be fully reliable, and which tend to last a long time). Perhaps the most important point for any decision maker to be aware of is that there is not any single drop-in substitute for all uses of hexavalent chrome. Further a substitute may work for one use but not for another. Substitution can affect other maintenance practices - so it can take some time to implement.

Detailed information on substitutes is gathered and shared at www.assetsdefense.org or www.asetdefense.org. This website provides information and assistance to improve weapons system performance and life-cycle cost while reducing or eliminating environmental safety and occupational health (ESOH) impacts from coatings and treatment processes that utilize hexavalent chromium.

3.3 Alternative techniques

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 and occupational asthma. 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 potassium 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 prioritisation², 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.

² 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 potassium 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/m³ (5-12 mg Cr (VI)/m³) 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 sensitivity has proved fairly persistent once developed. Contact with textiles colored with chromate-based pigments can be sufficient to exacerbate the dermatitis. The wearing of leather shoes tanned with chromates can produce dermatitis of the feet if these are allowed to remain sweaty. In sensitized individuals, the absorption of chromium by pulmonary and/or oral way could cause an exzematous reaction. After cutaneous exposure to chromic acid, erosions of the skin may occur. These « chrome holes » initially appear as papular lesions, either singly or grouped, with central ulceration.

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

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

Whereas potassium chromate has not been identified as a teratogen, other chromium (VI) compounds have been determined to be reprotoxic: sodium chromate, sodium dichromate, ammonium dichromate and potassium dichromate have been classified as toxic for reproduction (category 2). Please refer to the relevant Annex XV dossier.

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 finishing 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).

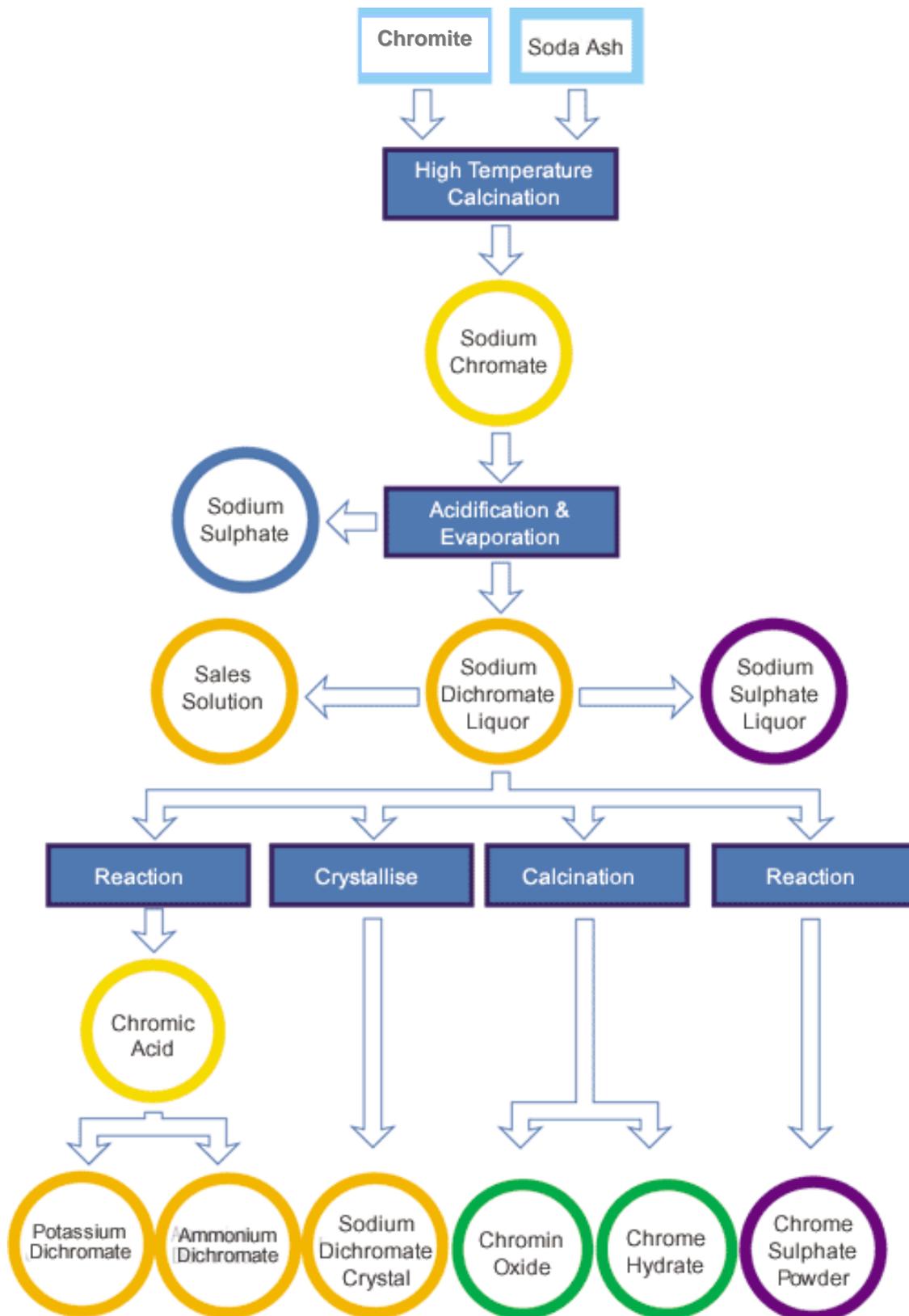


Figure A1: Example of chromium compounds manufacturing process (from ICDA website)

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 ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) 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 whose main ingredient is chromic anhydride. When mixed with acid, chromate ions CrO_4^{2-} , first form dichromate ions $\text{Cr}_2\text{O}_7^{2-}$, 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/m²). ECCS is always used lacquered. On the surface of the strip a coating mass between 50 and 140 mg/m² (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 dyeing 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 protonated 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 $\text{Cr}_2\text{O}_7^{2-}$ anion is used.

Reacting with dichromate in acid environment, $\text{Cr}_2\text{O}_7^{2-}$ anion is first fixed by ionic bond to the protonated amino groups of the wool and then reduced by reaction with wool reducing groups, among which the -S-S- cystine group:



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.