

**DATA ON MANUFACTURE, IMPORT, EXPORT, USES
AND RELEASES OF SODIUM DICHROMATE
AS WELL AS INFORMATION ON POTENTIAL
ALTERNATIVES TO ITS USE**

The technical work on this report has been led by Entec,
under framework contract ECHA/2008/2 (specific contract
ECHA/2008/02/SR5/ECA.227)

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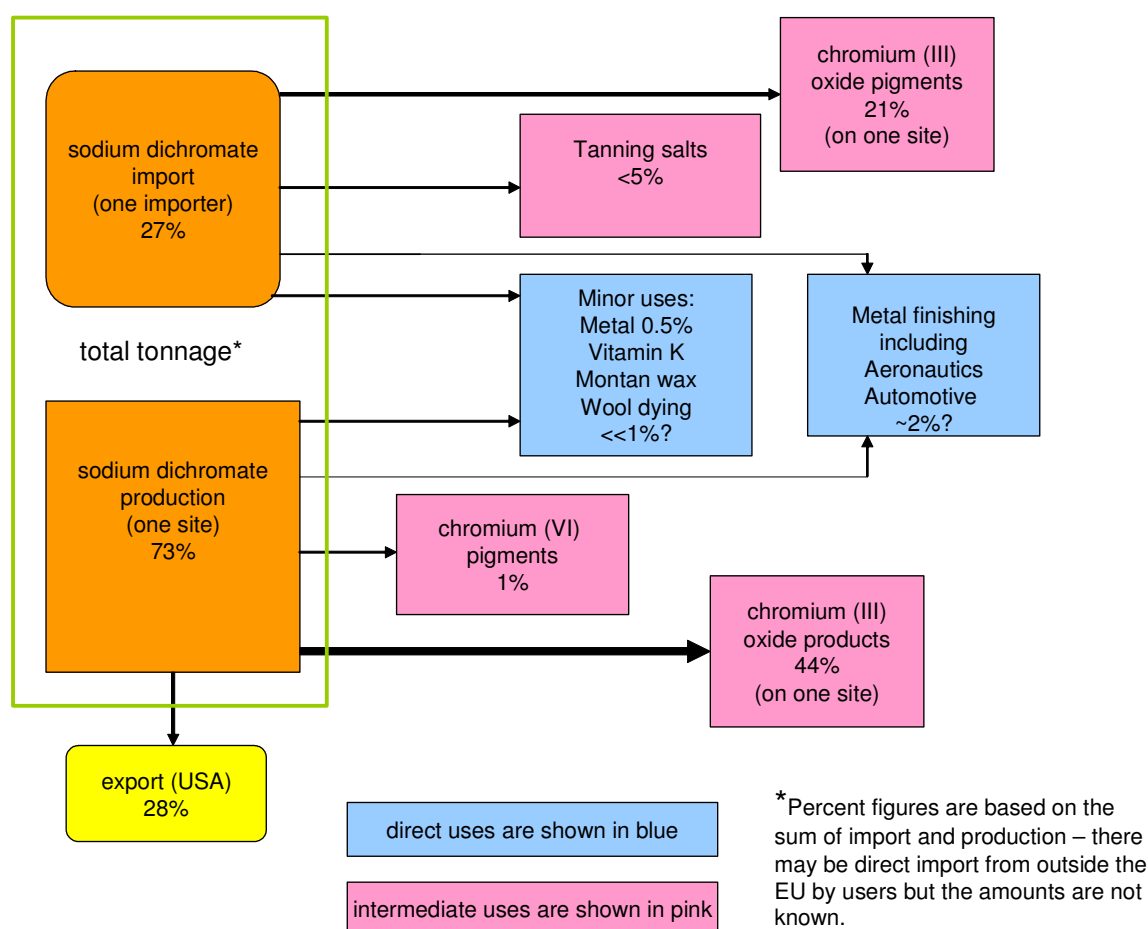
EXECUTIVE SUMMARY

This report presents data on the manufacture, use, releases and alternatives to sodium dichromate (dihydrate: EC No 234-190-3, CAS 7789-12-0 and anhydrous: EC No 234-190-3, CAS 10588-01-9), collated by Entec. In this report no distinction is made between sodium dichromate and sodium dichromate dihydrate as it appears that no such distinction is made in its manufacture and use.

The report has been produced according to a format and structure provided by ECHA. Draft reports have been reviewed and commented on by ECHA and this final report has been accepted by ECHA.

Consultation with industry indicated that the European production of sodium dichromate is significantly reduced from the 110 kilotonnes reported in the risk assessment report (EC, 2005) and is undertaken by a single manufacturer (Elementis) which is based in the UK. Import appears to be mainly from a single importer (Lanxess), although there may be other imports of sodium dichromate into the EU by users, but their identity and the volume is not known. The tonnages for production and import are therefore regarded to be commercially confidential and thus are presented in the confidential annex only (Annex 2 to this report).

An illustration of the main production, import and uses and is presented below (Figure 3.1 in the report).



A summary production, import and main uses (expressing quantities as percentages of the total quantity identified for this study), highlighting intermediate and non-intermediate uses (intermediate uses being exempt from authorisation) is set out below:

Table 0.1 Sodium dichromate summary of percent uses

Use	Percentage (of known EU production and import)	Intermediate use?	Except from authorisation?
Exported out of the EU	28%	N/A	Y
Production chromium (III) oxide	65%	Y	Y
Production of chromium (VI) pigments	<1%	Y	Y
Anticorrosion additive in coatings	<<1%	N	N
Production of chromium metal	<<1%	Y	Y
Metal finishing	~2%	N	N
Production of tanning salts	<5%	Y	Y
Production of montan wax	<<1%	N	N
Production of vitamin K	<<1%	N	N
Mordents for wool dyes	<<1%	N	N

The non-intermediate uses (and therefore those uses to which authorisation may apply if the substance was to be placed on Annex XIV of REACH) represent a small proportion of the total volume (around 2%). Nevertheless, as the total tonnage of this substance is still significant, the tonnage use in non-intermediate uses may still be of importance in terms of ‘high volume’ as a criterion for prioritisation¹.

Estimates of releases of sodium dichromate from manufacture and certain uses have been provided, largely based information from the risk assessment and risk reduction strategy reports. Further information on the releases of the substance per se has been difficult to gather as information is reported as either total chromium or hexavalent chromium. Nevertheless, for the non-intermediate uses there appears to be the potential for exposure of workers and possibility of releases to the environment.

Analysis of specific alternative substances and techniques has not been conducted. However the potential for the use of alternatives anticorrosion uses in the aeronautics industry, metal finishing in the metal packaging industry and for the synthesis of

¹ Article 58 (2) (c) of REACH – high volume is not specifically defined.

vitamin K, has been considered and the possibility for substitution has been indicated for uses in wood preservation and mordents for wool dyeing. It appears that for some industries the use of the substance (and in some cases hexavalent chromium in general) is diminishing (e.g. metal finishing and automotive industries), however for key uses such as for anticorrosion of metal parts and in paint systems in the aeronautics industry and for metal packaging that is used for food containers, that technically feasible alternatives do not exist or are not available because of specific industry rules requiring extensive testing of potential substitutes before use is permitted.

The information gathered for this report is based on information set out in the European Union Risk Assessment Report for chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate and potassium dichromate (EC, 2005), the Environmental Risk Reduction Strategy and Analysis of the Advantages and Drawbacks for Hexavalent Chromium (Defra, 2005) and the Human Health Risk Reduction Strategy for Chromates (HSE, 2007) as well as stakeholder comments from consultation on the Annex XV dossier for sodium dichromate (provided to Entec by ECHA) and consultation with the following:

- The International Chromium Development Association
- Elementis EU
- Lanxess
- ZVO – Central Agency of surface treatment
- Surface engineering association
- Aerospace and Defence Industries Association of Europe (ASD)
- Society of Motor Manufacturers and Traders
- European Automobile Manufacturers' Association (ACEA)
- Sonaca SA
- London & Scandinavian Metallurgical Company Ltd.
- Association for European Producers of Steel for Packaging (APEAL)
- European Confederation of Paint, Printing Ink and Artists' Colours Manufacturers Associations (CEPE)
- Town End (Leeds) Plc
- Völkper Spezialprodukte GmbH

1 Introduction

This report presents data on the manufacture, use, and alternatives to sodium dichromate (dihydrate: EC No 234-190-3, CAS 7789-12-0 and anhydrous: EC No 234-190-3, CAS 10588-01-9), collated by Entec over a period of 6 weeks. In this report no distinction is made between sodium dichromate and sodium dichromate dihydrate as it appears that no such distinction is made in its manufacture and use.

This report is intended to provide ECHA with information on the substance for:

1. Priority setting of substances in the candidate list for inclusion in the Annex XIV of the REACH Regulation.
2. Defining the conditions related to the entries on Annex XIV (cf. Article 58(1)).

The report has been produced according to a format and structure provided by ECHA. Draft reports have been reviewed and commented on by ECHA and this final report has been accepted by ECHA.

The starting point for study was the Annex XV dossier submitted by the French authorities to identify sodium dichromate as a substance of very high concern (SVHC). No additional information has been made available by the French competent authorities.

An EU risk assessment and risk reduction strategies for the environment and human health have been developed for hexavalent chromium substances (chromium trioxide, sodium chromate, sodium dichromate, ammonium dichromate and potassium dichromate). Therefore, given the timescales for this project and the significant information already developed, these reports are relied upon for relevant information where possible.

In addition the information presented here has been collected by consultation with relevant industry organisations and trade associations. The organisations contacted are as follows:

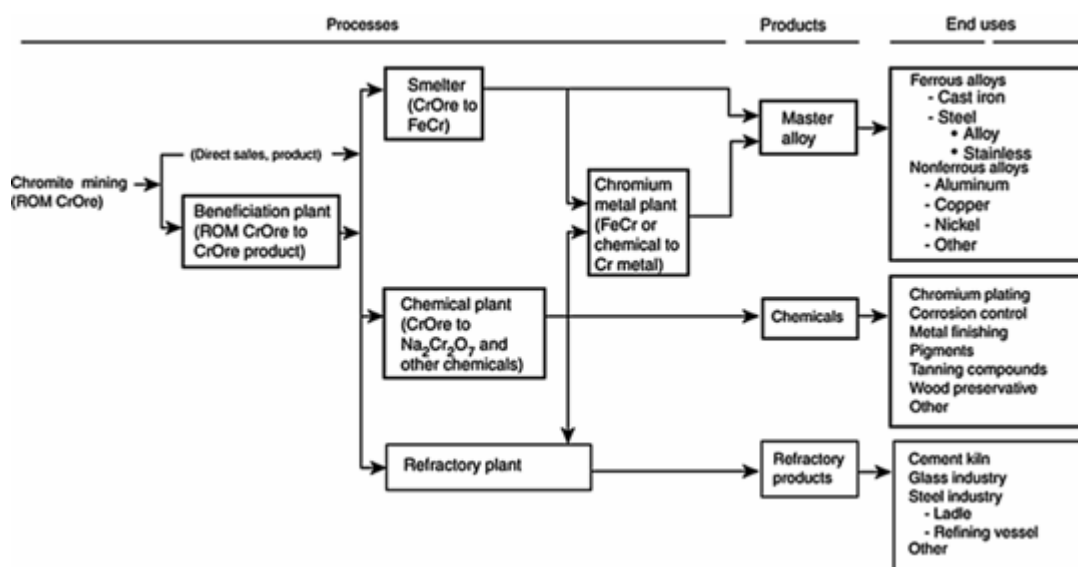
- The International Chromium Development Association
- Elementis EU
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- Society of Motor Manufacturers and Traders
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2 Information on manufacture, import and export and releases from manufacture

2.1 Manufacturing tonnages, sites and processes

The production process for sodium dichromate and other chrome substances and products are summarised in the figure below.

Figure 2.1 Processes, Products and end uses for chromium



From: Kirk Othmer Encyclopaedia of Chemicals Technology (2001)

Chromium-containing ore, chromite is mined in Russia, the Philippines, southern Africa and Finland. It contains chromium (III) oxide and is oxidised to sodium chromate during kiln roasting; acidification and evaporation of the product results in the production of sodium dichromate liquor and sodium sulphate. Sodium chromate is only used as an intermediate for the production of sodium dichromate. The majority of the sodium dichromate used in the EU (i.e. that which is not exported) is used as an intermediate (65% of total, 28% of total is exported²).

Information given in the risk reduction strategy for hexavalent chromium compounds indicates that, in 2006, the only manufacturer in the EU (Elementis based in the UK) ceased manufacturing chromium trioxide, potassium dichromate and ammonium dichromate. Therefore, only sodium dichromate is currently manufactured in the EU (HSE 2007) and this plant is in the UK. The production volume of sodium dichromate in 1997 was given as 110kt but it was reported in the environmental risk reduction strategy that production tonnage had significantly reduced by 2004.

Updated production tonnage information has been obtained from the International Chromium Development Association (ICDA) but, for reasons of confidentiality

² The total is comprised of the quantity produced in the EU and the quantity imported by the main producer and importer, respectively. There may be other import into the EU by users, but this is not known.

(because there is only one producer in the EU), this information has been supplied on the basis that it be kept confidential and has been included in the confidential annex to this report (Annex 2). However, the production tonnage is confirmed as reported in the environmental risk reduction strategy (Defra, 2005) to have significantly reduced from the figure reported in the RAR (110kt).

Information from the ICDA³ website indicates that the global production of sodium dichromate in 2006 was 850,000t.

2.2 *Import and export of the substance on its own or in preparations*

2.2.1 Substance on its own

The risk assessment report notes that Europe is a net exporter of chromium (III) and chromium (VI) products, but localised importing may occur from outside the EU.

Consultation with the manufacturing industry revealed that, of the sodium dichromate that produced in the EU and imported into the EU 28% is exported out of the EU to the USA (see confidential annex 2).

The major importer contacted for this study (Lanxess) owns mines in South Africa. Chromium ores are refined into various chromium (VI) compounds in South Africa and Argentina and then shipped into the EU both for internal use and further export. The import of sodium dichromate takes place as a solution. The 2007 import tonnages obtained from consultation with the main importer are presented in the confidential annex (Annex 2) and represent 27% of the total tonnage. The majority of the imported volume (c.80%) is transformed on-site to chromium (III) oxide pigments with the remaining volume being sold on for use in several applications, the major one being for the production of tanning salts.

It is possible that there are other smaller importers of sodium dichromate as such or in preparations. The potential importers were not identified for this report but may be revealed to ECHA through the registration process. For instance, a producer of chrome metal indicated that part of the sodium dichromate used for that purpose was imported from outside the EU⁴ (this is not indicated in the calculation of the proportion imported for this report).

2.2.2 Substance in preparations

No information on import of sodium dichromate in preparations has been collected for this report. This is explained by the difficulty in identifying uses of sodium dichromate in preparations. As consultation with main EU producer and importer did not highlight the use of sodium dichromate in wood preservatives (see section 3.1.2), it is possible that, if this use of sodium dichromate was confirmed, the quantities used for that purpose would be imported.

³ <http://www.icdachromium.com/pdf/REACH/Opening.Remarks.pdf> - accessed November 2008

⁴ Personal communication with London & Scandinavian Metallurgical Co Ltd (LSM), October 2008

2.3 *Import and export of articles containing the substance*

Sodium dichromate is used mainly as an intermediate. Of the sodium dichromate produced and imported into the EU the majority is exported, transformed to other chromium compounds or transported as an intermediate for transformation into other products. It is likely that only a very small percentage of sodium dichromate is contained as such in articles imported into and exported from the EU. Consultation with the aeronautics industry indicated that sodium dichromate is contained in articles manufactured and imported by the industry, largely from its use as an anti-corrosion agent in articles such as 'avionics' (electronics systems used air and space craft), landing gear and engines and in coating systems on aircraft⁵.

2.4 *Releases from manufacture*

2.4.1 *Releases to the working environment*

The human health risk reduction strategy (RRS) reported that, in 2004, there was one company in the EU manufacturing the five chromates, employing approximately 275 workers who could potentially be exposed (HSE 2007). Current information indicates that now sodium dichromate is the only chromium (VI) compound manufactured at this site, with an associated decrease in the number of workers potentially exposed. The manufacture of chromates at the site is carried out in enclosed processes, thereby reducing operator exposure.

The RAR (EC, 2005) indicated that the main areas for potential operator exposure could occur during the bagging of the product and during maintenance of the plant. Both these tasks could lead to inhalation and dermal exposure of the operators. However, as indicated in the human health RRS (HSE 2007), production of sodium dichromate solely as a solution has eliminated this source of exposure.

2.4.2 *Releases to the environment*

The environmental risk reduction strategy (Defra, 2005) considered the releases of chromium compounds from the European Pollutant Emission Register⁶ (EPER) database. The environmental RRS (Defra, 2005) reported data in 2005 (assumed to be 2001 data) for the EU15 (plus Hungary and Norway). Table 2.1 shows updated data from the EPER database (2004 data) for the EU 25. (Only those processes considered to be relevant to the production and use of sodium dichromate are presented).

⁵ Personal communication with ASD, November 2008

⁶ <http://eper.eea.europa.eu/eper/>

Table 2.1 Chromium emissions from IPPC installations in the EU 25 from the European Pollution Emission Register (EPER) 2004 data¹

Activity/description	Air (t)	Direct to water (t)	Indirect to water (t)
Basic inorganic chemicals or fertilisers	10.31	47.71	0.37
Surface treatment or products using solvents (>10t/d)	0.3	0.12	2.96
Metal industry	79.56	645.22	13.6
Tanning of hide and skins	-	0.21	155.42

¹ EPER <http://eper.eea.europa.eu/eper/> accessed October 2008

It should be noted that the EPER data reports releases of *all* chromium compounds, so does not show sodium dichromate on its own and does not discriminate between chromium (III) and chromium (VI) compounds or indeed any other valencies of the chromium ion. However, the data are still a very useful indicator of environmental releases, in particular because they are based, at least in part, on monitoring data.

Since it is known that the sole manufacturer of sodium dichromate is at a single site in the UK, it is possible to check the releases for this plant on the EPER database, again noting that these data are from 2004 and are for chromium and its compounds. These data are presented in Table 2.2.

Table 2.2 Chromium and its compounds releases from the production site in the UK UK EPER data¹

Year	Emission to air (kg/year)	Emission to water (kg/year)
2001	8,800	1,720
2004	7,780	1,480

¹ EPER <http://eper.eea.europa.eu/eper/> accessed October 2008

More recent data on the UK manufacturing site are available from the Anglo-Welsh Environment Agency's Pollution inventory. Reported releases are for total chromium.

Table 2.3 Chromium (total) releases from the production site in the UK Data from Environment Agency of England and Wales Pollution Inventory¹

Year	Emission to air (kg/year)	Emission to water ² (kg/year)
2005	6,919	1,941
2006	3,360	1,420
2007	2,930	1,800
1 Environment Agency 'What's in my back yard?' http://maps.environment-agency.gov.uk/wiyby 2 To river water		

The data reported in tables 2.1, 2.2 and 2.3 indicates releases to the environment of chromium compounds from production and processing. Sodium dichromate is of low volatility and is largely reported to be supplied as a solution, so it might be expected that this would limit the releases and workplace exposure of sodium dichromate. Nevertheless from the environmental release data there are releases of chromium to the environment from the manufacture of sodium dichromate, though it is not clear what proportion of this is sodium dichromate or even chromium VI.

3 Information on uses and releases from uses

3.1 Identification of uses

This study has aimed at updating the uses of sodium dichromate identified in the existing literature (RAR (EC 2005), environmental RRS (Defra, 2005) and human health RRS (HSE 2007). Table 3.1 summarises the known uses and the percentages of the total volume of sodium dichromate reported for this study (there may be other direct imports and uses that have not been quantified). From Table 3.1 it can be seen that the uses that are non-intermediate (and therefore of relevance to authorisation) represent as small proportion of the total tonnage. However, as the overall tonnage is high (although significantly less than the 110kt reported for the RAR (EC,2005), but still in the range 10 to 100 ktpa), then even small percentages can represent a significant use (1% = 100 to 1,000 tpa).

Table 3.1 Known uses of sodium dichromate and their relevance to authorisation

Use	Percentage (of known EU production and import)	Intermediate use?	Except from authorisation?
Exported out of the EU	28%	N/A	Y
Production chromium (III) oxide	65%	Y	Y
Production of chromium (VI) pigments	<1%	Y	Y
Anticorrosion additive in coatings	<<1%	N	N
Production of chromium metal	<<1%	Y	Y
Metal finishing	~2%	N	N
Production of tanning salts	<5%	Y	Y
Production of montan wax	<<1%	N	N
Production of vitamin K	<<1%	N	N
Mordents for wool dyes	<<1%	N	N

3.1.1 Sodium dichromate used as an intermediate

Consultation with the main European producer and importer indicated that the vast majority of the sodium dichromate present in the EU is used as an intermediate in the

synthesis of other chromium (VI) compounds or chromium (III) compounds. These compounds have a variety of uses, which are described below.

3.1.1.1 Manufacture of leather tanning salts (chromium (III) sulphates)

Basic chromium sulphates are used in the tanning of animal skins to produce leathers and they are made by either the inorganic or organic reduction of sodium dichromate. 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. In the past, some tanneries carried out on-site reduction of sodium dichromate. This practice is now rare; most tanneries are supplied with ready-made chromium tanning agents that contain no detectable levels of chromium (VI).

The exact numbers of workers involved in the manufacture of chrome tanning agents is unknown. The environment RRS suggested that approximately 150 employees are involved in the non-integrated manufacture of basic chromic sulphate for leather tanning.

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.

3.1.1.2 Manufacture of chromium (III) pigments

Chromium (III) oxide pigments may be made by a process involving reaction between ammonium sulphate and sodium dichromate, followed by thermal decomposition and washing to remove the sodium sulphate by-product. The RAR (EC, 2005) describes a process of mixing sodium dichromate with boric acid and water and heating in a furnace to produce green trivalent hydrated chromic oxide. The human health RRS (HSE 2007) suggests that this process is used to produce small quantities of pigment (tonnage not specified in the human health RRS).

Although there is a number of companies in the EU producing pigments and dyes, the exact number of workers involved was not reported in the human health RRS. Inhalation of sodium dichromate is unlikely since consultation for this current study indicated that it is supplied almost exclusively as a solution (although data from the RAR (EC, 2005) indicated the possibility for inhalation exposure for a number of uses (see table 3.3) and this is verified by monitoring data (see table 3.4) although exposure concentrations appear from these limited data to be low. Dermal exposure may occur during weighing, mixing of the ingredients and during weighing and charging of reactants to vessels.

3.1.1.3 Manufacture of chromium (VI) pigments

Chromium (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. Although primarily used in wet paints, chromium (VI) pigments may also be used in powder coating applications (Defra, 2005).

As with the manufacture of chromium III pigments, there are a number of companies in the EU producing pigments and dyes, the exact number of workers involved was not reported in the human health RRS. Inhalation of sodium dichromate is unlikely since consultation for this current study indicated that it is supplied almost exclusively as a solution however as notes above, the possibility for inhalation exposure have been indicated in other uses (see tables 3.3 and 3.4). Dermal exposure may therefore occur during weighing, mixing of the ingredients and during weighing and charging of reactants to vessels.

3.1.1.4 Production of chromium metal

A producer of chromium metal⁴ indicated they use sodium dichromate in a process based on the exothermic redox reaction with aluminium. This company indicated using approximately 450tpa of sodium dichromate. No information on the number of users of that kind has been collected.

However, information from the minor metals trade association⁷ indicates that the main processes to produce Cr metal involve chromium (III) oxide and not sodium dichromate. Indeed industry confirmed that there was only one company producing chrome metal using that process

3.1.2 Substance not used as an intermediate

3.1.2.1 Metal finishing

Metal finishing covers a wide range of varied and complex processes carried out by industry and involves both chemical and physical processing. The RRS reports that in the EU there are more than 18,300 installations known to carry out surface treatment of metals and plastics.

Approximately 440,000 people are employed in the European surface treatment industry, most of these in small or medium enterprises (SMEs) typically employing 10-80 people (HSE, 2007). However, not all of these installations will use chromium (VI) compounds. The human health RRS assumed that approximately 10% use chromium (VI); as such there could be approximately 2,000 installations employing 44,000 people across the EU. Clearly, if only the use of sodium dichromate is considered, then significantly fewer workers will be potentially exposed. In addition, from the consultation for this study and with reference to the RAR (EC, 2005) and environmental and human health risk reduction strategy reports (Defra 2005 and HSE 2007), it seems that there is a relatively small use of sodium dichromate *as such* in metal finishing applications, accounting for perhaps 2% of the total tonnage (see figure 3.1). It is understood that key users of sodium dichromate for metal finishing are in aeronautics industry and the metal packaging industry.

⁷ http://www.mmta.co.uk/uploaded_files/ChromiumMBM.pdf

Information from the human health RRS (HSE, 2007) indicates that chromium IV used in the metal treatment industry can be split into three basic types:

1) Electroplating - this involves the deposition of a metallic coating on the base material, includes decorative, hard/engineering and functional chromium plating and electrolytic chromium/chromium oxide coated steel (ECCS). Comments from surface treatment industry stated that sodium dichromate, dehydrate is not used in plating technology for electroplating. The use in the production process is clearly safe and unambiguously controllable⁸. Information on ECCS was gathered from the metals packaging sector trade association (APEAL) and is set out below.

2) Conversion coatings – this involves chemical treatment of metallic surfaces to give a barrier layer of complex chromium compounds to enhance corrosion protection on various metals. Examples are:

- anodising, where an electrolytic process is used to produce an oxide layer on the surface of aluminium and passivation; - it is understood that chromic acid is used for treatment of aluminium (Environmental RRS (Defra, 2005) passivation is addressed below in the aeronautics and metal packaging industry uses).
- chromating (a passivation process), which is used in nearly all areas of the steel processing industry and is an essential post-treatment step in zinc plating (galvanising) – this is addressed below for metal packaging industry use.
- coil coating is one particular sector using this process and the conversion coating provides an activated surface enabling the organic paint layer to adhere – we believe that possible use relevant to sodium dichromate is addressed below for metal packaging; and
- vitreous enamelling.

3) Brightening – This process may be part of the surface pre-treatment before another process, e.g. electroplating this process appear to use chromium trioxide Environmental RRS (Defra, 2005), so is not relevant to this study.

Information from the environmental RRS (Defra, 2005) indicates that the metal treatment sector is dominated by the chromium plating sector, a much smaller part of this sector is the use of chromium (VI) in passivates. Information from the UK industry indicates that the market for chromium (VI) in metal treatment has reduced considerably; between 1998 and 2003 the market for Cr (VI) plating chemicals was reduced by 53%. There has been a corresponding fall of 32% in the use of Cr (VI) based passivates. However, this trend may not be representative of the whole of the EU according to the sales figures of the producer of Cr (VI) compounds (env RRS).

Aerospace

Consultation with Aerospace and Defence Industries Association of Europe (ASD) and Sonaca (the latter commented on the Annex XV dossier) revealed that the main processes in the aeronautics industry are associated with anticorrosion of engines and airframes including:

⁸ ZVO – Central Agency of surface treatment comments to Annex XV dossier on sodium dichromate

- Passivation
- Sealing anodized layers on aluminium parts;
- Underlay for plating ;
- Electroplating; and
- Electroless nickel plating.

Consultation with the industry (ASD) revealed that many of the parts that are used to make aircraft are made by SMEs and are supplied to the large engine and airframe manufactures. Therefore processes using sodium dichromate are to a large extent used by small to medium sized specialist engineering companies. Large parts of the airframe will be made by the aircraft manufactures so there is also use of the substance by these large companies. At the time of writing no information on the amounts used in different processes by the aerospace industry was available (although it is understood that the industry is currently collecting these data)⁹.

Automotive

It is understood that chromium (VI) compounds are not used in new cars any longer, since the End-of-Life Vehicle directive 2000/53/EC banned its use¹⁰.

Metal packaging

For this study the Association of European Producers of Steel for Packaging¹¹ (APEAL) provided information on uses. The processes involved in steel packaging using the substance occur in only a few large plants in the EU. The processes are:

- Tinplate passivation - the substance is converted to chromium III and elemental chromium in the process
- Marking of tin-plate with chromium (III) oxide (CrO₃)
- Electrolytic chromium/chromium oxide coated steel (ECCS)

The process of passivation is used to make a stable steel-tin-lacquer system and prevents migration of metal components into the canned product. Only tinplate passivation and marking of tinplate involve the use of sodium dichromate, with tinplate passivation being the main use of the substance.

3.1.2.2 Wood preservation products

There is a suggestion that some sodium dichromate may still be used to manufacture wood preservation products. No confirmation of this has been made for the current report.

⁹ Personal Communication with ASD November 2008

¹⁰ (International) automotive task force on REACH communication via SMMT December 2008

¹¹ APEAL provided information for the risk reduction strategy and have also commented on the Annex XV dossier

There are a number of EU companies manufacturing copper chrome arsenate (CCA) wood preservation products, with approximately 150 workers being directly involved in the process according to the RRS. The environmental RRS also indicates that sodium dichromate can be used in other wood preservatives than CCA (e.g. CCB). However, wood preservatives are biocidal products and therefore subject to Directive 98/8/EC¹². Thus, if the active substances included in these products have been included in Annex I of the directive, these products should, in the future, be assessed before they are put on the market. If the active substances have not been included in Annex I of the directive, these products may not be placed on the market.

3.1.2.3 Mordant in wool dyeing

Sodium dichromate is used as a mordant in wool dyeing i.e. it is used to fix the dyes to the wool fibres. The dichromate is added to the dye bath after the dye has been dispersed through the fibres, in a process known as 'chroming'. However, it is possible for the dichromate to be added before the dye or at the same time. Chromium VI compounds are used in variable quantities depending on the dye used. In particular sodium dichromate is used as a fixative for black coloured dyes and imparts wash and light fastness to wool textiles. In the process the chromium ion is consumed by the dye and as it is used in approximately stoichiometric quantities there will be none or very little left in solution at the end of the process. In the UK there are a small number of dye houses (around five) that may still be using chromium based mordants¹³.

The total number of workers involved in this sector is unknown as the industry is diverse with many, mainly small, dyehouse operations (Human health RRS, HSE, 2007). The human health RRS gives as an example the number of UK workers in this industry sector who could potentially be exposed as in the low hundreds at most.

The human health RRS reports that 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 the dyeing vat, exposure is considerably reduced.

3.1.2.4 Manufacture of montan wax

Montan wax is a hard wax obtained by solvent extraction of certain types of lignite or brown coal. It is used for products such as car and shoe polishes, paints and as lubricant for moulding paper and plastics. Montan wax in polishes improves scuff resistance, increases water repellence and imparts high gloss.

In the RAR only one EU wax manufacturer was identified as using sodium dichromate to produce montan wax. Information in the RRS suggested that this may not be correct and there could be a number of other companies in the EU manufacturing montan wax. The largest manufacturer of montan wax in the world is Romonta GmbH located in Amsdorf, Germany¹⁴. Information gathered for this study

¹² Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market

¹³ Personal communication with Town End Colours December 2008

¹⁴ Poth Hill wax manufactures - www.poth-hille.co.uk

indicated that there is at least one other company producing montan wax that is also located in Germany.

The use only accounts for a very small percentage of the total consumption of sodium dichromate. According to the human health RRS, the process is totally enclosed and exposure is only likely to occur during sampling of the system and maintenance of the plant. No measured exposure data are available. At the time of writing information on the exact use of sodium dichromate in montan wax production (it is believed that the substance is used as a reducing agent), the amount used for this process, possible releases and alternatives is expected from a Germany based producer.

3.1.2.5 Anticorrosion agent

Sodium dichromate has been identified in the aerospace industry as an anticorrosion agent. It is used in as an active compound in multiple layer coating systems that may be comprised of up to ten layers, each layer being dependent on the properties of neighbouring layers. In these systems sodium dichromate (and other chromium VI compounds) function to form a protective 'self-sealing' layer if the coating is scratched thereby maintaining the protective coating that has to withstand abrasion and extremes of temperature.

3.1.2.6 Manufacture of vitamin K

According to the human health and environmental risk reduction strategies there is only one EU manufacturer of vitamin K¹⁵. The number of workers involved is unknown. Vitamin K is produced by oxidation of 2-methylnaphthalene with a solution of sodium dichromate acidified with sulphuric acid. Sodium dichromate is reduced to Cr (III) sulphate, which is sold to be used as tanning salts.

The human health RRS reports that (from the little information available) the manufacture of vitamin K is carried out in an enclosed system that reduces operator exposure. However both dermal and inhalation exposure could occur during unloading liquid sodium dichromate.

3.1.2.7 Industrial cleaning –

Aerospace industry

Consultation with the aerospace industry (ASD) revealed that sodium dichromate may also be used for specialist cleaning applications. For engine maintenance sodium dichromate and chromic acid solutions are used to 'de-smutt'(i.e. remove layers of exhaust soot and residues). It is understood that this procedure is only done by engine manufacturers under controlled conditions. No information was available on the concentrations used, the amount used for this purpose or whether any alternatives had been considered for the use.

Other cleaning use

¹⁵ Vitamin K represents a class of substances which contain the 2-methyl-1,4-naphthoquinone moiety.

It has been reported that sodium dichromate is used to clean glasswear. It is assumed that this is a very minor use and that the use is for glasswear for analysis purposes (such as in university research laboratories), for the removal of grease and persistent residues¹⁶.

3.1.2.8 Other miscellaneous uses

It has been reported that sodium dichromate can be used in ceramics¹⁷ and for the colouration of glass. Further information on these uses has not been gathered for this report. It is believed that chromium salts other than sodium dichromate are used for the colouration of glass.

3.2 Quantification of uses

The main uses of sodium dichromate are identified and discussed in the preceding section. There is one producer in the EU and one main importer; it is for this reason that the tonnages produced and imported are commercially confidential and are included in a confidential annex to this report. The human health RRS (HSE, 2007) states that sodium dichromate from production is supplied as a solution. This is also reported to be the case for imported and exported sodium dichromate, although some uses still appear to use powdered forms (see confidential annex – Annex 2).

Metal finishing

Quantities of sodium dichromate used for tinfoil passivation are presented in the confidential annex. Sodium dichromate is used as a solution, at a concentration of 20 to 30g/L, in two different processes, leading either to the formation of a layer containing tin and chrome (III) hydroxides, or to the formation of a layer containing chrome (III) hydroxide and metallic chromium. Under both processes, sodium dichromate is not present in the final product.

Further consultation with the European aeronautics industry (trade association ADS) revealed a large number of uses of sodium dichromate (and also other hexavalent chrome substances). They do not have figures on the tonnages used in the sector in the EU, but one company speculated that their use might be in the 10 tpa range so whole industry could be 1000 tpa + (this was a very rough estimate).

Production of Cr metal

The producer of Cr metal contacted indicated using approximately 450tpa of sodium dichromate.

Information from the minor metals trade association¹⁸ indicates that the main processes to produce Cr metal involve chromium (III) oxide and not sodium dichromate, confirming that this producer is the only EU company producing chrome metal using that process

¹⁶ Chemical Analysis in the Laboratory: A Basic Guide By Irene Mueller-Harvey, Richard M. Baker, Royal Society of Chemistry (Great Britain) Published by Royal Society of Chemistry, 2002
ISBN 0854046461, 9780854046461

¹⁷ Elementis sodium dichromate product sheet www.elementischromium.com

¹⁸ http://www.mmta.co.uk/uploaded_files/ChromiumMBM.pdf

3.2.1 Summary of quantification of uses

It can be seen from Figure 3.1 below that the majority of the sodium dichromate is used as an intermediate for the production of chromium (III) oxide. As this study is focused on sodium dichromate and further to this because these compounds are trivalent forms of chromium, further downstream use is not considered further. A significant amount of the sodium dichromate that is produced in the EU is exported. This leaves the remaining downstream uses of sodium dichromate to be tanning salts (which appears to be a not insignificant use) as well as minor uses including metal finishing, wool dyeing, manufacture of vitamin K, manufacture of chromium metal, use in wood preservation products and manufacture of montan wax.

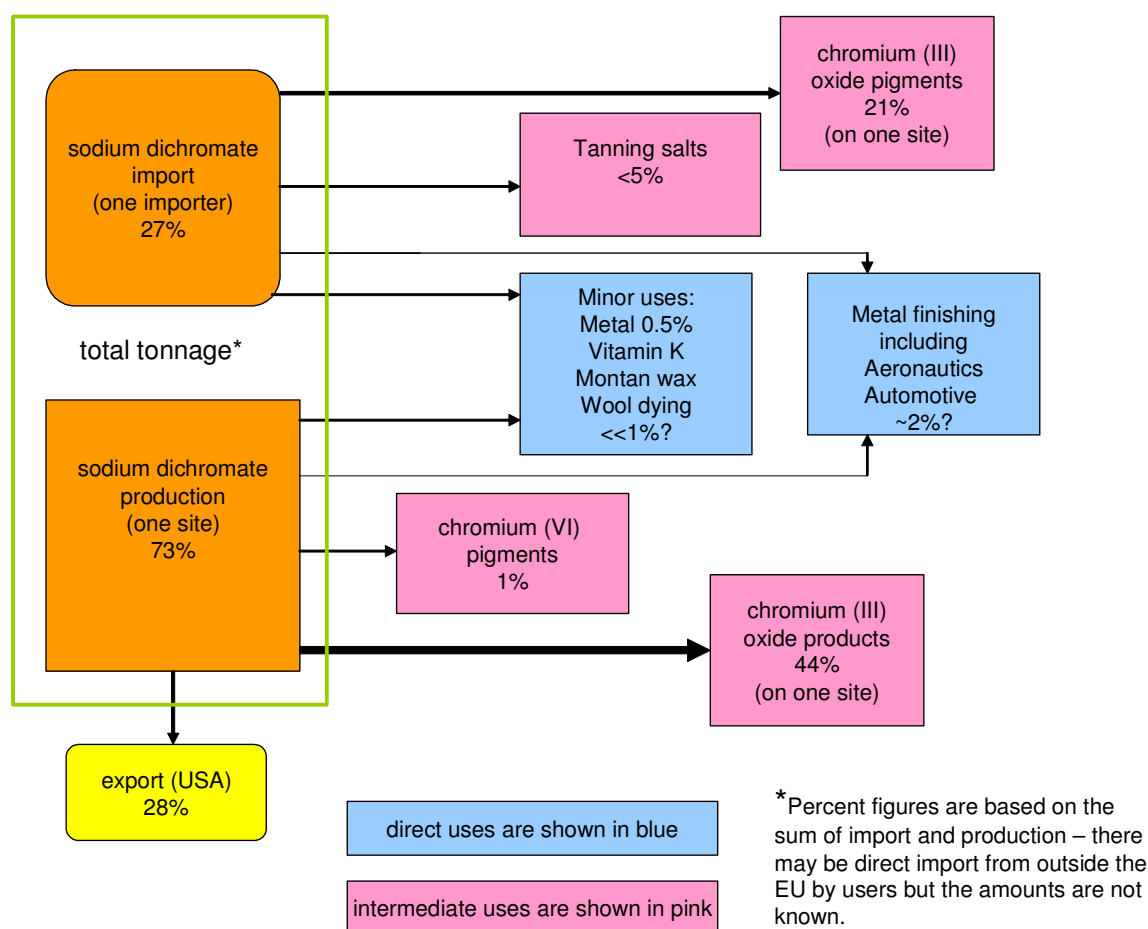


Figure 3.1 Production import and main uses of sodium dichromate

3.3 Quantification of releases from uses

3.3.1 Overview

This section of the report considers both releases of sodium dichromate to the environment and the exposure of workers to sodium dichromate in the workplace. Key points that should be made here are:

- That the environmental releases may be of importance to understand the possible impacts on the environment; estimates and measured data on releases can enable the control of the substance to be understood.
- For the workplace, however, the *exposure* of workers is of importance as this allows an understanding of the contact that humans may have with the substance rather than what is simply released (the later will be most likely captured by estimation of environmental releases anyway).

3.3.2 Releases to the environment

The local emissions of hexavalent chromium were considered in the RAR. These are largely based on predictions rather than measured data; these are presented in Table 3.2. No further predictions or measured data for sodium dichromate were made available for the purposes of the present study.

Table 3.2 Predicted chromium (VI) emissions expressed as total chromium (info from RAR)

Process	compartment	tonnes/year	kg/day	Continental (tonnes/year)
Pigment production	water	1.9	6.3	5.6
Chrome tanning salt production	water	4.2	14	38
Wood preservative formulation	water	2.1	6.9	8.2
Metal treatment formulation	Air	1.1	3.1	14
	water	0.93	3.7	12
Mordant dyeing	water	0.004	0.014	1.1

3.3.3 Exposure of workers

As the most important health end point is for lung cancer from inhalation of hexavalent chromium compounds, inhalation data is key for worker exposure. Inhalation exposure data is summarised in the RAR and is presented in Table 3.3.

Table 3.3 Summary of the inhalation exposure data from RAR.

Industry	Reasonable worst case (mg/m³)	Source	Number of samples
manufacture of the 5 chromates	0.02	measured data	1889
manufacture of other Cr containing chemicals			
- dyestuffs	0.5 (8hr) 1.5 (short term)	measured data judgement	39
- chrome tan	0.007	measured data	115
- manufacture Cr metal	0.01	measured data	73
- formulation metal treatment products	0.02	measured data	25
Use in metal treatment			
-passivation	0.001	measured data	42
manufacture of montan wax	0.004	EASE	
manufacture of vitamin K	0.0025	EASE	
use as a mordant in wool dyeing	0.5	measured data	3

The human health RRS presented reasonable worst-case inhalation exposures based on the 90th percentile of available measured data with professional judgment used where limited data were available. The EASE model was used to predict exposures for two scenarios (manufacture of Montan wax and vitamin K) where little or no information was available. Table 3.4 show exposure data collated since the completion of the RAR for the human health RRS.

Table 3.4 Inhalation data from human health RRS

Industry	Number of samples	Range of data (mg.m⁻³)
manufacture of the 5 chromates	180	0.005-0.007
manufacture of other Cr containing chemicals		
- dyestuffs	4	0.002, 0.0026 0.02, 0.052
- tanning	1	0.002
- manufacture Cr metal	2	<0.03, <0.02
- formulation metal treatment products	1	<0.0001
Use in metal treatment		
-passivation	2	0.003, <0.001
manufacture of montan wax	2	0.0055, <0.003
manufacture of Vitamin K	-	-
use as a mordant in wool dyeing	1	0.0003

3.3.4 Exposure limits

There is currently no harmonised EU OEL for the hexavalent chromates. The human health RRS set out relevant national exposure limits. These are presented in table 3.5.

Table 3.5 Occupational exposure limits (OELs) for EU Member States, from human health RRS (HSE, 2007)

Country	Compound	Limit (mg/m ³ as Cr)	Type of Limit	Notations
UK	Cr VI compounds	0.05	8-hr TWA (WEL)	Sen, BMGV
Germany	production of soluble Cr (VI) compounds	0.1	8-hr TWA (TRK)	Sh, EKA
	other Cr (VI) compounds	0.05		
Netherlands	Soluble Cr (VI) compounds	0.025 0.05	8-hr TWA STEL	
Sweden	Chromates and chromic acid	0.02 0.06	8-hr TWA STEL	
Finland	Cr (VI) compounds	0.05	TWA	
France	Cr (VI) compounds	0.05	8-hr TWA	
		0.1	STEL	

WEL	Workplace exposure limit
STEL	Short term exposure limit
TRK	Technical exposure limit
TWA	Time weighted average
Sen	Indication that the substance can cause occupational asthma
BMGV	Biological monitoring guidance value is available
Sh	Notation to indicate a skin sensitiser
EKA	Exposure equivalent values for biological monitoring

SCOEL has conducted a review of these compounds and the SCOEL recommendation has been published (SCOEL SUM/86 final February 2003). In view of the genotoxic properties of the hexavalent chromium compounds, SCOEL were not able to derive a health-based OEL. However, SCOEL did conduct a quantitative risk assessment for lung cancer, on the basis of which it was suggested that consideration could be given to an occupational exposure limit of 0.01 mg/m³ or 0.025 mg/m³ (8-hour TWA) for soluble Cr (VI) compounds. Directorate General Employment of the European Commission is proposing a study to assess the impact of introducing OELs for additional substances in Annex III of the Carcinogens Directive (2004/37/EC) – including substances for which a SCOEL recommendation was made. This includes an OEL for hexavalent chromium at the following possible values: 0.1 mg/m³; 0.05 mg/m³ and 0.025 mg/m³.

Comparing the measured data on inhalation exposure to hexavalent chromium (Table 2.4) with the lowest proposed level for the OEL (0.025 mg/m³) only one data point for use in dyestuffs is above this limit.

3.3.5 Dermal exposure

Table 3.5 shows the summary dermal exposure data from the RAR. With the exception of CCA use, all are based on predictions using the EASE model, as no measured dermal sampling data were available.

The data for CCA use are taken from a UK Health and Safety Executive (HSE) project and show the amount of Cr (VI) on the skin. Dermal exposure can occur at a number of stages in the wood treatment process, particularly when the bogie containing the treated wood is unloaded, during maintenance of the treatment vessel and from contact with contaminated surfaces. Exposures ranged from 1.37 - 41.71 mg Cr (VI) on the skin. The RWC of 16.5 mg Cr (VI) on the skin was based on the 90th percentile of the data.

Table 3.6 Summary of the dermal exposure data from RAR

Industry	Range of exposures (mg/cm ² /day)	Source
Manufacture of the five chromates	0 - 0.1	EASE
manufacture of other Cr containing chemicals - dyestuffs - chrome tan - manufacture Cr metal - formulation of metal treatment products	0.1 - 1 0 - 0.1 very low 0 - 0.1/ 0.1 - 1	EASE EASE EASE EASE
CCA use	1.37 - 41.71 mg Cr VI on skin RWC - 16.5 mg Cr VI on skin	Measured data
Use in metal treatment - mixing of solutions - adding to bath - dragout - re-threading steel strip	0 - 0.1 0 - 0.1 1 - 5 0.1 - 1	EASE
manufacture of montan wax	0.1 - 1	EASE
manufacture of Vitamin K	0 - 0.1	EASE
use as a mordant in wool dyeing	0.1 - 1	EASE

3.4 Uses of sodium dichromate and exemptions to inclusion in Annex XIV

Based on the information available for this study, it is felt that some of the uses identified could be considered as being subject to exemptions from the authorisation procedure.

Table 3.7 presents a summary of the uses of sodium dichromate, of the tonnages involved and of the downstream activities, along with the potential justifications for exemption from annex XIV.

Table 3.7 Uses of sodium dichromate and potential exemptions from annex XIV

Use	Tonnage (t)	Downstream activities	Potential exemptions
Manufacture of tanning salts	Confidential	leather tanning	On-site or transported isolated intermediates
Manufacture of pigments	Confidential	pigments	On-site or transported isolated intermediates
Metal finishing	Confidential	passivation of metal	
Production of Cr metal	450	Alloys	On-site or transported isolated intermediates
Manufacture of vitamin K	Unknown/minor	Vitamin K	May be considered as intermediate as used as reducing agent in manufacturing process
Manufacture of Montan wax	Unknown/minor	Montan wax	Not enough information on process
Wood preservatives	Unknown/minor	Timber	Use in biocidal products
Mordant in wool dyeing	Unknown/minor	Textile	
Sealant for anodised layers	Confidential	aeronautics	

4 Information on alternatives

4.1 Identification of alternative substances and techniques

4.1.1 Metal finishing

ECCS has been developed as an alternative to tinplate in order to preserve the natural reserves of tin. The function of the chromium coating is the same as for the passivation of tinplate. In that technique, chromium plating of steel strip (known as blackplate) is performed electrolytically in chromic acid baths (80-150 g/l). The coating obtained consists of chromium metal and chromium oxides.

Information from individual companies involved in metal passivation and set out in the environmental RRS (Defra 2005) suggested that there are signs that the industry may be moving away from chromium (VI) to either chromium (III) or chrome-free alternatives. Consultation with the Cobalt Development Institute¹⁹ (CDI) indicated that some research projects were ongoing, which tend to show that Cobalt-based plating could be an alternative to the use of chromium (VI) compounds.

Technical and economical feasibility and availability

ECCS can only be used with an additional organic coating. In addition, it is not suited for manufacturing 3-piece steel food cans or aerosols as it is less weldable than tinplate. Therefore, the use of ECCS is limited to about 20% of the total amount of steel for packaging, as an attractive alternative to tinplate for some applications (closures, 2-piece cans, etc ...).

On consultation with industry for this study, APEAL indicated that even though research programs are ongoing to substitute sodium dichromate in tinplate passivation, using chromium (III) or even chrome-free techniques, no solution has been found, fulfilling all of the following criteria:

- prevention of atmospheric oxidation of tin,
- ensuring organic coating adhesion and
- protection of steel from sulfuration by the can content.

Potential substitutes need to be validated over the whole shelf life of canned food (which is generally two to three years) in addition to storage time of steel at can manufacturing sites.

Aerospace

There are possible alternatives for a number of different uses, but none is presently known to fulfil the technical and airworthiness safety that is required for aircraft. In addition in many cases where possible alternative could be identified these could only be used for the production of new aircraft as maintenance of existing aircraft requires the use of the substances that are currently used because of compatibility with existing materials. A number of research projects have been funded into possible replacement products these largely focus on the replacement of hexavalent chromium

¹⁹ Personal communication with the Cobalt Development Institute, November 2008

rather than sodium dichromate per se. Need for authorisation of sodium dichromate would most likely lead to the use of other hexavalent chromium compounds²⁰.

4.1.2 Production of Cr metal

Alternative substances, such as potassium dichromate, and alternative techniques, such as electrolysis, exist for the production of Cr metal. However, this technique still uses either sodium dichromate or chromic acid.

4.1.3 Wood preservation products

As indicated in the human health RRS, restrictions on arsenic introduced under the Marketing and Use Directive (76/769/EEC) have an impact on chromates when used in CCA (copper, chromium, arsenate) in the wood preservative industry. These restrictions have led to increased use of two classes of alternative preservatives: either other Cr (VI) containing formulations which are not arsenic based, or ones containing no chromium. Arsenic pentoxide has not been supported under the Biocidal Products Directive (BPD) for use as an active agent in wood preservatives. Therefore, wood preservatives containing arsenic pentoxide must be removed from the market by 1st September 2006. Effectively this means that the use of CCA in wood preservatives has ceased.

The human health RRS also notes that in relation to other chromate-containing wood preservatives the European Commission agreed that chromates should be regarded as actives (i.e. active ingredients) in wood preservatives unless efficacy data can be provided to show otherwise. Data were provided in the UK proposing to show that chromates are not actives but these data were not regarded as convincing. Therefore the UK regards chromates as "actives" and has dealt with them under the BPD. This resulted in a ban on the presence of chromates in wood preservatives in the UK from September 2006. However, other Member States may still be permitting the use of chromates in wood preservatives pending the submission of efficacy data.

In addition, the human health RRS notes that, regardless of whether or not CrVI compounds are considered as actives, if they are present as components of wood preservatives then there is still a requirement to ensure that their human health risks, both in formulation and use, are adequately controlled under the biocidal products directive (98/8/EC).

4.1.4 Use as a mordant in dyeing

The UK textiles industry has provided information for the RRS that implies that in the UK, textile finishers are generally divided in three main groups:

- Those who have moved completely away from sodium dichromate or are in the process of doing so. This change has been driven by environmental/safety concerns and business pressures from customers who will not accept textiles treated with chromates;

²⁰ Personal communication with ASD, November 2008

- Those who are severely curtailing their use – e.g. from several tonnes per month at the beginning of the decade to a few kilos per month today; and
- SMEs that continue to use sodium dichromate to meet the specific needs of their customers, in quantities that range from tens of kilos to over a tonne per year.

Information gathered for this study suggested that there are a number of organic compounds that can be used in place of sodium dichromate as mordants (one example is vinylsulphones). These substances function by forming a covalent bond with the wool structure²¹.

4.1.5 Manufacture of vitamin K

According to one source²² there has been significant activity directed toward the search for a less toxic and more selective oxidizing agent than chromium in manufacture of vitamin K. For example, Hoechst has patented a process which uses organorhenium compounds. At a 75% conversion rate, a mixture of 86% of 2-methyl-1,4-naphthoquinone and 14% 6-methyl-1,4-naphthoquinone was obtained. Ceric sulfate (61) and electrochemistry have also been used.

²¹ • Town End (Leeds) Plc December 2008 personal communication

²² Kirk Othmer Encyclopaedia of Chemical Technology (2001), John Wiley and Sons.

5 References

EC (2005) European Union Risk Assessment Report Chromium trioxide, Sodium chromate, Sodium dichromate, Ammonium dichromate and Potassium dichromate.

EC Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market

Defra (2005) Environmental Risk Reduction Strategy and Analysis of the Advantages and Drawbacks for Hexavalent Chromium

HSE (2007) Human Health Risk Reduction Strategy for Chromates

Kirk Othmer Encyclopaedia of Chemical Technology (2001), John Wiley and Sons

Royal Society of Chemistry (Great Britain) (2002) Chemical Analysis in the Laboratory: A Basic Guide by Irene Mueller-Harvey, Richard M. Baker.

6 Disclaimers

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Annex 1: List(s) of information requirements for priority setting and specification of conditions for authorisation

Table 1: Overview on tasks related to work package 1 (grey shaded fields not relevant)

Manufacture, trade and formation	Process (narrative description)	Locations (number of M sites; spatial distribution) ²	Tonnage manufactured, imported, exported or formed	Releases to working environment ³	Releases to environment (t/y released to air, wastewater or to waste)
Elementis	Refining of chromite ore	Eaglescliffe (UK)	confidential	Unknown	7.78t to air 1.48t to waste water
Total Manufacture			confidential	unknown	9.26t*
Import subst. on its own			Confidential (see confidential annex)		
Import subst. in preparations			unknown		
Import subst. in articles ²			N/A		
Import into EU (total)			Confidential/unknown		
Export subst. on its own			confidential		
Export subst. in preparations			Unknown		
Export subst. in articles ¹			unknown		
Export from EU (total)			Confidential/unknown		
Global manufacture			unknown		
Unintentional formation during incineration (EU)	Unknown or N/A			Unknown or N/A	Unknown or N/A
Unintentional formation in processes (EU)	Unknown or N/A			Unknown or N/A	Unknown or N/A
Unintentional formation by transformation/degradation (EU)	Unknown or N/A			Unknown or N/A	Unknown or N/A
Total unintentional formation (EU)				Unknown or N/A	Unknown or N/A

1 A list of article types in which the substance is included shall be provided in addition.

2 In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the manufacturing structure and spatial distribution of manufacturing sites (e.g. in which Member States, regions, etc.) may suffice.

3 In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

* Based on EPER data for releases of all chromium compounds in the UK (2004 data). This is likely to be an overestimate. See section **Error! Reference source not found.** for explanations.

Table 2: Overview on tasks related to work package 2 (grey shaded fields not relevant)

Uses	Use Process (description: narrative and by use descriptor system)	Amount used (t/y)	Number of sites of use ¹ (#)	Spatial distribution of emission sites ¹	Releases to working environment ³	Releases to environment (t/y released to air, wastewater or to waste)
Formulation						
Wood preservation products		500	unknown	Unknown	Dermal exposure only	2.1t to water
Σ Formulation		500	unknown	Unknown	Only dermal exposure has been estimated (see section 2.3)	2.1*
End uses						
End Use 1						
End Use 2						
.....						
End Use n						
Σ End Uses		Σ t/y; uncertainty; trends	Σ #, trend	Overall geographical pattern; trend	Σ t/y; uncertainty; trends	Σ t/y; uncertainty; trends
Consumer use						
Substance in articles ²						
Substance in preparations						
Σ consumer use of subst. in articles and preparations		Σ t/y; uncertainty; trends				Σ t/y; uncertainty; trends

1 In quantitative or geographical terms exact specifications are only required if the number of sites is low. If there are many sites a semi-quantitative or qualitative description of the use structure and spatial distribution of sites of release (e.g. in which Member States, regions, etc.) may suffice.

- 2 A list of article types with the substance included and used by consumers shall be provided as well.
- 3 In case a quantification of releases is not possible a qualitative description of the emission situation at the workplace(s) shall be given and a semi-quantitative estimate of the exposure situation provided (e.g. no exposure – very high exp.).

Table 3: Overview of quantitative information requested at Member State level for individual years.

YEAR n	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1 (t/y)	Use 1 # sites	Use n (t/y)	Use n # sites
Member state								
Austria								
Belgium								
...								
Total								

YEAR n+1	Manufacturing (t/y)	Manufacturing # sites	Formulation (t/y)	Formulation # sites	Use 1 (t/y)	Use 1 # sites	Use n (t/y)	Use n # sites
Member state								
Austria								
Belgium								
...								
Total								

ANNEX 2: CONFIDENTIAL INFORMATION