15 June 2011

Draft background document for cobalt dichloride

Document developed in the context of ECHA's third Recommendation for the inclusion of substances in Annex XIV

Information comprising confidential comments submitted during public consultation, or relating to content of Registration dossiers which is of such nature that it may potentially harm the commercial interest of companies if it was disclosed, is provided in a confidential annex to this document.

1. Identity of the substance

Chemical name:	Cobalt dichloride
EC Number:	231-589-4
CAS Number:	7646-79-9

2. Background information

2.1. Intrinsic properties

Cobalt dichloride was identified as a Substance of Very High Concern (SVHC) according to Articles 57(a) as it is classified according to Annex VI, part 3, Table 3.1 of Regulation (EC) No 1272/2008 as a carcinogen category 1B[1], H350i (may cause cancer by inhalation), and was therefore included in the candidate list for authorisation on 28 October 2008, following ECHA's decision ED/67/2008. Pursuant to Commission Regulation (EC) No 790/2009 of 10 August 2009, cobalt dichloride is as of 1 December 2010 also classified in Annex VI, part 3, Table 3.1 as toxic for reproduction, Repr. 1B (H360F***: May damage fertility). An Annex XV dossier proposing the update of the entry of cobalt dichloride in the candidate list with its amended classification was prepared by ECHA upon request by the European Commission and submitted to the SVHC identification process in accordance with Art. 59 of the REACH Regulation. The entry for cobalt dichloride in the Candidate List will be updated accordingly in June 2011.

2.2. Imports, exports, manufacture and uses

2.2.1. Volume(s), imports/exports

[1] Classification in accordance with Regulation (EC) No 1272/2008 Annex VI, part 3, Table 3.1 List of harmonised classification and labelling of hazardous substances as amended and adapted to technical and scientific progress by Commission Regulation (EC) No 790/2009, OJ No L 235, p. 1, 5.9.2009

According to registration information the volume manufactured / imported in the EU is in the range of **1,000 – 10,000 t/y**. On the basis of tonnages reported to the Cobalt REACH Consortium (CoRC; RCOM, 2010; personal communication with EUROMETAUX, 2011), the annual production in the EU[2] was estimated in the same range.

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

In France, cobalt dichloride is produced by refining mattes of nickel of New-Caledonia. In the final steps of nickel extraction, some types of process generate cobalt dichloride. More generally the chemical action of hydrochloric acid on powder cobalt, cobalt oxide or carbonate cobalt generates cobalt dichloride that is used on site or sold (France, 2008).

Cobalt dichloride is reported to be largely produced and used as a solution (99%) with only a small portion of the production and use involving cobalt dichloride in powdered form (1%) (ECHA, 2009).

Workers in a factory in the Russian Federation producing cobalt acetate, chloride, nitrate and sulphates were reported to be exposed to cobalt in dust at concentrations of 0.05–50 mg/m^3 (IARC 2006, in the Netherlands, 2010; not mentioned, but assumed that concentration refers to Co^{2+}). At a different study, measured cobalt concentrations at workplaces with exposure to cobalt salts in a refinery were 68 – 89 $\mu g/m^3$ (range 1 – 7700 $\mu g/m^3$) (Lison 1994 in the Netherlands, 2010).

Five production sites are mentioned in the consultants report produced in the context of ECHA's first recommendation for inclusion of substances in Annex XIV (ECHA, 2009), located in France, Belgium, the UK, and Finland.

2.2.2.2. Uses and releases from uses

Uses

According to Registration data (additional info from other sources as mentioned below), cobalt dichloride is used in the EU in:

- ***Manufacture of other chemicals*** *(e.g. cobalt carboxylates);*

This seems also to include ***organic textile dyes*** (cobalt complexes of azo-dye derivates; the Netherlands, 2010) and use in ***other wet chemical processes***. Furthermore, cobalt dichloride seems to be used in the synthesis of ***tyre adhesion additives***, the synthesis of ***drying agents for paints***, and the manufacture of ***cobalt***

[2] In the background document for cobalt dichloride in the context of ECHA's first recommendation (ECHA, 2009), the total EU production had been estimated to be around 10,000t The current (2011) estimate of total production is found to be substantially lower than the initial estimate, according to the Cobalt REACH Consortium (personal communication with EUROMETAUX, 2011).

metal micronic powders for cutting tools (RCOM, 2008; RCOM, 2009; RCOM, 2011).

- ***Surface treatment processes****:*

These include metal surface treatment, non-metal surface treatment, or welding and soldering.

In electroplating (galvanoplasty) cobalt dichloride is electroplated as Co metal (RCOM, 2010). It is used in for electroplating High-Tech products, e.g. magnetic layers (RCOM, 2008). Further applications include for example Zn-(low)Co alloy plating and Co-Cr carbide composite plating that aim to deliver good corrosion and wear resistance (RCOM, 2011). For corrosion protection, cobalt dichloride is used in pre-treatment processes for zinc-coated surfaces. A coating is formed consisting essentially of ZnO containing Co^{2+} ions (RCOM, 2008). Areas of application include for instance the aerospace and automotive sectors (ECHA, 2009).

In applications of aluminium anodizing, cobalt dichloride is used to produce a range of shades from bronze to black and to improve the light fastness of the anodised layer. The pigmentation is achieved by precipitating CoS in the pores of the aluminium oxide layer (RCOM, 2008).

- *Formulation and industrial use* ***as water treatment chemical / oxygen scavenger / corrosion inhibitor****;*

For example, in water treatment cobalt dichloride is used as a catalyst in the decomposition of hypochlorites in effluents (RCOM, 2008).

- *Calcination/sintering process in the context of the manufacture/production of* ***inorganic pigments & frits, glass, ceramic ware*** *(in these cases: use as colorant or for discolouring),* ***varistors and magnets****:*

In ceramics, frits (glazes, enamels) and glass, cobalt salts (not necessarily all applications in these sectors are relevant for cobalt dichloride) are used as a colorant or a decolourant in the production process. Decolourising is assumed to be due to the catalytic effect of small amounts of Co(II) on bleaching actually performed by other oxidative substances (see e.g. Zhang et al., 1998, on a different application with similar function of Co^{2+}).

Cobalt salts are used in ceramic pigments and designated as underglaze stains, glaze stains, body stains, overglaze colours, and ceramic colours. Underglazes are applied to the surface of the article prior to glazing. The glaze stain uses cobalt colorants in the glaze. A body stain is mixed throughout the body of the ceramic. Overglaze colours are applied to the surface and fired at low temperatures. Ceramic colours are pigments used in a fusible glass or enamel and are one of the more common sources of the blue coloration in ceramics, china, and enamel ware (the Netherlands, 2010). Cobalt salts are also possibly used as bleaching agent in sanitary ceramics[3].

According to comments received from industry, cobalt dichloride is used in the manufacture of porcelain, and in glass as colorant (RCOM, 2008).

According to the Annex XV Dossier (France, 2008), cobalt dichloride is further used as dye mordant for glass industry (paints on glass surface). However, according to the Cobalt Development Institute (CDI; RCOM, 2008) cobalt dichloride is not used in glass paints/enamels, nor would it make much sense as an ingredient in the glass frit itself. According to the same comment, this use may be as a product or a precursor for a product that can be employed in a chemical vapour deposition (CVD) or physical vapour deposition (PVD).

Cobalt has been detected with a concentration of 560 mg/kg in one out of 12 glass and ceramic colours for hobby use (Danish Environmental Agency, 2005: Survey and assessments of chemical substances in glass and porcelain colours. Survey of chemical substances in consumer products No. 59; In RCOM, 2010).

Varistors are used for search protection in electrical and electronic products e.g. computers, office equipment, video and audio recording, communication equipment. No information has been provided regarding the exact function(s) of cobalt salts in the production of varistors and magnets (this is assumed to relate mainly to the magnetic properties of cobalt oxide).

- ***Humidity indication applications****, according to information from stakeholder consultation:*

Cobalt dichloride seems to be used as humidity indicator in several applications, such as in humidity indicator cards for military, export packaging, and semiconductor manufacturing. In those cases it is impregnated in paper cards, while it appears that it is regenerated after use (ECHA, 2009; RCOM, 2009).

There is uncertainty whether other applications currently occur in the EU. Comments received during stakeholder consultation suggest that cobalt dichloride is used as catalyst in the manufacture of pharmaceuticals. According to CDI (RCOM, 2008), cobalt dichloride is not used as a catalyst in organic reactions such as hydrogenation and desulphurisation. Cobalt metal and other inorganic cobalt compounds are used for this purpose. According to the Annex XV Dossier, cobalt dichloride is also used as a flux in magnesium refining. However, according to industry's knowledge European producers and recyclers of magnesium do not currently use this substance (CDI in RCOM, 2008). As all cobalt salts, cobalt dichloride is also used as analytical standard, while according to one comment this substance is used (at least at schools) among others in invisible inks (RCOM 2009).

[3] Sanitary ceramics comprise wash-bowls, glass bowls, baths, water massage baths, WC, bidets, seats, mixers, bathroom accessories, heating units, etc.

It is noted that cobalt has been detected in cosmetic kohl products (concentrations between 0.11 and 51 mg/kg) and in cosmetic henna products (concentrations between 0.59 and 1.1 mg/kg) (Danish Environmental Agency, 2005: Survey of chemical substances in consumer products No. 65; In RCOM, 2010).

Volumes per sector or use

According to information collected by the Cobalt REACH Consortium, relating to 2007 (RCOM, 2008; RCOM, 2011):

- Around 88 % of cobalt dichloride was used as an intermediate in the synthesis of other inorganic cobalt compounds
- Around 10 % was used in the synthesis of organic cobalt compounds (e.g. tyre adhesion additives and drying agents for paints)
- Less than 1 % was used in the synthesis of vitamin B12, and
- Small tonnages were used in the synthesis of pigments for textiles and of inorganic cobalt-containing pigments.

Additional small volumes appear to relate with surface treatment processes, humidity indicator cards (<<1 t/y), as well as production of animal food and veterinary products, according to the consultants report provided in the frame of ECHA's first recommendation for the inclusion of substances in Annex XIV (ECHA, 2009).

Releases from uses

The main route of occupational exposure of cobalt compounds is via the respiratory tract by inhalation of dusts, fumes and mists containing cobalt (IARC 1991 in RCOM, 2010). According to its classification, Cobalt dichloride may cause cancer by inhalation, with a low specific concentration limit of 0.01% for this hazard (it is noted that cobalt dichloride is also classified as toxic for reproduction)

No information regarding releases to the working environment is available.

Cobalt dichloride is reported to be largely produced and used as a solution (99%) with only a small portion of the production and use involving cobalt dichloride in powdered form (1%) (ECHA, 2009). Industry claims that uses in liquid solutions do not pose risk from inhalation from aerosolisation (RCOM, 2008); here it should be noted that there is no information available about the form in which the substance is used in applications in the scope of authorisation.

The UK Workplace exposure limit for cobalt and cobalt compounds is 0.1 mg/m^3 and the American Conference for Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) is 0.02 mg/m^3. Although the TLV has no legal status, it would generally be regarded as good practice to meet the TLV. UK Workplace exposure limits are normally set at levels that are believed to be achievable through good occupational hygiene practice (ECHA, 2009).

Overall, it seems likely that workplace exposures to cobalt dichloride are generally low. It is technically feasible to control airborne exposure concentrations to less than

0.1 mg/m^3 and concentrations in a large proportion of workplaces handling cobalt dichloride are likely to be less than 0.02 mg/m^3. Dermal exposure to cobalt dichloride can be readily controlled through the use of appropriately designed handling systems and procedures and the use of protective clothing and gloves where appropriate (ENTEC, 2008 in ECHA, 2009).

On the other hand, for example surface treatment is an activity carried out by numerous small and medium enterprises (SME), therefore a significant amount of workers may be exposed to this substance, with the chemical risk control in SME in Europe to be poor according to a number of reports (RCOM, 2009). Industry has argued that the use in surface treatment is safe, and that the main identified risk relates to the releases to the aqueous environment due to cobalt salts remaining in the aqueous solutions used, which is stated to be controlled by treatment of wastewater (RCOM, 2008).

According to further information from the public consultation (RCOM, 2009), the use of cobalt dichloride as humidity indicator is widespread, with the regeneration of silica gel siccatives (by heating the silica gel up to 150 or 180 ^{o}C and transferring and re-filling the regenerated granulate into the application system) to be accompanied by severe exposition to dust particles containing cobalt dichloride, and often not followed by appropriate risk management measures.

As regards consumer exposure, in a relevant study on porcelain dinnerware from Europe and Asia, which had been manufactured before mid-1970s and had hand-painted designs over the glaze, the extracted Co under acidic conditions was from <0.020 to 2.9 μg/mL (Sheets 1998 and ASTDR 2004 in the Netherlands, 2010).

All the above uses have been listed in the registration dossiers as industrial. Some of the produced mixtures containing cobalt dichloride can be assumed to be handled as well by professionals.

2.2.2.3. Geographical distribution and conclusions in terms of (organisation and communication in) supply chains

Information from the public consultation on the identification of substance as SVHC (RCOM, 2009) suggests that there are many small and medium enterprises involved in surface treatment processes. On the other hand, one company commented that the volume and the number of workers of the cobalt industry are in fact small (RCOM, 2010).

Based on the available information, it can be concluded, in particular for uses in the scope of authorisation, that the supply chains contain a small number of EU manufacturers and importers, and a medium number of downstream users, which represent a medium number of industry branches. In conclusion, according to the available information, the supply chains for cobalt dichloride appears to be of medium complexity.

2.3. Availability of information on alternatives[4]

As for cobalt dichloride and other cobalt salts a number of common uses have been registered, it can be reasonably assumed that such salts could in general replace cobalt dichloride in some of its applications.

According to the Cobalt REACH Consortium, the vast majority of the applications do actually not allow for mutual substitution of the cobalt salts for technical and/or economical reasons; even where it is chemically feasible to substitute the cobalt salts, it would not be practical on an industrial scale without involving excessive cost (further information is currently collected for the current applications; personal communication with EUROMETAUX, 2011).

Some information on specific uses is available in the Annex XV Dossier (France, 2008) or has been provided during the public consultation on the identification of cobalt dichloride as SVHC (RCOM: 2008, 2009, 2011). According to this information, cobalt salts are alternative to Cr(VI) in electroplating, with both groups of substances sharing similar hazardous inherent properties.

Regarding the use in self-indicating blue (anhydrous form) to pink (hydrated form) silica gels, it was reported that iron salts could be an alternative to cobalt dichloride (Inrs, 2007 in France, 2008). Phenolphthalein (a substance classified as carcinogen 1B) - in a concentration of 0.01% by weight – could be used as an indicator that changes from yellow when dry to green, and finally to deep blue when the gel has adsorbed approximately 5% of water by weight. While certain suppliers propose also other organic humidity indicators that give for example a colour change from orange to colourless (France, 2008).

Consultation with industry (ENTEC, 2008) regarding this use showed that alternatives to cobalt dichloride (e.g. other metal salts, such as iron or copper salts, as proposed by France in their Annex XV dossier) did not allow the same range of humidity indication and therefore these substances were not considered to be technically suitable. According to industry, the only alternative substance identified so far allowing humidity indicator cards to fulfil all quality and performance requirements specified in military and industrial standards is cobalt bromide, which probably has a similar hazard profile to cobalt dichloride.

No alternative substances or techniques to cobalt dichloride seem to have been identified for the other uses (ENTEC, 2008; RCOM: 2008,2009,2011).

2.4. Existing specific Community legislation relevant for possible exemption

No data available.

2.5. Any other relevant information (e.g. for priority setting)

No data available.

[4] Please note that this information was not used for the prioritisation.