20 December 2011

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. This confidential annex is not included in the public version of this background document.

1. Identity of the substance

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

This background document covers also the hydrated forms of Cobalt dichloride.

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 has been updated accordingly in June 2011.

2.2. Imports, exports, manufacture and uses

[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

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2.2.1. Volume(s), imports/exports

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, 2011b), the annual tonnage actually manufactured and/or imported in the EU is less than a third of the range maximum of 10,000.

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 (or other cobalt salts) generates cobalt dichloride that is used on site or sold (France, 2008; RCOM, 2011b).

Cobalt dichloride is predominantly supplied to downstream users as an aqueous solution (approximately 80% of EU tonnage). The solid form is mainly used in surface treatment applications (RCOM, 2011b).

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). According to the CoRC, these data are very unlikely to represent current cobalt dichloride exposure levels from industrial processes in the EU, with reference being made also to the Registration exposure scenarios that would demonstrate effective control of exposure (RCOM, 2011).

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 (and additional information from other sources as referenced 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; potentially rather a use of the diacetate salt, RCOM, 2011b) 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*** (cobalt carboxylates used as drier catalysts in alkyl based paints), and the manufacture of ***cobalt metal micronic powders for cutting tools*** (RCOM, 2008; RCOM, 2009; RCOM, 2011; RCOM, 2011b).

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

(Note: not necessarily all the described surface treatment application areas below are relevant for cobalt dichloride)

  - *Passivation / Anti-corrosion* (e.g. conversion layers/coatings on automotive parts, aerospace, military, marine, building, architectural, sanitary fitting, lighting, electrical etc.) (RCOM, 2011)
  - *Electroplating / Electroforming* (e.g. technical / magnetic / decorative plating; application in aerospace, automotive, telecommunication, electronics, storage media, military, household articles, watches, jewellery, metal logos, chains, buckles, medical technology, etc; electroplated as Co metal or alloys with nickel, tungsten, iron, molybdenum, chromium, zinc, precious metals, etc.); The function of the substance is to affect physical properties of surfaces, e.g. smoothness, hardness, brightness, ductility, resistance, porosity, or the production of record and compact discs (the Netherlands, 2010; RCOM, 2010; RCOM, 2011).
  - *Colour anodizing* (the pigmentation is achieved by precipitating CoS in the pores of the aluminium oxide layer (RCOM, 2008; RCOM, 2011))
  - *Electroless plating* (RCOM, 2011)

Those processes involve immersing components in aqueous solutions (Communication of CoRC to MSC, 2011). Applications that don't involve immersion (brush plating) have also been mentioned for cobalt dichloride, for the purpose of local repair (of corroded or worn areas) or for improvement of surface properties sometimes directly on assembled parts, without dismounting and transport (RCOM, 2011). In fact, among the Process categories (PROC) that have been associated with use in surface treatment processes in the registration dossiers is also PROC 7 ("Industrial spraying").

- *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). The substance is further used as oxygen scavenger, e.g. in sodium sulphite preparations. In that application, cobalt(II) dichloride acts as a catalyst that is increasing the rate and extent of removal of dissolved oxygen by the sodium sulphite, thereby reducing the risk of steam boiler failures due to corrosion by dissolved oxygen.

- *Calcination/sintering process in the context of the manufacture/production of* ***inorganic pigments & frits, glass, ceramic ware****:*

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In ceramics, frits (glazes, enamels) and glass, cobalt salts (cobalt dichloride is used in some, but not necessarily all such applications) 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 also possibly used as bleaching agent in sanitary ceramics[2].

Cobalt salts are used in ceramic pigments and designated as underglaze stains, glaze stains, body stains, overglaze colours, and ceramic colours. The underglaze is 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). According to the Annex XV Dossier (France, 2008), cobalt dichloride is further used as dye mordant for glass industry (paints on glass surface).

According to information provided by one company during the public consultation, cobalt dichloride is in fact a precursor in the manufacturing of cobalt oxides or cobalt dihydroxide. These cobalt oxides or cobalt dihydroxides are transformed by calcination into oxides used as pigments for « frits, glass, ceramic ware, varistors and magnets ». The same company noted that the majority of pigments producers directly use cobalt oxides in the manufacturing of pigments (RCOM, 2011b). Similarly, 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).

- ***As trace element in fermentation processes*** (RCOM, 2011b)

Substances produced include peptides, vitamins, enzymes, antibiotics, single-cell proteins, organic substances, etc.

- ***In fertiliser formulations and as animal feed supplement*** (RCOM, 2011b)

- ***Humidity indication applications*** (RCOM, 2009; RCOM,. 2011b)

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

Cobalt dichloride is used as humidity indicator in humidity indicator cards (HIC) for military, export packaging, and semiconductor manufacturing. (ECHA, 2009; RCOM, 2009). HIC have, according to information provided in the public consultation, replaced Humidity Indicating Silica Gel. HIC is a paper based product on which a cobalt dichloride solution is impregnated (mostly at concentrations of 0.1 to 0.3%). In contrast, Blue Indicating Silica Gel – as it is known in the industry – is silica gel coated with cobalt dichloride. According to the provided information, industry has been moving away from silica gel that was coated with cobalt dichloride due the dusting that can be inhaled (RCOM, 2011b). In the previous public consultation (RCOM, 2009) it was reported that cobalt dichloride is used widely as humidity indicator in laboratories (chemical, physical, biological, technological laboratories) as indicator in siccatives and that blue silica is still on the market. Regarding potential exposure, this has been considered to be of concern in particular during its regeneration for the purpose of reuse.

As all cobalt salts, cobalt dichloride is also used in analytical applications and diagnostic assays (RCOM, 2011b), while according to one comment this substance is used (at least at schools) among others in invisible inks (RCOM 2009).

- ***In diagnostics / as analytical reagent*** (RCOM, 2011b)

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).

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). Cobalt has been mentioned to be present in khol product as a naturally occurring impurity, in trace amounts, in this mineral. Similarly, henna has been mentioned to be a vegetable product containing natural traces of cobalt (RCOM, 2011b).

Volumes per sector or use

According to information collected by the Cobalt REACH Consortium, (RCOM, 2011b), the substance is used in the EU as follows:

- in the production of other chemicals, 97%
- in surface treatment, <2%
- as an oxygen scavenger/corrosion prevention in industrial water systems, <1%
- in medicinal products and as trace element in industrial cell culture, <1%
- as animal feed and as component of fertiliser formualtion, <<1%

- as humidity indicator, <<<1% (according to a company provided further information during the consultation, maximum 100 kg/y)
- in the manufacture of inorganic pigments for ceramic products (including glazes) & porcelain manufacture (decolourizing application), no specific tonnage information, assumed low

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)

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 size enterprises (SME), therefore a significant number of workers may be exposed to this substance, with the chemical risk control in SMEs in Europe being 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). In the public consultation of 2011, industry has referred to the exposure scenarios developed for the purpose of Registration and has provided further exposure-related information (mainly uses in surface treatment, fermentation, water treatment and humidity indication) (RCOM, 2011b).

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

No tangible information is available on the number of downstream users of cobalt dichloride in the EU, in particular for the uses in the scope of authorisation, with the cobalt industry (CoRC) estimating the number of sites not to be high (RCOM, 2011b).

Other industry organisations stated though that cobalt compounds are widely used by SMEs in many surface treatment processes and that these applications, including in decorative plating, are becoming increasingly important (RCOM, 2010; RCOM, 2011b). For example, as regards passivation of zinc or zinc alloy plating with Co(II) compounds, more than 3 billion pieces p.a. alone in Germany are treated for the automotive industry. Therefore, extrapolating on the European scale, there is uncertainty as to whether surface treatment in such dimensions could take place at a low/medium number of sites (not taken into account formulator sites and other uses in the scope of authorisation). The amounts of the Co(II) substances (including cobalt dichloride) used for surface treatment seem to be as well high, given the claimed specialty of the surface treatment uses and the relatively small amounts of cobalt needed per treated object.

CoRC confirmed that, in contrast to the initial survey, it now seems that there are many more facilities than expected (potentially thousands) involved in surface treatment with cobalt salt (mainly passivation treatment). CoRC further commented that use for passivation treatment is declining due to the availability of cobalt free alternatives and therefore the total number of sites is expected to decrease in the next years (communication of CoRC to MSC, 2011).

Therefore, based on the available information, it appears that, in particular for uses in the scope of authorisation, the supply chains contain a relatively small number of EU manufacturers and importers, and a higher number of downstream users.

2.3. Availability of information on alternatives[3]

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 and vice versa.

According to the Cobalt REACH Consortium, the vast majority of the applications do actually not allow for mutual substitution between 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 (personal communication with EUROMETAUX, 2011).

During public consultation (RCOM, 2011), industry provided some further arguments for the use in surface treatment and as humidity indicator, concluding that interchangeability between the cobalt salts included in ECHA's recommendation is not expected to occur at large-scale, and that case-by-case evaluation is deemed necessary.

It is acknowledged that cobalt dichloride may in some of its uses hardly be replaceable by another cobalt(II) salt. However, considering scientific knowledge in chemistry and the principal chemical processes taking place it appears very improbable that it would technically not be possible to replace cobalt dichloride in

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

at least some of its uses by another cobalt salt or that cobalt dichloride could not be used to replace other cobalt salts.

During consultation, also comments were provided with reference to existing suitable alternatives / alternatives under development for some uses (such cobalt-free passivation for zinc or zinc-alloy plating, RCOM, 2011b; or in humidity indicators, for certain humidity ranges, RCOM, 2010; RCOM, 2011b). In several comments, industry argued that no suitable alternatives have been identified (comments mainly referring to the use in surface treatment processes and as humidity indicator). (More) hazardous substances/technologies have also been referred to in some of the received comments, such as cadmium plating for zinc-cobalt plating, while Co(II) has replaced Cr(VI) in electroplating (RCOM, 2011).

2.4. Existing specific Community legislation relevant for possible exemption

There seems to be no specific Community legislation in force that would allow to consider exemption of (categories of) uses from the authorisation requirement on the basis of Article 58(2) of the REACH Regulation (see RCOM, 2011).

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

Not available.

3. Conclusions and justification

3.1. Prioritisation

Verbal-argumentative approach

Manufacture of other substances, including catalysts, textile dyes, tyre adhesion additives and driers, appear to be uses of the substance as intermediate. Furthermore, use in animal food supplement is considered to be outside the scope of authorisation. No concrete details that would allow a conclusion on their nature are available on some uses in the calcination process in the context of the manufacture / production of inorganic pigments & frits, glass and ceramic ware. Uses of cobalt dichloride in surface treatment processes, as water treatment chemical / oxygen scavenger / corrosion inhibitor, as fertiliser, as humidity indicator, and in fermentation processes appear to be in the scope of authorisation.

Therefore, taking account of the reported tonnage allocation to uses in the scope of authorisation, a relatively low volume appears to be used.

Sites using the substance in the scope of authorisation have been indicated by the Cobalt REACH Consortium to be not high, although significant uncertainty exists and this figure might be high.

Main route of occupational exposure is via the respiratory tract by inhalation of dusts, fumes and mists containing the substance. Worker exposure in industrial applications may be controlled in most instances but there are uses, e.g. in surface treatment, which include process steps with significant potential for exposure to dusts, fumes and aerosols containing the substance.

Based on the criteria, the substance has a moderate priority.

Scoring approach

Score			Total Score (= IP + V + WDU)
Inherent properties (IP)	Volume (V)	Uses – wide dispersiveness (WDU)	
Score: 0 -1 [4] (carcinogen 1B; toxic for reproduction 1B)	3 (Relatively low volume in the scope of authorisation)	Overall score: 2 * 3 = 6 Site-#: 2 (Used at a presumably medium number of sites) Release: 3 (for some uses risk of significant and potentially uncontrolled exposure)	9 - 10

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, cobalt dichloride gets a moderate priority for inclusion in Annex XIV.

It is moreover noted that cobalt dichloride should be grouped with the other cobalt(II) substances that are on the Candidate List in order to prevent evasion of a possible authorisation requirement by replacement of those cobalt(II) salts that are subject to authorisation with other equally hazardous cobalt(II) substances not included in Annex XIV.

Therefore, cobalt dichloride is recommended for inclusion in Annex XIV.

[4] Some information has been provided by the Cobalt Development Institute regarding a potential concentration threshold of cobalt (II) salts for eliciting cancer effects. For the sole purpose of this prioritisation step a score in the range 0 (carcinogenic with threshold) - 1 (carcinogenic without threshold) is assigned. This scoring does not pre-empt any conclusion by the Risk Assessment Committee when preparing its opinions on the future applications.

4. References

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http://echa.europa.eu/web/guest/identification-of-svhc

RCOM (2011): Responses to comments" document compiled from the commenting period on the identification of cobalt dichloride as SVHC (on the proposal to update the entry in the candidate list with the new classification; May 2011)

RCOM (2011b): Annex II to Responses to comments document (RCOM) on ECHA's draft 3rd recommendation for the group of recommended cobalt(II) substances – comments on cobalt dichloride.

http://echa.europa.eu/documents/10162/17232/rcom_cobalt_compounds_en.pdf