15 June 2011

Draft background document for cobalt(II) sulphate

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(II) sulphate
EC Number:	233-334-2
CAS Number:	10124-43-3

This background document covers also the hydrated forms of Cobalt(II) sulphate.

2. Background information

2.1. Intrinsic properties

Cobalt(II) sulphate was identified as a Substance of Very High Concern (SVHC) according to Articles 57(a) and (c) 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 as toxic for reproduction category 1B[1], H360F (may damage fertility), and was therefore included in the candidate list for authorisation on 15 December 2010, following ECHA's decision ED/95/2010.

2.2. Imports, exports, manufacture and uses

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, 2010; personal communication with EUROMETAUX, 2011), the annual production in the EU, corrected for export where data were available, was estimated in the same range.

[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

2.2.2. Manufacture and uses

2.2.2.1. Manufacture and releases from manufacture

Cobalt(II) sulphate is prepared by dissolving cobalt(II) oxide, hydroxide or carbonate in dilute sulphuric acid, followed by crystallisation. Crystallisation yields the commercial product, pink heptahydrate (Pantaik 2002 in the Netherlands, 2010).

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 μg/m^3 (range 1 – 7700 μg/m^3) (Lison 1994 in the Netherlands, 2010).

The CDI (Cobalt Development Institute) reported that manufacture and/or import facilities of the Cobalt REACH Consortia members for cobalt sulphate are located in Belgium, Finland, Norway and Germany (the Netherlands, 2010).

2.2.2.2. Uses and releases from uses

Uses

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

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

This includes also ***organic textile dyes*** (cobalt complexes of azo-dye derivates; the Netherlands, 2010; RCOM, 2010) and use in ***other wet chemical processes***. Furthermore, cobalt(II) sulphate is mentioned to be used in the manufacture of active substances for the production of batteries (it seems that production of batteries requires prior manufacture of another cobalt compound from cobalt(II) sulphate). This use concerns for example Li-ion and alkaline rechargeable (such as NiCd) batteries, which are used e.g. in the automotive market (HEV Vehicle and Electric Vehicle) and storage applications (for intermittent renewable energy generation; photovoltaic and wind) (industrial / portable batteries; RCOM, 2010; The Netherlands, 2010). According to the Cobalt Development Institute, cobalt(II) sulphate is also used in the manufacture of ***catalysts*** (personal communication with EUROMETAUX, 2011; no details available).

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

    - *Electrodeposition* (the Netherlands, 2010; RCOM, 2010): cobalt salts (not necessarily all the described applications below are relevant for cobalt(II) sulphate) are electroplated as Co metal or alloys with nickel, tungsten, iron, molybdenum, chromium, zinc, and precious metals. Applications include aerospace-, automotive-, telecommunication-,

electronics-, storage media-, military-, etc.- industries. 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.
  - *Colour anodizing*
  - *Non-electrodeposition*
  - *Welding and soldering processes*

- *Formulation (**as drier and pigment) in** - and **industrial** use of - **coatings and inks**;*

In the case of drier, the function relates to formation of coating (due to a catalysed oxidation of hydrocarbons) during the application of the formulated mixtures. Among potential products are also linoleum, paints, and lithographic inks, although at least one company considered the use of cobalt(II) sulphate in these products unlikely (the Netherlands, 2010; RCOM, 2010). No information is available on the concentration of cobalt(II) sulphate in such mixtures.

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

The formulated mixtures may be added e.g. to process water for protection of the pipes from corrosion by oxygen, or as micro-nutrient solution.

- *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**:*

Although the use of cobalt(II) sulphate in the production of inorganic pigments and frits has been registered, the Cobalt REACH Consortium (CoRC) does not have records of downstream users using the substance in such applications. On the basis of information provided by the Inorganic Pigments Consortium, CoRC deems it not likely that this specific substance is used in the manufacture of inorganic pigments or frits (RCOM, 2010).

In ceramics, frits (glazes, enamels) and glass, cobalt salts (not clear if relevant also for cobalt(II) sulphate) are used as a colorant or a decolourant in the production process. Decolorizing 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. 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). Cobalt salts are also possibly used as bleaching agent in sanitary ceramics[2].

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).

- ***Animal food supplement****, according to the Cobalt Development Institute (personal communication with EUROMETAUX, 2011).*

Information on further (to the above listed) uses was not possible to confirm on the basis of the available data. 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 (the Netherlands, 2010; RCOM, 2010; personal communication with EUROMETAUX, 2011[3]):

- above 90% of the cobalt(II) sulphate in the EU is used in the production of other chemicals (feed materials for other chemicals),
- up to 5% is used in the manufacture of catalysts and driers
- up to 5% is used in surface treatment and for the production of batteries
- up to 2% is used in the production of pigments (ink, ceramic, anodizing, textiles, glass, dyes) and in colorizing / decolorizing (in glass, pottery)
- up to 1% is used in animal food supplement

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(II) sulphate may cause cancer by inhalation, with a low specific concentration limit of 0.01% for this hazard (it is noted that cobalt(II) sulphate is also classified as toxic for reproduction).

[2] Sanitary ceramics comprise wash-bowls, glass bowls, baths, water massage baths, WC, bidets, seats, mixers, bathroom accessories, heating units, etc.
[3] Some use categories have been combined for reasons of commercial confidentiality.

Some measured concentrations have been reported in the literature for the dust in facilities producing cobalt salts (0.05–50 mg cobalt /m^3), and in a refinery (relating to cobalt salts use - 68 – 89 μg/m^3; range 1 – 7700 μg/m^3) (the Netherlands, 2010; RCOM, 2010).

The Cobalt REACH Consortium highlighted during the public consultation on the identification of the substance as SVHC that further exposure data is available, as having been provided to the Consortium Consultants, and which were considered in the detailed Exposure Scenarios that were prepared for the Registration Dossiers of cobalt salts. According to Germany, on the basis of toxicological and exposure data in the open literature, the occupational cancer risk is expected to be high (ROCM, 2010).

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 and articles can be assumed to be handled as well by professionals and consumers.

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

Estimates on the number of downstream users of cobalt(II) sulphate in the EU have been provided for combined use categories by the Cobalt REACH Consortium (CoRC; the Netherlands, 2010). According to these data (some double-counting may exist, according to CoRC), aprox. 90–115 sites (employing about 1000 workers) are involved in surface treatment processes, corrosion prevention, and manufacture of batteries; 10–15 sites relate to manufacture of driers and catalysts; 30-45 (~ 300 workers) sites involve in the production of pigments and decolourising applications. Finally, aprox. 40-80 sites manufacture other chemicals, and 25-35 sites relate to the animal food supplement sector.

Information from the public consultation on the identification of substance as SVHC (RCOM, 2010) suggests that there are many small companies involved in surface treatment processes, in particular in decorative plating, with applications in many metal and plastic components. 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).

Therefore, based on the available information, it can be concluded, in particular for uses in the scope of authorisation, that the supply chains contain a relatively small number of EU manufacturers and importers, and a high number of downstream users, which represent a medium number of industry branches. In conclusion, the supply chains for cobalt(II) sulphate appear to be of medium complexity.

2.3. Availability of information on alternatives[4]

As for cobalt(II) sulphate 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(II) sulphate 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 has been provided during the public consultation on the identification of cobalt(II) sulphate as SVHC (RCOM, 2010). According to this information, although alternative technologies to electroplating, and thus avoiding the use of cobalt salts, is possible for the production of Co-containing alloys, the coatings formed do not have the same nanostructures at relatively low cost. Furthermore, in an other comment it was stated that alternatives are available for the use of cobalt(II) sulphate in offset-printing.

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.

3. Conclusions and justification

3.1. Prioritisation

Verbal-argumentative approach

Relatively high volume used in the scope of authorisation. Widespread uses, as it appears that the substance is used at a high number of industrial settings and that the number of workers/ professional users involved might also be high.

Releases at workplaces in industrial settings seem to be controlled in most cases but some processes, involving handling of powder forms of the substance have a potentially significant exposure potential for industrial and - where relevant - professional workers. Recycling of imprinted paper and coated articles is a further source of potentially uncontrolled exposure.

In conclusion some uses can be considered as wide dispersive.

[4] Note : This information was not used for the prioritisation.

Therefore, based on the criteria, the substance gets high priority.

Scoring approach

Score			Total Score
Inherent properties (IP)	Volume (V)	Uses - wide dispersiveness (WDU)	(= IP + V + WDU)
Score: 0 -1 [5] (carcinogen 1B; toxic for reproduction 1B)	5 (Relatively high volume in the scope of authorisation)	Overall score: 3 * 3 = 9 Site-#: 3 (Used at a presumably high number of sites) Release: 3 (for some uses risk of significant and potentially uncontrolled exposure)	14 - 15

Conclusion, taking regulatory effectiveness considerations into account

On the basis of the prioritisation criteria, cobalt(II) sulphate gets high priority for inclusion in Annex XIV.

Therefore, **it is proposed to recommend cobalt(II) sulphate for inclusion in Annex XIV**.

As there are other cobalt(II) compounds on the Candidate List that could replace the substance in at least some of its uses, these other cobalt(II) compounds should be grouped with the substance and included in Annex XIV as well.

4. References

The Netherlands (2010): Annex XV dossier for the proposal for identification of Cobalt(II) sulphate as a CMR CAT 1 or 2, PBT, vPvB or a substance of an equivalent level of concern. Submitted by the Netherlands.
http://echa.europa.eu/doc/consultations/svhc/svhc_axvrep_netherlands_cmr_co-sulphate.pdf

Personal communication with EUROMETAUX (2011): Comments provided by the Cobalt REACH Consortium on clarification of information regarding the prioritisation of the cobalt salts

[5] Some information has been provided by the Cobalt REACH Consortium 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 authorisation applications.

RCOM (2010): “Responses to comments” document compiled from the commenting period on the identification of Cobalt(II) sulphate as SVHC (08.03.-22.04.2010).
http://echa.europa.eu/doc/about/organisation/msc/msc_rcoms2010/rcom_cobaltsulphate/rcom_cobaltsulphate_20101112.rtf
Zhang, X.-Z., Francis, R., Dutton, D., Hill, R. (1998) Decomposition of paracetic acid catalyzed by cobalt(II) and vanadium(V). Can. J. Chem. 76: 1064–1069.