

20 December 2011

Background document for cobalt(II) sulphate

Document developed in the context of ECHA's third Recommendation for 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(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 1B¹, H350i (may cause cancer by inhalation), and as toxic for reproduction category 1B¹, 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, 2011), the annual tonnage

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

manufactured and/or imported in the EU, corrected for export, is less than a third of the range maxima of 10,000.

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 (or other salts) in dilute sulphuric acid, followed by crystallisation. Crystallisation yields the commercial product, pink heptahydrate (Pantaik 2002 in the Netherlands, 2010; RCOM, 2011). It is noted that a large amount of cobalt sulphate is produced as a by-product in the manufacture of other metals, like nickel and copper; by removing cobalt impurities (RCOM, 2011).

Cobalt(II) sulphate is supplied / used in solid form or in solution (RCOM, 2011).

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/m³ (IARC 2006, in the Netherlands, 2010; not mentioned, but assumed that concentration refers to Co²⁺). In a different study, measured cobalt concentrations at workplaces with exposure to cobalt salts in a refinery were reported to be 68 – 89 µg/m³ (range 1 – 7700 µg/m³) (Lison 1994 in the Netherlands, 2010). According to the CoRC, these data are very unlikely to represent current cobalt sulphate 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).

The CDI (Cobalt Development Institute) and the CoRC reported that manufacture and/or import facilities of the Cobalt REACH Consortia members for cobalt sulphate are located in Belgium, Finland, Norway, Germany, and the UK (the Netherlands, 2010; RCOM, 2011).

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 derivatives; 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:**

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

- *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*

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(II) sulphate, 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").

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

In ceramics, frits (glazes, enamels) and glass, cobalt(II) sulphate is used as colorant or decolorant 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 Co²⁺). Cobalt salts are also possibly used as bleaching agent in sanitary ceramics².

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).

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

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).

- **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. According to industry's comments, cobalt sulphate is actually used in the synthesis of drying agents for paints and printing inks rather than directly as drier itself (RCOM, 2011).

- **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.

- **Animal feed supplement**, according to the Cobalt Development Institute (personal communication with EUROMETAUX, 2011).
- **As catalyst**, in organic synthesis (RCOM, 2011)
- **In fertiliser formulations** (RCOM, 2011)
- **As essential element in fermentation and for biogas production** (RCOM, 2011)

This use relates for example to the production of intermediates for antibiotics to preservatives, vitamins, food and technical enzymes, bio-based materials such as succinic acid, as well as to the production of biogas industry (e.g. associated to the sewage sludge treatment, bio-waste treatment, or agricultural manure treatment) (RCOM, 2011).

Information on potential further (to the above listed) uses could not be confirmed 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). Cobalt has been mentioned to be present in kohl 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.

Volumes per sector or use

According to information collected by the Cobalt REACH Consortium (RCOM, 2011), the use of cobalt(II) sulphate in the EU comprises:

- Manufacture of other chemicals. ~ 90%
- Use in surface treatment. < 5%
- Manufacture of inorganic pigments. <3%
- Manufacture of batteries. <1%
- Manufacture of catalysts. <<1%
- Use as an animal feed supplement. <1%
- Use as an oxygen scavenger/corrosion prevention in industrial water systems. <<1%
- Manufacture of textile dyes. <<1%
- Manufacture of drier and/or pigment in paints/inks. <<1%

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).

Some measured concentrations have been reported in the literature for the dust in facilities producing cobalt salts (0.05–50 mg cobalt /m³), and in a refinery (relating to cobalt salts use - 68 – 89 µg/m³; range 1 – 7700 µg/m³) (the Netherlands, 2010; RCOM, 2010).

The Cobalt REACH Consortium and other industry organisations highlighted during the public consultations that further exposure data is available to the Consortium Consultants, which was considered in the detailed Exposure Scenarios that were prepared for the cobalt salt Registration Dossiers. According to the German Competent Authority, on the basis of toxicological and exposure data in the open literature, the occupational cancer risk is expected to be high (RCOM, 2010). Industry has provided further exposure-related information during the public consultation 2011, mainly on the use in surface treatment, as well in water treatment (RCOM, 2011).

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

Data/estimations provided by CoRC during public consultation (RCOM, 2011) sum up below 100 sites for uses in the scope of authorisation, although for some of those uses no information on sites has been provided by industry. On the basis of all information available though there is relatively high uncertainty on the #-sites at which surface treatment is carried out, as explained below.

According to CoRC, cobalt(II) substances are used for surface treatment in small quantities and in highly specialised applications at some 10s of sites. (RCOM, 2011) However, other industry organisations stated 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, 2011). 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 (RCOM, 2011). Therefore, extrapolating on the European scale, there is uncertainty as to whether surface treatment in such dimensions could take place at less than 100 sites (not taken into account formulator sites and other uses in the scope of authorisation). The amounts of the Co(II) substances (including cobalt(II) sulphate) 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 high number of downstream users.

2.3. Availability of information on alternatives³

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 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 (EUROMETAUX, 2011).

During public consultation (RCOM, 2011), industry provided further arguments for the use in surface treatment, 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(II) sulphate 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 sulphate in at least some of its uses by another cobalt salt or that cobalt sulphate 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 as for the use of cobalt(II) sulphate in offset-printing, RCOM, 2010; or regarding cobalt-free passivation for zinc or zinc-alloy plating, RCOM, 2011). In several comments,

³ Note : Information on availability of alternatives was not used for the prioritisation.

industry argued that no suitable alternatives have been identified (comments mainly referring to the use in surface treatment processes). (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, active substances for the production of batteries, and pigments, appear to be uses of the substance as intermediate. Furthermore, use as 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 manufacture / production of inorganic pigments & frits, glass and ceramic ware. Uses of cobalt(II) sulphate in surface treatment processes, as water treatment chemical / oxygen scavenger / corrosion inhibitor, as drier/pigment, and as a catalyst (substance itself), in fertilisers and in fermentation / biogas production appear to be in the scope of authorisation.

Therefore, on the basis of the tonnage allocation per use a relatively high volume appears to be used in the scope of authorisation.

Widespread uses, as it appears that the substance is used at a high number of industrial sites, and that the number of workers that potentially could be exposed might also 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 gets high 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)	5 (Relatively high volume in the scope of authorisation)	Overall score: 3 * 3 = 9 Site-#: 3 (Used at a 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.

As there are other cobalt(II) compounds on the Candidate List that could replace the substance in at least some of its uses⁵, these other cobalt(II) compounds should be grouped with the substance and included in Annex XIV as well.

Therefore, cobalt(II) sulphate is recommend 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 preempt any conclusion by the Risk Assessment Committee when preparing its opinions on the future authorisation applications.

⁵ As Co(II) sulphate may be used to replace the other cobalt(II) substances in some of their uses.

4. References

- Communication of CoRC to MSC, 2011: "Summary information: Cobalt Salts and Inter-changeability", Room document ECHA/MS-21/040 provided by the Cobalt REACH Consortium via EUROMETAUX for the Member State Committee meeting 21 (7-9 December 2011).
- 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.
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- Personal communication with EUROMETAUX (2011): Comments provided by the Cobalt REACH Consortium on clarification of information regarding the prioritisation of the cobalt salts
- 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/web/guest/identification-of-svhc>
- RCOM (2011): Annex I to Responses to comments document (RCOM) on ECHA's draft 3rd recommendation for the group of recommended cobalt(II) substances – comments on cobalt(II) sulphate.
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- 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.