15 June 2011

Draft background document for cobalt(II) diacetate

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) diacetate
EC Number:	200-755-8
CAS Number:	71-48-7

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

2. Background information

2.1. Intrinsic properties

Cobalt(II) diacetate 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; personal communication with EUROMETAUX, 2011), the annual production in the EU, corrected for export, was estimated **below 1,000 t/y**.

2.2.2. 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

2.2.2.1. Manufacture and releases from manufacture

According to the Annex XV Dossier (references as following, in the Netherlands, 2010), cobalt(II) diacetate in produced on commercial scale by dissolving cobalt(II) carbonate or hydroxide in dilute acetic acid, followed by crystallization. Also, it may be prepared by oxidation of dicobalt octacarbonyl in the presence of acetic acid (Patnaik, 2002), or from powdered Co and acetic acid (The Merc Index, 14th Edition). The commercial product is manufactured and sold in the tetrahydrate form of the compound (Patnaik, 2002). It can be also prepared, by reflux of acetic acid solutions in the presence of cobalt(II) oxide, or by oxygenation of hot acetic acid solutions over cobalt metal (Kirk-Othmer 2010).

At a study mentioned in the Annex XV dossier, 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).

After consultation the Cobalt Development Institute (CDI) reported that manufacture and/or import facilities of the Cobalt REACH Consortia members for cobalt di(acetate) are located in Belgium, Finland, France, and the UK (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) diacetate is used in the EU in:

- ***Manufacture of other chemicals****;*

This includes also use in ***other wet chemical processes***. According to the Cobalt REACH Consortium, cobalt(II) diacetate is also used in the manufacture of ***catalysts*** (Hydrotreating; Oxidation catalyst; Hydrodesulphurisation; Fischer Tropsch (GTL); The Netherlands, 2010; RCOM, 2010; personal communication with EUROMETAUX, 2011).

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

    - *Electrodeposition* (the Netherlands, 2010; RCOM, 2010): cobalt salts (not necessarily all the described applications below are relevant for cobalt(II) diacetate) 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*

- *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 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. 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). 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).

- ***As a catalyst:***

As stated in the Annex XV Dossier, by far the main use of cobalt(II) diacetate is as a catalyst in the production of PTA, which is an intermediate for the manufacture of polyester fibres. Furthermore (the Netherlands, 2010; RCOM, 2010), cobalt(II) carboxylates, such as the oleate, acetate, and naphthenate, are used in the liquid-phase oxidations of p-xylene to terephthalic acid, cyclohexane to adipic acid, acetaldehyde to acetic acid, and cumene to cumene hydroperoxide. These reactions each involve a free-radical mechanism. Cobalt-catalyzed oxidations form the largest group of homogenous liquid phase oxidations in the chemical industry. According to additional information received during consultation (RCOM, 2010), cobalt(II) diacetate is used as a catalyst for the production of Dimethylterephthalate (DMT). It is only used in the form of aqueous solution. During the DMT production process

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

cobalt(II) diacetate is only lost within the esterification process resulting to metallic cobalt, which is recycled via extraction. DMT is purified by a distillation process.

- ***Production of plastics and/or PET:***

Cobalt(II) diacetate is used as catalyst for resin polymerisation. The final handling of PET articles has been registered as use by industrial, but as well as professional workers.

Furthermore, cobalt(II) diacetate is used as a dye for tinting clear PET bottles a light blue colour (the Netherlands, 2010). The use in PET tinting though is potentially soon to be phased out, according to information from the Committee of PET manufacturers in Europe (RCOM, 2010). Moreover, regarding the reference in the Annex XV dossier on the use of the substance as a catalyst in the manufacture of PET monomer, doubts were expressed during the stakeholder consultation by the Committee of PET manufacturers in Europe (RCOM, 2010).

- ***Manufacture of rubber adhesion agents:***

These agents are used for facilitating adhesion between steel and rubber in tyres. The function of the substance in the adhesive mixtures seems to be associated with adhesion promotion (RCOM, 2010).

- ***Animal food supplement ("feed grade materials")***

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[3]; RCOM, 2010):

- more than 70% of the cobalt(II) diacetate in the EU is used in the manufacture of catalysts – though, according to the information from the stakeholder consultation, a significant part of this amount may relate to the use of the substance itself as a catalyst, corresponding to at least several hundreds tonnes per year.
- up to 15% is used in the manufacture of chemicals (feed materials for other chemicals),
- up to 10% is used in surface treatment (anodizing) and alloys (hard metal)
- up to 5% is used in the production of pigments (ceramics, anodizing), dyes, and rubber adhesion

[3] Some use categories have been combined for reasons of commercial confidentiality.

- up to 5% is used as 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) diacetate may cause cancer by inhalation, with a low specific concentration limit of 0.01% for this hazard (it is noted that cobalt(II) diacetate 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 /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 prepared for the Registration Dossiers for 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).

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) diacetate 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. 10–15 downstream users relate to the manufacture of catalysts, 5-10 users in the production of other chemicals, 10-15 users involved in surface treatment and alloys, 10–15 in the production of pigments, dyes, and adhesion, and less than 10 sites are estimated to be involved in applications relating to animal food supplements. As mentioned above, it is further expected that a larger number of sites are involved in the use of the substance itself as a catalyst.

Based on the available information and the registered uses, 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, 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(II) diacetate appear to be of medium complexity.

2.3. Availability of information on alternatives[4]

As for cobalt(II) diacetate 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) diacetate 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).

According to industry comments (RCOM, 2010), unlikely / no viable alternatives are identified for the function as catalyst in various applications, while it is mentioned that available solutions exist and are currently being implemented for the use of cobalt(II) diacetate as colour modifier for PET materials.

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

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.

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

Scoring approach

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

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)	7 (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)	16 - 17

Conclusion, taking regulatory effectiveness considerations into account

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

Therefore, **it is proposed to recommend cobalt(II) diacetate 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) diacetate 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-diacetate.pdf

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) diacetate as SVHC (08.03.-22.04.2010). http://echa.europa.eu/doc/about/organisation/msc/msc_rcoms2010/rcom_cobaltdiacetate/rcom_cobaltdiacetate_20101119.rtf

[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 applications.