20 December 2011

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. This confidential annex is not included in the public version of this background 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; 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 **between 100 and 1,000 t/y**.

2.2.2. Manufacture and uses

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 is 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). Other cobalt salts can also be used in the manufacture of cobalt(II) diacetate (RCOM, 2011).

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). According to CoRC, this data is not specific to cobalt diacetate, with reference being made also to the Registration exposure scenarios that would demonstrate effective control of exposure (RCOM, 2011).

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). Updated information was provided during the public consultation on ECHA's draft recommendation (see confidential annex).

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:

- ***As a catalyst:***

The main use of cobalt(II) diacetate is as a catalyst in the manufacture of other chemicals, including in the production of purified terephthalic acid (PTA), dimethyl terephthalate (DMT), isophthalic acid (IPA), as well as in other oxidation processes. During the DMT production process cobalt(II) diacetate is only lost within the esterification process resulting in metallic cobalt, which is recycled via extraction. DMT is purified by a distillation process. PTA, IPA, and DMT are used as monomers in the polyester industry, including manufacture of PET packaging resins, PET film, and PET fibre (RCOM, 2010; RCOM, 2011).

PET is a polyester resin used as packaging material for mineral water and beverages, plus for a large number of food and non-food packaging applications.

Furthermore, it is widely used in fibre/clothing, technical filaments, packaging, nonwovens and engineering applications. DMT is in addition used for the manufacture of polybutyleneterephthalate (PBT), a thermoplastic engineering polymer with end uses in automotive, structural electrical parts and electrical connectors (RCOM, 2011).

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

Cobalt(II) diacetate is used as a dye for tinting clear PET bottles a light blue colour (the Netherlands, 2010). It is used for special products (PETG resins) requiring high quality colours level. The use in PET tinting though is currently being phased out, according to information from the Committee of PET manufacturers in Europe (RCOM, 2010; RCOM, 2011). Industry did not confirm the use of cobalt(II) diacetate as a catalyst in the manufacture of PET monomer (RCOM, 2010; RCOM, 2011).

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

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

  - *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* (RCOM, 2011)

Those processes involve immersing components in aqueous solutions (Communication of CoRC to MSC, 2011). Applications not involving immersion (brush plating) have also been mentioned for cobalt(II) diacetate, for the purpose of local repair (on corroded or worn areas) or 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 are also PROC 7 ("Industrial spraying") and PROC 10 ("Roller application or brushing"). However, one registrant has advised against surface treatment by spraying.

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

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) and potentially in the manufacture of ***organic textile dyes*** (RCOM, 2011).

- *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 salts (cobalt(II) diacetate 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).

Cobalt diacetate is also used as color modifier in PET polymers (see below). While downstream users have reported also the use of Cobalt diacetate in dyes (RCOM, 2011).

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).

- ***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).

- ***Manufacture of hardmetal powder (Cobalt-Tungsten carbide powder)*** (RCOM, 2011)

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

- ***As essential element for biogas production*** (RCOM, 2011)

- ***As analytical reagent in laboratories*** (RCOM, 2011)

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

Information on potential 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). 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 (RCOM, 2011).

Volumes per sector or use

According to information collected by the Cobalt REACH Consortium (RCOM, 2011):

- 70-80% is used as catalyst (according to the Committee of PET Manufacturers in Europe, less than 450t were used in the manufacture of PTA, IPA and DMT in Europe in 2011)
- Up to 10% is used as pigment in PET bottles, with the use currently being phased out
- Less than 5% is used in surface treatment
- Approximately 5% is used in the manufacture of other chemicals, and less than 1% in the manufacture of catalysts
- Less than 1% in the manufacture of inorganic pigments
- Approximately 1% is used in animal feed supplement
- Less than 1% is used in the production of hard metal powder
- Much less than 1% is used as rubber adhesion agent

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 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 prepared for the cobalt salt Registration Dossiers (RCOM, 2010; RCOM, 2011). 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 uses as a catalyst and in surface treatment (RCOM, 2011).

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

Industry involved in the use as catalyst provided information that the sites for that use in the EU are 10 (RCOM, 2011). CoRC's data/estimations provided 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) diacetate) used for surface treatment seem to be as well relatively high, given the claimed specialty of the surface treatment uses and the relatively small amounts of cobalt needed per treated object.

According to CoRC, cobalt(II) diacetate has been identified as only being used for surface treatment in certain gold-cobalt plating baths, usually for applications in fashion item accessories (e.g. metal logos, chains, buckels etc.) and is restricted to use in a single Member State (communication of CoRC to MSC, 2011). However, this statement is not in line with the information provided in the registration dossiers. These dossiers contain a much broader description for applications in surface treatment processes. Also during public consultation comments were received that indicate a broader application area for cobalt(II) diacetate in surface treatment (RCOM, 2011; see example of brushing application in section 2.2.2.2).

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).

Based on the available information, it appears, in particular for uses in the scope of authorisation, that the supply chains contains 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(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 and vice versa.

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 (personal communication with EUROMETAUX, 2011).

During public consultation (RCOM, 2011), industry provided some further arguments for specific uses (as catalyst, 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 diacetate 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 diacetate in at least some of its uses by another cobalt salt or that cobalt diacetate 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) diacetate as colour modifier for PET materials or cobalt-free passivation for zinc or zinc-alloy plating) (RCOM, 2011). In several comments, industry argued that no suitable alternatives have been identified (comments mainly referring to uses as catalyst or 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

[3] Please note that information on availability of alternatives was not used for the prioritisation.

Verbal-argumentative approach

Manufacture of other substances, including catalysts, textile dyes, 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, the manufacture and use of rubber adhesion agents, and the for manufacture of hard metal powder. Uses of Cobalt(II) diacetate as a catalyst (substance itself), in surface treatment processes, as colorant for PET, and in 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.

Sites using the substance in the scope of authorisation have been indicated by the Cobalt REACH Consortium to be below 100 (RCOM, 2011), although this figure might according to later provided information be much higher (Communication of CoRC to MSC, 2011).

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 moderate to high priority.

Scoring approach

Score			Total Score
Inherent properties (IP)	Volume (V)	Uses - wide dispersiveness (WDU)	(= IP + V + WDU)
Score: 0 -1 [4] (carcinogen 1B; toxic for reproduction 1B)	5 (Relatively high volume in the scope of authorisation)	Overall score: 2-3 * 3 = 6-9 Site-#: 2-3 (Used at a medium to high number of sites) Release: 3 (for some uses risk of significant and potentially uncontrolled exposure)	11 – 15

[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.

Conclusion, taking regulatory effectiveness considerations into account

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

It is moreover noted that cobalt(II) diacetate 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(II) diacetate is recommended for inclusion in Annex XIV.

4. References

Communication of CoRC to MSC, 2011: "Summary information: Cobalt Salts and Inter-changeability", Room document ECHA/MSC-21/2011/040 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) 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/documents/10162/adf55c9d-1277-4433-af63-983a580c2a53

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/web/guest/identification-of-svhc

RCOM (2011): Annex V to Responses to comments document (RCOM) on ECHA's draft 3rd recommendation for the group of recommended cobalt(II) substances – comments on cobalt(II) diacetate. http://echa.europa.eu/documents/10162/17232/rcom_cobalt_compounds_en.pdf