Assistance to the Commission on Technological Socio-Economic and Cost-Benefit Assessment Related to Exemptions from the Substance restrictions in Electrical and Electronic Equipment (RoHS Directive)
Final Report – Pack 6

Report for the European Commission DG Environment under Framework Contract No ENV.C.2/FRA/2011/0020

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Disclaimer

Eunomia Research & Consulting, Oeko-Institut and Fraunhofer Institute IZM have taken due care in the preparation of this report to ensure that all facts and analysis presented are as accurate as possible within the scope of the project. However no guarantee is provided in respect of the information presented, and Eunomia Research & Consulting and Oeko-Institut are not responsible for decisions or actions taken on the basis of the content of this report.

Contents

LIST OF FIGURES

LIST OF TABLES

1.0 Background and Objectives

The RoHS Directive 2011/65/EU entered into force on 21 July 2011 and led to the repeal of Directive 2002/95/EC on 3 January 2013. The Directive can be considered to have provided for two regimes under which exemptions could be considered, RoHS 1 (the former Directive 2002/95/EC) and RoHS 2 (the current Directive 2011/65/EU).

Under Framework Contract no. ENV.C.2/FRA/2011/0020, a consortium led by Eunomia Research & Consulting was requested by DG Environment of the European Commission to provide technical and scientific support for the evaluation of exemption requests under the new RoHS 2 regime. The work has been undertaken by Oeko-Institut and Fraunhofer Institute IZM, and has been peer reviewed by Eunomia Research & Consulting.

The approach to adjudicating on the case for exemptions has to take into account some new aspects under the RoHS 2 regime as compared to that of RoHS 1:

- The scope covered by the Directive is now broader as it covers all EEE (as referred to in Articles 2(1) and 3(1));
- The former list of exemptions has been transformed into Annex III and may be valid for all product categories according to the limitations listed in Article 5(2) of the Directive. Annex IV has been added and lists exemptions specific to categories 8 and 9;
- The RoHS 2 Directive includes the provision that applications for exemptions have to be made in accordance with Annex V. However, even if a number of points are already listed therein, Article 5(8) provides that a harmonised format, as well as comprehensive guidance – taking the situation of SMEs into account – shall be adopted by the Commission; and
- The procedure and criteria for the adaptation to scientific and technical progress have changed and now include some additional conditions and points to be considered. These are detailed below.

The new Directive details the various criteria for the adaptation of its Annexes to scientific and technical progress. Article 5(1)(a) details the various criteria and issues that must be considered for justifying the addition of an exemption to Annexes III and IV:

- The first criterion may be seen as a threshold criterion and cross-refers to the REACH Regulation (1907/2006/EC). An exemption may only be granted if it does not weaken the environmental and health protection afforded by REACH;
- Furthermore, a request for exemption must be found justifiable according to one of the following three conditions:
    - Substitution is scientifically or technically impracticable, meaning that a substitute material, or a substitute for the application in which the restricted substance is used, is yet to be discovered, developed and, in some cases, approved for use in the specific application;

- The reliability of a substitute is not ensured, meaning that the probability that EEE using the substitute will perform the required function without failure for a period of time comparable to that of the application in which the original substance is included, is lower than for the application itself;
- The negative environmental, health and consumer safety impacts of substitution outweigh the benefits thereof.

➢ Once one of these conditions is fulfilled, the evaluation of exemptions, including an assessment of the duration needed, now has to consider the availability of substitutes and the socio-economic impact of substitution, as well as adverse impacts on innovation, and life cycle analysis concerning the overall impacts of the exemption; and

➢ A new aspect is that all exemptions now need to have an expiry date and that they can only be renewed upon submission of a new application.

Against this background, and taking into account that exemptions falling under the enlarged scope of RoHS 2 can be applied for since the entry into force of the Directive (21.7.2011), the consultants have undertaken evaluation of a range of exemptions in this work (new exemption requests, renewing existing exemptions, amending exemptions or revoking exemptions).

The Report includes the following Sections:

Section 2.0	Project Set-up
Section 3.0	Scope
Section 4.0	Overview of the Evaluation Results
Section 5.0	Links from the Directive to the REACH Regulation
Sections 6.0 through 7.0	Evaluation of the requested exemptions handled in the course of this project.

2.0 Project Set-up

Assignment of project tasks to Oeko-Institut, started 24 July 2014. The overall project has been led by Carl-Otto Gensch. At Fraunhofer IZM the contact person is Otmar Deubzer. The project team at Oeko-Institut consists of Carl-Otto Gensch and the technical expert Yifaat Baron. Eunomia, represented by Adrian Gibbs, have the role of ensuring quality management.

3.0 Scope

Two new RoHS exemption requests have been evaluated through the course of the project. An overview of the exemption requests is given in

Table 4-1 below.

In the course of the project, a stakeholder consultation was conducted. The stakeholder consultation was launched for a duration of 10 weeks, between 31 October 2014 and 09 January 2015.

The specific project website (RoHS Evaluation website) was used in order to keep stakeholders informed on the progress of work: http://rohs.exemptions.oeko.info. The consultation held during the project was carried out according to the principles and requirements of the European Commission. Stakeholders who had registered at the website were informed through email notifications about new steps within the project.

Information concerning the consultation was provided on the project website, including a general guidance document, the applicant's documents for the exemption request, results of earlier evaluations where relevant, a specific questionnaire and a link to the EU CIRCABC website (Communication and Information Resource Centre for Administrations, Businesses and Citizens)[1]. All non-confidential stakeholder comments submitted during the consultation, were made available on the RoHS Evaluation website and on the EU CIRCABC website.

The evaluation of the stakeholder contributions led to further consultation including, *inter alia*, engaging with stakeholders in further discussion, further exchanges in order to clarify remaining questions, cross-checking and additional research with regard to the accuracy of technical arguments, and clarifications in respect of confidentiality issues.

The requests were evaluated according to the various criteria (cf. Section 1.0 for details). The evaluation appears in the following chapters. The information provided by the applicant and by stakeholders is summarised in the first sections. This includes a general description of the application and requested exemption, a summary of the arguments made for justifying the exemption, information provided

[1] EU CIRCABC website: https://circabc.europa.eu (Browse categories > European Commission > Environment > RoHS Evaluations, at top left, click on "Library")

concerning possible alternatives and additional aspects raised by the applicants and other stakeholders. In some cases, reference is also made to information submitted by applicants and stakeholders in previous evaluations, in cases where a similar request has been reviewed or where a renewal has been requested of a request reviewed in the past. The Critical Review follows these sections, in which the submitted information is discussed, to clarify how the consultants evaluate the various information and what conclusions and recommendations have been made. For more detail, the general requirements for the evaluation of exemption requests may be found in the technical specifications of the project.[2]

4.0 Overview of the Evaluation Results

The exemption requests covered in this project and the applicants concerned, as well as the final recommendations and proposed expiry dates are summarised in

Table 4-1. The reader is referred to the corresponding section of this report for more details on the evaluation results.

The – not legally binding – recommendations for Exemption Request 2014-1 and Exemption Request 2014-2 were submitted to the EU Commission by Oeko-Institut and have already been published at the EU CIRCABC website on 24 June 2015. So far, the Commission has not adopted any revision of the Annex to Directive 2011/65/EU based on these recommendations.

Table 4-1: Overview of the exemption requests, associated recommendations and expiry dates

No.	Requested Wording	Applicant	Recommendation	Expiry date
2014-1	Cadmium Anodes in Hersch cells for high-sensitivity oxygen sensors	*MOCON*, Inc.	Cadmium anodes in Hersch cells for oxygen sensors used in industrial monitoring and control instruments, where sensitivity below 10 ppm is required.	7 years from approval
2014-2	Lead in solders used to make electrical connections to temperature measure-ment sensors designed to be used periodically at temperature below -150°C	Lake Shore Cryotronics	Lead in solders of electrical connections to temperature measurement sensors in devices which are designed to be used periodically at temperatures below –150°C	30 June 2021

[2] Cf. under:
http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_IX/Project_Description_II_Pack_4.pdf

5.0 Links from the Directive to the REACH Regulation

Article 5 of the RoHS 2 Directive 2011/65/EU on "Adaptation of the Annexes to scientific and technical progress" provides for the

> "*inclusion of materials and components of EEE for specific applications in the lists in Annexes III and IV, provided that such inclusion does not weaken the environmental and health protection afforded by Regulation (EC) No 1907/2006*".

RoHS 2 does not further elaborate the meaning of this clause.

Regulation (EC) No 1907/2006 regulates the safe use of chemical substances, and is commonly referred to as the REACH Regulation since it deals with **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances. REACH, for its part, addresses substances of concern through processes of authorisation and restriction:

- Substances that may have serious and often irreversible effects on human health and the environment can be added to the candidate list to be identified as Substances of Very High Concern (SVHCs). Following the identification as SVHC, a substance may be included in the Authorisation list, available under Annex XIV of the REACH Regulation: *"List of Substances Subject to Authorisation"*. If a SVHC is placed on the Authorisation list, companies (manufacturers and importers) that wish to continue using it, or continue placing it on the market, must apply for an authorisation for a specified use. Article 22 of the REACH Regulation states that:

  > *"Authorisations for the placing on the market and use should be granted by the Commission only if the risks arising from their use are adequately controlled, where this is possible, or the use can be justified for socio-economic reasons and no suitable alternatives are available, which are economically and technically viable."*

- If the use of a substance (or compound) in specific articles, or its placement on the market in a certain form, poses an unacceptable risk to human health and/or to the environment that is not adequately controlled, the European Chemical Agency (ECHA) may restrict its use, or placement on the market. These restrictions are laid down in Annex XVII of the REACH Regulation: *"Restrictions on the Manufacture, Placing on the Market and Use of Certain Dangerous Substances, Mixtures and Articles"*. The provisions of the restriction may be made subject to total or partial bans, or other restrictions, based on an assessment of those risks.

The approach adopted in this report is that once a substance has been included into the regulation related to authorisation or restriction of substances and articles under REACH, the environmental and health protection afforded by REACH may be weakened in cases where, an exemption would be granted for these uses under the provisions of RoHS. This approach was adopted for evaluation of exemption requests following the approval of the RoHS recast in 2011 and has been applied in the re-

evaluation of the existing RoHS exemptions 7(c)-IV, 30, 31 and 40,[3] as well as for the evaluation of a range of requests assessed through previous projects in respect of RoHS 2.[4] Furthermore, substances for which an authorisation or restriction process is already underway are also reviewed, so that future developments may be considered where relevant.

When evaluating the exemption requests, with regard to REACH compliance, we have checked whether the substance / or its substitutes are:

- On the list of substances proposed for the adoption to the Candidate List (the Registry of Intentions);
- On the list of Substances of Very High Concern (SVHCs - the Candidate List);
- In the recommendations of substances for Annex XIV (recommended to be added to the Authorisation List);
- Listed in REACH Annex XIV itself (The Authorisation List); or
- Listed in REACH Annex XVII (the List of Restrictions).

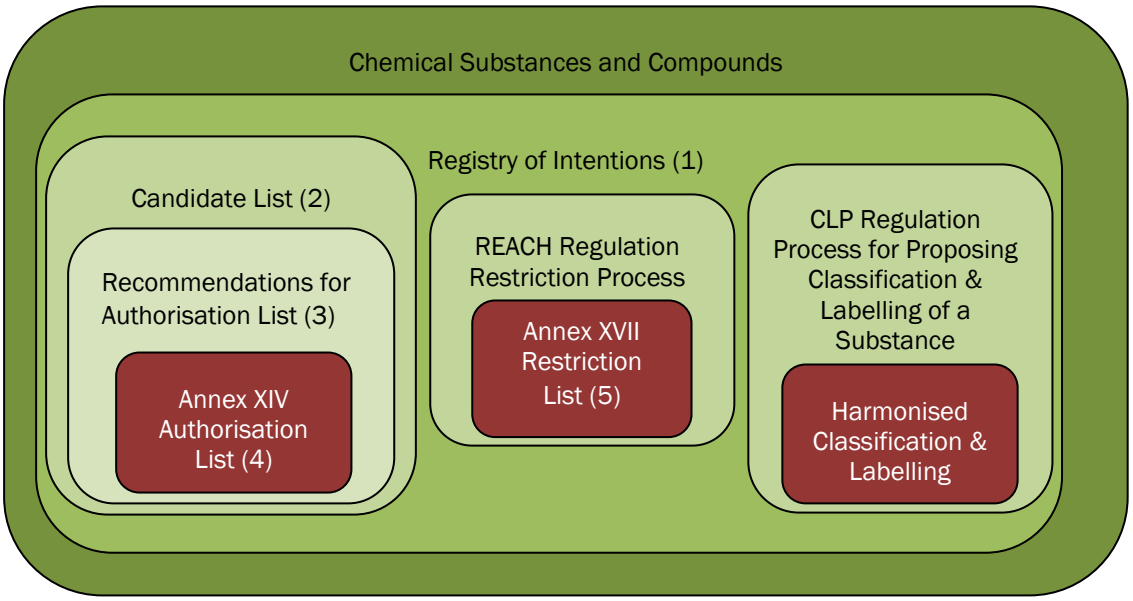
As the European Chemicals Agency (ECHA) is the driving force among regulatory authorities in implementing the EU's chemicals legislation, the ECHA website has been used as the reference point for the aforementioned lists, as well as for the exhaustive register of the Amendments to the REACH Legal Text.

Figure 5-1 shows the relationship between the two processes and categories. Substances included in the red areas may only be used when certain specifications and or conditions are fulfilled.

[3] See Zangl, S.; Blepp, M.; Deubzer, O. (2012) Adaptation to Scientific and Technical Progress under Directive 2011/65/EU - Transferability of previously reviewed exemptions to Annex III of Directive 2011/65/EU, Final Report, Oeko-Institut e. V. and Fraunhofer IZM, February 17, 2012, http://rohs.exemptions.oeko.info/fileadmin/user_upload/Rohs_V/Re-evaluations_transfer_RoHS_I_RoHS_II_final.pdf

[4] Gensch, C., Baron, Y., Blepp, M., Deubzer, O., Manhart, A. & Moch, K. (2012) Assistance to the Commission on technological, socio-economic and cost-benefit assessment related to exemptions from the substance restrictions in electrical and electronic equipment (RoHS Directive), Final Report, Oeko-Institut e. V. and Fraunhofer IZM, 21.12.2012 http://rohs.exemptions.oeko.info/fileadmin/user_upload/Rohs_V/RoHS_V_Final_report_12_Dec_2012_final.pdf

Figure 5-1: Relation of REACH categories and lists to other chemical substances



The following bullet points explain in detail the above-mentioned lists and where they can be accessed:

- Member States Competent Authorities (MSCAs) / the European Chemicals Agency (ECHA), on request by the Commission, may prepare Annex XV dossiers for identification of Substances of Very High Concern (SVHC), Annex XV dossiers for proposing a harmonised Classification and Labelling, or Annex XV dossiers proposing restrictions. The aim of the public Registry of Intentions is to allow interested parties to be aware of the substances for which the authorities intend to submit Annex XV dossiers and, therefore, facilitates timely preparation of the interested parties for commenting later in the process. It is also important to avoid duplication of work and encourage co-operation between Member States when preparing dossiers. Note that the Registry of Intentions is divided into three separate sections: listing new intentions; intentions still subject to the decision making process; and withdrawn intentions. The registry of intentions is available at the ECHA website at: http://echa.europa.eu/web/guest/addressing-chemicals-of-concern/registry-of-intentions;
- The identification of a substance as a Substance of Very High Concern and its inclusion in the Candidate List is the first step in the authorisation procedure. The Candidate List is available at the ECHA website at http://echa.europa.eu/web/guest/candidate-list-table;
- The last step of the procedure, prior to inclusion of a substance into Annex XIV (the Authorisation list), involves ECHA issuing a Recommendation of substances for Annex XIV. The ECHA recommendations for inclusion in the Authorisation List are available at the ECHA website at http://echa.europa.eu/web/guest/addressing-chemicals-of-

concern/authorisation/recommendation-for-inclusion-in-the-authorisation-list/authorisation-list;

- Once a decision is made, substances may be added to the Authorisation List available under Annex XIV of the REACH Regulation. The use of substances appearing on this list is prohibited unless an Authorisation for use in a specific application has been approved. The Annex can be found in the consolidated version of the REACH Legal Text (see below);
- In parallel, if a decision is made concerning the Restriction on the use of a substance in a specific article, or concerning the restriction of its provision on the European market, then a restriction is formulated to address the specific terms, and this shall be added to Annex XVII of the REACH Regulation. The Annex can be found in the consolidated version of the REACH Legal Text (see below); and
- As of the 16 of April 2015, the last amendment of the REACH Legal Text was dated from 23 March 2015 (Commission Regulation (EU) No 2015/282). The last consolidated version of the REACH Legal Text, dated 01 January 2015, was used to check Annex XIV and XVII: The consolidated version is available at the EUR-LEX website: http://eur-lex.europa.eu/legal-content/en/LKD/?uri=CELEX:32006R1907

In the following pages and tables, the various entries in REACH Annex XIV and Annex XVII are detailed as well as substances addressed in the various processes performed to identify SVHCs and subsequently to limit their use, where relevant, through addition of an entry in one of the annexes. These tables detail entries and processes of relevance for all of the substances listed in Annex II of the RoHS Directive (the RoHS restricted substances) and not only for substances relevant to the exemption requests evaluated in this report.

Table 5-1 lists those substances appearing in Annex XIV, subject to Authorisation, which are relevant to the RoHS substances dealt with in the requests evaluated in this project. As can be seen, at present, exemptions have not been granted for the use of these substances.

Table 5-1: Relevant entries from Annex XIV: The list of substances subject to authorisation

Designation of the substance, of the group of substances, or of the mixture	Transitional arrangements		Exempted (categories of)uses
	Latest application date (1)[5]	Sunset date (2)	
10. **Lead chromate** EC No: 231-846-0 CAS No: 7758-97-6	21 Nov 2013	21 May 2015	-
11. **Lead sulfochromate yellow** (C.I. Pigment Yellow 34) EC No: 215-693-7 CAS No: 1344-37-2	21 Nov 2013	21 May 2015	-
12. **Lead chromate molybdate sulphate red** (C.I. Pigment Red 104) EC No: 235-759-9 CAS No: 12656-85-8	21 Nov 2013	21 May 2015	-
16. **Chromium trioxide** EC No: 215-607-8 CAS No: 1333-82-0	21 Mar 2016	21 Sep 2017	-
17. **Acids generated from chromium trioxide and their oligomers** Group containing: **Chromic acid** EC No: 231-801-5 CAS No: 7738-94-5 **Dichromic acid** EC No: 236-881-5 CAS No: 13530-68-2 **Oligomers of chromic acid and dichromic acid** EC No: not yet assigned CAS No: not yet assigned	21 Mar 2016	21 Sep 2017	-
18. **Sodium dichromate** EC No: 234-190-3 CAS No: 7789-12-0 10588-01-9	21 Mar 2016	21 Sep 2017	-

[5] Article 58 (1) (c) of the REACH Regulation defines the significance of the sunset date and application date specified for substances listed in Annex XIV:
"(i) the date(s) from which the placing on the market and the use of the substance shall be prohibited unless an authorisation is granted (hereinafter referred to as the sunset date) which should take into account, where appropriate, the production cycle specified for that use"
"(ii) a date or dates at least 18 months before the sunset date(s) by which applications must be received if the applicant wishes to continue to use the substance or place it on the market for certain uses after the sunset date(s); these continued uses shall be allowed after the sunset date until a decision on the application for authorisation is taken [referred to as application date]"

Designation of the substance, of the group of substances, or of the mixture	Transitional arrangements		Exempted (categories of)uses
	Latest application date (1)[5]	Sunset date (2)	
19. **Potassium dichromate** EC No: 231-906-6 CAS No: 7778-50-9	21 Mar 2016	21 Sep 2017	-
20. **Ammonium dichromate** EC No: 232-143-1 CAS No: 7789-09-5	21 Mar 2016	21 Sep 2017	-
21. **Potassium chromate** EC No: 232-140-5 CAS No: 7789-00-6	21 Mar 2016	21 Sep 2017	-
22. **Sodium chromate** EC No: 231-889-5 CAS No: 7775-11-3	21 Mar 2016	21 Sep 2017	-
28. **Dichromium tris(chromate)** EC No: 246-356-2 CAS No: 24613-89-6	22 July 2017	22 January 2019	-
29. **Strontium chromate** EC No: 232-142-6 CAS No: 7789-06-2	22 July 2017	22 January 2019	-
30. **Potassium hydroxyoctaoxodizincatedichromate** EC No: 234-329-8 CAS No: 11103-86-9	22 July 2017	22 January 2019	-
31. **Pentazinc chromate octahydroxide** EC No: 256-418-0 CAS No: 49663-84-5	22 July 2017	22 January 2019	-

For the substances currently restricted according to RoHS Annex II: cadmium, hexavalent chromium, lead, mercury, polybrominated biphenyls and polybrominated diphenyl ethers and their compounds, we have found that some relevant entries are listed in Annex XVII of the REACH Regulation. The conditions of restriction are presented in

Table 5-2 below. Additionally, some amendments have been decided upon, and are still to be included in the concise version. These may be seen in Table 5-3.

Table 5-2: Conditions of restriction in REACH Annex XVII for RoHS substances and compounds

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
8. **Polybromobiphenyls; Polybrominatedbiphenyls (PBB)** CAS No 59536-65-1	1. Shall not be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin. 2. Articles not complying with paragraph 1 shall not be placed on the market.
16. **Lead carbonates**: (a) Neutral anhydrous carbonate (PbCO 3) CAS No 598-63-0 EC No 209-943-4 (b) Trilead-bis(carbonate)-dihydroxide 2Pb CO 3 - Pb(OH) 2 CAS No 1319-46-6 EC No 215-290-6	Shall not be placed on the market, or used, as substances or in mixtures, where the substance or mixture is intended for use as paint. However, Member States may, in accordance with the provisions of International Labour Organization (ILO) Convention 13, permit the use on their territory of the substance or mixture for the restoration and maintenance of works of art and historic buildings and their interiors, as well as the placing on the market for such use. Where a Member State makes use of this derogation, it shall inform the Commission thereof.
17. **Lead sulphates:** (a) PbSO 4 CAS No 7446-14-2 EC No 231-198-9 (b) Pb x SO 4 CAS No 15739-80-7 EC No 239-831-0	Shall not be placed on the market, or used, as substances or in mixtures, where the substance or mixture is intended for use as paint. However, Member States may, in accordance with the provisions of International Labour Organization (ILO) Convention 13, permit the use on their territory of the substance or mixture for the restoration and maintenance of works of art and historic buildings and their interiors, as well as the placing on the market for such use. Where a Member State makes use of this derogation, it shall inform the Commission thereof.
18. **Mercury compounds**	Shall not be placed on the market, or used, as substances or in mixtures where the substance or mixture is intended for use: (a) to prevent the fouling by micro-organisms, plants or animals of: — the hulls of boats, — cages, floats, nets and any other appliances or equipment used for fish or shellfish farming, — any totally or partly submerged appliances or equipment; (b) in the preservation of wood; (c) in the impregnation of heavy-duty industrial textiles and yarn intended for their manufacture; (d) in the treatment of industrial waters, irrespective of their use.
18a. **Mercury** CAS No 7439-97-6 EC No 231-106-7	1. Shall not be placed on the market: (a) in fever thermometers; (b) in other measuring devices intended for sale to the general public (such as manometers, barometers, sphygmomanometers, thermometers other than fever thermometers). 2. The restriction in paragraph 1 shall not apply to measuring devices that were in use in the Community before 3 April 2009. However Member States may restrict or prohibit the placing on the market of such measuring devices. 3. The restriction in paragraph 1(b) shall not apply to: (a) measuring devices more than 50 years old on 3 October 2007;

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
	(b) barometers (except barometers within point (a)) until 3 October 2009. 5. The following mercury-containing measuring devices intended for industrial and professional uses shall not be placed on the market after 10 April 2014: (a) barometers; (b) hygrometers; (c) manometers; (d) sphygmomanometers; (e) strain gauges to be used with plethysmographs; (f) tensiometers; (g) thermometers and other non-electrical thermometric applications. The restriction shall also apply to measuring devices under points (a) to (g) which are placed on the market empty if intended to be filled with mercury. 6. The restriction in paragraph 5 shall not apply to: (a) sphygmomanometers to be used: (i) in epidemiological studies which are ongoing on 10 October 2012; (ii) as reference standards in clinical validation studies of mercury-free sphygmomanometers; (b) thermometers exclusively intended to perform tests according to standards that require the use of mercury thermometers until 10 October 2017; (c) mercury triple point cells which are used for the calibration of platinum resistance thermometers. 7. The following mercury-using measuring devices intended for professional and industrial uses shall not be placed on the market after 10 April 2014: (a) mercury pycnometers; (b) mercury metering devices for determination of the softening point. 8. The restrictions in paragraphs 5 and 7 shall not apply to: (a) measuring devices more than 50 years old on 3 October 2007; (b) measuring devices which are to be displayed in public exhibitions for cultural and historical purposes.
23. **Cadmium** and its compounds CAS No 7440-43-9 EC No 231-152-8	For the purpose of this entry, the codes and chapters indicated in square brackets are the codes and chapters of the tariff and statistical nomenclature of Common Customs Tariff as established by Council Regulation (EEC) No 2658/87 (1). 1. Shall not be used in mixtures and articles produced from the following synthetic organic polymers (hereafter referred to as plastic material): —polymers or copolymers of vinyl chloride (PVC) [3904 10] [3904 21] —polyurethane (PUR) [3909 50] —low-density polyethylene (LDPE), with the exception of low-density polyethylene used for the production of coloured masterbatch [3901 10] —cellulose acetate (CA) [3912 11]

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
	—cellulose acetate butyrate (CAB) [3912 11] —epoxy resins [3907 30] —melamine-formaldehyde (MF) resins [3909 20] —urea-formaldehyde (UF) resins [3909 10] —unsaturated polyesters (UP) [3907 91] —polyethylene terephthalate (PET) [3907 60] —polybutylene terephthalate (PBT) —transparent/general-purpose polystyrene [3903 11] —acrylonitrile methylmethacrylate (AMMA) —cross-linked polyethylene (VPE) —high-impact polystyrene —polypropylene (PP) [3902 10] Mixtures and articles produced from plastic material as listed above shall not be placed on the market if the concentration of cadmium (expressed as Cd metal) is equal to or greater than 0,01% by weight of the plastic material. By way of derogation, the second subparagraph shall not apply to articles placed on the market before 10 December 2011. The first and second subparagraphs apply without prejudice to Council Directive 94/62/EC (13) and acts adopted on its basis. By 19 November 2012, in accordance with Article 69, the Commission shall ask the European Chemicals Agency to prepare a dossier conforming to the requirements of Annex XV in order to assess whether the use of cadmium and its compounds in plastic material, other than that listed in subparagraph 1, should be restricted. 2. Shall not be used in paints [3208] [3209]. For paints with a zinc content exceeding 10% by weight of the paint, the concentration of cadmium (expressed as Cd metal) shall not be equal to or greater than 0.1% by weight. Painted articles shall not be placed on the market if the concentration of cadmium (expressed as Cd metal) is equal to or greater than 0.1% by weight of the paint on the painted article. 3. By way of derogation, paragraphs 1 and 2 shall not apply to articles coloured with mixtures containing cadmium for safety reasons. 4. By way of derogation, paragraph 1, second subparagraph shall not apply to: — mixtures produced from PVC waste, hereinafter referred to as 'recovered PVC', — mixtures and articles containing recovered PVC if their concentration of cadmium (expressed as Cd metal) does not exceed 0.1% by weight of the plastic material in the following rigid PVC applications: (a) profiles and rigid sheets for building applications; (b) doors, windows, shutters, walls, blinds, fences, and roof gutters; (c) decks and terraces; (d) cable ducts; (e) pipes for non-drinking water if the recovered PVC is used in the middle layer of a multilayer pipe and is entirely covered with a layer of newly produced PVC in compliance with

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
	paragraph 1 above. Suppliers shall ensure, before the placing on the market of mixtures and articles containing recovered PVC for the first time, that these are visibly, legibly and indelibly marked as follows: '*Contains recovered PVC*' or with the following pictogram:  In accordance with Article 69 of this Regulation, the derogation granted in paragraph 4 will be reviewed, in particular with a view to reducing the limit value for cadmium and to reassess the derogation for the applications listed in points (a) to (e), by 31 December 2017. 5. For the purpose of this entry, 'cadmium plating' means any deposit or coating of metallic cadmium on a metallic surface. Shall not be used for cadmium plating metallic articles or components of the articles used in the following sectors/applications: (a) equipment and machinery for: — food production [8210] [8417 20] [8419 81] [8421 11] [8421 22] [8422] [8435] [8437] [8438] [8476 11] — agriculture [8419 31] [8424 81] [8432] [8433] [8434] [8436] — cooling and freezing [8418] — printing and book-binding [8440] [8442] [8443] (b) equipment and machinery for the production of: — household goods [7321] [8421 12] [8450] [8509] [8516] — furniture [8465] [8466] [9401] [9402] [9403] [9404] — sanitary ware [7324] — central heating and air conditioning plant [7322] [8403] [8404] [8415] In any case, whatever their use or intended final purpose, the placing on the market of cadmium-plated articles or components of such articles used in the sectors/applications listed in points (a) and (b) above and of articles manufactured in the sectors listed in point (b) above is prohibited. 6. The provisions referred to in paragraph 5 shall also be applicable to cadmium-plated articles or components of such articles when used in the sectors/applications listed in points (a) and (b) below and to articles manufactured in the sectors listed in (b) below: (a) equipment and machinery for the production of: — paper and board [8419 32] [8439] [8441] textiles and clothing [8444] [8445] [8447] [8448] [8449] [8451] [8452] (b) equipment and machinery for the production of: — industrial handling equipment and machinery [8425] [8426] [8427] [8428] [8429] [8430] [8431]

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
	— road and agricultural vehicles [chapter 87] — rolling stock [chapter 86] — vessels [chapter 89] 7. However, the restrictions in paragraphs 5 and 6 shall not apply to: — articles and components of the articles used in the aeronautical, aerospace, mining, offshore and nuclear sectors whose applications require high safety standards and in safety devices in road and agricultural vehicles, rolling stock and vessels, — electrical contacts in any sector of use, where that is necessary to ensure the reliability required of the apparatus on which they are installed. 8. Shall not be used in brazing fillers in concentration equal to or greater than 0.01% by weight. Brazing fillers shall not be placed on the market if the concentration of cadmium (expressed as Cd metal) is equal to or greater than 0.01% by weight. For the purpose of this paragraph brazing shall mean a joining technique using alloys and undertaken at temperatures above 450 °C. 9. By way of derogation, paragraph 8 shall not apply to brazing fillers used in defence and aerospace applications and to brazing fillers used for safety reasons. 10. Shall not be used or placed on the market if the concentration is equal to or greater than 0.01% by weight of the metal in: (i) metal beads and other metal components for jewellery making; (ii) metal parts of jewellery and imitation jewellery articles and hair accessories, including: — bracelets, necklaces and rings, — piercing jewellery, — wrist-watches and wrist-wear, — brooches and cufflinks. 11. By way of derogation, paragraph 10 shall not apply to articles placed on the market before 10 December 2011 and jewellery more than 50 years old on 10 December 2011.
28. Carcinogen category 1A or 1B or carcinogen category 1 or 2 According to Appendices 1 and 2: **Cadmium oxide** **Cadmium chloride** **Cadmium fluoride** **Cadmium Sulphate** **Cadmium sulphide** **Cadmium (pyrophoric)** **Chromium (VI) trioxide**	Without prejudice to the other parts of this Annex the following shall apply to entries 28 to 30: 1. Shall not be placed on the market, or used, — as substances, — as constituents of other substances, or, — in mixtures, for supply to the general public when the individual concentration in the substance or mixture is equal to or greater than: — either the relevant specific concentration limit specified in Part 3 of Annex VI to Regulation (EC) No 1272/2008, or, — the relevant concentration specified in Directive 1999/45/EC where no specific concentration limit is set out in Part 3 of Annex VI to Regulation (EC) No 1272/2008.

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
Zinc chromates including zinc potassium chromate **Nickel Chromate** **Nickel dichromate** **Potassium dichromate** **Ammonium dichromate** **Sodium dichromate** **Chromyl dichloride; chromic oxychloride** **Potassium chromate** **Calcium chromate** **Strontium chromate** **Chromium III chromate; chromic chromate** **Sodium chromate** **Lead Chromate** **Lead hydrogen arsenate** **Lead Nickel Salt** **Lead sulfochromate yellow; C.I. Pigment Yellow 34;** **Lead chromate molybdate sulfate red; C.I. Pigment Red 104;**	Without prejudice to the implementation of other Community provisions relating to the classification, packaging and labelling of substances and mixtures, suppliers shall ensure before the placing on the market that the packaging of such substances and mixtures is marked visibly, legibly and indelibly as follows: 'Restricted to professional users'. 2. By way of derogation, paragraph 1 shall not apply to: (a) medicinal or veterinary products as defined by Directive 2001/82/EC and Directive 2001/83/EC; (b) cosmetic products as defined by Directive 76/768/EEC; (c) the following fuels and oil products: — motor fuels which are covered by Directive 98/70/EC, — mineral oil products intended for use as fuel in mobile or fixed combustion plants, — fuels sold in closed systems (e.g. liquid gas bottles); (d) artists' paints covered by Directive 1999/45/EC; (e) the substances listed in Appendix 11, column 1, for the applications or uses listed in Appendix 11, column 2. Where a date is specified in column 2 of Appendix 11, the derogation shall apply until the said date.
29. Mutagens: category 1B or category 2 According to Appendices 3 and 4: **Cadmium chloride** **Cadmium fluoride** **Cadmium Sulphate** **Chromium (VI) trioxide** **Potassium dichromate** **Ammonium dichromate** **Sodium dichromate** **Chromyl dichloride; chromic oxychloride** **Potassium chromate** **Sodium chromate**	
30. Toxic to reproduction: category 1A or 1B or toxic to reproduction category 1 or 2 According to Appendices 5 and 6: **Cadmium chloride** **Cadmium fluoride** **Cadmium Sulphate** **Potassium dichromate**	

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
Ammonium dichromate **Sodium dichromate** **Sodium chromate** **Nickel dichromate** **Lead compounds with the exception of those specified elsewhere in this Annex** **Lead Arsenate** **Lead acetate** **Lead alkyls** **Lead azide** **Lead Chromate** **Lead di(acetate)** **Lead hydrogen arsenate** **Lead 2,4,6-trinitroresorcinoxide, lead styphnate** **Lead(II) methane-sulphonate** **Trilead bis- (orthophosphate)** **Lead hexa-fluorosilicate** **Mercury** **Silicic acid, lead nickel salt**	
47. **Chromium VI** compounds	1. Cement and cement-containing mixtures shall not be placed on the market, or used, if they contain, when hydrated, more than 2 mg/kg (0.0002%) soluble chromium VI of the total dry weight of the cement. 2. If reducing agents are used, then without prejudice to the application of other Community provisions on the classification, packaging and labelling of substances and mixtures, suppliers shall ensure before the placing on the market that the packaging of cement or cement-containing mixtures is visibly, legibly and indelibly marked with information on the packing date, as well as on the storage conditions and the storage period appropriate to maintaining the activity of the reducing agent and to keeping the content of soluble chromium VI below the limit indicated in paragraph 1. 3. By way of derogation, paragraphs 1 and 2 shall not apply to the placing on the market for, and use in, controlled closed and totally automated processes in which cement and cement-containing mixtures are handled solely by machines and in which there is no possibility of contact with the skin. 4. The standard adopted by the European Committee for Standardization (CEN) for testing the water-soluble chromium (VI) content of cement and cement-containing mixtures shall be used as the test method for demonstrating conformity with paragraph 1.
63. **Lead** and its compounds CAS No 7439-92-1 EC No 231-100-4	1. Shall not be placed on the market or used in any individual part of jewellery articles if the concentration of lead (expressed as metal) in such a part is equal to or greater than 0.05% by weight. 2. For the purposes of paragraph 1:

Designation of the substance, of the group of substances or of the mixture	Conditions of restriction
	(i) 'jewellery articles' shall include jewellery and imitation jewellery articles and hair accessories, including: (a) bracelets, necklaces and rings; (b) piercing jewellery; (c) wrist watches and wrist-wear; (d) brooches and cufflinks; (ii) 'any individual part' shall include the materials from which the jewellery is made, as well as the individual components of the jewellery articles. 3. Paragraph 1 shall also apply to individual parts when placed on the market or used for jewellery-making. 4. By way of derogation, paragraph 1 shall not apply to: (a) crystal glass as defined in Annex I (categories 1, 2, 3 and 4) to Council Directive 69/493/EEC (14); (b) internal components of watch timepieces inaccessible to consumers; (c) non-synthetic or reconstructed precious and semiprecious stones (CN code 7103, as established by Regulation (EEC) No 2658/87), unless they have been treated with lead or its compounds or mixtures containing these substances; (d) enamels, defined as vitrifiable mixtures resulting from the fusion, vitrification or sintering of minerals melted at a temperature of at least 500 °C. 5. By way of derogation, paragraph 1 shall not apply to jewellery articles placed on the market for the first time before 9 October 2013 and jewellery articles produced before 10 December 1961. 6. By 9 October 2017, the Commission shall re-evaluate this entry in the light of new scientific information, including the availability of alternatives and the migration of lead from the articles referred to in paragraph 1 and, if appropriate, modify this entry accordingly.

Table 5-3: Summary of relevant amendments to Annexes not updated in the last concise version of the REACH Regulation

Designation of the substance, of the group of sub-stances, or of the mixture	Conditions of restriction	Amended Annex	Amendment date
Addition of **Entry 62** concerning: (a) **Phenylmercury acetate** EC No: 200-532-5 CAS No: 62-38-4 (b) **Phenylmercury propionate** EC No: 203-094-3	1.Shall not be manufactured, placed on the market or used as substances or in mixtures after 10 October 2017 if the concentration of mercury in the mixtures is equal to or greater than 0.01% by weight. 2.Articles or any parts thereof containing one or more of these substances shall not be placed on the market after 10 October 2017 if the concentration of mercury in the articles or any part thereof is equal to or greater than 0.01% by weight.'	Annex XVII, entry 62	20 Sep 2012

Designation of the substance, of the group of sub-stances, or of the mixture	Conditions of restriction	Amended Annex	Amendment date
CAS No: 103-27-5 (c) **Phenylmercury 2-ethylhexanoate** EC No: 236-326-7 CAS No: 13302-00-6 (d) **Phenylmercury octanoate** EC No: - CAS No: 13864-38-5 (e) **Phenylmercury neodecanoate** EC No: 247-783-7 CAS No: 26545-49-3			
Addition of items 5-7 to entry 47. **Chromium VI** compounds	5. Leather articles coming into contact with the skin shall not be placed on the market where they contain chromium VI in concentrations equal to or greater than 3 mg/kg (0.0003% by weight) of the total dry weight of the leather. 6. Articles containing leather parts coming into contact with the skin shall not be placed on the market where any of those leather parts contains chromium VI in concentrations equal to or greater than 3 mg/kg (0.0003% by weight) of the total dry weight of that leather part. 7. Paragraphs 5 and 6 shall not apply to the placing on the market of second-hand articles which were in end-use in the Union before 1 May 2015.'	Annex XVII, entry 47	27 March 2014. The amend-ment shall apply from 1 May 2015.

As of 17 April 2015, the REACH Regulation Candidate list includes those substances relevant for RoHS listed in Table 5-4. Proceedings concerning the addition of these substances to the Authorisation list (Annex XIV) have begun and shall be followed by the evaluation team to determine possible discrepancies with future requests of exemption from RoHS (new exemptions, renewals and revokals)[6]:

[6] Updated according to http://echa.europa.eu/web/guest/candidate-list-table

Table 5-4: Summary of relevant substances currently on the REACH Candidate List

Substance Name	EC No.	CAS No.	Date of Inclusion	Reason for inclusion
Cadmium Fluoride	232-222-0	7790-79-6	17 Dec 2014	Carcinogenic (Article 57 a); Mutagenic (Article 57 b); Toxic for reproduction (Article 57 c); Equivalent level of concern having probable serious effects to human health (Article 57 f)
Cadmium Sulphate	233-331-6	10124-36-4 31119-53-6	17 Dec 2014	Carcinogenic (Article 57 a); Mutagenic (Article 57 b); Toxic for reproduction (Article 57 c); Equivalent level of concern having probable serious effects to human health (Article 57 f)
Cadmium chloride	233-296-7	10108-64-2	16 June 2014	Carcinogenic (Article 57a);
Cadmium sulphide	215-147-8	1306-23-6	16 Dec 2013	Carcinogenic (Article 57a); Equivalent level of concern having probable serious effects to human health (Article 57 f)
Lead di(acetate)	206-104-4	301-04-2	16 Dec 2013	Toxic for reproduction (Article 57 c);
Cadmium	231-152-8	7440-43-9	20 Jun 2013	Carcinogenic (Article 57a); Equivalent level of concern having probable serious effects to human health (Article 57 f)
Cadmium oxide	215-146-2	1306-19-0	20 Jun 2013	Carcinogenic (Article 57a); Equivalent level of concern having probable serious effects to human health (Article 57 f)
Pyrochlore, antimony lead yellow	232-382-1	8012-00-8	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead bis(tetrafluoroborate)	237-486-0	13814-96-5	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead dinitrate	233-245-9	10099-74-8	19 Dec 2012	Toxic for reproduction (Article 57 c)
Silicic acid, lead salt	234-363-3	11120-22-2	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead titanium zirconium oxide	235-727-4	12626-81-2	19 Dec 2012	Toxic for reproduction (Article 57 c)

Substance Name	EC No.	CAS No.	Date of Inclusion	Reason for inclusion
Lead monoxide (lead oxide)	215-267-0	1317-36-8	19 Dec 2012	Toxic for reproduction (Article 57 c)
Silicic acid ($H_2Si_2O_5$), barium salt (1:1), lead-doped[7]	272-271-5	68784-75-8	19 Dec 2012	Toxic for reproduction (Article 57 c)
Trilead bis(carbonate)dihydroxide	215-290-6	1319-46-6	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead oxide sulfate	234-853-7	12036-76-9	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead titanium trioxide	235-038-9	12060-00-3	19 Dec 2012	Toxic for reproduction (Article 57 c)
Acetic acid, lead salt, basic	257-175-3	51404-69-4	19 Dec 2012	Toxic for reproduction (Article 57 c)
[Phthalato(2-)]dioxotrilead	273-688-5	69011-06-9	19 Dec 2012	Toxic for reproduction (Article 57 c)
Tetralead trioxide sulphate	235-380-9	12202-17-4	19 Dec 2012	Toxic for reproduction (Article 57 c)
Dioxobis(stearato)trilead	235-702-8	12578-12-0	19 Dec 2012	Toxic for reproduction (Article 57 c)
Tetraethyllead	201-075-4	78-00-2	19 Dec 2012	Toxic for reproduction (Article 57 c)
Pentalead tetraoxide sulphate	235-067-7	12065-90-6	19 Dec 2012	Toxic for reproduction (Article 57 c)
Trilead dioxide phosphonate	235-252-2	12141-20-7	19 Dec 2012	Toxic for reproduction (Article 57 c)
Orange lead (lead tetroxide)	215-235-6	1314-41-6	19 Dec 2012	Toxic for reproduction (Article 57 c)
Sulfurous acid, lead salt, dibasic	263-467-1	62229-08-7	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead cyanamidate	244-073-9	20837-86-9	19 Dec 2012	Toxic for reproduction (Article 57 c)
Lead(II) bis(methanesulfonate)	401-750-5	17570-76-2	18 Jun 2012	Toxic for reproduction (Article 57 c)
Lead diazide, Lead azide	236-542-1	13424-46-9	19 Dec 2011	Toxic for reproduction (article 57 c),
Lead dipicrate	229-335-2	6477-64-1	19 Dec 2011	Toxic for reproduction (article 57 c)
Dichromium tris(chromate)	246-356-2	24613-89-6	19 Dec 2011	Carcinogenic (article 57 a)
Pentazinc chromate octahydroxide	256-418-0	49663-84-5	19 Dec 2011	Carcinogenic (article 57 a)
Potassium hydroxyoctaoxodizincatedichromate	234-329-8	11103-86-9	19 Dec 2011	Carcinogenic (article 57 a)

[7] *[with lead (Pb) content above the applicable generic concentration limit for 'toxicity for reproduction' Repr. 1A (CLP) or category 1 (DSD); the substance is a member of the group entry of lead compounds, with index number 082-001-00-6 in Regulation (EC) No 1272/2008]*

Substance Name	EC No.	CAS No.	Date of Inclusion	Reason for inclusion
Lead styphnate	239-290-0	15245-44-0	19 Dec 2011	Toxic for reproduction (article 57 c)
Trilead diarsenate	222-979-5	3687-31-8	19 Dec 2011	Carcinogenic and toxic for reproduction (articles 57 a and 57 c)
Strontium chromate	232-142-6	7789-06-2	20 Jun 2011	Carcinogenic (article 57a)
Acids generated from chromium trioxide and their oligomers. Names of the acids and their oligomers: Chromic acid, Dichromic acid, Oligomers of chromic acid and dichromic acid.	231-801-5, 236-881-5	7738-94-5, 13530-68-2	15 Dec 2010	Carcinogenic (article 57a)
Chromium trioxide	215-607-8	1333-82-0	15 Dec 2010	Carcinogenic and mutagenic (articles 57 a and 57 b)
Potassium dichromate	231-906-6	7778-50-9	18 Jun 2010	Carcinogenic, mutagenic and toxic for reproduction (articles 57 a, 57 b and 57 c)
Ammonium dichromate	232-143-1	7789-09-5	18 Jun 2010	Carcinogenic, mutagenic and toxic for reproducetion (articles 57 a, 57 b and 57 c)
Sodium chromate	231-889-5	7775-11-3	18 Jun 2010	Carcinogenic, mutagenic and toxic for reproduction (articles 57 a, 57 b and 57 c)
Potassium chromate	232-140-5	7789-00-6	18 Jun 2010	Carcinogenic and mutagenic (articles 57 a and 57 b).
Lead sulfochromate yellow (C.I. Pigment Yellow 34)	215-693-7	1344-37-2	13 Jan 2010	Carcinogenic and toxic for reproduction (articles 57 a and 57 c))
Lead chromate molybdate sulphate red (C.I. Pigment Red 104)	235-759-9	12656-85-8	13 Jan 2010	Carcinogenic and toxic for reproduction (articles 57 a and 57 c)
Lead chromate	231-846-0	7758-97-6	13 Jan 2010	Carcinogenic and toxic for reproduction (articles 57 a and 57 c)
Lead hydrogen arsenate	232-064-2	7784-40-9	28 Oct 2008	Carcinogenic and toxic for reproduction (articles 57 a and 57 c)

Substance Name	EC No.	CAS No.	Date of Inclusion	Reason for inclusion
Sodium dichromate	234-190-3	7789-12-0, 10588-01-9	28 Oct 2008	Carcinogenic, mutagenic and toxic for reproduction (articles 57a, 57b and 57c)

Additionally, Member States can register intentions to propose restrictions or to classify substances as SVHC. The first step is to announce such an intention. Once the respective dossier is submitted, it is reviewed and it is decided if the restriction or authorisation process should be further pursued or if the intention should be withdrawn.

As at the time of writing (April 2015), it cannot yet be foreseen how these procedures will conclude. It is thus not yet possible to determine if the protection afforded by REACH Regulation would in these cases consequently be weakened by approving the exemption requests dealt with in this report. For this reason, the implications of these decisions have not been considered in the review of the exemption requests dealt with in this report. However, for the sake of future reviews, the latest authorisation or restriction process results shall be followed and carefully considered where relevant.[8]

As for prior registrations of intention, dossiers have been submitted for the substances listed in table Table 5-5.

Table 5-5: Summary of substances for which a dossier has been submitted, following the initial registration of intention

Restriction / SVHC Classification	Substance Name	Submission Date	Submitted by	Comments
Restriction	Cadmium and its compounds	17 Jan 2014	Sweden	Artist paints
	Cadmium and its compounds	17 Oct 2013	ECHA	Amendment of the current restriction (entry 23) on use of paints with TARIC codes [3208] & [3209] containing cadmium and cadmium compounds to include placing on the market of such paints and a concentration limit.

[8] European Chemicals Agency (ECHA), Registry of intentions to propose restrictions: http://echa.europa.eu/registry-of-current-restriction-proposal-intentions/-/substance/1402/search/+/term (last accessed 22 August 2012)

Restriction / SVHC Classification	Substance Name	Submission Date	Submitted by	Comments
	Lead and lead compounds	18 Jan 2013	Sweden	Placing on the market of consumer articles containing Lead and its compounds
	Chromium VI	20 Jan 2012	Denmark	Placing on the market of leather articles containing Chromium VI
	Phenylmercuric octanoate; Phenylmercury propionate; Phenylmercury 2-ethyl-hexanoate; Phenylmercury acetate; Phenylmercury	15 Jun 2010	Norway	Mercury compounds
	Mercury in measuring devices	15 Jun 2010	ECHA	Mercury compounds
	Lead and its compounds in jewellery	15 Apr 2010	France	Substances containing lead
SVHC Classification	Cadmium fluoride	04 Aug 2014	Sweden	CMR
	Cadmium sulphate	04 Aug 2014	Sweden	CMR
	Cadmium chloride	03 Feb 2014	Sweden	CMR; other;
	Cadmium sulphide	05 Aug 2013	Sweden	CMR; other;
	Lead di(acetate)	05 Aug 2013	Netherlands	CMR
	Cadmium	04 Feb 2013	Sweden	CMR; other; Substances containing Cd
	Cadmium oxide	04 Feb 2013	Sweden	CMR; other; Substances Containing Cd
	Trilead dioxide Phosphonate; Lead Monoxide (Lead Oxide); Trilead bis(carbonate)di-hydroxide; Lead Dinitrate; Lead Oxide Sulphate; Acetic acid, lead salt, basic; Dioxobis(stearato)trilead; Lead bis(tetrafluoroborate); Tetraethyllead; Pentalead tetraoxide sulphate; Lead cyanamidate; Lead titanium trioxide; Silicic acid ($H_2Si_2O_5$), barium salt (1:1), lead-doped; Silicic acid, lead salt; Sulfurous acid, lead salt, dibasic; Tetralead trioxide sulphate; [Phthalato(2-)]dioxotrilead; Orange lead (lead tetroxide);	30 Aug 2012	ECHA	CMR; substances Containing Lead

Restriction / SVHC Classification	Substance Name	Submission Date	Submitted by	Comments
	Fatty acids, C16-18, lead salts; Lead titanium zirconium oxide			
	Lead(II) bis(methanesulfonate)	30 Jan 2012	Netherlands	CMR; Amides
	Lead styphnate; Lead diazide; Lead azide; Lead dipicrate	01 Aug 2011	ECHA	CMR; Substances containing lead
	Trilead diarsenate			CMR; Arsenic compounds
	Strontium Chromate	24 Jan 2011	France	CMR; Substances containing chromate
	Acids generated from chromium trioxide and their oligomers: Chromic acid; Dichromic acid; Oligomers of chromic acid and dichromic acid	27 Aug 2010	Germany	CMR; Substances containing chromate
	Chromium Trioxide	02 Aug 2010	Germany	CMR; Substances containing chromate
	Sodium chromate; Potassium chromate; Potassium Dichromate	10 Feb 2010	France	CMR; Substances containing chromate
	Lead chromate molybdate sulfate red (C.I. Pigment Red 104); Lead sulfochromate yellow (C.I. Pigment Yellow 34)	03 Aug 2009	France	CMR; substances Containing Lead
	Lead Chromate	03 Aug 2009	France	CMR; Substances containing chromate
	Lead hydrogen arsenate	27 Jun 2008	Norway	CMR; Arsenic compounds
	Sodium dichromate	26 Jun 2008	France	CMR; Substances containing chromate

Concerning the above-mentioned processes, as at present, it cannot be foreseen if, or when, new restrictions or identification as SVHC might be implemented as a result of this proposal; its implications have not been considered in the review of the exemption requests dealt with in this report. In future reviews, however, on-going research into restriction and identification as SVHC processes and the results of on-going proceedings shall be followed and carefully considered where relevant.

Table 5-6 shows the check of substitutes and alternative materials of relevance to the exemption requests evaluated in the course of this project for specific provisions under REACH, e.g. conditions of restriction in REACH Annex XVII and Annex XIV. The evaluation and recommendations of each exemption request that are presented in

the following chapters will only briefly refer to the relationship to the REACH Regulation, indicating the results of the REACH check described below.

Table 5-6: In progress: Check of conditions of restriction and authorisation in REACH Annex XVII and Annex XIV, for possible substitutes

Request No.	Substance or compounds	Specific provisions etc. under REACH
2014-1	No relevant substitutes named	n.a
2014-2	No relevant substitutes named	n.a

6.0 Exemption Request No. 2014-1: "Cadmium Anodes in Hersch cells for high-sensitivity oxygen sensors"

Abbreviations

Cat. 9	RoH2 Annex I, Category 9: Monitoring and control instruments including industrial monitoring and control instruments;
Cd	Cadmium
IMCI	Sub Cat. 9 industrial monitoring and control instruments, as defined in RoHS Article 3(24): industrial monitoring and control instruments' means monitoring and control instruments designed for exclusively industrial or professional use;
MOCON	Mocon Inc., the applicant.
NiCd	Nickel cadmium
NIST	National Institute of Standards and Technology
Pb	Lead;
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
ZrO_2	Zirconium dioxide

6.1 Background

MOCON [9] explains that Hersch Cells are used in high-sensitivity oxygen sensors capable of measuring oxygen concentrations below 100ppm. Cadmium (Cd) is present in the anodes of Hersch Cells, used in specialized, high sensitivity oxygen sensors, where, the range of oxygen detection is from 80ppt to 70ppm. An Annex IV exemption presently exists for the use of lead (Pb) in anodes of oxygen sensors.[10] While Pb is less toxic than Cd, lead anodes are unable to provide the levels of sensitivity (measurements of tens or hundreds of parts per trillion) and stability

[9] MOCON (2014a), Mocon, Inc. Original Application for Exemption, submitted 28.4.2014, available under: http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-1/Mocon-Exemption_Request_Public.pdf

[10] MOCON later specifies that Annex IV Ex. „1b Lead anodes in electrochemical oxygen sensors" is meant.

required by certain industries. Therefore, the request is made for Cd in equipment designed for sensitivity ranges where Pb is unsuitable. Against this background, MOCON request an exemption for:

"*Cadmium Anodes in Hersch cells for high-sensitivity oxygen sensors*"

The exemption is requested to be added to Annex IV and for a duration of 7 years.

Hersch cells for high-sensitivity oxygen sensors are applied in several sectors, some of them are according to the applicant's contribution critical in the sense of socioeconomic costs (see Section 6.3.3).

It is understood that MOCON is currently the only supplier of Cd based Hersch cell sensors for the global market[11].

6.1.1 Amount of Cadmium Used under the Exemption

According to MOCON [12], "the net number of sensors placed on the EU market per year is below 50 units".

The average mass of cadmium used within this application, which was sent to the EU over the last three years was ≤0.528 kg/year. However, since 1991 MOCON has had a recycling program where customers are instructed to send back the sensors when they are replaced or when the instruments are thrown out. On the basis of the average quantity of sensors which are sent back to MOCON containing Cd it is estimated that the net amount of added Cd to the EU associated with these sensors is ≤0.329 kg/year. [13]

It is important to note this is the maximum amount of cadmium placed on the market per year. This is because many of these instruments may still be in use or in inventory and not in use. The customer may have also properly recycled the sensor somewhere else, and so this is explained to reflect the worst-case scenario.[14]

6.2 Description of Requested Exemption

Due to the very specific application, Sections 6.2 through 6.4 are, by necessity, based on information provided by the applicant and other stakeholders and do not necessarily reflect the view of the consultants.

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[11] MOCON (2014b), Mocon Inc. Answers to Clarification Questions, submitted 23.10.2014, available under: http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-1/RoHS_Question_Response.pdf

[12] MOCON (2015c), E-mail communication from 23.04.2015

[13] Op. cit. MOCON (2014a)

[14] Ibid.

Electrochemical oxygen sensors are essentially small fuel cells, which use oxygen as fuel to generate current, where the size of the current is proportional to the concentration of oxygen. Within the cell an electrochemical reaction occurs:[15]

> *"The Coulox[16] oxygen [or Hersch Cell] sensor is a fuel cell that performs in accordance with Faraday's Law… A Hersch cell operates by introducing a sample gas to an electrolytic solution; in this case it is potassium hydroxide (KOH)… When exposed to oxygen, the Coulox generates an electrical current that is proportional to the amount of oxygen entering the sensor. The Coulox sensor has a carbon cathode and a Cd anode. The cathodic and anodic reactions respectively:*
>
> *1/2O2 + H2O +2e⟶ 2OH-*
>
> *Cd + 2OH- -2e⟶ Cd (OH)2*
>
> *The electrons create an electrical current, which can be used to calculate the amount of oxygen entering the Coulox sensor. As annotated, each oxygen molecule entering the Coulox results in four free electrons creating an electrical current. One mole of oxygen (22.4 liters at 0C and 760 mmHg) would produce four Faradays of current. With one Faraday = 96,500 Ampere-seconds, each mole of oxygen will produce 4 x 96,500 = 3.86 x 105 Ampere-seconds… This creates a current which is used to coulometrically determine the concentration of oxygen in solution with the electrolyte."*[17]

Coulometric detection methods in electrochemical analysis refer to detection methods in which the current is directly proportional to the flow rate of the substance involved in the electrochemical reaction, and the amount of charge, which flows, is proportional to the amount of substances taking part in the reaction.[18]

To demonstrate this in more practical terms, MOCON [19] explain: *"One cc of oxygen in 24 hours = 0.000199 Amperes of current. This means that the sensor has a sensitivity as little as 100 picoamps and a repeatability of 500 picoamps…"*

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[15] Goodman, P. (2006), Reliability and Failure Analysis : Review of Directive 2002/95/EC (RoHS) Categories 8 and 9 – Final Report, Prepared for the EU COM, Copyright ERA Technology Limited 2006, Section 10.1.3, available under: http://ec.europa.eu/environment/waste/weee/pdf/era_study_final_report.pdf, last accessed 09.03.2015

[16] It is understood that the Coulox® is MOCON's coulometric sensor.

[17] Op. cit. MOCON (2014a)

[18] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8, available under: http://goldbook.iupac.org/C01367.html, last accessed 09.03.2015

[19] Op. cit. MOCON (2014a)

6.3 Applicant's Justification for Exemption

MOCON [20] explain that alternative substances exist and are commonly used in oxygen sensors. However, for specialized applications, where stable sensitivity for measurements at the ppt level is required, there are no available substitutes. Pb is commonly used as an anode in oxygen sensors, however, it is stated that Cd has specific properties, which are necessary for high-sensitivity applications. MOCON [21] explain the main reasons why the Cd Hersch Cell oxygen sensors cannot be replaced with other technologies:

- *"The Hersch cadmium cell is "Coulometric" and follows Faraday's Law even at ppt levels. This means calibration is not required at these extreme low levels.*
- *The solubility of cadmium in KOH (electrolyte) is very low, therefore it does not migrate (like other metals) to the sensing electrode, precipitate or block the sensing electrode sights. This gives the Hersch cadmium cell extraordinary long stable sensitivity life (years). Other metals do not have the life, sensitivity or stability.*
- *It is recognised by ASTM (D-3985, F-1307, F-1927, F-2622), TAPPI, ISO, JIS, DIN and other standards worldwide."*

Additional properties of importance for the Hersch cell are provided by MOCON in a later communication[22] noting among others:

- *"Flat discharge curve (accuracy);*
- *Sensor life (charge);*
- *Inherent method of maintaining electrolyte heath over years;*
- *Temperature independent;*
- *Oxygen efficiency measurement >95%;*
- *Sensor response (fast);*
- *Specific to Oxygen (Limited cross sensitivity)."*

"In 1978 The Hersch cell had a sensitivity of 0.1 cc/m²·day (34.7ppb). Over the next 53 years improvements were made to achieve much lower levels of sensitivity. Currently the sensor has enough sensitivity to see 0.001 cc/m²·day (0.347ppb). Even at this level we have customers who would like to see even lower. The OLED and Solar panel industries would like to measure ten times lower than that at 0.0001 cc/m²·day (0.0347ppb). To get to this point it will take at least another three years of research and development.[23]

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[20] Op. cit. MOCON (2014a)

[21] Ibid.

[22] MOCON (2015a), Answers to 2nd round of clarification questions, submitted per e-mail on 24.2.2015

[23] Op. cit. MOCON (2014b)

By using Cd, the instrument is able to measure oxygen transmission down to 0.0005 cc/m2 x day which equals 170 ppt and a sensitivity of 0.0001 cc/m2 x day (equal to 34 ppt). It should be noted that 70 ppm is the highest level of oxygen that is measurable still remaining linear. The Cd is very specific to oxygen and has very few interfering gases. The sensitivity that the cadmium exhibits to oxygen without degrading over long periods of time (years) enables the sensors to have a long operative time; i.e., the long-term stability of the sensor sensitivity (years); over which the > 95% efficacy to oxygen detection does not change.[24]

6.3.1 Possible Alternatives for Substituting RoHS Substances

It is understood that there are other types of oxygen sensors, which do not contain Cd. However, *MOCON* [25] explains:

- *"All other sensor technologies require that a membrane be present to keep the electrolyte from leaving the sensor. When the membrane is present the sensors no longer directly measure all of the oxygen. This requires that the sensor be calibrated. To accurately calibrate the sensors a NIST traceable gas must be used. There are some manufacturers who claim they can make a NIST traceable gas down to 10ppm but when MOCON contacted NIST they stated they have never seen a gas that low…*[26]
- *This is critical because the lowest level of NIST calibration gas is 1 Mole% oxygen (10,000 ppm). The best "Certified" gas is about 10 ppm (± 20%) which is still 10,000 times away from where the user needs to measure accurately. All competing technologies require calibration at the testing range of interest, which there are no standards below 10 ppm.*[27]
- *There are other technologies which have been researched but they too have their own limitations. In fact MOCON uses several of these other technologies in other less sensitive instruments. They include Pb, ZrO_2 and Optical Fluorescence. These technologies all measure oxygen as low as single ppm levels and all require frequent calibration with certified gases. Other technologies have been researched but have been met with their own limitations. These include Tunable Laser Diodes, Pb, ZrO_2, other electrochemical sensors and Optical Fluorescence. They all have to be calibrated because there is no direct measurement of oxygen taking place."*[28]

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[24] Op. cit. MOCON (2014a)

[25] Op. cit. MOCON (2014b)

[26] Ibid.

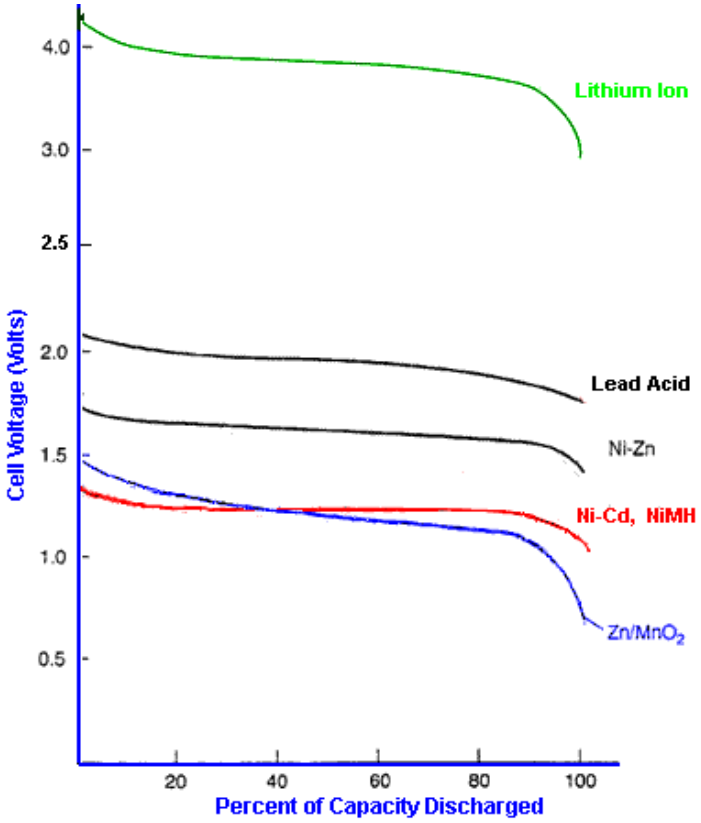
[27] Op. cit. MOCON (2014a)

[28] Op. cit. MOCON (2014b)

Available technologies for oxygen sensors are also described by Dr. Paul Goodman in section 10.1.3 of a reliability and failure analysis of Cat. 8 and Cat. 9 applications prepared for the EU COM[29]. This section of the study focuses on Pb based oxygen sensors and reviews various alternatives for such sensors. As it is understood that such sensors are less sensitive than the Hersch cells, their alternatives are not further discussed here, though a summary can be viewed in Appendix A.1.0

A flat discharge curve is explained to be important for the accuracy of the sensor. MOCON [30] provide the following diagram comparing the discharge curve of the NiCd sensor (used in the Hersch cell) with other sensors such as a lead-acid sensor. The cell voltage of a Pb sensor is explained to decay constantly over the entire curve (↓6-7%) from 10% to 90% range. The NiCd is almost flat over the same discharge range. Since there is no calibration gas at the ppb and ppt levels of oxygen this becomes an important characteristic of Cd. A comparison of the discharge curve of the NiCd sensor with other sensors is shown in Figure 6-1.

Figure 6-1: Comparison of discharge curve of NiCd sensor (used in the Hersch cell) with other sensors



Source: Op. cit. MOCON (2015a)

[29] Op. cit. Goodman (2006)

[30] Op. cit. MOCON (2015a)

The applicant summarises that alternatives for the Cd Hersch Cell that can fulfil its respective applications are currently not known.[31]

6.3.2 Environmental Arguments

MOCON emphasizes the limitations of possible alternatives to justify their request. Such alternatives are not observed as comparable in their performance to the Cd based Hersch Cells. Thus, MOCON does not provide detail as to possible direct environmental and health impacts related to these alternatives.

The consultants assume that Cd is considered to be more toxic than Pb, in light of the lower threshold specified for it in Annex II of the Directive (0.01 and 0.1% weight respectively). However, MOCON [32] explain that Cd has specific properties, which are necessary for high-sensitivity applications and it is understood that Pb oxygen sensors would not cover the same measurement range in light of their lower sensitivity.

Since 1991, MOCON [33] has maintained a program where end-of-life sensors are returned to its facility in the United States for recycling. Every sensor, which contains Cd plaques and is shipped to clients, has a label marked: "RETURN EXPENDED SENSOR TO MOCON FOR DISPOSITION" on the device. This is a global label, which is present on every sensor installed or shipped. When MOCON receives back the Cd [sensors], they are shipped to Green Lights Recycling Inc., which has stated that the Cd is designated for recycling and reuse, and not sent to a landfill. For sensors placed on the EU market, it is estimated that ≥ 0.199 kg/annum of Cd is recycled through this practice. The applicant notes that it is also possible that some articles are recycled by EU-based WEEE service providers, which means that the total amount could be higher.

6.3.3 Socio-economic Impact of Substitution

To clarify possible socio-economic impacts, MOCON [34] explains that there are several users of high-sensitivity oxygen sensors requiring ppt measurements. Applications affecting human health and the environment include:

- "*The pharmaceutical industry uses Hersch cell sensors to ensure certain medications are protected from oxygen. This is required to maintain strength, and therefore public safety. The high instrument sensitivity is required to manufacture some medicines, which are very sensitive to even trace amounts of oxygen.*
- *Freshness and Safety in food packaging design, which requires ppt sensitivity, is the largest application of Hersch cell sensor technology. This affects consumer safety and potentially human health.*

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[31] Op. cit. MOCON (2014a)

[32] Ibid.

[33] Ibid.

[34] Ibid.

- *The solar panel industry relies on ppt oxygen sensors instruments to measure their high oxygen barriers. Oxygen barriers are required in order to prolong the lifetime of the panels. Long-lasting Solar Panels are necessary to generate "green" energy; which results in benefits for the environment.*
- *Similarly, the OLED industry requires oxygen barriers in order to create OLED screens. Only very sensitive instruments using Hersch cells are capable of measuring at the levels they require."*

Concerning the question, if the impacts of substitution outweigh the benefits thereof, MOCON [35] make a statement in reference with some of the industries mentioned in which oxygen sensors based on the Hersch Cell's Cd anode are used. It is explained that for the net gain associated with eliminating 0.52 kg of Cd annually from the EU market, *"substitution of Hersch cells with lead-based instruments would result in (among other impacted industries):*

- *Specific medicines being unable to be reliably manufactured;*
- *Loss of integrity in food packaging design;*
- *Decreased lifespan of solar panels."*

6.3.4 Road Map to Substitution

It is understood that MOCON is investigating other anode materials for use as substitutes for the Cd sensor, but there are proprietary issues that need to be overcome to begin studies on different materials. It is further explained, "*the length of a sensor development project can be 1 year or 10 years or never. The last electrochemical sensor development took 6-7 years. The last improvement (not the same as development) made in the Cd Coulox sensor took 3 years (only one component changed). It depends on how many components or materials or geometries have to be changed to accommodate the new anode*".[36]

6.4 Stakeholder Contributions

No contributions were received during the stakeholder consultation concerning this request.

6.5 Critical Review

6.5.1 REACH Compliance - Relation to the REACH Regulation

Section 5.0 of this report lists Entry 23 restricting the use of Cd and its compounds in Annex XVII of the REACH Regulation. This entry restricts the use of Cd in various materials and articles, including:

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[35] Op. cit. MOCON (2014a)

[36] Op. cit. MOCON (2015a)

- In mixtures and articles produced from a number of synthetic organic polymers referred to as plastic materials (paragraph 1);
- In paints and painted articles (paragraph 2 & 3);

In cadmium plated articles or components of articles used and manufactured in various sectors (paragraph 5 & 6 - see detail in

- Table 5-2 in Section 5.0);
- Brazing fillers (paragraph 8 & 9);
- Jewellery (paragraph 10 & 11);

To clarify the relevance of the various restrictions, MOCON were asked if the application for which this exemption request has been made could be in the scope of the restrictions addressed in Item 23.

MOCON [37] explains that "*the items listed in Annex 1: REACH List of Restrictions (Annex XVII) Item 23 are not related to the Hersch cell*". When asked if the application for which this exemption request has been made is covered by one of the items in restriction 23 MOCON details:

> "*1. Does not cover our application, not producing plastic materials*
> *2. Does not cover our application, not producing paint*
> *3. Does not cover our application, not producing mixtures for safety reasons*
> *4. Does not cover our application, not recycling plastics*
> *5. Does not cover our application, not plating cadmium*
> *6. Does not cover our application, not plating cadmium*
> *7. Does not cover our application, not plating cadmium for aerospace or safety devices*
> *8. Does not cover our application, not brazing*
> *9. Does not cover our application, not brazing for aerospace or safety devices*
> *10. Does not cover our application, not producing jewellery*
> *11. Does not cover our application, did not produce jewellery before Dec 10, 2011*"

On this basis, it can be followed that the Hersch cell oxygen sensors would not be affected by this entry.

Entry 28 and 30 of Annex XIV of REACH stipulate that various cadmium compounds shall not be placed on the market, or used, as substances, constituents of other substances, or in mixtures for supply to the general public. A prerequisite to granting the requested exemption would therefore be to establish whether the intended use of cadmium in this exemption request might weaken the environmental and health protection afforded by the REACH Regulation related to these entries.

In the consultants' understanding, the restriction for substances under entries 28 and 30 of Annex XVII does not apply to the use of Cd in this application. Cd used as an

[37] MOCON (2015b), Mocon Inc., Response to 3rd round of clarification answers, submitted per email on 20.04.2015

anode material in oxygen sensors placed on the market. In the consultants' point of view this is not a supply of Cd and its compounds as a substance, mixture or constituent of other mixtures to the general public. Cd is part of an article and as such, entries 28 and 30 of Annex XVII of the REACH Regulation would not apply. Additionally, the sensors of relevance are products that are not provided to the general public, but to industrial users requiring high-sensitivity oxygen measurement.

No other entries relevant for the use of cadmium in the requested exemption could be identified in Annex XIV and Annex XVII (status March 2015).

Based on the current status of Annexes XIV and XVII of the REACH Regulation, the requested exemption would not weaken the environmental and health protection afforded by the REACH Regulation. An exemption could thus be granted if other criteria of Art. 5(1)(a) apply.

6.5.2 Scientific and Technical Practicability of Substitution

MOCON [38] provides information concerning alternative types of oxygen sensors, as well as concerning alternative substances that could be used to replace Cd in the anode, explaining that these alternatives could not substitute or eliminate the use of Cd in the Hersch cell sensors. MOCON claims that the exemption is in line with Article 5(1)(a) since the

> "*elimination or substitution via design changes or materials and components which do not require any of the materials or substances listed in Annex II is scientifically or technically impracticable*".

MOCON further explains that an Annex IV application exemption presently exists for lead in anodes of oxygen sensors. While lead is understood to be less toxic than cadmium, MOCON state that lead anodes are unable to provide the levels of sensitivity (measurements of tens or hundreds of parts per trillion) and stability required by certain industries. Therefore, the request is made for cadmium in equipment designed for sensitivity ranges where lead is unsuitable.

It is understood that, although alternative technologies exist on the market, these would not be suitable for applications that require the high sensitivity of the Cd Hersch Cell. It can also be followed that the frequent need to calibrate other sensors would further limit their use in the measurement range for which the Cd Hersch cell is used, as also reflected in the statement below:

> *"These technologies all measure oxygen as low as single ppm levels and all require frequent calibration with certified gases. Other technologies have been researched but have been met with their own limitations. These include Tunable Laser Diodes, Pb, ZrO2, other electrochemical sensors and Optical Fluorescence. They all have to be calibrated because there is no direct measurement of oxygen taking place"* [39]

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[38] Op. cit. MOCON (2014a)

[39] Op. cit. MOCON (2014b)

One could argue if this explanation should be interpreted as a lack of alternatives, or as a limitation of the existing ones in terms of their reliability within the measurement range for which the Hersch cell is applied. However, in any case, the consultants can follow that on this basis an exemption would be justified in line with Article 5(1)(a), as at least one of the criteria is fulfilled.

6.5.3 Scope of the Requested Exemption – Product Categories and Sub-Groups

MOCON [40] originally requested the exemption "*Cadmium anodes in Hersch cells for high-sensitivity oxygen sensors*" to be added to Annex IV and specified that the exemption was relevant for industrial monitoring and control instruments (IMCI - Sub-Cat. 9 Industrial).

MOCON were asked to clarify if sensors are used for other than industrial monitoring and control purposes and answered that *"The instruments containing the Hersch cell are analytical equipment which measure oxygen. There is no other use known for the Hersch cell outside of analytical equipment."*[41]

On this basis, it is concluded that the exemption is only needed for IMCI, which need to comply with the RoHS substance restrictions starting 22.07.2017. This understanding was reflected in the formulation of the stakeholder consultation questionnaire, furthermore asking stakeholders whether they agreed with the scope of the exemption. As no contributions were made, it is concluded that the applicability of a possible exemption could be limited to IMCI. This aspect is reflected in the proposed wording formulation recommended in Section 6.6.

6.5.4 Environmental Arguments

MOCON [42] provides information concerning the waste management program of its sensors at end-of-life, estimating that ≥ 0.199 kg/annum of Cd is recycled through returning end-of-life sensors to the vendor. Putting this in context, MOCON estimates the average annual mass of cadmium sent to the EU over the last three years associated with these devices is in the order of 0.5 kg.

MOCON further notes that it is possible that some articles may be recycled by EU-based WEEE service providers, which would mean that the overall amount recycled is possibly higher. The consultants cannot follow this view. It is plausible that the remaining sensors are indeed collected through existing WEEE collection schemes. In this sense, it can be followed that such sensors are to be handled with other WEEE and shall not be sent to landfills. However, the market price for Cd is relatively low[43] and is not expected to motivate recyclers to target the sensors for specific recycling

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[40] Op. cit. MOCON (2014a)

[41] Op. cit. MOCON (2014b)

[42] Op. cit. MOCON (2014a)

[43] See for example Cd prices for the last 6 months under http://www.metalprices.com/p/CadmiumFreeChart

programs, particularly given the small Cd quantities at hand (less than 1 kg of Cd/annum) and the small number of sensors placed on the market per annum (net number below 50 units). Of the remaining sensors not returned to the vendor, these are very unlikely to all reach a recycling facility where a successful cadmium extraction and recycling operation may be practiced for these uncommon devices. Though the remaining sensors are probably properly handled, the consultants cannot conclude on the basis of the available information that more than the estimated 0.199 kg/annum Cd is recycled from used sensors. That said, MOCON does not refer to the environmental aspects of the sensors as its main argumentation for justifying an exemption. The legislation dictates that as long as one of the Article 5(1)(a) criteria is fulfilled an exemption could still be granted.

6.5.5 Discussion of Wording Formulation

The applicant has requested an exemption with the following wording formulation.

"Cadmium Anodes in Hersch cells for high-sensitivity oxygen sensors"

Though this formulation limits the applicability of a future exemption for Cd to its use in anodes in Hersch cells, in the consultants' opinion the reference to a sensitivity level remains vague in the formulation *"high sensitivity sensors"*. To avoid misuse of a possible exemption, the consultants would recommend limiting the scope of application of an exemption to the relevant level of sensitivity at which the use of Cd in the Hersch cell is indispensable.

The applicant[44] has stated that the Hersch Cell Cd anode is used in high-sensitivity oxygen sensors capable of measuring oxygen concentrations below 100ppm, also specifying that this application is used where, the range of oxygen detection is from 80ppt to 70ppm. In the consultants opinion, though it can be followed from these statements that the Cd-based Hersch Cell can be used at these sensitivities, data was not provided in the application or in the initial clarification rounds, to confirm that other oxygen measurement technologies cannot be used to cover part of the measurement range below 100 ppm. The consultants' believe this is also reflected in the applicants statement "*lead anodes are unable to provide the levels of sensitivity (measurements of* ***tens or hundreds of parts per trillion****) and* ***stability*** *required by certain industries*". MOCON [45] states that *"there is no NIST traceable gas or method to calibrate below 10ppm"*, however this would still mean that other technologies could be used for sensitivities above 10 ppm, as long as the need for calibrations is feasible.

On this basis, the applicant was requested to clarify if there are overlaps between the range of measurement of the Hersch cell and other measurement technologies in which Cd is not in use. It was further asked if other requirements would limit the use

[44] Op. cit. MOCON (2014a)

[45] Op. cit. MOCON (2014b)

of alternative technologies in the overlapping range (i.e., the need for frequent calibration to retain sensitivity). MOCON [46] responded that:

> *"Other oxygen measurement technologies are numerous… over ninety percent (90%+) of all oxygen sensors measure somewhere in the range of 0.1% (1000 ppm) to 100% O_2. There are even some that can measure from 0.01% (100 ppm) to 21% O_2. There are a handful that can measure from 1ppm to about 10,000 ppm (1% O_2). And there are only 2 or 3 oxygen sensors (lead electrochemical) that can measure below 1ppm (100ppb)… but none of these technologies have "80 ppt" oxygen sensitivity. As can be seen there are only a couple of sensors that have some overlap with the Coulox (Hersch) sensor, but these sensors don't meet RoHS requirements either (lead)."*

Regarding calibration requirements, the applicant further explains:[47]

> *"All of the above sensor technologies have calibration and accuracy problems at levels below 10ppm of oxygen…because they are not Coulometric… This is critical because 99.9% of the measurement range for Permeation testing is below the lowest available calibration gas (10ppm) and far below the 2 mole% (20,000 ppm) lowest available reference gas from NIST… If this technology (Hersch cell) is rejected the entire packaging industry would be left without a standard oxygen permeation measurement method. Also the safety of food would be in jeopardy."*

The consultants conclude that the scope of a possible exemption could thus be limited to the range of measurement below which other technologies cannot measure. The consultants can follow the applicants statement that there are no alternatives for the Hersch Cell in specialized applications, where stable sensitivity for measurements at the ppt level is required. It is also understood that technologies that could measure below 10 ppm in theory would not be practical in light of the problems with calibration at this level. MOCON have explained that 99.9% of the measurement range for permeation testing is below this level, and it is thus assumed that the Hersch cell is also used mainly for measurement of such sensitivities. However, it was not clear whether some of the applications of the Hersch cell are dedicated specifically to measurements within the 10-ppm to 70 ppm range, in cases where frequent calibration is a disadvantage. MOCON were thus asked, whether the sensors are sometimes used specifically for measurements within this range, in cases where frequent calibration must be avoided. MOCON [48] responded:

> *"Yes, the standard measurement range for the permeation instrument is up to 70 ppm, this is not a "supplementary" range, but the practical useable range for the instrument… Typically there are not applications for which only the 10-70 ppm range is required, standard usage of the instrument utilizes the entire range."*

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[46] Op. cit. MOCON (2015b)

[47] Ibid.

[48] MOCON Inc. (2015d), e-mail communication from 01.06.2015

In a later communication, MOCON [49] further confirmed that limiting the scope of a possible exemption, by using a 10 ppm threshold related to the required measurement sensitivity, would be adequate. Such a "threshold" though limiting the areas where the device could be applied based on the required measurement sensitivity, is not understood to affect the ability of the device to measure levels higher than the suggested threshold.

As mentioned in Section 6.5.3, it is understood that the application is only used in industrial monitoring and control instruments, and it is thus further recommended to limit the exemption to this product category.

6.5.6 Conclusions

Article 5(1)(a) provides that an exemption can be justified if at least one of the following criteria is fulfilled:

- their **elimination or substitution** via design changes or materials and components which do not require any of the materials or substances listed in Annex II is scientifically or technically impracticable;
- the **reliability** of substitutes is not ensured;
- the total negative **environmental, health and consumer safety impacts** caused by substitution are likely to outweigh the total environmental, health and consumer safety benefits thereof.

From the information provided by MOCON, it is clear that there exist alternative oxygen sensors, some of these also containing Pb, which is also a restricted substance under the RoHS Directive. Nonetheless, it can be followed that alternative technologies (with Pb and without) do not provide the same sensitivity and accuracy related to the Hersch Cell sensors at the relevant measurement range - oxygen measurement at very low levels. Though some of the other technologies could be applied at such levels in theory, the explanation that their need for calibration at such levels would not allow their use in practice can be followed. In this sense, though alternatives may exist that could be used for high sensitivity measurements, it is understood that the calibration limitations would not provide for a sensor with comparable sensitivity and reliability below a measurement level of 10ppm oxygen. Below this level, an exemption would thus be in line with Art. 5(1)(a), as at least one of the three main criteria would be fulfilled. As this threshold is understood to be related to the sensitivity performance requirement of some measurement applications, the devices ability to measure above this level in practice is understood not to be affected.

The applicant has explained that the length of a sensor development project can vary from 1 to 10 years, assuming it is successful. To demonstrate this, examples are given as to the development time required the last time one component was changed in a sensor (this being 3 years), and the development time for the last produced new

[49] MOCON Inc. (2015e), e-mail communication from 11.06.2015

electrochemical sensor (6-7 years). The applicant has requested the exemption for the maximum duration of 7 years. On the basis of prior knowledge of the redesign cycles common for IMCI, the consultants can follow that additional time could also be needed once a candidate was found in order to bring it onto the market in the form of an oxygen sensor (e.g. time for redesign and recertification). The consultants thus find it plausible that a suitable substitute shall not come onto the market within the next 7 years.

6.6 Recommendation

The consultants recommend granting an exemption as follows:

> *Cadmium anodes in Hersch cells for oxygen sensors used in industrial monitoring and control instruments, where a sensitivity below 10 ppm is required.*

The exemption duration is recommended to be 7 years from the time the exemption is approved.

Should an exemption be granted, it should be added to Annex IV of the RoHS Directive.

6.7 References Exemption Request 2013-6

Goodman (2006) Goodman, P. (2006), Reliability and Failure Analysis : Review of Directive 2002/95/EC (RoHS) Categories 8 and 9 – Final Report, Prepared fort he EU COM, Copyright ERA Technology Limitted 2006, Section 10.1.3, available under: http://ec.europa.eu/environment/waste/weee/pdf/era_study_final_report.pdf,http://ec.europa.eu/environment/waste/pdf/era_study_final_report.pdf last accessed 09.03.2015

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7.0 Exemption Request No. 2014-2: "Lead in solders used to make electrical connections to temperature measurement sensors designed to be used periodically at temperature below -150°C"

Abbreviations

Ag	Silver
Au	Gold
He	Helium
K	Kelvin (0 K = –273.15°C)
LSC	Lake Shore Cryotronics
mK	milli-Kelvin
NTC	Negative Temperature Coefficient
OEM	Original Equipment Manufacturer
Pb	Lead
Pd	Palladium
PPMS	Physical Properties Measurement Systems
PTC	Positive Temperature Coefficient
RTD	Resistance Temperature Detectors
Sn	Tin

7.1 Demarcation of the Requested Exemption from Exemptions in RoHS Annex IV

Exemption 26 in RoHS Annex IV covers the use of "*lead in*

- *solders on printed circuit boards,*
- *termination coatings of electrical and electronic components and coatings of printed circuit boards,*
- *solders for connecting wires and cables,*
- *solders connecting transducers and sensors,*

that are used durably at a temperature below –20°C under normal operating and storage conditions."

Lake Shore Cryotronics (LSC) produces sensors that are temporarily used at temperatures below –150°C under normal operating and storage conditions, as reported by LSC[50]. Exemption 26 in RoHS Annex IV therefore does not cover the use of lead in LSC's sensors in devices where they are only operated temporarily below –20°C.

Exemption 27 in RoHS Annex IV authorises the use of "*lead in*

- *solders,*
- *termination coatings of electrical and electronic components and printed circuit boards,*
- *connections of electrical wires, shields and enclosed connectors,*

which are used in

(a) magnetic fields within the sphere of 1 m radius around the isocentre of the magnet in medical magnetic resonance imaging equipment, including patient monitors designed to be used within this sphere, or

(b) magnetic fields within 1 m distance from the external surfaces of cyclotron magnets, magnets for beam transport and beam direction control applied for particle therapy."

LSC[51] agrees that exemption 27 covers parts of its sensor applications, but excludes the uses of the sensors in other types of equipment that are not described in the above exemption, as is the case for most of the applications listed on page 47.

LSC[52] requests an exemption to be added to Annex IV for

"Lead in solders used to make electrical connections to temperature measurement sensors designed to be used periodically at temperatures below -150°C."

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[50] LSC (2014a), Lake Shore Cryotronics exemption request document "Lake Shore Submission.pdf", retrievable from http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-2/Lake_Shore_Submission.pdf; accessed 27 January 2015

[51] LSC (2014b), Lake Shore Cryotronics document "20141002_answers_Questionnaire-1_Clarification_Exe-Req-2014-2", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM; retrievable from http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-2/20141002_answers_Questionnaire-1_Clarification_Exe-Req-2014-2.pdf; accessed 27 January 2015

[52] Op. cit. LSC (2014a)

7.2 Description of Requested Exemption

7.2.1 Technical Background

According to LSC[53], cryogenic sensors are used in a very wide variety of applications, both for research and in original equipment manufacturer (OEM) equipment. Many of the uses are out of scope of RoHS such as in satellites, and in the Hubble Space telescope, which has been in use for 24 years already.

LSC[54] states that the following types of cryogenic sensors are available:

- positive temperature coefficient (PTC) resistance temperature detectors (RTDs) such as platinum detectors;
- negative temperature coefficient (NTC) RTDs such as germanium and Cernox detectors;
- diodes such as silicon; and
- capacitance type diodes.

The characteristics of these temperature sensors, as provided by LSC[55], are identified in

Table 7-1.

Table 7-1: Characteristics of temperature sensors in the scope of the exemption request

Type	Temperature range (K)	Immunity to ionising radiation	Performance in magnetic fields
Semiconductor (diodes)	1.4 to 500		Fair
NTC	0.01 to 325 (depends on material)	Yes	Cernox and RuO2 have good performance
Capacitance	1.4 to 290		Excellent
PTC	0.65 to 873 (depends on type)	Yes	Fair above certain temperatures

Source: LSC[56]

LSC[57] describes the sensors as very small components, for example 3 mm x 2 mm, 1.5 mm x 0.6 mm x 0.25 mm, 1.3 mm diameter discs. All of them have two or four

[53] Op. cit. LSC (2014a)

[54] Ibid.

[55] Ibid.

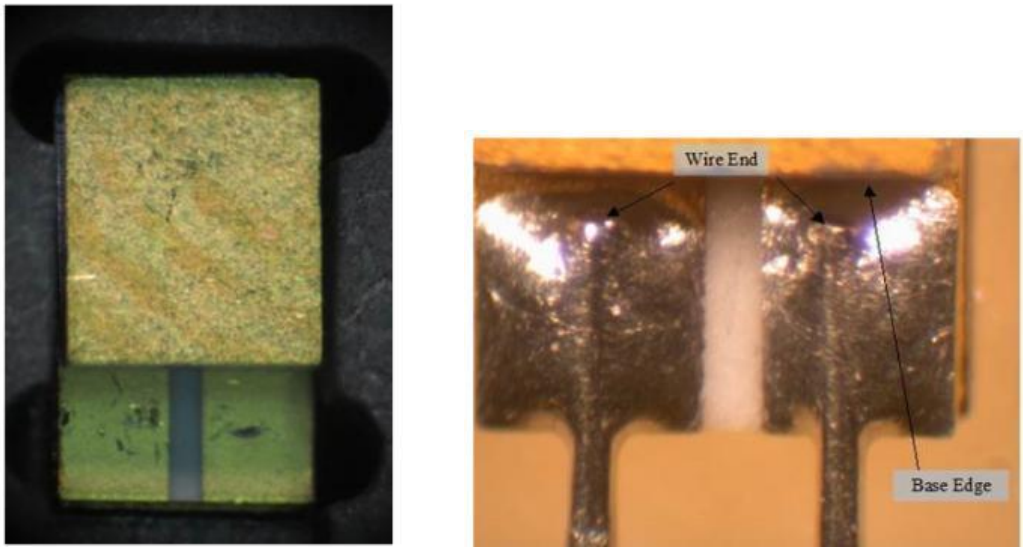
[56] Ibid.

[57] Ibid.

electrical connections, but not all use solder to make electrical connections. Close up photographs of typical sensor subassemblies are shown in

Figure 7-1.

Figure 7-1: CX[58] Sensor subassembly prior to external leads attachment (left), close-up of pad after attachment with Sn63Pb37 Solder



Source: LSC[59]

LSC[60] explains that each type of sensor has different material and design requirements. A wide variety of sensor designs are used because each application has different size, function and performance requirements. Some types of sensors must use only non-magnetic materials, which excludes nickel barrier layers and magnetic alloys. Copper and gold plated copper terminals and palladium/silver thick-film material are commonly used as non-magnetic termination coatings on a wide variety of electrical components.

According to LSC[61], a few types of PTC sensors are designed for cryogenic measurement, so tin-based lead- free solders cannot be used. These sensors are sold directly to end-users who use them in their own equipment that they construct for

[58] A CX (Cernox™) SD is a thin film resistance temperature sensor that is used at temperatures as low as 100 mK. (273.05 °C) according to
LSC (2015c). Lake Shore Cryotronics document "Questionnaire-5_Exe-Req-2014-2_answered.docx", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 8 April 2015

[59] Op. cit. LSC (2014a)

[60] Ibid.

[61] Ibid.

own use, as well as to OEMs who make commercial equipment. LSC[62] claims that within the scope of the RoHS Directive, its sensors are only used in equipment of categories 8 and 9 as described by RoHS Annex I (medical devices and monitoring and control instruments). Examples of such OEM equipment are:

- Dilution refrigerators: temperature measurements down to 8 mK (milli-Kelvin);
- Adiabatic demagnetization refrigerators: temperature measurements down to 50 mK;
- Closed cycle refrigerators: temperature measurements down to 4 K (-269.15°C);
- He3 refrigerators: temperature measurements down to 300 mK (–272.85°C);
- He4 refrigerators: temperature measurements down to 1 K (–272.15°C);
- High magnetic field-based characterization systems: Measurements down to around 1.2 K (–271.95°C);
- He bath cryostats: temperature measurements down to 1 K (–272.15°C);
- Dry (cryogen-free) systems: temperature measurements down to 8 mK (-273.142°C);
- Sensors sold to universities and used for research and development. These may be used for many years, and in some cases decades, at a wide range of temperatures.

LSC[63] highlights the main characteristic of the above applications, which is that the sensors measure very low temperatures (down to 0.01 K; –273.14°C) and may also measure higher temperatures up to 873 K (~ 600°C). The time at any temperature will be extremely variable depending on the application. In some, the sensor will be at very low temperatures for many years, in other applications, temperature will rise and fall so that sensors are at low temperature for many shorter periods.

LSC[64] explains that solder with 37% lead is used for electrical connections to cryogenic sensors to prevent the formation of thick intermetallic phases, whiskers, and tin pest.

7.2.2 Amount of Lead Used under the Exemption

The requested exemption would allow the use of lead in lead solders for the applications described here. LSC[65] uses lead solder with 37% of lead. LSC[66]

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[62] Ibid.

[63] Op. cit. LSC (2014a)

[64] Ibid.

[65] Ibid.

[66] Op. cit. LSC (2014b)

estimates that far less than 10 kg of lead would be used under this exemption for the European Union market.

7.3 Applicant's Justification for the Exemption

LSC[67] explains that lead is a component of the solder used to make electrical connections to the sensors. During use, the solder bond experiences very large temperature changes including very low temperature. As a result of these changes, high levels of stress can be imposed on the solder joint. Lead is added to the solder for several reasons (LSC[68]):

- Lead most effectively inhibits tin pest phase transformation occurring with tin and its alloys at low temperature;
- Lead-tin solder is relatively ductile at low temperature. It is much more flexible than the most commonly used lead-free solders, welded bonds and conductive adhesives;
- Very low electrical resistivity within the temperature range of use and relatively high thermal conductivity;
- Resistance to oxidation and corrosion in conditions of use; and
- Lead gives a high resistance to tin whisker formation on electroplated tin coatings.

LSC[69] highlights that when soldering, it is important to avoid forming too thick intermetallic phases as these are brittle and can crack under stress. Lead solder melts at lower temperatures than most lead-free solders and its wetting properties are superior. Intermetallic phases with lead solders tend to be thinner and so are less susceptible to brittle fracture. This is also important on silver palladium (Ag/Pd) thick-film terminations because, the entire thickness of the Ag/Pd layer can be lost if the soldering temperature is too high and if the Ag/Pd is in contact with molten solder for too long. Ag/Pd/Sn intermetallic phases form, which are relatively brittle and prone to cracking.

LSC[70] explains that some types of sensors are hermetically sealed with gold-tin solder and so electrical connections must be made with a lower temperature bonding method, which excludes the use of welding and brazing due to their high process temperatures. Other sensors are made of ceramic materials to which electrical connections are made directly by soldering to metallised pads. These ceramics are relatively brittle materials so brazing or welding are unsuitable as the high temperature would cause cracking.

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[67] Op. cit. LSC (2014a)

[68] Ibid.

[69] Ibid.

[70] Ibid.

LSC[71] states that lead based solders have had a very long and successful history of use at cryogenic temperatures, for over 50 years and have proven to be very reliable. Review of published literature has identified very few studies that evaluated lead-free solders to determine whether they will or will not be reliable with devices cycled at low temperatures. This literature indicates that potential failure modes which can occur with high tin solders in cryogenic applications include tin pest, embrittlement and cracking on thermal cycling. These devices are stressed during the large temperature cycles. From ambient temperature down to 1 K (–272.15 °C) represents a temperature range of around 292 °C. Evaluations of lead-free solders have not been carried out at these very low temperatures to find reliable substitute solders. The lack of substitutes with proven reliability is a concern to users of these sensors who require long-term high reliability.

LSC[72] quotes the literature. *"Wiring connections made with solders containing a high percentage of tin can embrittle and crack after repeated thermal cycling between room temperature and cryogenic temperatures."*[73] The following alloys should preferably be used *"For electrical wiring: 63%Sn-37%Pb or 63%Sn-36.65%Pb-0.35%Sb eutectic solder (T_{melt} = 183 °C); or 93%Pb-5.2%Sn-1.8%Ag for a higher melting-temperature solder (T_{melt} = 299 °C). The antimony in the alternative lower T_{melt} solder minimizes embrittlement and cracking, a potential problem that can occur in high-tin solders after repeated thermal cycling to cryogenic temperatures."*[74]

In reference to the above citation, LSC[75] quotes the comment of Lake Shore Director of Metrology and physicist John Krause, PhD: *"Several years ago I contacted the author about this comment. He made this comment based more on observations than any accumulation of data and he had no hard data to give me. He gave me the name of another person to talk to, which I can't remember, but that never came through with anything more firm."*

LSC[76] states that the reliability of an alternative bonding method will require very lengthy research and testing because many of the failure modes that occur at very low temperature cannot be accelerated.

LSC[77] lists alternative bonding materials and technologies as potential alternatives to SnPb solder.

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[71] Op. cit. LSC (2014a)

[72] Ibid.

[73] Jack W. Ekin (2006) *Experimental Techniques for Low-Temperature Measurements*, in Oxford University Press, p.162

[74] Jack W. Ekin (2006) *Experimental Techniques for Low-Temperature Measurements*, in Oxford University Press, p.105

[75] Op. cit. LSC (2014a)

[76] Ibid.

[77] Ibid.

7.3.1 Substance Alternatives

7.3.1.1 Lead-free Solder Alloys

It can be understood that various lead free solder alloys have been tested, however LSC argues that the reliability of such substitutes to be applied as alternatives is insufficient in cryogenic applications in the scope of the requested exemption.

7.3.1.1.1 Resistance to Tin Pest

Tin pest has been known for many decades but most research has been carried out at temperatures between −50 and −30 °C because the phase transformation occurs most rapidly within this temperature range and because testing at liquid helium temperatures is difficult to carry out. The rate of tin pest transformation depends on two distinct processes occurring. The first is nucleation where minute α-phase tin particles are formed within the β-phase tin. The driving force for nucleation is the temperature distance between 13 °C and the actual temperature. The driving force for nucleation increases as the temperature drops. Nucleation usually requires a defect such as a grain boundary or a particle of impurity, but the time for nucleation to occur varies considerably. (LSC[78])

The second process is phase transformation where the α-phase grows from the initial nucleation sites. The rate at which this occurs also varies considerably depending on the alloy composition and its history as this affects crystal structure, as well as on the temperature. (LSC[79])

The Open University research tested SnCu, SnAg, SnAgCu and SnZnBi alloys that were treated to simulate the effects on real solder joints and so are more realistic. The alloys were cast with three different cooling rates and the most realistic, fast cooling showed the highest likelihood of phase transformation. All samples are included in the table below, which shows the percentage of samples that exhibit more serious signs of phase transformation. (LSC[80])

Table 7-2: Percentage of samples with phase transformation

Alloy	−18 °C 8 years	−18 °C 10 years	−40 °C 8 years	−40 °C 10 years
SnPb	none	with 11.4%	none	37.5%
SnCu	35.8%	71.7%	14%	58.1%
SnAg	3.8%	22.9%	37.3%	98.7%

[78] Op. cit. LSC (2014a)

[79] Ibid.

[80] Ibid.

Alloy	−18°C 8 years	−18°C 10 years	−40°C 8 years	−40°C 10 years
SnAgCu	24.2%	56.6%	10%	20%
SnZnBi	100% of samples suffered from tin pest at −40°C after six years	100% of samples suffered from tin pest at −40°C after six years	100% of samples suffered from tin pest at −40°C after six years	100% of samples suffered from tin pest at −40°C after six years

Source: Open University; source as indicated by LSC[81]

Research published in 2005 by a Japanese solder manufacturer found the percentages of transformation at −45°C as identified in

Table 7-3. (LSC[82])

Table 7-3: Percentages of test samples with phase transformation at −45°C

Additive to 99.99% tin	After 10 hours	After 30 hours
Tin only	80%	100%
0.01% Sb	100%	100%
0.01% Cu	100%	100%
0.01% Zn	100%	100%
0.01% Ag	5%	78%
0.01% Bi	0.5%	3.0%
0.01% Pb	0%	0%

Source: Keith Sweatman (2005) Suppression of Tin Pest in Lead-free Solders, JEDEX conference, San Jose, USA; source as indicated by LSC[83]

According to (LSC[84]), these results confirm that copper accelerates the transformation whereas silver delays but does not prevent transformation, compared to pure tin, but

[81] Op. cit. LSC (2014a)

[82] Ibid.

[83] Ibid.

[84] Ibid.

is far less effective than lead. It is often claimed that antimony can suppress tin pest but these results show that small additions are ineffective. Apart from lead, 0.01% bismuth had the greatest delaying effect but even after only 30 hours, 3% had transformed so that after sufficient time, the transformation would be complete. Lead was the most effective with no phase transformation being observed in this test. Solders used with cryogenic sensors however experience much lower temperatures than –45 °C, and the sensors are used within a wide range of temperatures.

The report of Oeko[85] contains more details on tin pest and how it affects the reliability of solder joints.

7.3.1.1.2 Suitability for Soldering to Non-magnetic Terminals

As nickel barrier layers cannot be used, LSC[86] claims it is important that wetting times are short and substrate dissolution rates are as low as possible, so that the solder pad is not lost completely during soldering, and that brittle intermetallic layers are as thin as possible to avoid brittle fracture.

7.3.1.1.3 Ductility

According to LSC[87], there is no published research into the effect of thermal cycles that include very low temperatures and so it is possible only to estimate the likely effect on reliability. It is known that all solders become harder and much more brittle as temperature decreases, and most lead-free solders are harder than SnPb. Harder solders are likely to induce higher stress levels that would be more likely to cause more damage to the substrate or the solder. Relatively soft and ductile materials can deform to relieve any stresses that will occur as a result of differential thermal expansion that will occur when temperature changes, whereas brittle materials will not deform so high stress forces will be induced. When attached to brittle ceramic materials that are used for some types of sensors, the high strain imposed by very hard and non-ductile solder substitutes may cause damage to the ceramic or cause metallised bonds used for electrical connections to detach from the surface of the sensors.

7.3.1.1.4 Tin Whiskers

LSC[88] claims that tin whiskers grow from tin and tin alloys that are under compressive stress and can cause short circuits. Tin whiskers usually grow fairly slowly so that

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[85] Oeko (2012), Gensch, C.-O.; Baron, Y.; Blepp, M.; Manhart, A.; Moch, K., Oeko-Institut; Deubzer, O., Fraunhofer IZM: Assistance to the Commission on technological, socio-economic and cost-benefit assessment related to exemptions from the substance restrictions in electrical and electronic equipment (RoHS Directive), December 2012; retrievable from http://rohs.exemptions.oeko.info/fileadmin/user_upload/Rohs_V/RoHS_V_Final_report_12_Dec_2012_Final.pdf; accessed 28 January 2015, p. 66 et seq.

[86] Op. cit. LSC (2014a)

[87] Ibid.

[88] Ibid.

failures occur after many years or even decades. This is usually associated with electroplated tin as this is often in compressive stress. The behaviour of lead-free solders at very low temperature has not been studied over long periods and tin whisker formation cannot be ruled out.

7.3.1.1.5 Long-term Reliability at Low Temperatures

According to LSC[89], there is very little research on the low temperature properties of lead-free solders that has been published.

Table 7-4 summarizes the properties of lead-free alloys.

Table 7-4: Overview on suitability of lead-free alloys for low temperature applications

Alloy type	Melting range	Tin pest susceptibility	Suitability
Sn5Sb	232 – 240°C	Resistant	Melting point too high
Sn-25Ag-10Sb	233°C	Not known	Melting point too high.
58%Sn42%Bi	138°C	Not known	Low melting temperature but may be too brittle. Bismuth alloys have poor thermal fatigue resistance[8].
57%Sn42%Bi1%Ag	139 – 140°C	Not known	More malleable than 58Sn42Bi. Fatigue resistance concern.
SnAgBi (+others) (Sn3.3Ag4.7Bi, Sn3.5Ag1Bi, various SnAgCuBi)	Typically 208 – 213°C	Not known but probably inferior to SnPb	Uncommon but available lead-free solders that have been used for laptop PCs (SMT only). Fatigue resistance similar to tin/lead but little data on reliability available.
SnAgIn		Test results available only for 20 months at -18°C	Very uncommon solder with little reliability data available
SnCu	227°C	Very susceptible	M.pt. 217°C. Used for wave soldering but too high temp for complex multilayer PCBs with heavy components
SnAg (+Cu)	217°C (eutectic alloy)	Susceptible	Common lead-free used for wave and SMT
Sn9Zn, Sn8Zn3Bi	189 - 199	Inferior to SnPb	Requires very corrosive fluxes which can damage other parts of the equipment. Zinc solders are susceptible to corrosion and so are rarely used

[89] Op. cit. LSC (2014a)

Source: LSC[90]

7.3.1.1.6 Solder Wetting on Non-magnetic Terminals

LSC[91] refers to research that has shown that all of the commercially available types of tin-based lead-free solders have higher substrate dissolution rates and longer wetting times. This is explained in part to be due to the higher soldering temperature needed for lead-free solders, but the absence of the lead phase also appears to have an impact. Comparative tests have been published by Asahi, a solder manufacturer[92], in which a variety of alloys were compared by wave soldering a standard printed circuit board using a soldering temperature of 245 °C.

Table 7-5: Wetting times of solder alloys at 245 °C wave soldering

Alloy composition	Wetting time (seconds)
Tin/lead	0.6
Sn0.7Cu	1.0
Sn3.5Ag	1.4
Sn3.5Ag3.0Bi	1.7
Sn4Ag0.5Cu	1.9

Source: LSC[93]

LSC[94] states that the temperature affects wetting times, but depending on the solder alloy and its melting point. It is therefore unrealistic to compare tests at 245 °C because SnPb is typically soldered at ~235 °C whereas lead-free alloys may be at ~255 °C. At these temperatures, Asahi's test results show that SnPb has considerably shorter wetting time:

SnPb at 235 °C ~ 0.77 seconds

SnAgCu at 255 °C ~ 1.28 seconds

LSC[95] explains that during soldering, the substrate metal dissolves in molten solder at a rate that depends on the alloy composition as well as being proportional to the

[90] Op. cit. LSC (2014a)

[91] Ibid.

[92] http://www.asahisolder.com/Publication/Comparative.pdf; source as referenced by LSC (2014a)

[93] Op. cit. LSC (2014a)

[94] Ibid.

[95] Ibid.

temperature. The dissolution rate increases as the temperature is raised. Research by two organisations is shown below to illustrate this effect with copper as a substrate.

Table 7-6: Copper dissolution rate of different alloys at different temperatures

Solder alloy	Copper dissolution rate (µm/s) in 275°C solder bath[96]	Copper dissolution rate (µm/s) in wave soldering at specified temperature[97]
SnPb	1.8	~1.38 at 255°C (72°C above melting point)
SnCu	2.7	3.28 at 275°C (~48°C above melting point)
SnAg	4.4	3.28 at 275°C (~54°C above melting point)
Sn3.7Ag0.7Cu	-	2.3 at 275°C (~58°C above solidus) or 3.3 at 300°C (~80°C above solidus)

Source: LSC[98]

LSC[99] interprets these results to show that the risk of complete loss of copper substrate is higher with lead-free solders than with tin-lead solder. Nickel barrier coatings react with liquid solder much more slowly, but cannot be used as they are magnetic. Silver and gold substrates also dissolve in liquid solder as rapidly as copper. One manufacturer (Syfer) of non-magnetic passive components with silver/palladium end terminations without nickel barrier layers advises that one type of these components can be soldered at 240°C for at most 20 seconds. At the standard lead-free reflow temperature times, no more than 7 seconds is acceptable to avoid a too thick intermetallic layer forming between the tin, silver and palladium. Another manufacturer (Temex) states in their technical datasheet that the maximum time (for one of their components) at 260°C with the non-magnetic versions must be less than 10 seconds, whereas components with nickel barriers can be at 260°C for 120 seconds. Lake Shore's sensors are usually hand soldered, where temperature control is difficult and so complete dissolution and loss of the sensor's terminal coatings is likely to occur with lead-free solders on nonmagnetic sensors without a nickel barrier layer.

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[96] D. Di Maio, C. P. Hunt and B. Willis, "Good Practice Guide to Reduce Copper Dissolution in Lead-Free Assembly", Good Practice Guide No. 110, 2008, National Physical Laboratory, UK; source as referenced by LSC (2014a)

[97] C. Hunt and D. Di Maio, "A Test Methodology for Copper Dissolution in Lead-Free Alloys", National Physical Laboratory, UK; source as referenced by LSC (2014a)

[98] Op. cit. LSC (2014a)

[99] Ibid.

7.3.1.1.7 Resistance to Vibration

According to LSC[100], most research with lead-free solders has been carried out to simulate and accelerate the conditions experienced by consumer, household and IT products although some military-type applications have also been considered. Some of the tests involve brief excursions below 0 °C (down to -40 °C) but the time at low temperature in total is always relatively short and almost no research has been carried out at liquid helium temperatures. So apart from the risk of tin pest, the long term reliability of lead-free solder joints at very low temperatures is not known. Solders become less ductile as the temperature decreases and so at very low temperature they can become very brittle. Lead-free solders are less ductile than tin lead at room temperature. Examples for un-annealed alloys are:

Eutectic tin 37% lead	Vickers hardness = 12.9
Tin 4.7% silver 0.7%copper	Vickers hardness = 21.9

LSC[101] claims that many types of equipment can experience vibration and also big temperature fluctuations, which can have detrimental effects on solder joints. Vibration and temperature cycling typical of consumer and IT equipment has been extensively studied but there has been no research carried at the low temperatures that occur in types of equipment in which Lake Shore sensors are used. Research has shown that lead-free solders are more susceptible to failure than eutectic tin lead solders when exposed to vibration with high g-forces.[102] There is therefore an unquantifiable risk that lead-free solders that will be very brittle at low temperature, will have a greater risk of failure at very low temperatures than ductile tin-lead solders if vibration or stress, due to temperature changes, occurs.

7.3.1.1.8 Thermal Fatigue Research

LSC[103] states that thermal fatigue is a well-known cause of failure due to cracking of solder joints. This is due to cyclic stress and is well understood for tin-lead and a lot of research has been carried out with lead-free solders but not at the very low temperatures experienced by Lake Shore sensors. Research and development to simulate stresses that occur at “normal” temperatures of 10 to 40 °C may not be applicable at temperatures down to 1 K (–272.15 °C).

LSC[104] stresses that thermal fatigue research shows that lead-free solders are inferior to tin-lead at high stress level, whereas at lower stress levels they appear to be superior. Stress levels are likely to increase as temperature drops from ambient

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[100] Op. cit. LSC (2014a)

[101] Ibid.

[102] Various research studies, e.g. http://www.jgpp.com/projects/lead_free_soldering/April_4_Exec_Sum_Presentations/JTR%20Reliability%20Conclusions%20March%2028%202006.pdf; source as referenced by LSC (2014a)

[103] Op. cit. LSC (2014a)

[104] Ibid.

temperature to 1 K (–272.15°C) – a range of nearly 300°C, where the solder will become very brittle. High stress and brittle solder would suggest poor reliability for lead-free solders but as yet, no research is available to determine the true behaviour.

LSC[105] reports that a variety of solder alloys have been suggested for use at cryogenic temperatures but there has been only very limited research carried out and very little published. Indium solders are softer and more ductile than tin-lead and some limited researched has been carried out for their use in space applications, down to -150°C[106]. This research showed that thermal fatigue life is affected by the type and thickness of the intermetallic phase that forms. Also, fatigue life is shorter (failure after fewer cycles) at very low temperatures. For example, with soldering to 0.5 µm gold metallisation, at –55°C, under the test conditions used, there were 6,500 cycles to failure, but at –150°C, there were only 2,500 cycles to failure. Lake Shore sensors are used at below –250°C, so the number of cycles to failure is likely to be even less if the solder will be less ductile, although tests at this temperature were not carried out or reported.

LSC[107] refers to Vishay, which has published a guide to soldering strain gauges for use at cryogenic temperatures[108]. The optimum alloys for long life at cryogenic temperatures are an alloy with 93.5% lead (plus tin and silver) and SnPb with a trace addition of antimony. Vishay say that tin 5% antimony can be used at cryogenic temperatures but warn that it is “quite brittle” and so will not be suitable for Lake Shore sensors as these can experience vibration and thermal cycling. Vishay do not recommend tin/silver (presumably due to tin pest).

7.3.1.1.9 Other Properties of Relevance

LSC[109] puts forward further arguments against the use of lead-free solders in its sensors. These arguments are identical to those of the applicant that requested the exemption which resulted in Exemption 26 of Annex IV and can be checked there.[110]

7.3.1.2 Electrically Conductive Adhesives

According to LSC[111], conductive adhesives are a potential alternative to solders. This alternative is however only very rarely used to assemble electrical circuitry because its long term reliability and performance (i.e. permanent low electrical resistance) is usually inadequate for most applications, either because its initial resistance is not sufficiently low or due to a gradual increase in resistance that occurs due to loss of

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[105] Op,. cit. LSC (2014a)

[106] http://drum.lib.umd.edu/bitstream/1903/8768/1/umi-umd-5787.pdf; source as referenced in LSC (2014a)

[107] Op. cit. LSC (2014a)

[108] http://www.vishaypg.com/docs/11023/soldacce.pdf; source as referenced in LSC (2014a)

[109] Op. cit. LSC (2014a)

[110] Cf. Oeko (2012), p. 47 et seqq.

[111] Op. cit. LSC (2014a)

metal-metal contact within the bond due to movements caused by expansion/contraction or due to oxidation of base-metals such as copper used for substrates. It will also not be suitable for use in this application because the bonds to components must be resistant to vibration and large temperature changes including very low temperatures where most adhesives will become extremely brittle. The electrical conductivity will also be inferior to solder alloys.

7.3.1.3 Welded or Brazed Bonds

LSC[112] says that brazing and welding avoids the use of tin so that tin pest is not an issue. However, these bonding techniques cannot be used to build electrical circuitry between copper wires and electronic components because the very high temperatures (> 500 °C for brazing and > 1,000 °C for welding) would destroy most of the types of sensors that are used, as well as the printed circuit board material on which they may be mounted. Brazing and spot welding are used on some types of sensors but cannot be used on types that are heat-sensitive or are damaged by thermal shock (most ceramic types).

7.3.1.4 Mechanical Connections such as Crimps

LSC[113] states that mechanical connections are unsuitable for the very small sensors made by LSC. Where an electrical connection needs to be made to a very small ceramic or glass surface, there is nothing for a crimp to "grip". Mechanical connections can also be unreliable if repeated temperature cycles occur, because this causes differential movements that abrade the surface. This causes loss of thin precious metal coatings and the exposed base-metal substrates will oxidise. The amount of oxide will increase every time there is sideways movement until the amount is enough to cause high electrical resistance and an open circuit (this process is known as "fretting").

7.3.2 Environmental Arguments

LSC[114] claims that the use of potential substitutes like lead-free solders will shorten the lifetime of products, which will increase the quantity of waste electrical and electronic equipment. There will also be an increase in materials and energy consumption required to manufacture replacement equipment and sensors. LSC[115] says silver is one of the lead-free solder ingredients that has a significant detrimental environmental impact, mainly during the manufacturing and refining life cycle phases but the overall life cycle of silver cannot be directly compared with the overall lifecycle of lead to determine which will have the inferior environmental life cycle impact.

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[112] Op. cit. LSC (2014a)

[113] Ibid.

[114] Ibid.

[115] Ibid.

LSC[116] does not expect impacts on consumer safety and on health unless the increased quantity of waste has a health impact on workers who recycle waste electrical and electronic equipment.

7.3.3 Road Map for Substitution

LSC[117] claims that very extensive testing will be needed to avoid using the small amount of lead, which would be used under the requested exemption. All lead-free solders are unlikely to be suitable because of the risk of tin pest, as described in Section 7.3.1. Lead-free solders need to be evaluated to establish the sensor lifetimes under the conditions of use. One of the likely causes of failure is due to tin pest, but testing for this cannot be accelerated and so is likely to require very long periods for testing. LSC[118] are aware that some of its customers use their sensors for at least 15 years. Another potential failure cause is embrittlement (cracking within solder joints). Any potential alloys attached to sensors will need to be thermally cycled at the same temperature ranges that LSC's sensors experience in use. This type of testing can take many years, because acceleration factors for accelerated tests are not known. Although industry now has some experience with temperature cycling between –40 and 200°C, there are no published test results at cryogenic temperatures. Solders are much more brittle at very low temperatures so their thermal cycle behaviour is likely to be very different at –250°C than at –40°C.

Accelerated testing, to shorten testing times, to simulate use at very low temperature is not reliable unless the acceleration factor is known and this cannot be determined until solders have been used for at least 15 years at cryogenic temperature. It will therefore require many years to carry out this research and this exemption is needed for the maximum validity period.

LSC[119] explains that it tested a very uncommon solder: eutectic AuSn (gold-tin) with a few types of sensors. Solder wetting is poor and the soldering process is very difficult to carry out (poor yields were achieved) as it must be carried out in a vacuum. LSC therefore has abandoned this alloy due to the very poor wetting achieved, which is likely to result in early failures of solder bonds. AuSn is rarely used by the electronics industry for this type of soldering due to the difficulty of achieving good bonds and so there is no published research available that describes its long-term reliability at cryogenic temperatures.

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[116] Op. cit. LSC (2014a)

[117] Ibid.

[118] Ibid.

[119] Ibid.

7.4 Stakeholders' Contributions

One supporting document was submitted to the online consultation. The supporter, however, wished to remain anonymous. The information could therefore not be taken into account.

JBCE[120] submitted a document during the stakeholder consultation, which relates exemption 7a in RoHS Annex III to the requested exemption. Exemption 7a in RoHS Annex III allows the use of lead in high melting point solders with a lead content of at least 85%.

LSC requests, however, the authorisation to use solders with only 37% of lead. The JBCE document was therefore not followed up during the evaluation.

7.5 Critical Review

7.5.1 REACH Compliance – Relation to the REACH Regulation

Section 5.0 of this report lists entry 28 and entry 30 in Annex XVII of the REACH Regulation, stipulating that lead and its compounds shall not be placed on the market, or used, as substances, constituents of other substances, or in mixtures for supply to the general public. A prerequisite to granting the requested exemption would therefore be to establish whether the intended use of lead in this exemption request might weaken the environmental and health protection afforded by the REACH regulation.

In the consultants' understanding, the restriction for substances under entry 28 and entry 30 of Annex XVII does not apply to the use of lead in this application. Pb used in solders for sensor contacts, in the consultants' point of view is not a supply of lead and its compounds as a substance, mixture or constituent of other mixtures to the general public. Pb is part of an article and as such, entry 30 of Annex XVII of the REACH Regulation would not apply. Additionally, such devices using cryogenic sensors are products that are not provided to the general public, but to users other than private ones, e.g. to hospitals and scientific institutions.

No other entries relevant for the use of lead in the requested exemption could be identified in Annex XIV and Annex XVII (status April 2015).

Based on the current status of Annexes XIV and XVII of the REACH Regulation, the requested exemption would not weaken the environmental and health protection afforded by the REACH Regulation. An exemption could therefore be granted if other criteria of Art. 5(1)(a) apply.

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[120] JBCE (2015) Japanese Business Council in Europe (JBCE) document "20150112___JBCE____Comment_on_public_cousulation_of_Exemption_request_2014-2.pdf", retrieved from "http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-2/20150112___JBCE____Comment_on_public_cousulation_of_Exemption_request_2014-2.pdf; submitted during the stakeholder consultation

7.5.2 Scientific and Technical Practicability of Lead Substitution or Elimination

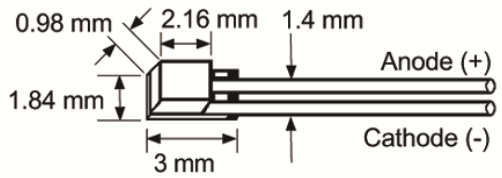
The evaluation of the exemption requests resulting in exemptions 25 and 26 of RoHS Annex IV[121] showed that, once soldering is required, lead-free solders cannot be used in cryogenic applications. They are prone to tin pest, which seriously affects the reliability of the appliances.

LSC[122] mentions, however, that not all of its sensors use solder to manufacture external electrical connections. In principle, connections other than soldering are thus available so that the use of lead can be eliminated. With the information retrieved from the LSC[123] exemption request and the online consultation questionnaire LSC (2015a), it could not be clarified under which conditions exactly connections other than soldering are feasible. Several rounds of questionnaires[124] and a phone conference were required to clarify this question.

LSC[125] explain that internal bonds use either ultrasonic wire bonding or soldering with gold-silicon or gold- tin and are thus lead-free. Depending on the device and package type, external connections on the sensors are either soldered, brazed or spot welded. LSC[126] states that cryogenic sensors need to have external connections (leads) to connect them with the instrumentation that is used to read these devices. The instrumentation could never physically fit near the sensor let alone withstand cryogenic conditions. Instead, the instrumentation is installed in a benign location outside of the experimental region and connected to the sensor leads using one of several available special alloy extension wires.

Figure 7-2 shows a typical sensor with leads and its dimensions.

Figure 7-2: Sensor with external connections (leads)



Source: LSC[127]

[121] Cf. Oeko (2012), page 47 sqq. and page 85 sqq.

[122] Op. cit. LSC (2014a)

[123] Ibid.

[124] See LSC (2015b),c,d

[125] LSC (2015a), Lake Shore Cryotronics document "Questionnaire-3_Exe-Req-2014-2.pdf", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 10 February 2015

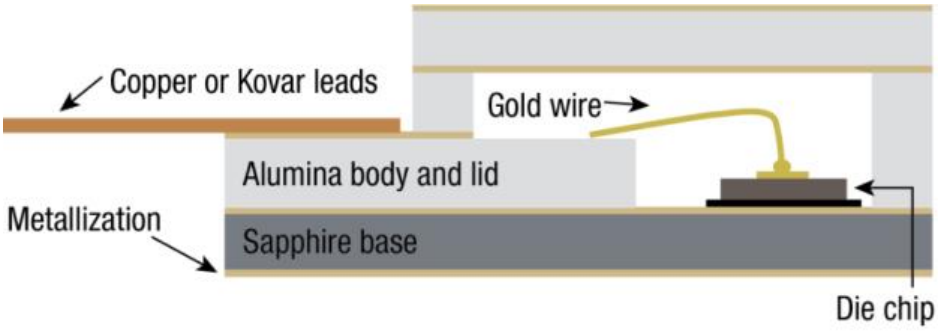
[126] LSC (2015d), Lake Shore Cryotronics document "Questionnaire-6_Exe-Req-2014-2_answered.docx", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 16 April 2015

[127] Op. cit. LSC (2015c)

According to LSC[128], the temperature measurement in harsh cryogenic environments is based on the sensor's resistance or voltage. For voltage based temperature sensors, the leads can be brazed to the sensor, which eliminates the need to use solder and thus also avoids the use of lead in the assembly of the sensor. An example are subassemblies with Kovar leads as illustrated in

Figure 7-3.

Figure 7-3: Sensor subassembly with brazed Kovar or soldered copper leads



Source: LSC[129]

LSC[130] describes that the Kovar leads are brazed on prior to mounting the sensing element, prior to making the internal electrical bonds, and prior to the final hermetic lid seal process, which are all done on-site at Lake Shore. The finished device is lead-free. Such Kovar leads are extremely durable and have worked well for several of LSC's sensor applications, primarily silicon diode temperature sensors.

According to LSC[131], the drawback to Kovar is that it is magnetic and has a high resistance. These properties make it unsuitable for resistance temperature sensors. The resistance sensors require low resistance leads to minimize potential measurement errors. They are also often used in magnetic fields where the presence of any extraneous magnetic material can either distort the field or create errors in whatever experiment is being done.

For LSC[132], the best choice for this application is copper instead of Kovar leads. To date, LSC[133] has not been successful in obtaining acceptable pre-brazed copper leads to the subassembly contact pads, mainly because of concerns about oxidation of the copper during brazing and the durability of the completed assembly. Cryogenic

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[128] Op. cit. LSC (2015d)

[129] Op. cit. LSC (2015d)

[130] Ibid.

[131] Ibid.

[132] Ibid.

[133] Ibid.

resistance temperature sensors require a solid mechanical joint, which at the same time does not impact the low level signals involved. These sensors are typically operated at the few millivolt level with measurement resolutions in the sub-microvolt range. At this time, the only option for typical sensor applications is therefore soldering. Custom attachments, such as spot welding and wire bonding of gold leads, have been done for specific applications but these tend to be extremely fragile and prone to breaking.

In summary, LSC can braze Kovar leads to the unassembled sensor packages of voltage-based temperature sensors, while the copper leads of resistance-based sensors need to be soldered to the sensor package.

Besides the use of solders to attach copper leads to resistance temperature sensors, LSC[134] states that extension wires are needed to enable the installation of the sensors into customers' applications such as SQUID magnetometers, PPMS (physical properties measurement systems,) and cryo-test platforms that include cryostats, dilution refrigerators, and closed cycle refrigerators. The extension wires are soldered to the Kovar leads and to the copper leads using lead solders, as these connections are still in the cryogenic area, where lead-free solders may suffer from tin pest causing reliability problems. Brazing or welding instead of soldering is impossible as the higher process temperatures, in comparison with soldering, would destroy the sensors.

LSC[135] explains that for many applications, the customer applies the extension wires at its facility and requires only a leaded[136] sensor from Lake Shore. However, for certain applications, LSC is requested to provide the sensor with pre-attached extension leads. The requested extension wire can either replace the sensor leads or be attached to the sensor leads, depending upon application specifics.

LSC[137] describes that, besides enabling the installation, one main purpose of the special extension leads is to prevent heat leaking from the outside environment into the sensor through the connecting wires. Wires with poor thermal conduction such as phosphor bronze (CuSnP) or manganin (CuMnNi) are typically used. The wire is to be heat sunk at multiple points through the various temperature stages. Without the proper use of this extension wire, LSC's customers' products may not reach their required base temperature or may not measure properly.

The different sensor types require different numbers of connections soldered with lead solder:

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[134] Op. cit. LSC (2015c)

[135] Ibid.

[136] Meaning a sensor equipped with external connections, not with the substance lead (Pb).

[137] Op. cit. LSC (2015c)

- In voltage temperature sensors, the extension wires are soldered to the Kovar leads.
- In resistance temperature sensors:
    - The copper leads are soldered to the sensor assembly, and
    - The extension wires are soldered to the copper leads.

So resistance temperature sensors have at least four soldered connections, while voltage temperature sensors have only two solder connections. LSC was asked why voltage temperature sensors cannot replace resistance temperature sensors at least in applications where no magnetic fields are involved in order to reduce the amount of lead solders.

LSC[138] replied that the voltage-based sensors (diode temperature sensors) cannot replace the resistance sensors. Each sensor type has unique characteristics that make it more or less suitable depending upon the application and temperature range:

- The voltage-based sensors are easier to use and require simpler instrumentation to measure them. They are available with predetermined tolerances to standard calibration curves, which makes costly, individual calibrations unneeded when precise temperature measurement is not required. (LSC[139])
- Resistance sensors offer a higher level of performance when considering all sensor characteristics, such as calibration accuracy, self-heating, and stability. Resistance sensors are the sensor of choice for the more critical temperature measurements and typically are more expensive. (LSC[140])

From the applicant's above arguments, the reviewers conclude that the two temperature sensor types have different properties and that the voltage based sensors cannot fully replace the resistance-based ones to restrict the use of lead solder to the technically required minimum. As the resistance temperature sensors are more expensive, there would also be no incentive to use them instead of the cheaper voltage temperature sensors.

Based on the available information, the reviewers conclude that lead solders cannot be substituted or eliminated in the external contacts of temperature sensors that are used periodically at temperatures below –150 °C. Thus, on the basis of the Art. 5(1)(a) criteria, granting an exemption would be justified.

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[138] Op. cit. LSC (2015d)

[139] Ibid.

[140] Ibid.

7.5.3 Discussion of Wording Formulation

The applicant proposed the following wording for the requested exemption:

> *"Lead in solders used to make electrical connections to temperature measurement sensors designed to be used periodically at temperature below –150 °C"*

This wording would in principle allow using the exemption for applications where the temperature sensors are not exposed to cryogenic conditions. To exclude misuse, the reviewers propose a slightly different wording:

> *"Lead in solders of electrical connections to temperature measurement sensors in devices which are designed to be used periodically at temperatures below –150 °C."*

LSC[141] agreed to this revised wording.

Technically and scientifically, the justification of the exemption is very similar to exemptions 26 and 27 of RoHS Annex IV. The core technical constraint for the exemptions is the tin pest phenomenon occurring at low temperatures. Exemptions 26 and 27 expire on 30 June 2021. Due to the technical similarity, the consultants recommend the same expiry date for this requested exemption, so that exemptions 26, 27 and this new exemption could be reviewed together in the case that competent stakeholders were to ask for a further extension.

7.6 Recommendation

The applicant provided evidence that lead in solders to contact temperature sensors in devices operated periodically below –150 °C currently cannot be substituted or eliminated. In absence of contrary information, the reviewers recommend granting the exemption in line with Art. 5(1)(a)(i).

The reviewers propose the following wording for the exemption, which should be added to Annex IV as requested by LSC[142]:

> *"Lead in solders of electrical connections to temperature measurement sensors in devices which are designed to be used periodically at temperatures below –150 °C."*

As the technical background of this exemption is similar to Exemptions 26 and 27 of RoHS Annex IV, the consultants recommend that the expiry date match the date given in these exemptions, which is 30 June 2021.

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[141] LSC (2015b), Questionnaire-4_Exe-Req-2014-2_answered.docx "Questionnaire-4_Exe-Req-2014-2_answered.docx", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 9 March 2015

[142] LSC (2014a), Questionnaire-4_Exe-Req-2014-2_answered.docx "Questionnaire-4_Exe-Req-2014-2_answered.docx", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 9 March 2015

Instead of adding a new exemption, the technically similar background and the partial coverage of the applicant's use of lead with exemption 26 in the consultants' opinion would alternatively justify amending exemption 26 of RoHS Annex IV as follows (the addition shown in bold):

"Lead in

- *— solders on printed circuit boards,*
- *— termination coatings of electrical and electronic components and coatings of printed circuit boards,*
- *— solders for connecting wires and cables,*
- *— solders connecting transducers and sensors,*

that are used durably at a temperature below –20 °C under normal operating and storage conditions;

- ***— solders of electrical connections to temperature measurement sensors in devices which are designed to be used periodically at temperatures below –150 °C.**"*

The expiry date of this amended exemption would remain 30 June 2021.

7.7 References Exemption Request 2014-2

JBCE (2015) Japanese Business Council in Europe (JBCE) document "20150112___JBCE____Comment_on_public_cousulation_of_Exemption_request_2014-2.pdf", retrieved from "http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-2/20150112___JBCE____Comment_on_public_cousulation_of_Exemption_request_2014-2.pdf; submitted during the stakeholder consultation

LSC (2014a) Lake Shore Cryotronics exemption request document "Lake Shore Submission.pdf", retrievable from http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-2/Lake_Shore_Submission.pdf; accessed 27 January 2015

LSC (2014b) Lake Shore Cryotronics document "20141002_answers_Questionnaire-1_Clarification_Exe-Req-2014-2", sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM; retrievable from http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_6/2014-2/20141002_answers_Questionnaire-1_Clarification_Exe-Req-2014-2.pdf; accessed 27 January 2015

LSC (2015a) Lake Shore Cryotronics document “Questionnaire-3_Exe-Req-2014-2.pdf”, sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 10 February 2015

LSC (2015b) Questionnaire-4_Exe-Req-2014-2_answered.docx “Questionnaire-4_Exe-Req-2014-2_answered.docx”, sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 9 March 2015

LSC (2015c) Lake Shore Cryotronics document “Questionnaire-5_Exe-Req-2014-2_answered.docx”, sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 8 April 2015

LSC (2015d) Lake Shore Cryotronics document “Questionnaire-6_Exe-Req-2014-2_answered.docx”, sent via e-mail by Betsey Kraus, Lake Shore Cryotronics Inc., to Otmar Deubzer, Fraunhofer IZM, on 16 April 2015

Oeko (2012) Gensch, C.-O.; Baron, Y.; Blepp, M.; Manhart, A.; Moch, K., Oeko-Institut; Deubzer, O., Fraunhofer IZM: Assistance to the Commission on technological, socio-economic and cost-benefit assessment related to exemptions from the substance restrictions in electrical and electronic equipment (RoHS Directive), December 2012; retrievable from http://rohs.exemptions.oeko.info/fileadmin/user_upload/Rohs_V/RoHS_V_Final_report_12_Dec_2012_Final.pdf; accessed 28 January 2015

A.1.0 Appendix: Summary of Goodman Review of Alternatives for Lead Based Oxygen Sensors

Available technologies for oxygen sensors are described by Dr. Paul Goodman in section 10.1.3 of a reliability and failure analysis of Cat. 8 and Cat. 9 applications prepared for the EU COM.[143] The section of the study focuses on Pb based oxygen sensors and reviews various alternatives for such sensors.

Such sensors use a Pb anode, having the advantage that it does not corrode in the cell spontaneously, and so does not produce a current in the absence of oxygen. Such sensors also have a reasonably long life of 1-2 years and do not consume energy in their operation, so that the batteries used by portable oxygen meters have long lives. Pb cell based sensors are robust and can withstand vibration and shock without damage. They are however not suitable for use with hot gases. [144] Neither are they as sensitive in their measurements as the Cd Hersch Cell, as MOCON have explained.[145]

Regarding substance substitutes, Goodman explains that many other metals could principally be used, however all suffering from various disadvantages as detailed below. It should be kept in mind that these alternatives were reviewed in comparison with Pb sensors and not in comparison with the Hersch cell. However, it is understood for the details that they would not be potential substitutes for Hersch cells either.

- **Zinc** corrodes spontaneously and so greatly shortens the life of the sensor, also giving a continuous but variable background current that makes low oxygen concentrations impossible to measure;
- **Tin, nickel** and **copper** undergo passivation: when these metals oxidise, they form an inert protective oxide coating that prevents further reaction. **Nickel** and **copper** as well as **iron** are also not suitable for oxygen reduction, meaning that the cell would not operate; This could be changed by imposing a voltage from an external power source, however this would add weight to the sensor and also mean that the battery is consumed more quickly, making the sensors unsuitable for portable applications.
- **Indium** may be suitable though it too can undergo passivation. However indium is produced in small quantities, and its supply is explained to be insufficiently available to replace the estimated 10 tonnes of Pb used per annum in oxygen sensors.

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[143] Goodman, P. (2006), Reliability and Failure Analysis : Review of Directive 2002/95/EC (RoHS) Categories 8 and 9 – Final Report, Prepared for the EU COM, Copyright ERA Technology Limited 2006, Section 10.1.3, available under: http://ec.europa.eu/environment/waste/weee/pdf/era_study_final_report.pdf, last accessed 09.03.2015

[144] Op. cit. Goodman, P. (2006)

[145] Op. cit. MOCON (2014a)

- **Aluminium** was not considered, as it also undergoes passivation. Even if this could be prevented, it would react violently with the electrolyte.
- **Gold, platinum and silver** do not oxidize and their electrode potentials are too close to those of the cathode.

Goodman also details alternative types of sensors to explain that the use of Pb based sensors could not be eliminated:

- **Paramagnetic sensors** are explained to be less practical in size and cost as well as susceptible to orientation, vibration and shock, with a risk of large errors in the presence of other paramagnetic gases as well as strong magnetic fields.
- **Potentiometric sensors** – most metals cannot be used in place of Pb as they give the cathode an electrode potential not suitable for oxygen reduction. However, by controlling the cathode's electrode potential with an external power-source, any metal could be used as an anode. This would however shorten the sensor life in light of changes to the composition of the electrolyte though in some cases this could be similar to electrochemical sensors. The main drawback is that their design is more complex, requiring control electronics and a constant power-source to operate.
- **Zirconia sensors** – are designed for measurement of oxygen in gases and operate at 700°C. For this reason they are mainly applied in flue gas monitoring and engine management. They consume power to maintain their operating temperature and their accuracy can be poor as their response is affected by other gases.