RoHS 2011/65/EU

Annex IV Application Exemption Request

Date of submission: April 28, 2014

1. Name and contact details

1) Name and contact details of applicant:

Company:	MOCON, Inc.	Tel.:	763-493-6370
Name:	Mike Howe	E-Mail:	mhowe@mocon.com
Function:	Product Development Manager	Address:	7500 Mendelssohn Ave N, Brooklyn Park, MN 55428 USA

2) Name and contact details of responsible person for this application (if different from above):

Company:	_____	Tel.:	_____
Name:	_____	E-Mail:	_____
Function:	_____	Address:	_____

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2. Reason for application:

Please indicate where relevant:

x Request for new exemption in:

☐ Request for amendment of existing exemption in

☐ Request for extension of existing exemption in

☐ Request for deletion of existing exemption in:

☐ Provision of information referring to an existing specific exemption in:

☐ Annex III x Annex IV

No. of exemption in Annex III or IV where applicable: _____

Proposed or existing wording:

Cadmium Anodes in Hersch cells for high-sensitivity oxygen sensors

Duration where applicable:

7 years (per Directive 2011/65/EU Article 5.2)

☐ Other: _____

3. Summary of the exemption request / revocation request

An Annex IV application exemption is requested for cadmium in Hersch cells for high-sensitivity oxygen sensors capable of measuring oxygen concentration below 100ppm. Using a Hersch Cell, the range of oxygen detection is from 80ppt to 70ppm.

With reference to Article 5.1.(a), this exemption is made for the following reason:

> *— 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,*

An Annex IV application exemption presently exists for lead in anodes of oxygen sensors. While lead is less toxic than cadmium, 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.

Of the industries requiring high-sensitivity oxygen measurement, the following industries provide examples where human health or the environment would be placed at risk if the technology were to become unavailable:

- Manufacture of certain pharmaceutical products which are sensitive to extremely low levels of oxygen
- Integrity of food packaging design
- Lifespan of solar panels, which require a high oxygen barrier to ensure component integrity

There are other industries requiring highly sensitive oxygen measurements; however the above examples were chosen to identify socioeconomic costs.

The net environmental benefit to refusing this exemption request would be minimal, amounting to the removal of at most, 0.52 kg of cadmium from the European waste stream per year.

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4. Technical description of the exemption request / revocation request

(A) Description of the concerned application:

1. To which EEE is the exemption request/information relevant?

Name of applications or products:

Cadmium is present in the anodes of Hersch cells, which are used in specialized, high sensitivity oxygen sensors where parts per trillion (ppt) measurements are required.

a. List of relevant categories: (mark more than one where applicable)

☐ 1	☐ 7
☐ 2	☐ 8
☐ 3	x 9
☐ 4	☐ 10
☐ 5	☐ 11
☐ 6	

b. Please specify if application is in use in other categories to which the exemption request does not refer:

None

c. Please specify for equipment of category 8 and 9:

The requested exemption will be applied in

x monitoring and control instruments in industry

☐ in-vitro diagnostics

☐ other medical devices or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?

(Indicate more than one where applicable)

☐ Pb x Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substance:

Cadmium anodes are used in oxygen sensors for specific applications when a high degree of sensitivity and long-term instrument stability is required. Given the absolute nature of the sensor, it is the only possible instrument where no calibration is necessary.

4. Content of substance in homogeneous material (%weight):

CONFIDENTIAL

5. Amount of substance entering the EU market annually through application for which the exemption is requested: **≤ 0. 528 kg / year**

This is based on worst-case analysis.

CONFIDENTIAL

The exemption applicant is the only current supplier of the requested technology; therefore the exact figure is obtained by counting total sales over the period of 2011-2013, annualizing, and multiplying by amount of substance per unit.

CONFIDENTIAL

6. Name of material/component: Hersch Cell

7. Environmental Assessment: _____

LCA: ☐ Yes

☐ No

The average mass of cadmium sent to the EU over the last three years was ≤0.528 kg/year. However, since 1991 we have had a recycling program where we instruct our customers to send back the sensors when they are replaced or the instruments are thrown out. On average we see about CONFIDENTIAL: XX% of our sensors which contain the cadmium come back to the US for proper recycling. So the net result of added cadmium to the EU was ≤0.329 kg/year.

It is important to note this is the maximum amount of cadmium added 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. So this is worst case senario.

(B) In which material and/or component is the RoHS-regulated substance used, for which you request the exemption or its revocation? What is the function of this material or component?

A Hersch cell operates by introducing a sample gas to an electrolytic solution; in this case it is potassium hydroxide (KOH).

How the Coulox Sensor Works

The Coulox oxygen sensor is a fuel cell that performs in accordance with Faraday's Law. When exposed to oxygen, the Coulox generates an electrical current that is proportional to the amount of oxygen entering the sensor.

Overview

The Coulox sensor has a Carbon cathode and a cadmium anode. The cathodic and anodic reactions respectively:

$1/2O_2 + H_2O + 2e \rightarrow 2OH^-$

$Cd + 2OH^- - 2e \rightarrow Cd(OH)_2$

The electrons create an electrical current, which can be used to calculate the amount of oxygen entering the Coulox sensor.

How Much Current is Produced?

As noted, 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 $4 \times 96{,}500 = 3.86 \times 10^5$ Ampere-seconds.

In more practical terms:

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 repeatibility of 500 picoamps.

To illustrate that; if you were to take the entire population of the world and multiply it by 40, so 280 billion people, and asked the sensor to find any one specific person it would pick them out!

This creates a current which is used to coulometrically determine the concentration of oxygen in solution with the electrolyte.

Lead is commonly used as an anode in this application; however cadmium has specific properties which are necessary for high-sensitivity applications.

Therefore, an application exemption for cadmium in anodes of Hersch cells for high-sensitivity oxygen sensors is requested.

(C) What are the particular characteristics and functions of the RoHS-regulated substance that require its use in this material or component?

The two major reasons why certain industries are unable to substitute cadmium Hersch cell oxygen sensors:

- The Hersch cadmium Cell is "Coulometric" and follows Faraday's Law at ppt levels. This removes the need to calibrate at these extreme low levels.

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 application requires accurate measurements. Competing technologies (exempt lead in particular) require calibration at the testing range of interest, for which there are no standards below 10 ppm.

- The solubility of cadmium in KOH (electrolyte) is very low, therefore 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; on the order of years. Other metals do not have the life, sensitivity or stability.

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5. Information on Possible preparation for reuse or recycling of waste from EEE and on provisions for appropriate treatment of waste

1) Please indicate if a closed loop system exist for EEE waste of application exists and provide information of its characteristics (method of collection to ensure closed loop, method of treatment, etc.)

Yes. Since 1991, the applicant has maintained a program where end-of-life sensors are returned to the applicant's facility in the United States for recycling.

Every sensor which is shipped with cadmium has a label marked: "RETURN EXPENDED SENSOR TO MOCON FOR DISPOSITION" somewhere on it. This is a global label which present on every sensor installed or shipped. When MOCON receives back the cadmium, it is shipped to Green Lights Recycling Inc. where Green Lights stated that the cadmium is designated recycle and reuse. This means that it is reused in other things and not sent to a landfill.

2) Please indicate where relevant:

☐ Article is collected and sent without dismantling for recycling

☐ Article is collected and completely refurbished for reuse

☐ Article is collected and dismantled:

- ☐ The following parts are refurbished for use as spare parts: _____
- x The following parts are subsequently recycled: Cadmium plaque

☐ Article cannot be recycled and is therefore:

- ☐ Sent for energy return
- ☐ Landfilled

3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:

☐ In articles which are refurbished _____

Articles which are returned:

x In articles which are recycled: Approximately ≥ 0.199 kg/year

Articles which are not returned:

x In articles which are sent for energy return or landfilled: ≤.329 kg/year

Note: It is possible that some of these articles have been recycled by EU-based WEEE service providers without the knowledge of the applicant. Therefore, a net value of ≤0.329 kg/year represents an upper limit. In addition, some of these instruments may still be in use or in inventory at the customers' facilities.

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6. Analysis of possible alternative substances

(A) Please provide information if possible alternative applications or alternatives for use of RoHS substances in application exist. Please elaborate analysis on a life-cycle basis, including where available information about independent research, peer-review studies development activities undertaken

An application exemption exists in annex IV:
1b. Lead anodes in electrochemical oxygen sensors

(B) Please provide information and data to establish reliability of possible substitutes of application and of RoHS materials in application

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7. Proposed actions to develop possible substitutes

(A) Please provide information if actions have been taken to develop further possible alternatives for the application or alternatives for RoHS substances in the application.

The applicant currently manufactures several oxygen sensors, not all of which rely on cadmium. However, the sensors using other anode materials (lead) are suitable only for other applications that do not require the high sensitivity of the cadmium Hersch cell application.

(B) Please elaborate what stages are necessary for establishment of possible substitute and respective timeframe needed for completion of such stages.

At this time, it cannot be confidently stated that an alternative material exists. None is currently known. Section 8.(B).3 of this document references an analysis performed for the European Commission in which the consultant explores various metals which can potentially be used as anodes in oxygen sensors. He concludes that lead and cadmium comprise the only two viable metals for scientific reasons. Please refer to 8.(B).3 for more detail.

As is shown elsewhere in this request, lead is unsuitable for ppt measurements.

8. Justification according to Article 5(1)(a):

(A) Links to REACH: (substance + substitute)

1) Do any of the following provisions apply to the application described under (A) and (C)?

☐ Authorisation

- ☐ SVHC
- **X** Candidate list
- ☐ Proposal inclusion Annex XIV
- ☐ Annex XIV

☐ Restriction

- ☐ Annex XVII
- ☐ Registry of intentions

☐ Registration

2) Provide REACH-relevant information received through the supply chain.
Name of document: _____

(B) Elimination/substitution:

1. Can the substance named under 4.(A)1 be eliminated?
   - ☐ Yes. Consequences? _____
   - **x** No. Justification: See 8(b).2
2. Can the substance named under 4.(A)1 be substituted?
   - ☐ Yes.
     - ☐ Design changes:
     - ☐ Other materials:
     - ☐ Other substance:
   - **x** No.

Justification:

Alternative substances exist and are commonly used in oxygen sensors. However, for specialized applications where stable sensitivity on the order of parts per trillion is required, there are no available substitutes.

The basic type of oxygen sensor used is a Hersch Cell. By using cadmium, the instrument is able to measure oxygen transmission down to 0.0005 cc/m^2 x day which equals 170 ppt (parts per trillion) and a sensitivity of 0.0001 cc/m^2 x day (equal to 34 ppt).

Another advantage is the long term stability of the sensor sensitivity (years); over which the > 95% efficacy to oxygen detection does not change. It should be noted that 70 ppm is the highest level of oxygen measurable and still be linear.

It is believed that the technology has another 100 to 1000 times more sensitivity for future development. This level of sensitivity has been requested by some users of the technology.
It should be noted that the sensor measurement is a direct absolute (Coulometric) measurement of oxygen and follows Faraday's Law. Second, the cadmium is very specific to oxygen and has very few interfering gases. Third is the sensitivity the cadmium has to oxygen without degrading over long periods of time (years).

There are several major reasons why certain industries are unable to substitute Hersch cell oxygen sensors:

- 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.

- 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.

- The solubility of cadmium in KOH (electrolyte) is very low, therefore 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.

3. Give details on the reliability of substitutes (technical data + information):

Available technologies for oxygen sensors are described by Dr. Paul Goodman in section 10.1.3 of *Reliability and Failure Analysis : Review of Directive 2002/95/EC (RoHS) Categories 8 and 9 – Final Report*[1]

In the context of lead as an anode material in electrochemical oxygen sensors, Dr. Goodman investigates several possible materials.

He evaluates several possible Pb substitutes and concludes that:

- Zn is unsuitable due to its high corrosion rate. This provides an unpredictable reference current and therefore precludes its use in anything but rudimentary measurements.
- Sn, Al, and In self-passivate, which prevents reaction from continuing after a short period.
- Ni, Cu, Fe are unsuitable due to the necessity of adding an external power supply.
- Au, Pt, Ag are unsuitable due to electrode potential issues.

Cadmium is dismissed by Dr. Goodman as it is more toxic than lead.

However, for measurement of oxygen concentrations on the order of hundreds or tens of ppt, lead does not provide adequate sensitivity (ppt) or the “Coulometric” (absolute) accuracy and characteristics.

Sensor technologies discussed in ERA Report 21006-0383 “Alternative types of sensors” are comparator type sensors which do not have the sensitivity, accuracy or the Coulometric characteristics the Hersch Cell has.

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
    1) Environmental impacts: See below
    2) Health impacts: See below
    3) Consumer safety impacts: See below

There are several users of high-sensitivity oxygen sensors requiring ppt measurements. Applications affecting human health and the environment include:

[1] Retrieved from http://ec.europa.eu/environment/waste/pdf/era_study_final_report.pdf 2013-01-30

- 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 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.

- 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.

⇨ Do impacts of substitution outweigh benefits thereof?

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

For the net gain of eliminating 0.52 kg of cadmium annually from the European market.

Please provide third-party verified assessment on this: _____

(C) Availability of substitutes:

a) Describe supply sources for substitutes: _____

b) Have you encountered problems with the availability? Describe: _____

c) Do you consider the price of the substitute to be a problem for the availability?

☐ Yes ☐ No

d) What conditions need to be fulfilled to ensure the availability? _____

(D) Socio-economic impact of substitution:

⇨ What kind of economic effects do you consider related to substitution?

☐ Increase in direct production costs

☐ Increase in fixed costs

☐ Increase in overhead

x Possible social impacts within the EU

x Possible social impacts external to the EU

☐ Other: _____

⇨ Provide sufficient evidence (third-party verified) to support your statement: _____

9. Other relevant information

Please provide additional relevant information to further establish the necessity of your request:

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10. Information that should be regarded as proprietary

Please state clearly whether any of the above information should be regarded to as proprietary information. If so, please provide verifiable justification:

The format "CONFIDENTIAL" has been used throughout the document to denote confidential information.

Confidential information consists of:

- Exact metallurgy of the anode (because this information is a trade secret)
- Sales figures used to quantify amount of substance placed on market (because sales figures would benefit competitors, are unnecessary for scientific analysis of the merits of this request, and could be used to reverse engineer the anode metallurgy given the mass of cadmium placed on the market)