



- (a) wide-range measurements with a conductivity range covering more than 1 order of magnitude (e.g. range between 0,1 mS/m and 5 mS/m) in laboratory applications for unknown concentrations;
- (b) measurements of solutions where an accuracy of +/- 1 % of the sample range and where high corrosion resistance of the electrode are required for any of the following:
  - (i) solutions with an acidity < pH 1;
  - (ii) solutions with an alkalinity > pH 13;
  - (iii) corrosive solutions containing halogen gas;
- (c) measurements of conductivities above 100 mS/m that must be performed with portable instruments.

Duration where applicable:

7 years

Other: \_\_\_\_\_

### **3. Summary of the exemption request / revocation request**

Platinized Platinum electrodes are absolutely necessary for the measurement of wide range, high accuracy, high reliability for high concentration of acid and alkali.

Platinized Platinum electrodes is a platinum electrode coated with a very thin layer of platinum black that can increase the effective surface area by a factor of 1,000. In order to achieve the above performance, lead is used in the electro deposition process of platinum black. The elimination of lead in the plating solution has been studied by many electrochemists for several decades, however there are no research paper to eliminate or substitute the substance.

Therefore, we apply for the extension of the exemption ANNEX IV #37 for Lead in platinized platinum electrodes, an additional period of 7 years for category 9.

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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:

Platinized Platinum electrodes for measurement instruments

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

- |                            |                                       |
|----------------------------|---------------------------------------|
| <input type="checkbox"/> 1 | <input type="checkbox"/> 7            |
| <input type="checkbox"/> 2 | <input type="checkbox"/> 8            |
| <input type="checkbox"/> 3 | <input checked="" type="checkbox"/> 9 |
| <input type="checkbox"/> 4 | <input type="checkbox"/> 10           |
| <input type="checkbox"/> 5 | <input type="checkbox"/> 11           |
| <input type="checkbox"/> 6 |                                       |

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

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

The requested exemption will be applied in

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     Cd     Hg     Cr-VI     PBB     PBDE

3. Function of the substance:

Platinum black electrodeposition is done to enlarge the surface area of metal electrodes, enabling the surface area of the electrodes to enlarge about 1,000 times of the flat electrodes without platinum black plating.

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

Depends on type of electrodes.

5. Amount of substance entering the EU market annually through application for which the exemption is requested:

Please supply information and calculations to support stated figure.

Total amount of the restricted substance (Pb):

According to the composition of the plating solution, small part of lead is contained in the platinum black on the electrode. The amount of lead, in the EU market, in the platinized platinum electrodes for measurement instruments, which is prepared by the method with the plating solution of the composition, would be less than 1 gram per year. (Please refer to 4.(B) )

6. Name of material/component: Thin layer of platinum black

7. Environmental Assessment:

LCA:  Yes

No

**(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?**

[The component for which an exemption is requested]

Lead in platinized platinum electrodes.

[Characteristics]

Platinized platinum electrode is the platinum electrode covered with a thin layer of platinum black. Small part of lead is concentrated in the layer of platinum black during the electrodeposition process.

Platinum is used because it prevents chemical reaction in the solution.

Performance of electrode as catalyst and its electric capacitance is proportional to its surface area.

Platinum black electrodeposition is done to enlarge the surface area of metal electrodes, enabling the surface area of the electrodes to enlarge about 1,000 times of the flat electrodes without platinum black electrodeposition.

Platinized platinum electrode is the high performance electrode in various applications.

In electrochemistry, the standard potential of a chemical species is measured as voltage difference between the oxidation-reduction potential of hydrogen and the species using the standard hydrogen electrode because the oxidation-reduction potential of hydrogen is zero volts.

The standard hydrogen electrode is a thin platinum plate with platinum black electrodeposition on its surface. The platinum functions as a catalyst to efficiently stimulate the oxidation-reduction reaction of hydrogen and platinized electrode is used to create larger surface area of the electrode so as to generate stable oxidation-reduction potential. The standard hydrogen electrode is one of the applications of the platinized platinum electrode for measurement.

[Platinization method]

Platinization is conducted using the plating solution prepared from water solution of 30g/L of hydrogen hexachloroplatinate(IV) hexahydrate (CAS#:18497-13-7) and 0.25g/L of lead(II) acetate trihydrate (CAS#:6080-56-4). A suitable plating apparatus consists of a 6 V d.c. supply, a variable resistor, a milliammeter, and two electrodes. Good platinized coatings are obtained using from 1.5 to 3 C/cm<sup>2</sup> of electrode area. For example for an electrode having a total area (both sides) of 10 cm<sup>2</sup>, the plating time at a current of 20 mA would be from 12.5 to 25 min. The current density may be from 1 to 4 mA/cm<sup>2</sup> of electrode area. Plate the electrodes one at a time with the aid of another electrode with alternating the D.C. current direction. During the plating, agitate the solution gently. This method is described in EN27888:1993 (ISO 7888:1985), "Water quality - Determination of electrical conductivity". This method provides good adherence of the platinum black to the substrate.

[The equipment utilizing platinized platinum electrode]

For example, electrical conductivity meters are used for inspecting and testing various kinds of water, such as water in rivers, seawater, distilled water, drinking water, industrial water, and industrial effluents.

[The structure and principle of electrical conductivity meters]

**AC two electrode method.**

The figure 1 illustrates AC two electrode method with two electrodes put into the solution, applying AC power forming stable voltage waves and measuring the value of electric current through the solution.

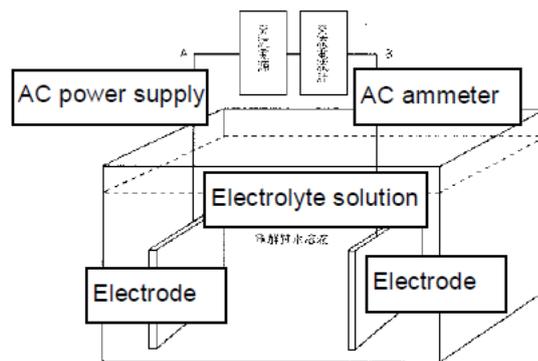


Figure 1 The principle of the AC two electrode method.

The measurement of electrical conductivity by the AC two electrode method causes the transfer of charge between an electron in the electrode and a ion in the solution on the surface of the electrode (electrode reaction). Here, equivalent circuit between electrode A and B becomes complex as described in figure 2.

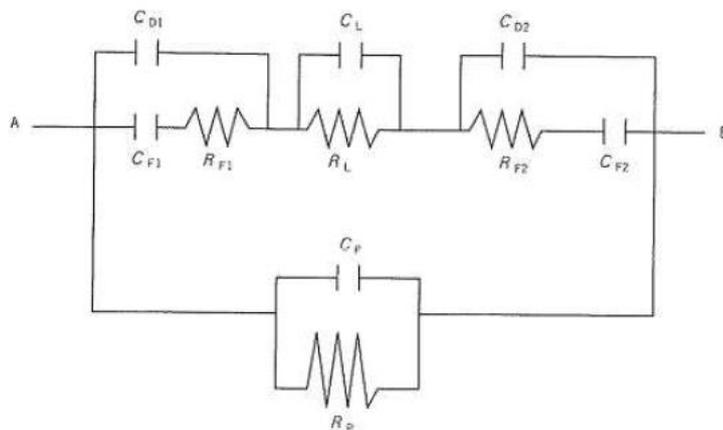


Figure 2 The equivalent circuit of AC two electrode method

The symbols denote as follows:

- $R_L$ ; the electrical resistance between the electrodes to be measured,
- $C_L$ ; the capacitance according to the permittivity of the solution created between electrodes,
- $C_{D1}$  and  $C_{D2}$ ; the capacitance according to the electric double layers created on the surfaces of the electrodes,
- $C_{F1}$ ,  $C_{F2}$ ,  $R_{F1}$  and  $R_{F2}$ ; the capacitances and electrical resistances according to the electrode reaction on the surfaces of the electrodes,
- $C_P$  and  $R_P$ ; the shunt capacitance and the electrical resistance connected to the electrodes with wire leads and others. If the measurement of the electrical resistance between electrodes is susceptible to the  $C_P$  capacitance, the

effect can be reduced with covering the lead wires with shield.  $C_L$  is to be considered only if the solution is as highly resistant as an insulator.

The impedance caused by electrode reaction and others needs to be sufficiently reduced in comparison with the electrical resistance between the electrodes  $R_L$  when the electric conductivity of the solution is measured. High frequency of the alternative voltage reduces the capacitive impedance. Although the equivalent circuit of the cell is complicated, the equivalent circuit of the Figure 2 can be simplified by use of electrodes with precious metal (Pt electrodes are often used) to prevent chemical reaction in the solution and platinum black electrodeposition with which the capacitances apart from  $C_{D1}$  and  $C_{D2}$  can be ignored. The capacitances of  $C_{D1}$  and  $C_{D2}$  are increased by use of platinum black electrodeposition and adequately high frequency of AC power, enabling highly accurate measurement of electric conductivity.

As mentioned above, electric capacitance is generated on the surface of electrodes and in the liquid interface of reagents. The polarization impedance of electric double layers is equivalent to  $1/(2\pi f C_{D1,2})$ . The increase of the polarization impedance adds the electrical resistance of the reagent, resulting in measurement error.  $2\pi f C_{D1,2}$  needs to be greater in order to measure it correctly.

Here,  $2\pi f = \omega$  (circular frequency)

$C_{D1,2}$  = electric capacity of the metal electrodes

The capacity of the metal electrode  $C_{D1,2}$  is proportional to the surface area. Platinum black electrodeposition is done to enlarge the surface area of metal electrodes, enabling the surface area of the electrodes to enlarge about 1,000 times of the flat electrodes without platinum black plating.

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

Platinum black electrodeposition is done to enlarge the surface area of metal electrodes, enabling the surface area of the electrodes to enlarge about 1,000 times of the flat electrodes without platinum black plating.

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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.)**

No information

**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: \_\_\_\_\_

The following parts are subsequently recycled: \_\_\_\_\_

Article cannot be recycled and is therefore:

Sent for energy return

Landfilled

Some are collected and some cannot be recycled.

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

In articles which are refurbished \_\_\_\_\_

In articles which are recycled \_\_\_\_\_

In articles which are sent for energy return \_\_\_\_\_

In articles which are landfilled \_\_\_\_\_

Total amount of the restricted substance (Pb):

According to the composition of the plating solution, small part of lead is contained in the platinum black on the electrode. The amount of lead, in the EU market, in the platinized platinum electrodes for measurement instruments, which is prepared by the method with the plating solution of the composition described above, would be less than 1 gram per year.

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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**

The elimination of lead in the plating solution has been studied by many electrochemists for several decades, and some reviews have been also issued<sup>1)</sup>. But platinized platinum electrode, at which lead(II) acetate is used as the component of the plating solution, is still required to measure the solutions with low electrical conductivity accurately. As of 30<sup>th</sup> June 2017, there is no research paper on the alternative substances. Therefore, there are no alternative substance.

<sup>1)</sup>PLATINIZED PLATINUM ELECTRODES

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Received July 29, 1970 (Revised Manuscript Received October 23, 1970)

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

As of 30<sup>th</sup> June 2017, useful alternative technologies are not proposed.

1) Other type of electrode:

Platinized platinum electrode shows superb characteristics especially in low electric conductivity and low dissolved hydrogen area.

2) Other method of platinum black electrodeposition:

Electrodeposition using lead acetate is superb in resulting surface area and adherence of platinum black to the substrate platinum as shown in the reference <sup>1)</sup>.

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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.**

As of 30<sup>th</sup> June 2017, there are no alternatives.

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

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**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
  - Candidate list
  - Proposal inclusion Annex XIV
  - Annex XIV
- Restriction
- Annex XVII
  - Registry of intentions
- Registration

A few lead compounds are mentioned but this substance in this application is not referred to.

- 2) Provide REACH-relevant information received through the supply chain.

Name of document: None

**(B) Elimination/substitution:**

1. Can the substance named under 4.(A)1 be eliminated?

- Yes. Consequences? \_\_\_\_\_
- No. Justification:

If the measurement requires wide range, high accuracy, high reliability for high concentration of acid and alkali, small size etc, Platinized Platinum electrodes are necessary. As mentioned in 4.(B), Platinized Platinum electrode is required in order to measure, for example, electrical conductivity

on the basis of EN27888:1993 / ISO 7888:1985 standard. With all latest technologies, it is not possible eliminate lead concentration no more than 0.1%.

2. Can the substance named under 4.(A)1 be substituted?

Yes.

Design changes:

Other materials:

Other substance:

No.

Justification: Same as 8 (B) 1

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

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to

1) Environmental impacts: N/A

2) Health impacts: N/A

3) Consumer safety impacts: N/A

⇒ Do impacts of substitution outweigh benefits thereof?

Please provide third-party verified assessment on this: N/A

**(C) Availability of substitutes:**

a) Describe supply sources for substitutes: N/A

b) Have you encountered problems with the availability? Describe: N/A

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? N/A

**(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

Possible social impacts within the EU

Possible social impacts external to the EU

Other: \_\_\_\_\_

⇒ Provide sufficient evidence (third-party verified) to support your statement: N/A

## **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:**

There is no information should be regarded to as proprietary information.

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