Questionnaire for Further Clarification

Exemption Request "Hexavalent chromium in alkali dispensers for in-situ production of photocathodes"

Background

The Öko-Institut together with Fraunhofer IZM has been appointed within a framework contractfor the evaluation of applications for granting, renewing or revoking an exemption to be included in or deleted from Annexes III and IV of the new RoHS Directive 2011/65/EU (RoHS 2) by the European Commission.

You have submitted the above mentioned request for exemption which has been subject to a first completeness and understandability check. As a result we have identified that there is some information missing and a few questions to clarify before we can proceed with the online stakeholder consultation on your request. Therefore we kindly ask you to provide answers for the following questions and to reformulate your request if necessary.

Questions

1. In your proposal different applications are mentioned:
    - Photocathodes used in X-ray image intensifier systems
    - Photocathodes used in photomultiplier tubes (used for measurement of electromagnetic radiation)

   For which of these applications a further exemption from the requirements of the RoHS-Directive will be needed? In your proposed wording you limit your request to X-ray image intensifiers. Please clarify the scope of the exemption request.

   COCIR is concerned with an exemption for image intensifiers only. We mention this as other sectors of industry may also have an interest in this exemption.

2. Would a reference to medical devices help to further specify your exemption request (e.g. Hexavalent chromium in alkali dispensers used to create photocathodes in X-ray image intensifiers for medical applications)?

This would be helpful. The types of image intensifiers used in medical devices require this type of alkali dispenser but non-medical image intensifiers can use different technology

3. Could you please provide the CAS-number of the substances used in CrVI alkali dispensers (e.g. of Cs_2CrO_7, Zr/Al, ZrO_2, Al_2O_3, Cr_2O_3, Cs)? Image intensifiers

predominantly use the following types of CrVI alkali dispensers for photocathode production:

1. Cs2CrO4
2. K2CrO4

Substance	CAS number
Cs_2CrO_7	56320-90-2
Zr/Al	12004-83-0
ZrO_2	1314-23-4
Al_2O_3	1344-28-1
Cr_2O_3	1308-38-9
Cs	7440-46-2
Cs2CrO4	13454-78-9
K2CrO4	7789-00-6

4. In your proposal, you state that alternative CrVI-dispensers are available, notably the products by SAES and Alvatec. On page 8, the problems associated with theAlvatec product are laid out. It is mentioned that the different melting points of indium (to seal the tube), of glass and the evaporation temperature of the alkali dispenser lead to problems such as a premature escape of alkali metals. Could you please further specify these problems and also provide melting and evaporation temperatures for the used materials in comparison to CrVI-dispensers? The only CrVI free dispensers available on the market up till now are from Alvatec. The SAES products are still in development. Indium has a melting point of 156.60 °C. The Indium seal referred to is the seal of the Alvatec dispenser itself. Image intensifiers are baked / degassed at about 200 °C to remove contamination / gasses while they are evacuated. 200 °C is well above the melting point of Indium resulting in breakage of the seal before evaporation. As a result of the broken seal some of the content of the dispenser is lost resulting in loose particles inside the image intensifier which are unacceptable as they appear randomly in X-ray images and could give misleading and incorrect diagnoses. Another negative effect of losing part of content of the dispenser is that the amount available for evaporation becomes too small resulting in a poor photo cathode causing very poor image quality.

5. Could you please also clarify the role of indium in the Alvatec and the CrVI-dispensers? Is indium used in both manufacturing processes or only with the Alvatec dispensers? If

no indium is used with CrVI-dispensers, what other means is used to seal the tube? Would this technology be transferable to the Alvatec-dispensers? Indium is used to seal the Alvatec dispensers (see question 4) and is not used for CrVI-dispensers. CrVI-dispensers do not use a seal at all. A different design is used to avoid early loss of the content. Currently only Alvatec dispensers with Indium seal are available. We don't know whether it is possible to change the Alvatec design into an alternative design, but given the fact that it is not available at least (major) development effort is required. Looking at the amount of time still available between now and July 21, 2014 it is not possible that a new product can be developed and released (technical and regulatory wise) for usage in an image intensifier as part of medical X-ray equipment.

6. Furthermore, it is stated that when using the Alvatec product, high electric currents are used to heat the dispenser. According to the applicant, the electric current heats the electrical wires, which can lead to cracks and leaks in the glass. On the other side, the applicant also states that current CrVI-dispensers also require heating via electric current. Could you please give information on the differences between these two types of heatings/currents? Could high temperatures be avoided using wires with other diameters? This statement mainly holds for glass photomultiplier tubes but is much less of an issue for image intensifier designs. We have no data on wire diameter.

7. You mention that SAES offers a dispenser based on dichromate salts. Can you provide any data and information on the applicability of this dispenser type for in-situ production of photocathodes? Could you please also provide more information on the used substances of this product? These dispensers are still in development at SAES. Specifications are not known yet, but products might become available in the course of 2012, although this is not certain.

8. You mention that digital detection systems contain Cd, Pb or Hg. Could you please specify this information by further specifying the substances used (names and CAS-numbers) and the mass per devices (e.g. Cd per digital detection system). Here, it would also be good to receive information on potential differences between different types of digital detector systems. Could you further provide a comparison of types, applications and masses of RoHS-substances used in both types of systems (image intensifier systems[1] and digital detector systems)?

[1] In addition tothe substances used in the photocathodes, it would also be important to get comprehensive information allowing a holistic comparison of the two systems. With regards to image intensifier systems this also includesRoHS-substances in other components such as phosphors. Answer - Medical image intensifiers use cadmium in phosphors – we estimate ~0.006mg of Cd in a 25cm diameter image intensifier (hence the

The most commonly used digital detectors are based on silicon with a thin layer of scintillator material that contains thallium. We estimate that one silicon detector will contain only a few tens of milligrams of thallium (this depends on the size of the detector). Thallium doped caesium iodide scintillator does not appear to have a CAS number. The CAS number for thallium iodide is 7790-30-9and that of caesium iodide is 7789-17-5

Less common but having the advantage of requiring lower radiation doses are new cadmium telluride and cadmium zinc telluride detectors. For example, one detector of 20 x 20 x 6mm and typically will contain 6.5 grams of cadmium. CdZnTe CAS is 303114-50-3 andCdTe CAS is 1306-25-8. Image intensifiers contain besides 0.00228 – 0.00342 grams of CrVI, 0.0051 – 0.011 grams Cadmium in the phosphor layer, depending on the size.

9. You mention that digital detector systems require higher radiation doses for some types of treatment (e.g. for single exposure imaging). Could you please provide more information on the differences in X-ray dose and its relation to cancer risks? (A lot of this information was already provided within the exemption request for “Cadmium in phosphor coatings in image intensifiers for X-ray images” – it would be good to provide this information again for a transparent stakeholder process).

Procedures that require continuous real-time imaging subjects patients to higher radiation doses if digital detectors are used than with image intensifiers. This is because a higher noise level is acceptable with analogue image intensifiers than with digital detectors. Higher doses are needed with digital detectors to ensure that electronic noise is insignificant and do not hide important features. Continuous imaging is used, for example for angiography where the patient’s blood vessels are viewed while stents etc. are fed through to reach blockages (see http://en.wikipedia.org/wiki/Angiography). The additional X-ray dose that patient’s are exposed to where digital detectors are used is extremely varied and is not possible to quantify as this is controlled to a large extent by medical staff. For many procedures, no additional dose is needed by digital detectors but this depends on the image quality that can be tolerated. Doctors try to use the lowest dose possible to achieve an acceptable image. The dose depends on the type of procedure, the type of X-ray system, the patient and what the doctor is trying to see. Under some circumstances, image intensifier systems can require lower X-ray doses than digital systems but this cannot be quantified.

Effect of increased radiation dose on human health

previous exemption request) but no other RoHS substances are used. The input phosphor is sodium doped caesium iodide and does not contain thallium.

It is understood that there is a linear relationship between radiation dose and risk of cancer. Therefore a 10% increase in X-radiation dose leads to 10% more people having cancer from the radiation. The International Commission on Radiological Protection (ICRP)[2] has determined that the risk coefficient is 5% at 1 Sievert although this is a very high dose and low mS doses are more typical of medical imaging. One of the highest X-ray doses used for imaging is used for cardiology where continuous irradiation is needed to view blood vessels during surgical procedures. Huda[3] has established that typical CT doses which are similar to cardiology doses cause about 1 person in 1,000 (0.12%) to have cancer. In this case, a 10% increase in radiation dose will cause statistically one additional person in 10,000 to have cancer. Clearly, it is important to minimise radiation doses and the "Directive 97/43/Euratom – Medical Exposures Directive" requires that all patient exposures are optimised and so if implementation of RoHS were to result in higher doses, this would conflict with existing EU legislation.

10. You mention various efforts into alternative substances and production technologies that emit alkali metals, both internal and external. When did efforts to redesign production start? Efforts did start back in 2006 and where mainly focused on designing in CrVI free dispensers. Since only one dispenser was available on the market (Alvatec product) the effort was limited to this product. Unfortunately this attempt failed, see also question 4. As soon or in case SAES launches their CrVI free products, new attempts will be done again to design in this product. Critical remains SAES' time to market. This in view of the time left between now and July 21, 2014. Releasing (technical and regulatory wise) such an important component in an image intensifier as part of a medical X-ray device requires a significant amount of time. For the reasons explained in the dossier, external dispensers have not been considered as alternatives to internal dispenser designs.

11. In chapter 4.2 of your request, you mention that "most current II designs use internal alkali dispensers although it is possible to connect an external alkali dispenser to the II or PMT and then to remove the dispenser after fabrication […]". This implies that production of CrVI-free photocathodes is at least partly established on an industrial scale. Could you please provide more information on this production type? We are unable to provide more details of these designs. See answer to Q10.

12. You mention that in end-of-life management, "the mass of output hexavalent chromium in image intensifiers is extremely small and is safely treated as hazardous waste to be

[2] ICRP publication 103 "The 2007 Recommendations of the International Commission on Radiological Protection.

[3] W. Huda, W. T. Rowlett and U. J. Schoef "Radiation dose at cardiac computed tomography: facts and fiction" J. Thorac. Imaging, 2010 Aug; 25(3) p 2014

converted into trivalent chromium […]". Could you please give more information on end-of-life management of X-ray devices? In particular, information on collection rates and pre-processing technologies would help the evaluation process. Where a used X-ray system is taken back by manufacturers, still – functioning image intensifiers are either re-used or are treated as hazardous waste. When IIs become waste, the materials are recycled wherever possible. Manufacturers have contracts with recyclers in all countries who treat the waste alkali dispensers as stainless steel and so recover the iron and chromium content. COCIR has no data on the proportion of end-of-life image intensifiers that are collected because these can be disposed of by a variety of routes and most are not recorded. For example, there are no records if equipment is sold outside the EU or if the hospital arranges for disposal of non-functioning equipment.

13. You repeatedly refer to potential negative socio-economic consequences for the case, no exemption would be granted (e.g. higher equipment costs and subsequent impacts on healthcare). Could you support and quantify your assertions by sound evidence, possibly also providing external research and studies?

One of the justifications for this exemption is only indirectly related to equipment cost. Hospitals have limited budgets for new equipment so if X-ray imaging equipment prices were higher because cheaper image intensifier systems were not available, then hospitals would delay purchase of new equipment and be forced to continue to use old equipment which will have a negative impact on human health (of its patients). We do not believe that this is a socio-economic or cost issue but is a human health issue. The study carried out by ERA for the Commission into the possibility of including categories 8 and 9 in the scope of RoHS found that healthcare budgets are fixed and so if prices rise, hospitals could buy less new equipment. The section "Effect of equipment age on healthcare" of the dossier explains the effect of equipment age on healthcare.

14. In chapter 8 you estimate "that only 5 to 10 grams of hexavalent chromium is placed on the EU market annually by this application". Could you please provide the data and calculations used for this estimate? Please find below the calculation details for global annual production quantities. The following assumptions have been made:

The following data is based on one representative manufacturers products who are assumed to have ~12% market share. The EU is estimated to have one third of the global market. The table below is for this one manufacturer2 image intensifiers:

Size Image intensifier	Weight CrVI per II (g)	Annual quantity (pcs)	Total weight (g)
23 cm	0.00228	1200	2.74
31 cm	0.00342	500	1.71
38 cm	0.00342	300	1.03
		Total (global)	5.48

The estimated annual global consumption of CrVI in this application is ~45.7 grams

Therefore the total EU quantity of CrVI for this application is 13.7 grams

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Note that 15cm IIs are supplied only for repair of existing systems and so are excluded from RoHS.

15. In chapter 9 of your request you lay out a potential roadmap to substitute CrVI-free alkali dispensers. In this roadmap you estimate the time for R&D and reliability testing to take 4 years after 2013. In addition, you estimate another year for the approval-process under the Medical Devices Directive. Could you further explain the basis of this estimation? What types of redesigns do in fact need approval under the Medical Devices Directive? It is not possible to know the whole potential roadmap, because II manufacturers don't drive the steps after release of CrVI-free dispensers on image intensifier level. The timing of release on image intensifier level depends on the time to market of the SAES alternative (see also our comments on questions 5 and 10). Currently the SAES CrVI-free dispensers which are still in development and is currently the only possible feasible alternative. If the SAES alternative becomes available before the end of 2012, a release on image intensifier level is possible in 2014 (if successful). This is in line with availability of new designs of CrVI-free II in 2015 for medical device (X-ray equipment) level. This type of design change, which affects the X-ray image system, will definitely require approval under the MDD which will additional years before sales in the EU are permitted.

16. What is the typical lifetime of the photocathodes usedin X-ray image intensifier systems and photomultiplier tubes? For photomultiplier these are likely to be equal to the lifetime of the image intensifier which is (on average) up to 7 years depending on the application.