MIRION TECHNOLOGIES

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Exemption Request Form

Date of submission:

1. Name and Contact Details

1) Name and Contact Details of Applicant:

Company:	Mirion Technologies	Tel.:	+44 (0) 1252 391890
Name:	Clive Dixon	E-Mail:	cdixon@mirion.com
Function:	Design Group Manager	Address:	2, Columbus Drive, Southwood Business Park, Farnborough, Hampshire, GU14 0NZ, UK

2) Name and Contact Details of Responsible Person for this Application (if different from above):

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

2. Reason for Application:

Please indicate where relevant:

- Request for new exemption in: Annex III
- 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
  - Annex IV
- No. of exemption in Annex III or IV where applicable:
- Proposed or existing wording: Cadmium in video cameras designed for use in environments exposed to ionising radiation with a dose rate in excess of 100Gy/hour and a total dose in excess of 100KGy with a centre resolution greater than 450 TV Lines
- Duration where applicable: maximum validity period
- Other:

3. Summary of the Exemption Request/Revocation Request

This exemption is requested to allow the use of cadmium as a photo-detector in ionising radiation tolerant video camera tubes. These cameras are used in nuclear facilities to remotely observe operations and inspect various parts of a nuclear reactor for fabrication defects. They are exposed to high doses of gamma and other radiation that will rapidly damage all other available types of video camera. The cadmium-based photo-detector has optimal optical performance to enable clear images to be obtained. Most video cameras today use CCD or CMOS silicon detectors that cannot be used in high radiation environments whereas the few remaining “vidicon” camera tube types that are commercially available contain RoHS substances (lead or cadmium) and the type with lead (Plumbicon) is less light sensitive and is not gamma radiation tolerant.

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: Video cameras that are designed to be used inside high radiation exposure environments such as in nuclear power plants and radioactive waste management facilities.

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

☐ 1	☐ 7
☐ 2	☐ 8
☒ 3	☒ 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:

c. Please specify for equipment of category 8 and 9:
The requested exemption will be applied in

- monitoring and control instruments in industry YES
- 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)
   Cadmium

3. Function of the substance: Visible light detection and imaging with resistance to ionising radiation, especially gamma radiation

4. Content of substance in homogeneous material (% weight): 58.7% (Cd in CdSe)

5. Amount of substance entering the EU market annually through application for which the exemption is requested: 0.03 to 0.12 grams to support stated figure.

   Manufacturers of Chalnicon tubes do not provide data on the cadmium content. However, the cadmium selenide layer is probably 0.5 to 2 µm thick[1] and an illustrative example tube[2] has a target active area of 15 mm diameter = 176mm^2. In this example, the CdSe volume is 0.09 to 0.35 mm^3. As the density of CdSe is 5.82 g/cm^3, the mass is 0.5 to 2 milligrams of CdSe per tube. The cadmium content of CdSe is 59% Cd so each tube contains 0.3 to 1.2 milligrams of cadmium.

   Mirion estimate that less than 100 cameras with Chalnicon tubes which are in scope of the RoHS directive are placed on the EU market annually so the total amount of cadmium is about 0.03 to 0.12 grams of cadmium per year..

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[1] Many publications give different values, but this range is from US patent 4614891. Thickness of 50 to 300 nm (0.05 to 0.3 microns) is given in; "Growth and characterization of semiconducting cadmium selenide thin films" by K. N. Shreekanthan, B. V. Rajendra, V. B. Kasturi, and G. K. Shivakumar, Cryst. Res. Technol. 38, No. 1, 30 – 33 (2003) and 6 microns from;
http://www.researchgate.net/profile/Yuriy_Gnatenko2/publication/263363816_Study_of_the_correlation_between_structural_and_photoluminescence_properties_of_CdSe_thin_films_deposited_by_close-spaced_vacuum_sublimation/links/00b4953aaaf2501ca2000000.pdf

[2] http://www.electron.spb.ru/data_eng/LI501.pdf

6. Name of material/component: Cadmium used as cadmium selenide based semiconductor detectors. A thin layer of cadmium selenite (CdSeO3) is also used.

7. Environmental Assessment:
LCA: ~~Yes~~
No Not applicable to this exemption request

(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?

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The Nuclear industry has always had a requirement for cameras that are radiation tolerant to 1-2MGy against gamma radiation. These cameras are used for inspection and general surveillance activities in Nuclear power stations while they are also used to monitor various operations in waste processing plants such as those found at the Sellafield nuclear fuel waste processing facility in the UK.

These cameras fundamentally achieve their high radiation tolerance by using a thermionic image sensor (camera tube), which was the image sensor used in all types of camera in the 1960's. These sensors used a light sensitive semiconductor layer on the faceplate of the tube referred to as the target layer. Originally there were a number of different target layers manufactured, however over the years, this image sensor has been replaced by CCD and CMOS sensors in other industries leading to the demise of the thermionic image sensor. Currently there is only one suitable type of thermionic image sensor that is in production called the Chalnicon whose target layer contains 58.7% cadmium.

CCD and in particular, CMOS radiation tolerant technologies have advanced over the past ten years driven primarily by the medical and space industries. However, these sensors have not yet reached the radiation tolerance levels of the Chalnicon tube or those required by the nuclear industry. As a result it is necessary for Mirion Technologies (IST) Ltd to apply for an exemption to allow the use of cadmium in the Chalnicon tube for ROHS 2 compliance.

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

The cadmium selenide layer is required to be sensitive to visible light of all wavelengths visible to the human eye with a high sensitivity and most importantly to have a very high resistance to ionising radiation.

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.)

The equipment is likely to become radioactive in use, so has to be treated as a radioactive hazardous waste. Radioactive hazardous waste is strongly regulated in the EU and so will not enter waste streams with other electrical equipment. Radioactive waste is regulated in the EU[3] by the "Radioactive Waste and Spent Fuel Management Directive".

2) Please indicate where relevant: See 5.1 above.

- Article is collected and sent without dismantling for recycling
- Article is collected and completely refurbished for reuse
- Article is collected and dismantled:

[3] https://ec.europa.eu/energy/en/topics/nuclear-energy/radioactive-waste-and-spent-fuel

- 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

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

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

There are many types of video camera that have been developed, each having different characteristics. As stated above, these have largely been replaced by CCD and CMOS detectors and designs with some radiation tolerance have been developed but these are not able to withstand the high radiation levels in the most demanding environments, such as in nuclear reactors.

The main requirement of the video camera is resistance to very high exposure levels of ionising radiation that occurs in nuclear environments which includes α, β and γ radiation. Shielding can protect the electrical circuitry but visible light has to reach the light detector and so it is not possible to block the ionising radiation which will damage most light sensitive materials. The types of camera detectors that have been developed include:

Vidicon – several types of camera tubes have been developed, although only a few are still manufactured. These include**:**

- Chalnicon – use cadmium selenide detectors and were first developed in the early 1970s and cameras using these tubes are available from several suppliers, but the tubes are made by only one manufacturer that we are aware of.
- Tubes with antimony trisulphide photodetector, but are no longer manufactured.
- Several designs use lead oxide detector (e.g. Plumbicon). Some designs are intended for X-ray imaging using fluoroscopy (this converts X-rays to a visible image that is imaged by the camera).The number of manufacturers is uncertain (for example, Matsushita has ceased production) and there may be none. Plumbicon are not radiation tolerant and so are not suitable as substitutes for Chalnicon.
- Saticon camera tubes use selenium / tellurium / arsenic photoconductor detectors with a layer of antimony trisulphide. These are no longer produced. One suppler advertises Plumbicon tubes (which contain lead) as alternatives[4] to Saticon.
- Silicon diode photoconductor are described by Burle[5], but no known manufacturers exist. However, they are not designed to be exposed to intense ionising radiation.
- Newvicon camera tubes use zinc selenide but also contains cadmium. Apparently available from at least two suppliers[6], but are no longer manufactured and so cannot be used as a substitute. Some types are designed to have sensitive near infrared response.

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[4] http://www.nimaging.com/products/tubes/

[5] "Photosensitive camera tubes and devices handbook", Burle, download from http://www.r-type.org/pdfs/pctdh.pdf

[6] http://www.nimaging.com/products/tubes/ and http://frank.pocnet.net/other/Matsushita/Matsushita_Vidicon-Tubes.pdf

In practice, the only commercially available camera tube with sufficient radiation tolerance is the Chalnicon tube, all other types are either no longer produced (and would have been inferior) or are not sufficiently radiation tolerant for nuclear applications. Several suppliers advertise radiation tolerant cameras which contain Chalnicon tubes and there are also a few suppliers of Chalnicon tubes, but there appears to be only one Chalnicon tube manufacturer (others have ceased production).

Important characteristic for cameras used for observations in nuclear facilities are:

- Sensitivity to visible light
- Low dark current – signal generated in complete darkness
- Stability with temperature
- Image burn-in – this can occur after a long period with a static image and can appear to remain after the objects are moved
- Flare – due to reflected light from the detector surface. Very high light adsorption properties prevent this effect.
- Radiation tolerance and image not affected by radiation

Several of the Vidicon-type camera tubes cannot be considered as alternatives because they also contain RoHS substances, i.e. those that have lead oxide (e.g. Plumbicon) and zinc cadmium selenide (Newvicon) photodetectors.
Of the rest, Chalnicon tubes have the highest visible light sensitivity, lowest dark current and best temperature stability and are not susceptible to image burn-in or flare. Typical comparative data is as follows[7]:

Type	**Signal current nA/µW at 450nm**	**Signal current nA/µW at 600nm**	**Dark current at 30˚C (nA)**	**Dark current at 50˚C (nA)**
Chalnicon	340	430	1	6
Sb_2S_3	120	70	20	>50
Plumbicon (lead oxide)	270	80	2 (from Naraganset XQ2182 data sheet)	
Silicon diode	270	460	10	40
Newvicon	250	430	7 (from Naraganset XQ1440X data sheet)	

As far as light sensitivity is concerned, what is more important is to be close to unity quantum yield in the entire eye sensitive visible light range and as shown in reference 7; this behaviour is closest for Chalnicon.

Solid state cameras

Silicon based such as Charge Coupled Devices (CCD) and CMOS were first introduced in the 1980s. These are made on single crystal silicon substrates with defined, very small areas of extremely thin photosensitive layers and associated interconnection circuitry. Due to the very fine structure and thin layers, these are readily damaged by ionising radiation so cannot be used in locations with high levels of ionising radiation. Furthermore, the image is degraded by radiation significant dose rates (>1KGy (appears as snow!). These limitations are due to charge trapping within the silicon oxide layer that creates electric fields within the device that affect its operation. Neutrons damage the crystal structure of the silicon that equally affects the operation of the solid state sensor.

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

Not applicable as no alternative with required performance exist.

[7] "Photosensitive camera tubes and devices handbook", Burle, http://www.r-type.org/pdfs/pctdh.pdf and "Operating Features for Chalnicon", Technical Information , Aug 1987, Hamamatsu.

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.

Obtaining a clear image at locations exposed to high levels of ionising radiation is not readily achievable because of the radiation induced noise (snow effect), The radiation also rapidly damages the camera causing rapid failure. This is a serious problem in nuclear facilities as it is dangerous for workers to enter to replace them. Vidicon cameras are significantly more radiation resistant than CCD and CMOS types and so have to be used. Also, Chalnicon cameras have several technical advantages described above in section 6 (A). Resistance to ionising radiation can be achieved by using physical barriers such as thick layers of heavy metals such as lead or tungsten but these cannot be used at the viewing position where optically transparent materials must be used. Lenses that do not discolour (go brown) have been developed and glass with a high lead content is an effective barrier to alpha and beta-radiation, but is less effective with gamma-radiation. As a result, the only remaining option is to use a photoconductive material that is resistant to gamma and other ionising radiation. Chalnicon was developed in the 1970s and since has been widely used inside nuclear reactors and nuclear reprocessing facilities because of its unique combination of optical performance and radiation resistance. The choice of photoconductor materials for Vidicon cameras is very limited. The material must be a semiconductor with suitable optical and electrical properties and all possible materials have been evaluated over the last 50 or so years and so it is difficult to envisage any alternative materials that would have all of the required properties and reliability.

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

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

(A) Links to REACH: (substance + substitute) – referring to cadmium selenide and cadmium selenite

1) Do any of the following provisions apply to the application described under (A) and (C)?
   - Authorisation **No**
   - SVHC **No**
   - Candidate list **No**
   - Proposal inclusion Annex XIV **No**
   - Annex XIV **No**
   - Restriction **No**
   - Annex XVII **No**
   - Registry of intentions **No**
   - Registration **Not applicable**

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

(B) Elimination/substitution:

1. Can the substance named under 4.(A)1 be eliminated?
   - Yes. Consequences?
   - No. Justification: - **See answer to Q6.**

2. Can the substance named under 4.(A)1 be substituted?
   Yes.
   - Design changes:
   - Other materials:
   - Other substance:

   No.
   Justification: **See answer to Q6.**

3. Give details on the reliability of substitutes (technical data + information): Alternative cameras do not have all of the required properties. Those with similar optical performance such as CCD and CMOS will fail due to radiation damage. Other types of Vidicon camera tubes either do not give the required performance or are much less resistant to radiation and so will be

less reliable due to their lower resistance to ionising radiation as explained in answer to Q6. Shorter lifetimes are not acceptable as plant operators need to view their facilities remotely as operators will be severely harmed if exposed to these environments. Therefore they are not easily able to replace cameras that fail**.**

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
   1) Environmental impacts:
   2) Health impacts:
   3) Consumer safety impacts:
   - Do impacts of substitution outweigh benefits thereof?**, There are no substitutes**

Please provide third-party verified assessment on this: Not applicable

(C) Availability of substitutes: None that are suitable – see Q6

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

(D) Socio-economic impact of substitution: Not applicable

- 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:

9. Other Relevant Information

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

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: