1st Questionnaire Exemption No. 13b (renewal request)

Exemption for „Cadmium and lead in filter glasses and glasses used for reflectance standards“

Abbreviations and Definitions

Cd	Cadmium
Pb	Lead

Background

The Oeko-Institut has been appointed within a framework contract[1] for the evaluation of an application for granting 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.[1]

Spectaris e.V has submitted the above mentioned request for exemption which has been subject to a first evaluation. The information you have referred has been reviewed and as a result we have identified that there is some information missing and a few questions to clarify concerning your request.

Questions

1. The original exemption refers to glasses used for reflectance standards. You state in this regard:

   > Other: This renewal request does not include or describe reflectance standards as these are different to optical filters in terms of applications, materials and function. Justification for renewal of this exemption for reflectance standards should be provided by reflectance standard manufacturers.

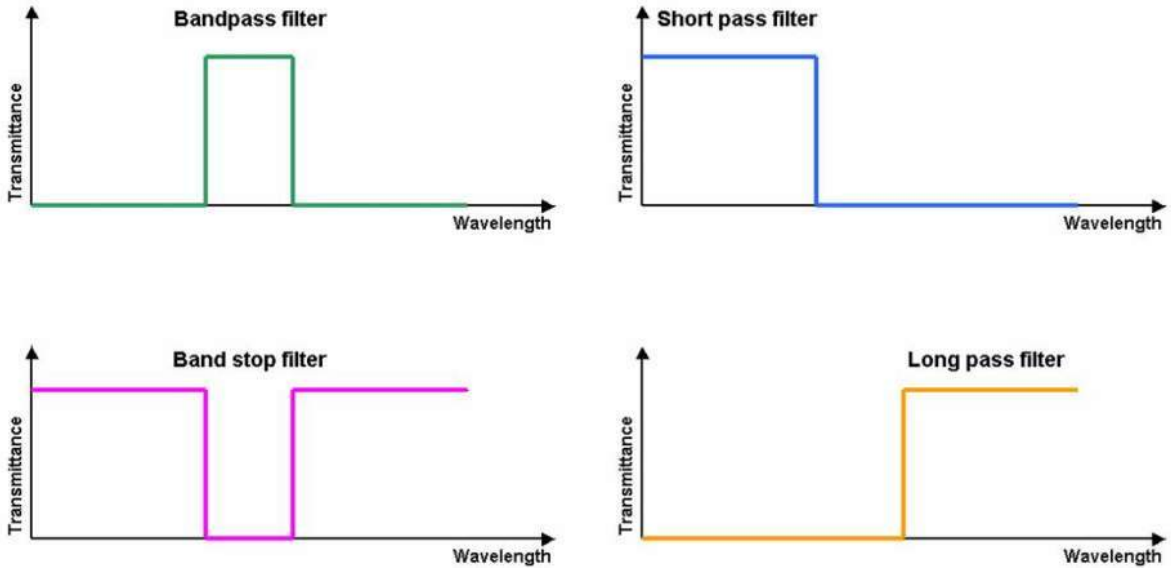
   a. Do you mean that your request only regards use of Cd and Pb in filter glasses, whereas use of Cd and Pb for reflectance standards would need to be supported by such manufacturers? Yes
   b. If this is so, why do you request to renew the original formulation of the exemption? A reflectance standard manufacturer has informed Spectaris that cadmium-free reflectance standards have not been developed and so they still need the exemption and so no change in the current wording is needed. Spectaris is not expert on reflectance standards and so cannot provide evidence to justify this aspect of the exemption, but we expect that reflectance standard manufacturers will

[1] Contract is implemented through Framework Contract No. ENV.C.2/FRA/2011/0020 led by Eunomia

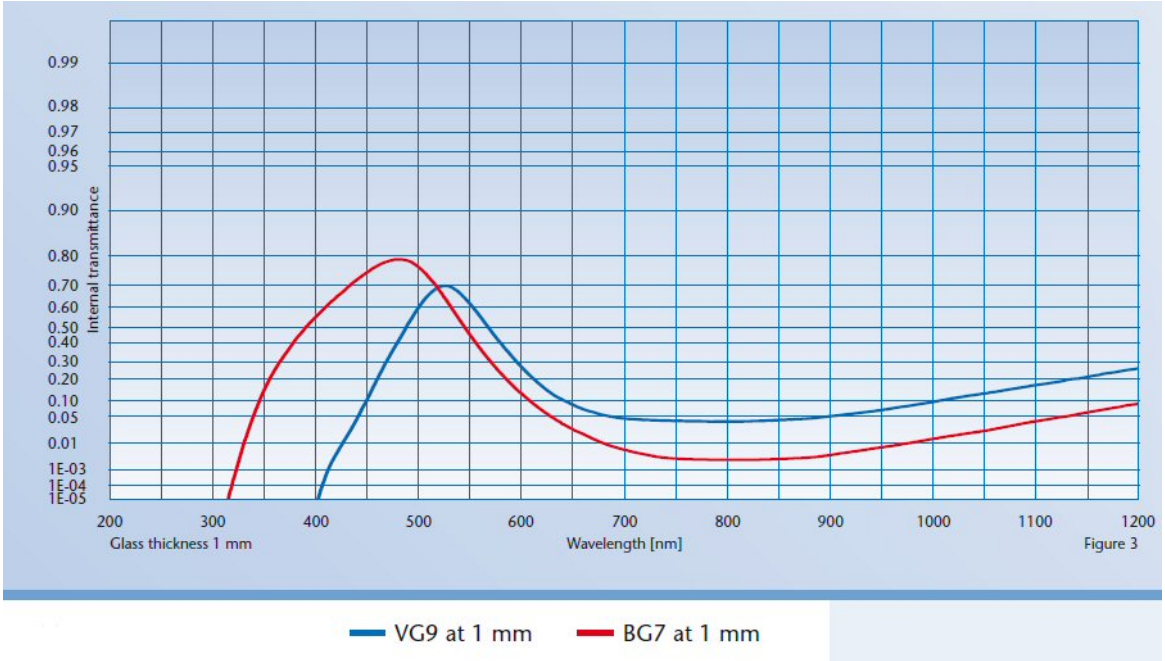
submit detailed evidence as part of the stakeholder consultation for this exemption renewal request.

c. In case justification is not provided for use in reflectance standards, please provide a formulation for the applications for which your members have need for this exemption. Cadmium and lead in filter glasses.

2. Please detail names of manufactures for both Cd based filter glasses and for lead based filter glasses (i.e.,VG9 glasses). Schott AG, Hoya Japan, Isuzu Japan, Kopp Glass USA, Yinxing China, Haian Baode China
What are the “unique properties” (s. pg. 26) of Pb that are important for establishing the technical performance required in applications where VG9 glasses are used? i.e., what are the substance properties which prevent the use of substance alternatives? Just like all filters band pass filters such as VG9 should have very steep edges for the separation of the desired transmitted light from the undesired light which is to be strongly blocked. The separation should occur at well-defined wavelengths.

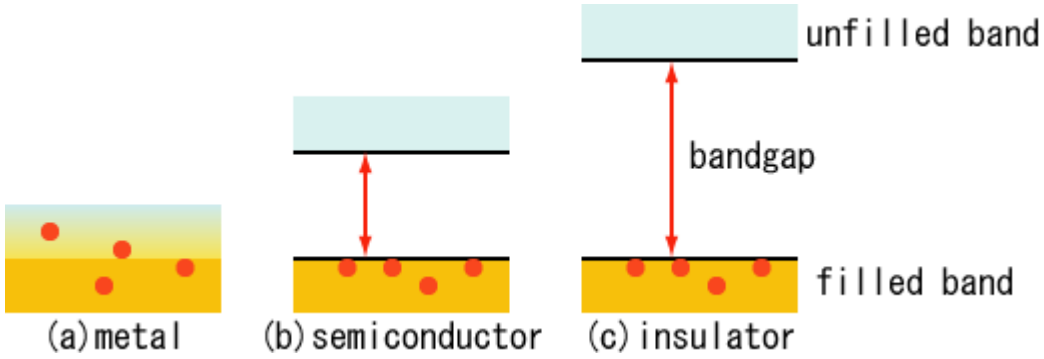


Comparison of the ideal filter characteristics with real filter glasses show that they do not reach 100 percent transmittance and edges are smooth.

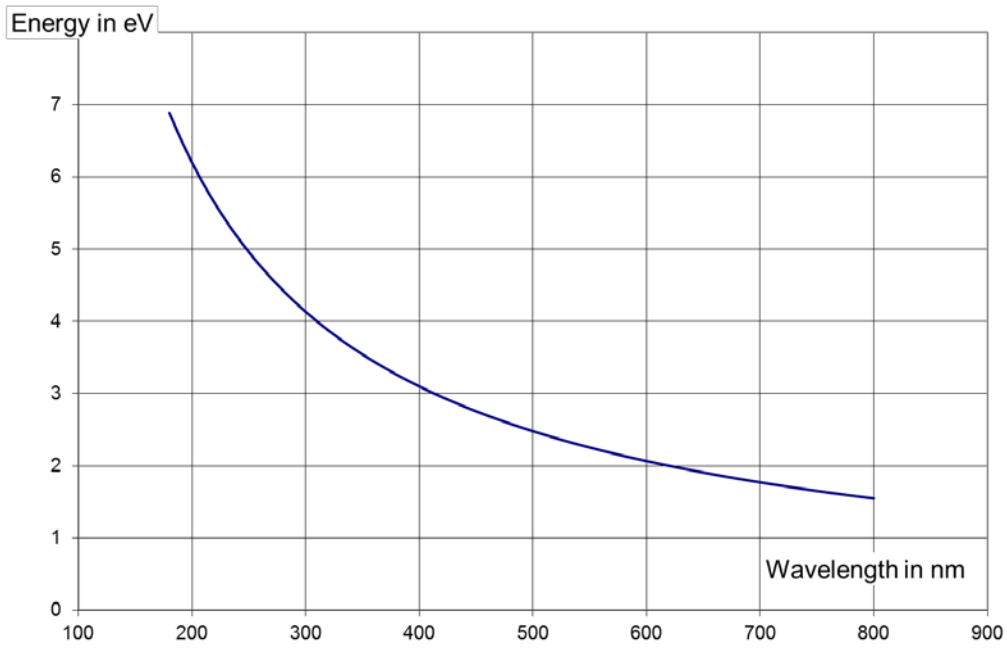


3. With metrology applications false light coming from wavelength ranges, which should be blocked off but still have some residual intensity due to the smooth edges, will reduce signal to noise ratio and thus give inferior reliability and poor image quality. The task in developing such glasses is to find compositions leading to steepest slopes and highest transmission. Mineral filter glasses consist of a base glass and coloring chemical elements. However, one is not free to choose combinations arbitrarily. Only few elements have the required light absorption bands. In the case of VG9 they are copper and chromium III in combination. In different base glasses the absorption bands of these coloring agents will shift in position and vary in width. For VG9 the optimized base glass is a silicate glass with 15 % lead oxide in its composition. Other variants will decrease filter characteristics quality.
4. What are the properties of Cd that are important for establishing the “wavelength sharp cut-off” property, explained to be the performance aspect for which it is used in various applications and for which substitutes are said not to be available? This is explained in the exemption renewal request document from Spectaris in section 4A.3 on pages 9 to 11 and section 6 on pages 19 to 22. On page 11 in the exemption application we wrote:

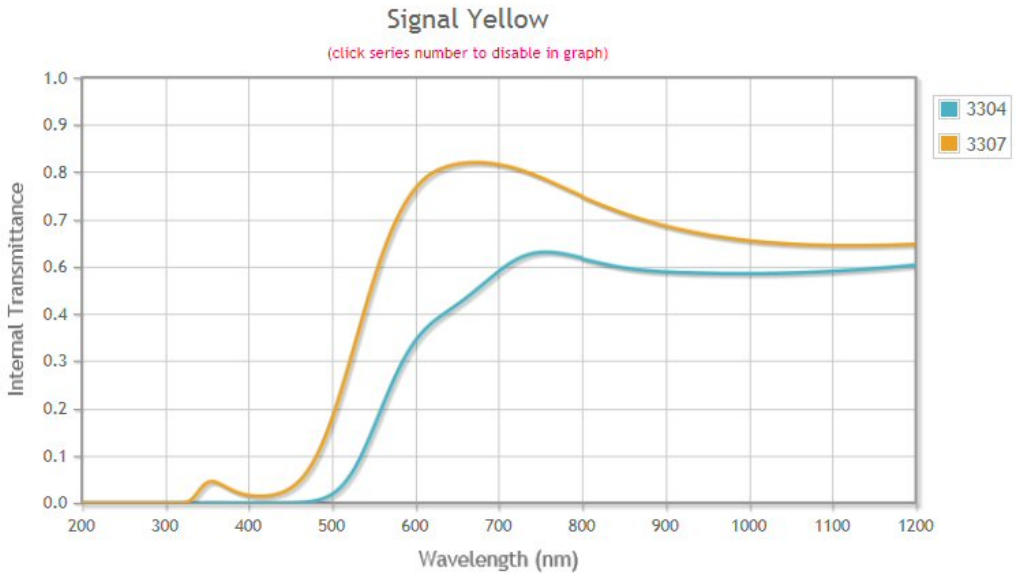
   “The cadmium compound initially appears to disperse to give a colourless clear glass. This is then heated to nucleate and crystallise very small (sub-micron), coloured cadmium chalcogenide particles that are dispersed in a colourless matrix.”
   The steep slope effect is based on the semiconductor electron band gap characteristic of the microcrystals formed by the cadmium compounds.



In order to cross the gap, electrons must have energy higher than the threshold value given by the gap width. For the glass type GG495 e.g. this energy lies at 2.5 eV. All light with higher energy will be strongly absorbed. Just below this energy electrons cannot surpass the gap anymore and light will be fully transmitted.
This semiconductor property for its microcrystal lying in the desired energy range and even allowing adjusting the gap width and thus the absorption edge position with a temper process is absolutely unique for the cadmium chalcogenides. No other compounds have been found that perform this function.



5. It is understood that there are 3 types of alternatives which could replace the use of Cd filter glasses. On page 19 it is mentioned that where possible these have been applied in some applications, however cannot be used to replace Cd filter glasses in applications in which it is still used.
    a. On what basis do you assume that where alternatives are available, that they are applied instead of Cd filter glasses? If the strict tolerances on steep slopes are not required customers change to cheaper alternatives such as yellow glass e.g. from company Kopp USA.



Also coated filters are cheaper than colored filters. They can be used if transmissive sidebands and the angular dependence of coated filters are acceptable.
Plastic filters are also much cheaper than the colored filter glasses. They will be used, when filter function tolerances are not stringent and visual color perception is the more important aspect than strict wavelength separation. Plastic and coated filters can block unwanted light only to residual transmission of about 1 %. If this is acceptable they may be used instead of filter glasses, which block unwanted light light to 0,000001 % and below. The very high blocking is needed in applications where safety and reliability is essential.

b. Can you estimate how successful substitution efforts have been since the first Directive (RoHS 1) came into force? What was the ration of Cd based and Cd-free filter glasses manufactured in the past and at present? There is no cadmium free steep slope filter glass even though the search for a replacement with the same filter properties was started at least around 1990. The application of these glasses was always restricted to niches with especially high requirements. For 2007 we estimated the world-wide production of all suppliers together around 60 tons per year. The estimation is coarse since we do not get any real numbers from other companies than Schott. If there was an influence by RoHS1 it is not observable separate from the year-to-year variations.

c. Please provide some examples concerning applications in which substitution efforts have allowed the substitution of Cd. You may refer both to substance substitution within the glass as well as technology developments that have allowed the elimination of the need for Cd. Some examples have been provided in section. 6, pages 19 – 26. When the steep absorption edge is not required, other filters can be used. But if the sharp absorption edge is required the choice will be with the Cd-containing filters. For metrology application with their high requirements on filter characteristics there was no replacement to our knowledge, since there is no alternative with the same performance. For photographic filter applications it can be expected that image processing software can imitate a filter effect so that amateur photographers probably bought less yellow orange and red filters. For professional users with higher requirements this may not be the same.

d. For example, have the developments in digital technologies allowed eliminating the need for Cd in certain devices through the use of digital processing software? If an image is distorted when the cut-off-edge was not sharp enough, digital processing software will not make the image better.

6. You mention that lead is used only in one type of filter glass named VG9. As PB is used in a single component (in use in a number of applications), it would be possible to split the exemption (Pb exemption and Cd exemption) and limit an exemption for Pb in filter glasses only for their use in VG9 glasses (or in a suitable term used to describe such glasses). Please explain why an unlimited exemption has been requested for Pb in filter glasses? VG9 is presently the last glass type out of a family of green filter glasses which originally consisted of seven types. The reduction to one single glass type was done with the catalogue issued in 2005 due to low market requirement. A future need for the presently not offered glass types cannot be excluded. Also, VG9 is a Schott proprietary glass type. Other manufacturers may use lead in different glass filter types (these are likely to be similar to VG9). Further restriction to glass families or glass types would not lead to any useful improvement. A separate exemption for lead in filter glass would result in 13a, 13b and 13c. This will create extra work for the EC and industry at the next renewal to write and assess three requests instead of two, but will not affect the amount of RoHS substance used. 13b is not an unlimited exemption as lead is used in filter glass of only for one specific formulation (VG9). Exemption 13 has allowed the use of lead in filter glass since 2006 but this is the only filter type that uses lead.
7. On page 27, you detail that none of the Cd compounds regulated under REACH are used in filter glasses. Please detail what Cd and Pb compounds are used in filter glasses to allow confirming this statement. As explained on page 27, when cadmium compounds are added to optical glass to produce an optical filter, very small dispersed particles form in the glass matrix. The exact composition of the dispersed particles is uncertain as chemical analysis of these very small particles is very difficult / impossible. However, there is evidence that these particles are non-stoichiometric compounds that contain cadmium, sulphur and zinc from the glass matrix. To achieve a “steep edge”, the dispersed particles are most likely to be a type of semiconductor and as such will not have an exact stoichiometric chemical formula, such as of “CdS or $CdZnS_2$”. The same holds true for Pb compounds contained in filter glasses where it will be present as a complex multi-element mixed oxide.

Please note that answers to these questions are to be published as part of the available information relevant for the stakeholder consultation to be carried out as part of the evaluation of this request. If your answers contain confidential information, please provide a version that can be made public along with a confidential version, in which proprietary information is clearly marked.