Questionnaire 2 COCIR Exemption 11 of RoHS Annex IV

Lead in alloys as a superconductor and thermal conductor in MRI

Acronyms and Definitions

TCB thermal conductor bonds

1. Background

Bio Innovation Service, UNITAR and Fraunhofer IZM have been appointed1 by the European Commission through for the evaluation of applications for the review of requests for new exemptions and the renewal of exemptions currently listed in Annexes III and IV of the RoHS Directive 2011/65/EU.

You submitted information to substantiate your request for the renewal of the above-mentioned exemption. This information was reviewed and as a result, we ask you to kindly answer the below questions for further clarification of your request until 19 May 2021 latest.

2. Questions

1) You explain in your exemption application: *"Nb alloys are superconductors only at temperatures below 9.4 K. They are either immersed in liquid helium which has a boiling temperature of 4.2 K or they are in good thermal communication through thermally conducting bonds with a cooling system that operates at ~4.2 K."*

   a) We assume that these thermally conducting bonds (TCBs) are the "thermal conductor" functionality of lead and lead alloys addressed in the exemption. Is this correct, or is there any other use bonds made from lead and/or lead alloys which are only acting as thermal conductors?

      Lead is also used in thermal conductors (SnPb solder) to equilibrate temperature within the cold zone, with lead providing the function of the prevention of the Sn from causing pest or whiskers.

   b) Would it be possible that you provide a graph showing the principal construction of these thermal communication construction?

      A cross sectional illustration is currently being sourced and will be communicated as soon as possible.

   c) Which materials do these TCBs connect?

      The TCBs mechanically and thermally conntect the superconducting wire entering and exiting the superconducting coils to theelectrical circuit of the magnet. Each MRI

[1] It is implemented through the specific contract 070201/2020/832829/ENV.B.3 under the Framework contract ENV.B.3/FRA/2019/0017

manufacturer has their own proprietary designs so there is variation in the materials that are most suitable and used.

d) Do these thermally conductive bonds have electrical functionalities as well, i.e. do electrical currents pass through them?

Yes.

e) Are the TCBs exposed to stronger magnetic fields?

Yes, the TCBs are exposed to intense magnetic field from MRI coil which range from 0.3 to 7 Tesla and higher.

f) Does superconductivity influence the thermal conductivity as well so that the loss of superconductivity of TCBs would crucially deteriorate the thermal conducicitivity?

No.

g) Which solders are used for these thermal bonds: Metallic lead and/or PbBi and/or other lead-containing alloys?

Lead/bismuth alloy is used.

h) To avoid the use of lead, can TCBs be made from other material be used if the TCBs have no electrical functionality?

No, the TCBs need to have electrical functionality.

i) We understand that the direct immersion into liquid helium of the superconductor is an alternative construction to the design with cooling via thermally conducting bonds. Are there specific technical reasons or conditions why or when the one or the other cooling mode is or even has to be used? We know that each MRI manufacturer may have proprietary designs. Please, however, explain the technical/physical pros and cons of these cooling modes beyond requirements of proprietary designs.

It is important to note that irrespective of the cooling mechanism, the same technical function of the superconducting electrical connection is required, with them being used in both immersive and cryogen free designs.

The benefit of using a cooling system, rather than immersion in helium, is that the small amounts of helium lost during maintenance, if a fault occurs or in the event of a emergency are avoided. This is important because the global helium supply is very limited and global shortages have occurred.

2) In table 1 of your submission you describe and comment the properties of several alternative superconducting materials which might be candidates to replace lead and lead alloys. SnIn, the most promising substitute, has a lower Hc than PbBi, but still a much higher Hc than metallic lead which is also used, and even 100 mT after its degradation are still more than the 80.34 mT of Pb, and the Tc is still above 4.2 K.

a) Why is the Hc of SnIn alloys a problem in the light of the above?

A refernce point of PbBi should be used as a point of comparision, rather than metallic Pb as this is not used. SnIn alloys have a lower critical current than PbBi which is the optimal choice for MRI. In addition to this the Hc of SnIn alloys is less than 100 mT after degradation, this does not mean that it is 100 mT, but rather is consistenly lower than this and is dependant on a variety of factors such as the aging conditions and length of aging. <100mT is too low.

b) Are metallic lead bonds only used for TCBs, or also to conduct eletrical currents?

PbBi is also used to conduct electrical currents.

3) You state in your exemption request that SnIn with the addition of third elements have been shown to increase the critical field and critical current values, which are, however, lower than that of lead or lead-bismuth alloy. BiSnIn and SnInSb alloys have been shown to be superior to SnIn, but are very inferior to lead-bismuth.

a) In table 1, the Hc of SnIn is already higher than that of Pb, and additions of third elements further improve Hc. We assume that the values in table 1 are correct and that your above statement only applies to PbBi, but not for metallic lead. Correct?

Yes, PbBi is the most commonly used superconductor and has a much higher Hc than lead or SnIn.

b) What are Tc, Hc and Jc of these two ternary alloys compared to Pb, PbBi and SnIn (please indicate quantitatively)?

Alloy	Tc	Critical field	Critical current
PbBi	8.4K (ref 4 of exemption 11 request)	3.5T (ref 4 of exemption 11 request) or 1.7T from ref 3 of our request)	Ca. 2 x 10^8A/m^2 at 0.1T, 1.3 x 10^8A/m^2 at 0.2T (ref 4 of exemption 11 request)
Sn35In50Bi15	6.9K (Ref 2) (6.5K from ref 4 of exemption 11 request)	0.18 T (Ref 2)	<10^7A/m^2 at 0.1T, but zero (i.e. resistive) at 0.2T (ref 4 of exemption 11 request)

Pure lead is not included here as it is very inferior to PbBi, so is now rarely used.

4) Lead is used even though its Hc is only 80.34 mT, while SnIn has 640 mT, andPbBi 1,770 mT. This covers a broad range. We are aware that the bonding materials used need to be placed in

[2] https://www.researchgate.net/publication/285627426_Microstructure_and_superconducting_properties_of_Sn-In_and_Sn-In-Bi_alloys_as_Pb-free_superconducting_solders

areas of lower magnetic field strength, which means that Hc influences the contructive freedom. What is the minimum Hc required to still allow the necessary degree of constructive choices?

In practice, lead is very rarely used and PbBi is the optimum alloy. Each MRI manufacturer has their own proprietary designs and there are differences in field strengths depending on the model in question. As a singular example from one manufacturer, a minimum Hc of 400mT would be required, although it is important to note that other manufacturers may have differnet values. However, it can be stated that a higher Hc is always preferable as image quality improves as the field strength increases.

5) According to the Oxford study which you reference, cold-pressing technologies are promising, provided oxidation of the filaments is prevented, which was achieved by using a standard tinning method to prevent filament oxidation. The resulting joints exhibited good metallurgical interface between NbTi filaments. The study reports that the Cu matrix was removed by etching in HNO_3, no hydrofluoric acid used. Your interpretation of the study's results seem to deviate from the authors' opinion. Could you kindly let us know why you arrive at this different result?

The paper's author clearly states that this option is not yet a commercially viable solution and more research is needed. This is one of the planned avenues of investigation which will be explored in the coming years.

6) You state in your exemption request that "Bonding using a mixture of lead-free BiInSn solder with a dispersion of strands of NbTi superconductor have been evaluated[3]. This gave superior performance to the BiInSn solder alloy alone, but was very inferior to PbBi alloy solder.

a) We find BiInSn solders tested in the reference, but cannot find these composite solders in the referenced source. Maybe they are addressed in a different reference?

The reference is "Novel Superconducting Joints for Persistent Mode Magnet Applications", by Tayebeh Mousavi, et al., Electronics and Photonics Vol 1, part 51. June 2016[4]

b) Could you please quantify the performance parameters (Tc, Hc, Jc) of these composite solders?

These are not given in the abstract of this paper, however the values for BiSnIn are given above.

c) Could you please also let us know whether these solders would be used as TCBs and/or as superconductors?

These were investigated as possible superconducting bonds, but were found to be unsuitable as the results were too inconsistent. They have not been assessed as TCBs.

[3] Lead-Free Persistent Mode Joints Between NbTi Wires, T J Davies, M Bristow, T Mousavi, A Thomas, M Lakrimi, C R M Grovenor and S C Speller, dowloaded from https://www.stfc.ac.uk/files/superconducting-joints-for-magnet-applications; source as referenced by COCIR 2020 a.

[4] Abstract available from https://www.cambridge.org/core/journals/mrs-advances/article/abs/novel-superconducting-joints-for-persistent-mode-magnet-applications/480EEE76F9DBF16B7C791AC9DD49D727

7) While you mention NbSn-superconductors next to the NbTi ones, your further arguments for the use of lead are related to the NbTi superconductors only. What is the situation with NbSn superconductors?

MRI usually uses NbTi but NbSn may also be used. Nb−Ti is a solid solution phase whereas Nb_3Sn is an intermetallic phase. Due to the difference of their intrinsic superconducting properties, they have different ranges of applications. NbSn may be used at higher magnetic fields than NbTi, but NbTi is easier to process so is more common in commercial MRI.

Please note that answers to these questions may be published as part of the review 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.

It would be help the review process if you could kindly provide the information in formats that allow copying text, figures and tables to be included into the review report.