Supporting evidence for exemption request 14 "Lead in alloys as a superconductor and thermal conductor in devices that depend on superconductivity for their operation"

1. Name and address of applicant

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2. Introduction

Exemption request 14 is to allow the use of lead in cryocooler cold head in any equipment that require cryocoolers but specifically for category 9 equipment such as NMR. Cryo-coolers are also used in medical equipment such as Magnetoencephalography (MEG).

Cryocoolers are used in all these devices to achieve and maintain the very low temperatures needed to keep helium as a liquid, which is used to keep at a temperature that is low enough for superconduction of superconducting materials. Superconducting Magnets are used for Magnetic Resonance Imaging (MRI), nuclear magnetic resonance (NMR) chemical analysis and in cyclotrons. Very low temperatures are also needed for Magnetoencephalography (MEG) systems. The superconducting magnets used for MRI, NMR, etc., and the superconducting quantum interference devices (SQUID) of MEG, are held at the temperature of liquid helium which is 4K (-269°C) to maintain the superconducting properties that are essential for providing very powerful magnets for MRI and high-end NMR and also for ultrasensitive SQUID magnetic field detectors.

Helium is now considered an irreplaceable natural resource and evaporating it into the atmosphere will be considered more and more wasteful. Also, there appears to be lack of production capacity causing difficulties in deliveries and the associated contracts. Availability of long-term Helium delivery contracts limited in several countries. Minimizing or eliminating He consumption of MEG-systems is of considerable and rising economical, ecological, and practical importance. Although not commercially used yet in MEG, the availability of reasonably priced closed cycle cryocoolers offers a possibility to this end. In MRI, closed-cycle cryocoolers are widely used for this purpose.

In total, the use of Helium of a MEG system, if no cryocooler is used, comprises annually roughly 5000 liters of liquid. The cost of liquid helium has risen continuously over the past ten years and now represents an obstacle to adopting magnetoencephalography. This translates into annual running costs of approximately 50,000 EUR per system. Over a ten-year lifetime of a magnetoencephalography system, the running costs amount to roughly one fourth of the overall investment (excluding personnel costs). A cryocooler-based closed-loop helium reliquefaction system would significantly reduce (but not eliminate) these running costs.

In addition to the ecological, environmental, and economical aspects, the logistics and downtime required by the weekly refills of the system further complicates the adoption of magnetoencephalography. A closed-loop helium reliquefaction system would substantially reduce the involvedness of the technology by entirely eliminating the weekly refills and the associated logistics.

The above withstanding, it is prudent to assume that most new MEG customers would choose to purchase the proposed reliquefaction system. It should also be assumed that the introduction of the reliquefaction system increases demand for the magnetoencephalography system by reducing the aforementioned obstacles to adoption.

3. Cryocoolers

Two types of cryocoolers have been mainly used to cool various types of equipment, like superconducting magnets, to low temperatures: Gifford-McMahon and Pulse Tube coolers. Both are based on cyclic compression and expansion of the working gas, here Helium. During the expansion cycle the expanding and cooling gas flows through a regenerator, a heat exchanger with a high heat capacity and low longitudinal thermal conductivity, and cools it. During compression warm gas flows through the cold regenerator in the cold head of the device and is cooled down prior to the next expansion cycle. The cycle is repeated continuously resulting in cooling of the cold head.

In Gifford-McMahon (GM) devices the actuating force is accomplished by valves and high - and low pressure reservoirs (compressor inlet and outlet) driving the displacer, a mechanical piston which causes the gas to flow back and forth through the regenerator.

In the Pulse Tube cooler the displacer is eliminated. There are no mechanical moving parts in the cooler, except for the compressor and a rotating valve causing the pressure and flow variation in the cold head. The proper gas motion in phase with the pressure is achieved by means of a gas tank/reservoir, connected to a combination of a flow tube, “pulse tube”, and a regenerator via an orifice. The oscillating gas flow through the orifice separates the heating and cooling effects as the displacer does in GM-devices.

These are relatively simple devices that alternately compress and expand helium. When helium is compressed its temperature increases (as do all gases). The generated heat is adsorbed by a material referred to as the “regenerator” which is contained in the “cold head”. The cooled and compressed helium is then allowed to expand whereupon it cools (all gases cool when they expand) so that overall during the compression/expansion cycle, there is a decrease in temperature. With helium it is possible after repeated compression / cooling / expansion to reach and maintain 4K temperature at which several metals are superconductors, to reliquefy helium gas, and, therefore, to minimize the liquid helium loss. The regenerator material must have high thermal conductivity and high specific heat capacity at liquid helium temperatures. The thermal properties of materials at ambient are very different to those at 4K and so the commonly used metals used in domestic refrigerators and freezers are not suitable at 4K. The specific heat of most metals decreases with temperature and the values for most metals are very low at 4K which makes them unsuitable for this application.

Research has shown that lead is a particularly good material in this application as it has high thermal conductivity and high thermal capacity at 4K, which is superior to metals such as aluminium and copper. Lead is also a superconductor at 4K and so has a very high thermal conductivity, far higher than non-superconducting materials. Large temperature fluctuations induce stresses but at very low temperature, most materials become very brittle but lead is relatively ductile and so is resistant to damage.

As the electrical interference of the running cryocooler of either type is too high for MEG measurements, the system still uses liquid helium as refrigerant, and the cryocooler is used intermittently for cooling and liquefying the helium back to the system during when the MEG is not in use, e.g. during the night. The goal is to achieve a duty cycle without loss of helium to atmosphere and, therefore, without need of liquid helium refills.

Due to technical constraints (e.g. temperature profiles which affect the performance), GM type cryocoolers seem to be better suited for the intermittent operation. GM-coolers are also more robust and are commonly used commercially in MRI-systems. Vibration and acoustic noise generated by the cooler should not be a problem as the cooler is off during measurements, provided that the regenerator materials themselves are not very magnetic. When the optional reliquefaction system is installed but not operational, the cryogenic system shall function as if no reliquefaction system was installed.

A typical cooling power required is on the order of a few Watts at 4 K. Lead is used as it has particularly good thermal properties at temperatures below 40K and is used in the first stage of two-stage pumps. Rare earth materials are also be used for <10K so are used as the second stage and they have been proposed in research publications to replace lead, however they exhibit unfavourable magnetic properties which has a detrimental effect on the signal quality particularly to MEG but also MRI so replacement is not straightforward (see P. Goodman report, Cobham Technical Services, ERA Technology report 2009-0394, section 3.2).

Cryocoolers are not made by manufacturers of MEG or NMR and so commercially available coolers are used from specialist manufacturers such as Sumitomo Heavy Industries, Brookes Automation and others. Cryocoolers are designed for specific minimum temperatures and different thermal conductors and designs are needed depending the temperature and performance that is required. Both rare earth and lead metals are used depending on the required temperature and for liquid helium temperatures, both are currently necessary although formulations used are proprietary to cryocooler manufacturers. Cryocoolers that are suitable for MEG all contain lead at present so there are no lead-free alternatives.

Coolers used for MRI are also based on lead cold-heads. The amount of lead in a commercial cold-head is not known to us as this is proprietary to cryocooler manufacturers. The environmental impact of lead in cryocoolers is predominantly determined by other uses because at present there are of the order of 10-20 MEG systems units sold annually world-wide with slight increase expected in future – only a fraction of the number of cryocoolers needed for MRI and other applications including may that are excluded from the scope of RoHS as they are large-scale stationary industrial tools (e.g. cryopumps used in semiconductor fabrication).

The best performance magnets for MRI, NMR and cyclotrons is achieved by using very powerful superconducting magnets and these are made using Niobium alloy superconducting wire. These alloys include Nb3Sn and NbTi are superconductors at temperatures below 18K and 9.2K respectively and so these need to be cooled with liquid helium. The so-called "high temperature" superconductors such as yttrium-barium-copper-oxide (YBCO) which becomes superconducting below 92K were developed in the 1980s but are ceramic materials and are too brittle to be made into electromagnets especially where severe vibration occurs. Also, superconducting properties degrade in powerful magnetic fields and so only certain alloys are suitable for MRI, cyclotrons and the best performing NMR all of which use very powerful magnets. The most powerful magnets currently used for MRI are 7 Tessla and so NbTi superconductors are used for MRI because they remain superconducting in magnetic fields of up to 15 Tesla.

4. Magnetoencephalography

MEG as a product is far from being mass-market, and each system is a dedicated permanent installation for professional use, also installed and de-installed by professionals. The lead in the cold head is contained in confined closed modules where it can also be effectively removed and recycled at end-of life of an MEG system.

The health benefits of MEG clearly outweigh the environmental and health risks associated with the use of the small amounts of lead in this exemption.

SQUID detectors of Magnetoencephalography (MEG) are used to detect extremely small electrical signals within the brain. This is used to generate 3D maps of the brain by detecting and mapping minute brain signals. These signals are extremely small (of the order of femtoteslas – 1/1,000,000,000,000th the strength of a typical domestic magnet) and one manufacturer's MEG, for example has 300 special superconducting quantum interference devices (SQUIDs) used as detectors. The detection of such small signals is only possible in the absence of external electrical noise and this noise can be eliminated only by cooling the detector to liquid helium temperatures.
Helium is a rare and expensive element with very limited natural supply and so it is essential to minimize losses as there is no alternative to helium to maintain very low temperature needed for MRI, MEG, etc. The MRI and MEG equipment are filled with liquid helium when they are manufactured and should not lose this helium for several years before more needs to be added. Helium is maintained at 4K by specially designed compact and efficient refrigeration devices developed by Gifford and McMahon.

5. Analysis of possible alternatives

This exemption is justified because there are no other materials or designs that can currently be used to replace the types of cryocoolers currently used for MEG and other applications. Medical equipment and analytical instrument manufacturers can only use cryocoolers that are commercially available and these currently contain lead thermal conductors as the regenerator. Research into substitute materials is being carried out and publications shows that several possible alternative materials are being evaluated but no lead-free commercial cryocoolers are yet available for liquid helium temperatures which are suitable for MEG and many other applications for cryocoolers.

Cryocoolers that used at liquid helium temperatures are two-stage devices which use both lead and rare earth metals. Lead is ideally suited between 10 and 50K whereas rare earths such as Er_3Ni are used to achieve lower temperatures of less than 10K.
One type of material that has been researched since the 1990s is the rare earth metal erbium. This metal is classified as a critical material because world supply is limited so that a large increase in consumption may not be possible in the short term.

Cold head regenerator materials must be good thermal conductors, have high thermal capacity at very low temperature and be resilient to large temperature changes. This limits the choice to metals and ideally they should not be brittle. Lead meets all of these requirements but very few, if any other materials meet all of the essential requirements. The specific heat of lead decreases with temperature as do most other materials. However, many metals undergo a phase transition at very low temperature and the specific heat values of a few metals rises at temperatures close to 4K when they undergo this phase transition and so there are some metals with higher specific heat values than lead although their thermal conductivity may be lower and many are brittle materials.
Research publications state that rare earth alloys including ErNi, Er_3Ni, $ErNi_2$, $DyNi_2$, Nd, $HoNi_2$ and GdRh all have reasonably high volumetric specific heat values and so are possible candidates as regenerator materials for cryocoolers. They do however suffer from several disadvantages:

- NMR, MRI and MEG are extremely sensitive to magnetic materials which cannot be used within the detection zones of the instruments. All rare earth metals are strongly paramagnetic (and nickel is also magnetic) and so could be highly detrimental to the sensitivity of these machines and so cannot be located close to the instrument.
- Rare earths, despite their name are not especially rare although supplies are limited and they are regarded as being critical metals in the EU. Some rare earth metals are fairly abundant such as neodymium (although demand currently exceeds supply) whereas others including erbium (the most promising candidate) are available only in extremely small quantities. Demand of many rare earth metals exceeds supply and most is produced in China who is imposing export quotas so that manufacturers outside of China may be unable to use rare earth metals except in very small quantities.
- Rare earth compounds with nickel such as ErNi are very brittle and so are very difficult to produce in the useful shapes needed for cryocooler cold heads unlike lead. Erbium itself however is fairly ductile although is more difficult to fabricate than lead.

6. Re-use and recycling of materials from waste EEE

At end of life, the MEG, NMR, cyclotron, etc would be recycled to recover valuable materials, which are mainly metals. These are all professional products and so would never be treated with municipal waste. The equipment is large and heavy so that it cannot be disposed of easily except by professional recyclers. Large items of electrical equipment that have high metals content are nearly always collected, dismantled and valuable metals recovered for reuse. The cryocooler cold head is one part of these large instruments and so would be recycled with the other parts using traditional metals recovery processes. Steel, aluminium, copper and lead can easily be separated and recovered with high yields.

7. Proposed plan to develop substitutes and timetable

Manufacturers of MEG and MRI do not make the liquid helium cooling systems such as the cold head – these are manufactured by their suppliers who produce these products for a wide variety of industries. At least one cold head manufacturer is currently carrying out research into substitutes for lead and is planning to launch the first lead-free cryocooler in 2012 although research is incomplete and so this could be delayed. This manufacturer has found that replacing lead in some types of cryocooler is much more difficult than in others and with some types, it is not yet possible to achieve the performance that is achieved with lead. It is not expected that a lead-free version of the type of cryocooler used for MEG will be available until 2014 at the earliest and as technical issues are yet to be resolved, this may be a later date.

If a suitable "lead-free" device can be developed for evaluation by medical device manufacturers, the time required for evaluation, reliability testing, clinical trials and approval under the Medical Devices Directive could be up to 6 years. Currently there is no certainty that a lead-free design will be developed and available in 2014 but in any event, these cannot be used with MEG for treating patients until they have been validated in clinical trials and approved under the Medical Device Directive and this would appear to be unlikely before 2020.

8. Proposed wording for exemption

Item 11 of Annex IV of the recast RoHS directive is intended to exempt the use of lead when used as a superconductor and also when used in cryocoolers as a thermal conductor when for MRI. As the same designs of cryocoolers are also used for MEG, NMR and cyclotrons, these types of equipment could be added to item 11or the definition could be changed to include all cryocoolers as there are also other types of analytical instrument that utilises cryocoolers. Cryocoolers are used only as parts of category 8 and 9 products and with equipment that is excluded from the scope of RoHS such as large-scale stationary industrial tools.

An alternative proposed new definition for Annex IV to cover the use of lead as a superconductor and also in cold heads of cryocoolers could be:
Lead in alloys used as a superconductor and used as a thermal conductor in cryocooler cold heads.