Application for granting new Exemption: Lead used in pin connector systems requiring non-magnetic connectors

1. Name and address of applicant

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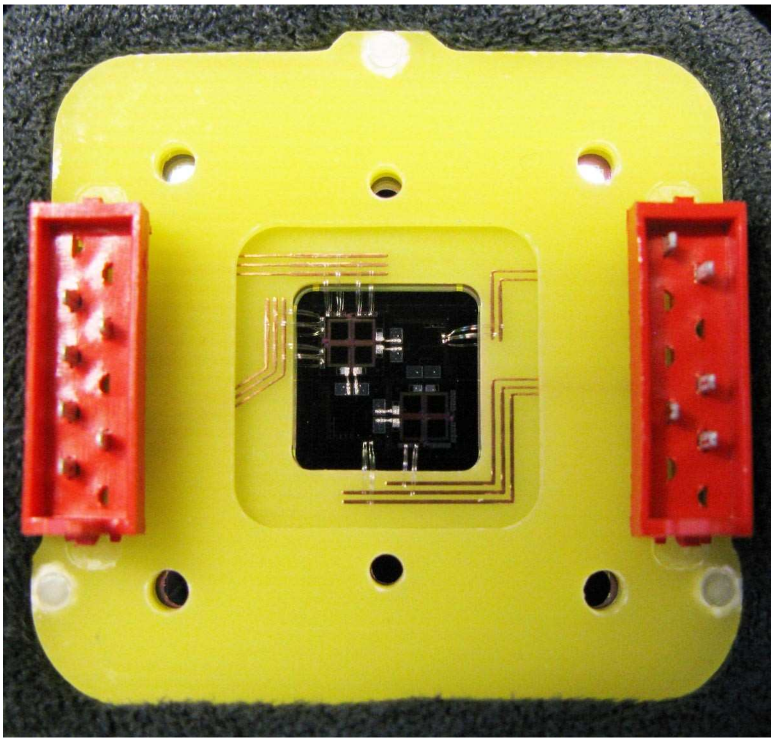
2. Summary of the application

Magneto-EncephaloGraphy (MEG) is a relatively new technique for generating 3D images of the brain using Superconducting Quantum Interference Device (SQUID) detectors. These detectors are cooled to 4K in liquid helium and measure extremely small electrical signals, meaning the pins used in the connectors must be non-magnetic and resistant to very low temperatures. This severely limits the choice of materials that can be used and the only suitable materials are copper pins with tin/lead alloy electroplated coatings. Pure tin and all other tin alloy coatings cannot be used as they are more susceptible to failure from tin pest than tin/lead which has a reasonable resistance. Precious metals silver and gold inter-diffuse with copper so that copper migrates to the surface where it oxidises causing an increased electrical resistance which is prevents the detection of the very weak signals. No substitute material has been identified that can replace lead and no alternative designs found that can be used to make reliable plug-in electrical connections.

3. Description of materials and equipment for which the exemption is required

Magneto-encephalography (MEG) is a fairly new technique that 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 product, for example has 300 special superconducting quantum interference devices (SQUIDs) used as detectors. The SQUID detectors are cooled to 4K with liquid helium and connected electrically with special non-magnetic connectors. These connectors will be very cold although not superconducting and must be non-magnetic to avoid interfering with the detection of very small brain signals. An example is shown below:



Nickel is the most common barrier coating used on electrical connectors of this type which is used between the copper or copper alloy terminals and the external coating of which tin/lead, tin, silver or gold are most frequently used. However nickel cannot be used in this application as it is a strongly magnetic metal and so would impair the performance of the MEG. Copper is used as the base metal for the metal connector terminals because it is physically strong and is an excellent electrical conductor at 4K. Copper however tarnishes in air to form an electrical insulator and so it must be coated with a material that does not tarnish and is a good electrical conductor at 4K.

4. Justification for exemption– Article 5 criteria

The justification for this exemption is that there are no alternative connector coating materials available that will not fail prematurely. Connector coatings must have a high electrical conductivity, i.e. metals such as tin, gold, silver, gold, etc. at 4K and this must not deteriorate in use As MEG SQUID detectors are used to detect extremely small signals, electrical conductivity must be very high and so any combination of metals that will have resistance that increases over time will be unsuitable. Gold or silver plated onto copper but separated by an electroplated nickel barrier is commonly used for connectors but nickel cannot be used for this application. Without nickel, copper rapidly diffuses into gold and silver and when it reaches the surface, it will oxidise causing an increase in electrical resistance. Copper reacts with tin to form an intermetallic layer at the copper/tin interface and so copper does not normally reach the surface unless the tin coating is very thin or the part is used at 100°C or hotter so that intermetallic formation is accelerated and all of the tin is consumed. Tin-copper intermetallic formation will be extremely slow however at 4K.

Tin and most of its alloys cannot however be used because they undergo a phase transformation (tin pest) at low temperatures, which causes the tin coating to form a powder with a high electrical resistance. The coating must also be ductile to allow connector pins to be inserted into sockets (this eliminates brittle metals such as bismuth) and must be non-magnetic and so excludes nickel, iron, cobalt, etc. Section 4 below explains the technical issues that mean that only tin/lead alloy coatings are technically suitable for this application

No alternative designs are possible as connectors are needed to connect and disconnect the SQUID detectors to the electrical measurement system. Permanent soldered or brazed connections are unsuitable for this application.

5. Analysis of possible alternatives

The table below lists the potential alternative materials that are currently used by the electronics industry for connector coatings with comments on their suitability in this specific application.

Connector terminal coating	Comments
Tin lead alloys	Non-magnetic and stable at liquid helium temperatures. Resistant to tin whiskers. Low electrical resistivity at 4K.
Tin, tin silver and tin copper alloys	Will undergo phase change and disintegrate – “tin pest” (see below) and also susceptible to tin whiskers
Tin bismuth	Bismuth retards tin pest phase transformation but is less effective than lead. Tin bismuth is susceptible to tin whiskers, especially as a nickel barrier layer cannot be used. Not readily available as a coating.
Rhodium	Contact material used in reed relays. Unsuitable as moderately paramagnetic
Silver	Tarnishes to give electrically insulating surfaces and inter-diffuses with copper
Nickel	Unsuitable as strongly ferromagnetic
Gold	Unsuitable without nickel barrier because copper from the terminal will diffuse into gold and then oxidize at the surface to give electrically insulating surface layers
Silver palladium alloy	Alloys with high silver content tarnish. Palladium increases magnetic susceptibility and increases electric contact resistance. Electroplating is very difficult, usually applied as thick film material which is not practical for connectors

5.1. “Tin pest” phase transformation.

It is well known that tin coatings suffer from tin pest at low temperature but the behaviour of tin alloy coatings is less well studied. One researcher[1] showed that 99.99% pure tin suffers complete transformation after only 30 hours at -45°C.

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[1] “Suppression of Tin Pest in Lead-free Solders” by Keith Sweatman, JEDEX conference, San Jose, USA 2005

Research with tin and its alloys has not been carried out at 4K so its performance is not known. Research by Plumbridge[2] at the Open University has shown that tin based solder alloys such as those containing bismuth can suffer from tin pest sooner than tin-lead alloy although this research was into bulk alloys whereas electroplated coatings may behave differently. This research has shown after testing a range of commercial alloys at -18°C and -40°C for over 10 years, that some alloys such as SnCu suffer tin pest sooner at -18°C whereas others such as SnAg suffer tin pest sooner at -40°C. This research also showed that tin/lead solder also eventually suffers from tin pest at both temperatures although it has been used in applications such as MRI for many decades without problems which indicates that at the much lower temperatures, the rate is sufficiently reduced for the solder to survive the normal life of the equipment. However this cannot be certain for any other alloys, especially if they have been shown to suffer from tin pest more quickly than tin/lead. The Open University research is studying SnCu, SnAg, SnAgCu and SnZnBi. All alloys have been studied so far for over 10 years at both temperatures except for SnZnBi which has results published after only six years. This research is summarised below. This includes data for what are referred to as "tested" samples. These are alloys that are treated to simulate the effects on real solder joints and so are more realistic than the untested samples but will be different to electroplated coatings used on connectors. Alloys were cast with three different cooling rates and the most realistic, fast cooling showed the most likelihood of phase transformation but all samples are included in the table below which shows the percentage of samples that show more serious signs of phase transformation:

Table 1. Percentage of solder samples exhibiting tin pest phase transformation

Alloy	-18°C 8 years	-18°C 10 years	-40°C 8 years	-40°C 10 years
SnPb	none	11.4%	none	37.5%
SnCu	35.8%	71.7%	14%	58.1%
SnAg	3.8%	22.9%	37.3%	98.7%
SnAgCu	24.2%	56.6%	10%	20%
SnZnBi	100% of samples suffered from tin pest at -40°C after six years			

These results show that all of the substitute alloys tested suffer from tin pest much sooner than SnPb, especially the standard lead-free alloys that are now widely used by the electronics industry. This research also shows that a lead-free solder containing bismuth is also unsuitable as it suffered from tin pest after less than 6 years, much sooner than SnPb.

Evidence that bismuth is less effective than lead additions to tin coatings is available from research published in 2009. This describes a case study where electroplated tin connectors suffered from tin pest after low temperature storage. This investigation found that 5% lead addition was effective at preventing tin pest but 0.5% bismuth or antimony were less effective[3]. 0.5% bismuth additions are fairly standard for coatings on connector terminals. The Open University research is the only work on tin pest which has studied tin alloys for over 10 years at low temperature. All other work is much shorter and so where this showed no transformation occurred, this result is of little value as phase transformation may

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[2] W. J. Plumbridge, "Further Observations on tin pest formation in solder alloys", J. Electronic Materials, Vol 39 (4), p 433, 2010.

[3] N. D. Burns, "A tin pest failure", J. Failure Analysis and Prevention, Vol 9 (5), p 461, 2009

take longer than the tests were carried out and no comparison with tin/lead can be made. Tin pest cannot be accelerated unlike other physical processes because cooling slows the transformation rate and heating up to just below 13°C drastically slows the nucleation rate. No transformation occurs at higher temperatures.

Tin alloys used in MEG will experience much lower operating temperatures than -45°C as is being used in the Open University research. The effect of temperature on tin pest is that as this decreases, the thermodynamic energy to cause the phase transformation increases but the rate of physical processes decreases with temperature. It is therefore difficult to predict what might happen at much lower temperatures and very little published research is available. The overall rate of transformation depends on both nucleation and transformation. Published research has shown that transformation rates depend on the temperature[4] as shown in the table below:

Temperature	Theoretical transformation rate m/s
-10°C	1.5×10^{-5}
-20°C	1×10^{-5}
-30°C	0.6×10^{-5}

Nucleation rates depend on many variables including alloy composition, cooling rate, work history, etc. as well as temperature and so overall tin pest failure rates are impossible to predict and so must be measured.

5.2. Tin whiskers

Tin whiskers are thin rods of tin that grow spontaneously from electroplated tin coatings. These have been known for many decades and have caused the failure of a wide variety of electrical equipment as a result of short circuits. Only since the introduction of the RoHS directive has intensive research been carried out to determine its causes and identify measures to minimise the risk. This research has shown that whiskers form where the tin has compressive stress which can have many different causes. The US organisation International Electronics Manufacturing Initiative (iNEMI) has co-ordinated a lot of research and published guidance on methods to minimise whisker formation[5]. However these recommendations cannot all be adopted with non-magnetic pin connectors. Of the potential substitutes available, only tin and tin alloys electroplated onto copper terminals are viable because non-magnetic metals such as copper tarnish to give a high contact resistance. iNEMI recommend avoiding tin plated onto copper by using gold electroplated onto nickel or tin electroplated onto nickel but these are not suitable options for this application as nickel is magnetic. iNEMI state that if tin is plated onto copper, it should be baked at 150°C within 24 hours to form a thin uniform intermetallic layer. This is also impractical with connectors containing heat sensitive plastic parts (also, tin suffers from tin pest). One of the sources of stress is due to the formation of irregular crystals of tin/copper intermetallic phases that grow between copper substrates and tin plated coatings. Barrier layers and heat treatment prevent irregular tin/copper formation but are not options for this application.

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[4] http://www.electroiq.com/index/display/packaging-article-display.articles.advanced-packaging.volume-15.issue-11.features.tin-pest-in-tin-rich-solders.html

[5] iNEMI has published guidance on mitigation measures against tin whiskers based on many years research, http://thor.inemi.org/webdownload/projects/ese/tin_whiskers/Pb-Free_Finishes_v4.pdf

Another source of stress in connectors is deformation of the tin that occurs when connector pins are inserted. In this application, this stress is unavoidable. There appears to be no alternatives to lead addition to prevent tin whiskers for this application.

The behaviour of tin whiskers at very low temperatures (close to 4K) is not known and no published research has been found. If very low temperatures increase stress levels in the tin coating, this could increase the risk of whisker formation but without long-term research this risk is not known.

6. Life cycle assessment

6.1. Alternative pin coatings

Alternative lead-free terminal coatings include tin on copper, tin alloys on copper and either silver or gold on copper although as explained above, none of these are technically viable alternatives for this application. The life cycles of these materials are briefly described below:

6.2. Mining and refining of metals used to make solders

Tin is widely available as tin ores and production of tin metal is straightforward.

Lead is mined in large quantities as a primary metal with about 8 million tonnes per year being produced. Consumption world-wide is increasing despite the RoHS restrictions due to its main uses for batteries and as a building material. Extraction and refining of lead from its ores is well controlled in most countries so that lead pollution does not occur. Sulphur dioxide is produced as a by-product which is used to make sulphuric acid.

Silver and gold mining **c**reates large amounts of waste and consumes much more energy than tin or lead refining. The quantities of emissions of hazardous substances are far greater than from lead refining. The US EPA has published an extensive life cycle analysis comparing tin/lead with lead-free alloys[6] and this shows that alloys containing silver have much larger environmental impacts than tin/lead in the production phase. Cyanide is used for extraction and refining silver and gold and accidents causing serious environmental damage have occurred.

Bismuth arises as a by-product from mining other metals including lead. It is a relatively rare metal occurring at low concentrations so that significant quantities of energy are required to extract and refine this metal. Availability is not an issue.

6.3. Assembly and use of medical equipment

No differences during this life cycle phase unless premature failure were to occur due to tin pest or tin whiskers. Reliability with lead-free alloys is uncertain (tin pest and tin whiskers) and there is a risk that they may cause unexpected failures. These failures would have a negative impact on healthcare as the equipment will not being available at hospitals when needed. As MEG are expensive, hospitals will have only one machine available.

End of life

Lead: Recycling of electrical scrap at end of life can be carried out safely using modern safe processes that are available in the EU and elsewhere. Only if unsafe recycling processes are carried out in developing countries would lead pose a risk

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[6] See full life cycle analysis of lead-free and lead-based solders
http://www.epa.gov/dfe/pubs/solder/lca/index.htm

although this is small due to the very small amount of lead used in this application.
Silver and gold: It is likely that recyclers will want to recover silver and gold from equipment at end of life. There are safe and very efficient processes used by professional recyclers in the EU and elsewhere but there is a risk that unsafe methods using very hazardous chemicals such as nitric acid and cyanide might be used in developing countries where unsafe recycling occurs.
Other tin alloy additives including tin (Bi and Cu) may also be recovered by modern efficient recycling processes but bismuth is difficult to recycle without suitable complex processes and its presence reduces the value of printed circuit board scrap.

7. Additional information

Although only small numbers of MEG are placed on the EU market annually, each contains ~ 1000 connectors of this type and one manufacturer estimates that the total quantity of lead used in this application is 100g per year for worldwide sales for one manufacturer and there are only 4 or 5 MEG manufacturers in total worldwide. Total lead placed on the EU market is estimated at approximately 100grams (assuming EU is 20% of the world market and each of the five manufacturers use the same amount of lead).

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

At end of life, the pin connectors can be reused or recycled for metals recovery. The standard method for efficient metals recovery used for all types of electrical equipment is smelting and is ideally suited to these components. Copper, tin and lead are recovered with high yields by EU recyclers and emissions are well within the limits imposed by EU legislation

9. Proposed plan to develop substitutes and timetable

Although there are no obvious candidate materials for evaluation, any potential materials would be evaluated by exposure for long periods in the operating conditions experienced by these pin connectors. The test conditions will need to be representative of the operational conditions to ensure that electrical resistance remains low and if tin or tin alloys are evaluated, that tin whiskers do not form and tin pest does not occur. As tin pest cannot be accelerated, this work will take many years with as long as 10 years testing being ideal. Should a suitable lead-free material be found, two years reliability testing in MEG equipment will be needed to collect data that will be needed to gain approval under the medical devices directive (MDD). The timescale is as follows:

Research to identify potential alternatives	1 – 2 years
Testing of alternative materials	10 years minimum
Reliability testing with MEG	2 years
Submission for MDD approval	1 year

This indicates that from R & D starting in 2011, a usable substitute will not be available until at least 2026.

10. Proposed wording for exemption

Lead used in pin connector systems used at temperatures below -20°C requiring non-magnetic connectors