Lake Shore
CRYOTRONICS

RoHS exemption Request Form
Date of submission: 23 May 2014

1. Name and contact details

1) Name and contact details of applicant:

Company:	Lake Shore Cryotronics	Tel.:	(614) 212-1537
Name:	Betsey Krause	E-Mail:	Betsey.krause@lakeshore.com
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2) Name and contact details of responsible person for this application (if different from above):

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

2. Reason for application:

Please indicate where relevant:

- Request for new exemption in: Annex IV
- Request for amendment of existing exemption in Annex IV (item 26)
- 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:

Lead in solders used to make electrical connections to temperature measurement sensors designed to be used periodically at temperature below -150C.

- Duration where applicable: Valid for at least 7 years
- Other:

3. Summary of the exemption request / revocation request

This request is to exempt the use of lead in solders used to make electrical connections to precision sensors that are designed to be used at and cycled through cryogenic temperatures.

Investigations have shown that there are no alternative materials or designs available that are suitable for making electrical connections to cryogenic sensors, due to the combination of essential properties that are required.

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: Cryogenic sensors that are used at low temperatures

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

b. (exemption removed in July, 2011)

1		7	
2		8	Medical devices
3		9	Monitoring and control instruments
4		10	
5		11	
6			

b. Please specify if application is in use in other categories to which the exemption request does not refer: No

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 - Yes

2. Which of the six substances is in use in the application/product?
(Indicate more than one where applicable)
Lead (Pb)

3. Function of the substance:

Lead is a component of the solder used to make electrical connections to cryogenic sensors. Lead based solder is used when tinning wire, when attaching leads (electrical wire) to the sensor body and when attaching the sensor to QC/ Calibration probes for testing in liquid helium, etc.

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

37%

5. Amount of substance entering the EU market annually through application for which the exemption is requested:
CONFIDENTIAL – PLEASE SEE SEPARATE DOCUMENT

Please supply information and calculations to support stated figure.
CONFIDENTIAL – PLEASE SEE SEPARATE DOCUMENT

6. Name of material/component:

Lead in Tin/ Lead Solder. (63wt%Sn/37wt%Pb)

7. Environmental Assessment:
LCA: Yes –

No – LCA not applicable because this exemption is justified because there are no technically suitable substitute materials or designs that are known to be sufficiently reliable.

(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?
Cryogenic sensors are used in a very wide variety of applications, both for research and in OEM equipment. Many of the uses are out of scope of RoHS such as in satellites, Hubble Space telescope (in use so far for 24 years), etc.

The following types of cryogenic sensors are available:

- positive temperature coefficient (PTC) RTD (resistance temperature detector) such as platinum,
- negative temperature coefficient (NTC) RTDs such as germanium and Cernox,
- diodes such as silicon and capacitance types.

Characteristics of these sensors include:

Type	Temperature range (K)	Immunity to ionising radiation	Performance in magnetic fields
Semiconductor (diodes)	1.4 to 500		Fair
NTC	0.01 to 325 (depends on material)	Yes	Cernox and RuO2 have good performance
Capacitance	1.4 to 290		Excellent
PTC	0.65 to 873 (depends on type)	Yes	Fair above certain temperatures

The sensors are very small components, examples include; 3 x 2 mm, 1.5 x 0.6 x 0.25 mm, 1.3 mm diameter disc and all have two or four electrical connections. Not all use solder to make electrical connections and each type of sensor has different material and design requirements. A wide variety of sensor designs are used because each application has different size, function and performance requirements.

- Some types of sensors must use only non-magnetic materials and so nickel barrier layers and magnetic alloys cannot be used. Copper and gold plated copper terminals and palladium/silver thick-film material are commonly used as non-magnetic termination coatings on a wide variety of electrical components, but when soldering, it is important to avoid forming too thick intermetallic phases as these are brittle and can fail by cracking when stressed. As leaded solder melts at a lower temperature than most lead-free solders and its wetting properties are superior, the intermetallic phase thickness tends to be thinner and so is less susceptible to brittle fracture. This is also important on silver palladium thick-film terminations because, the entire thickness can be lost if the soldering temperature is too high and if the Ag/Pd is in contact with molten solder for too long. Ag/Pd/Sn intermetallic phases form which are relatively brittle. This is explained in more detail in answer to Q6.

- Some types of sensor are hermetically sealed with AuSn solder and so electrical connections must use a lower temperature bonding method to make electrical connections. This prevents the use of welding and brazing to make connections, due to the high temperature of these processes.

- Some sensors are made of ceramic materials to which electrical connections are made directly by soldering to metallised pads. These ceramics are relatively brittle materials so brazing or welding are unsuitable as the high temperature would cause cracking.

- A few types of PTC sensors are designed for cryogenic measurement so tin-based lead- free solders cannot be used. These sensors are sold directly to end-users who use them in their own equipment that they construct for own use as well as to OEMs who make commercial equipment. Examples of types of OEM equipment that are in scope of RoHS in which these sensors are used include:

- Dilution refrigerators: temperature measurements down to 8 mK
- Adiabatic demagnetization refrigerators: temperature measurements down to 50 mK
- Closed cycle refrigerators: temperature measurements do to 4 K
- He3 refrigerators: temperature measurements down to 300 mK
- He4 refrigerators: temperature measurements down to 1 K
- High magnetic field-based characterization systems: Measurements down to ~1.2 K
- He bath cryostats: temperature measurements down to 1 K
- Dry (cryogen-free) systems: temperature measurements down to 8 mK
- Sensors sold to Universities and used for R&D. These may be used for many years and in some cases decades at a wide range of temperatures.

The main characteristic of these applications is that the sensors measure very low temperature (down to 0.01K) and may also measure higher temperatures up to 873K. The time at any temperature will be extremely variable depending on the application. In some, the sensor will be at very low temperature for many years, in others applications, temperature will rise and fall so that sensors are at low temperature for many shorter periods.

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

Lead is a component of solder used to make electrical connections to the sensors. Sensors are made from a variety of different materials such as metals, ceramics and glassy materials. In use, the solder experiences very large temperature changes including very low temperature and as a result of these changes, high levels of stress can be imposed. Lead is added to the solder because:

- Lead is the most effective additive that inhibits tin pest phase transformation occurring with tin and its alloys at low temperature
- Lead / tin solder is relatively ductile at low temperature (much more flexible than the most commonly used lead-free solders, welded bonds and conductive adhesives).
- Very low electrical resistivity within the temperature range of use and relatively high thermal conductivity
- Resistance to oxidation and corrosion in conditions of use

- Lead gives a high resistance to tin whisker formation on electroplated tin coatings

Lead based solders have had a very long and successful history of use at cryogenic temperatures, for over 50 years and have proven to be very reliable. Review of published literature has identified very few studies that evaluated lead-free solders to determine whether they will or will not be reliable with devices cycled at low temperature (these publications are described here). Potential failure modes that can occur with high tin (Sn) solders in cryogenic applications include tin pest, embrittlement and cracking on thermal cycling. These devices are stressed during the large temperature cycles – ambient to 1K is a temperature range of 292K. Evaluation of lead-free solders have not been carried out at these very low temperatures to find reliable substitute solders. The lack of substitutes with proven reliability is a concern to users of these sensors who require long-term high reliability. Reliability of an alternative bonding method will require very lengthy research and testing because many of the failure modes that occur at very low temperature cannot be accelerated.

In reference to the following citation, Lake Shore Director of Metrology and physicist John Krause, PhD commented, *"Several years ago I contacted the author about this comment. He made this comment based more on observations than any accumulation of data and he had no hard data to give me. He gave me the name of another person to talk to, which I can't remember, but that never came through with anything more firm."*

> *"Wiring connections made with solders containing a high percentage of tin can embrittle and crack after repeated thermal cycling between room temperature and cryogenic temperatures."* (**Experimental Techniques for Low-Temperature Measurements** by Jack W. Ekin, Oxford University Press, 2006, p.162.)

Ekin also gives his preferences for soldering electrical wires on and reiterates his high tin comment:

> *"For electrical wiring: 63%Sn-37%Pb or 63%SN-36.65%Pb-0.35%Sb eutectic solder (T_{melt} = 183°C); or 93%Pb-5.2%Sn-1.8%Ag for a higher melting-temperature solder (T_{melt} = 299°C). The antimony in the alternative lower T_{melt} solder minimizes embrittlement and cracking, a potential problem that can occur in high-tin solders after repeated thermal cycling to cryogenic temperatures."* (**Experimental Techniques for Low-Temperature Measurements** by Jack W. Ekin, Oxford University Press, 2006, p.105.)

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.)

Not applicable. Closed loops do not exist because used sensors are not returned to the manufacturer.

2) Please indicate where relevant:

- Article is collected and sent without dismantling for recycling **Yes**
- Article is collected and completely refurbished for reuse

- Article is collected and dismantled:
  - 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

Sensors are supplied to OEMs who use these in their products and who will be responsible for compliance with the EU WEEE directive. Lake Shore has not been able to determine the fate of their products at end of life although in the future, most category 9 products (which will contain sensors) should be collected for recycling in compliance with the requirements of the WEEE directive. The sensors are however not likely to be collected and recycled separately.

3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:
Amount of material used is confidential and provided in separate confidential document. The proportions in each route below are not known but it is expected that most will be recycled.

- 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

The potential alternatives to SnPb solder are alternative bonding technologies. These are:

Possible Lead-free solder alloy substitutes	Resistance to tin pest: Tin pest has been known for many decades but most research has been carried out at temperatures between -50 and -30°C because the phase transformation occurs most rapidly within this temperature range and because testing at liquid helium temperatures is difficult to carry out. The rate of tin pest transformation depends on two distinct processes occurring: • The first is nucleation where minute α-phase particles are formed within the β-phase. The driving force for nucleation is the difference in temperature between 13°C and the actual temperature and so the driving force for nucleation increases as the temperature drops. Nucleation usually requires a defect such a grain boundary or a particle of impurity but the time for nucleation to occur varies considerably. • The second process is phase transformation where the α-phase grows from the initial nucleation sites. The rate at which this occurs also varies considerably depending on the alloy composition and its history (as this affects crystal structure) as well as the temperature.

More details on tin pest are described below.

Suitability for soldering to non-magnetic terminals - As nickel barrier layers cannot be used, it is important that wetting times are short and substrate dissolution rates are as low as possible so that the solder pad is not lost completely during soldering and that brittle intermetallic layers are as thin as possible to avoid brittle fracture. Lead-free solders are compared with leaded solders below.

Ductility - There is no published research into the effect of thermal cycles that include very low temperatures and so it is possible only to estimate the likely effect on reliability. It is known that all solders become harder and much more brittle as temperature decreases and most lead-free solders are harder than SnPb. Harder solders are likely to induce higher stress levels that would be more likely to cause more damage to the substrate or the solder. Relatively soft and ductile materials can deform to relieve any stresses that will occur as a result of differential thermal expansion that will occur when temperature changes, whereas brittle materials will not deform so high stress forces will be induced. When attached to brittle ceramic materials that are used for some types of sensors, the high strain imposed by very hard and non-ductile solder substitutes may cause damage to the ceramic or cause metalised bonds used for electrical connections to detach from the surface of the sensors. Softer solders based on indium are discussed the section “thermal fatigue research” below.

Tin whiskers – Tin whiskers grow from tin and tin alloys that are under compressive stress and can cause short circuits. Tin whiskers usually grow fairly slowly so that failures occur after many years or even decades. This is usually associated with electroplated tin as this is often in compressive stress. The behaviour of lead-free solders at very low temperature has not been studied over long periods and tin whisker formation cannot be ruled out.

Electrically conductive adhesives

An alternative to solders is conducting adhesives. This is however only very rarely used to assemble electrical circuitry because its long term reliability and performance (i.e. permanent low electrical resistance) is usually inadequate for most applications, either because its initial resistance is not sufficiently low or due to a gradual increase in resistance that occurs due to loss of metal-metal contact within the bond due to movements caused by expansion/contraction or due to oxidation of base-metals such as copper used for substrates. It will also not be suitable for use in this application because the bonds to components must be resistant to vibration and large temperature changes including very low temperatures where most adhesives will become extremely brittle. The electrical conductivity will also be inferior to solder alloys.

Welded or brazed bonds

Brazing and welding avoids the use of tin so that tin pest is not an issue. However, these bonding techniques cannot be used to build electrical circuitry between copper wire and electronic components because the very high temperatures (>500℃ for brazing and >1000℃ for welding) would destroy most of the types of sensors that are used, as well as the printed circuit board material on which they may be

	mounted. Brazing and spot welding are used on some types of sensors but cannot be used on types that are heat-sensitive or are damaged by thermal shock (most ceramic types).
Mechanical connections such as crimps	These are unsuitable for the very small sensors made by Lake Shore, particularly where an electrical connection needs to be made to a very small ceramic or glass surface, there is nothing for a crimp to “grip”. Mechanical connections can also be unreliable if repeated temperature cycles occur, because this causes differential movements that abrade the surface. This causes loss of thin precious metal coatings and the exposed base-metal substrates will oxidise. The amount of oxide will increase every time there is sideways movement until the amount is enough to cause high electrical resistance and an open circuit (this process is known as “fretting”).

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

> There is only very limited useful research available but this indicates that lead-free solder reliability will be inferior when sensors are used at very low temperatures.

Tin Pest Research

Past research results have been rather confusing due to very inconsistent results, believed to be due to variables that affect the rate at which nucleation occurs as well as the rate of phase transformation neither of which were understood or adequately controlled. Low levels of impurities are now known to be important, but in early research these were not accurately determined because analysis techniques of sufficient accuracy were not available. Other variables that affect rates of both nucleation and transformation include cold working, thermal history, the rate of cooling of solder, aging of solder, the effect of creep; all of which have all been found to affect the rate of tin pest phase transformation, some to a considerable extent. Research at the Open University by Plumbridge[1] showed that pre-treatment of solder samples in ways that real solder joints experience gives samples which had a much higher phase transformation rates than samples that were cast and slowly cooled.

In the Open University research, tin pest nucleation was found to take many years with some alloys. After nucleation, transformation from white to grey tin occurs as the nucleated particles grow. The rate of phase transformation depends on temperature and as with most chemical and physical processes, this decreases as the temperature drops. The kinetics of tin pest are therefore very complex but the net result is that the phase transformation is usually fastest between ~-30 and -50°C. Other elements added to tin significantly alter the tin pest behaviour. Some metals such as lead, antimony and bismuth retard tin pest whereas others such as copper and iron appear to increase the transformation rate. Metals that dissolve in tin such as lead usually retard tin pest as the solution of metals is less susceptible whereas metals such as copper that form solid inter-metallic phases increase the rate of transformation possibly due to the inter-metallic crystals acting as nucleation sites, although this may be an oversimplification.

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

Although there is a lot of research into tin pest published, this frequently provides contradictory results. This is partly because tin pest transformation rates depend on all of the alloying elements including trace impurities that are present at very low concentrations and which are usually not controlled. Research shows that high purity tin with intentional additions can give very fast phase transformations whereas commercial purity solders can take longer due to multiple trace impurities.

There are several other limitations with published research that is relevant to this exemption request. Firstly, most research is carried out over a period of less than two years (post graduate studies are usually completed within three years) but this is not sufficiently long with commercial alloys to determine if and when tin pest will occur because equipment lifetimes are much longer. Unlike other physical processes, it is not possible to artificially accelerate tin pest. Many physical processes are accelerated by raising the temperature but this is not possible for tin pest because if temperature is increased, nucleation is retarded and no transformation will occur if the temperature exceeds 13°C. Research therefore needs to be carried out for periods that are similar to the lives and temperature histories of the electrical equipment in which Lake Shore sensors are used, this can be up to ten or more years, but may not be at a fixed temperature with large fluctuations possible. Another problem is the temperature at which research is carried out. The rate of phase transformation slows with decreasing temperature and so most research is carried out between ~-30 and -50°C to obtain results in as short a time as possible (although this can still take many years). Lake Shore sensors are used in a wide range of temperature including down to 0.01K. At very low temperature, nucleation will be faster due to the larger temperature difference, but phase transformation rates may be reduced, although this is not known as no data is published. However it is likely that phase transformation will be slower at liquid helium temperatures than at -30 and -50°C, and so much longer research trials are needed. It is very difficult to determine by how much the rate is slowed at lower temperatures and whether a solder alloy will survive the required product lifetime based on research carried out at only one temperature, such as at ~-30°C. There are no other data points published for rates at very low temperature to allow extrapolation.

The only published long term research is by the UK Open University which has shown after testing a range of commercial solder 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 this alloy has been proven to be suitable for Lake Shore's cryogenic sensors. However a reliable lifetime is uncertain for all other tin alloys, especially if they have been shown to suffer from tin pest more rapidly than tin/lead.

The Open University research has been studying SnCu, SnAg, SnAgCu and SnZnBi. All alloys for over 10 years at both temperatures with 10 year data published, 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. Alloys were cast with three different cooling rates and the most realistic, fast cooling showed the highest 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:

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 possible substitute alloys suffer from tin pest sooner than SnPb, especially the standard lead-free solders 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.

Research published in 2005 by a Japanese solder manufacturer found the following percentages of transformation at -45°C[2].

Additive to 99.99% tin	% of samples exhibiting phase transformation	
	After 10 hours	After 30 hours
Tin only	80%	100%
0.01%Sb	100%	100%
0.01%Cu	100%	100%
0.01%Zn	100%	100%
0.01%Ag	5%	78%
0.01%Bi	0.5%	3.0%
0.01%Pb	0%	0%

These results confirm that copper accelerates the transformation whereas silver delays but does not prevent transformation, compared to pure tin, but is far less effective than lead. It is often claimed that antimony can suppress tin pest but these results show that small additions are ineffective. Apart from lead, 0.01% bismuth had the greatest delaying effect but even after only 30 hours, 3% had transformed so that after sufficient time, the transformation would be complete. Lead was the most effective with no phase transformation being observed in this test. Further evidence that bismuth is less effective than lead is from research published in 2009 that 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].

Solders used with cryogenic sensors however experience much lower temperatures than -45°C, and the sensors are used within a wide range of temperatures. The overall rate of tin pest depends on both nucleation and transformation rates. Published research has shown that theoretical 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}

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

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

[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

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. Alloy composition is one factor and Plumbridge found that tin pest occurred more quickly with SnCu and SnAgCu at -18°C than at -40°C whereas SnAg and SnPb was more rapid at -40°C than at -18°C. These differences are probably due to differences in both nucleation and transformation rates at these two temperatures and therefore it is impossible to predict how long tin pest will take to occur with lead-free alloys at all of the wide range of temperatures cryogenic sensors are used.

Very little research with tin/bismuth solders at very low temperatures could be found except for the work described above that indicates that it will be inferior to tin/lead. The US standard ASTM B545 states that "*where electroplated tin coatings are subject to long-term storage or used at very low temperatures, it may be advisable to co-deposit small amounts (<1%) of bismuth, antimony, or lead with the tin. These alloying additions, particularly the first, have been shown to inhibit the transformation*". Also, the US Federal specification QQ-S-571 recommends 0.27% antimony addition to tin to prevent tin pest. The only other possible alloy addition where some research has been carried out is with additions of antimony.

The research described above however shows that very low concentrations of antimony are ineffective but tin/antimony solders with several percent of antimony is described in a patent application for cryogenic pumps as being resistant to tin pest at temperatures as low as 4K[5]. SnSb solder is also recommended for cryogenic use by Vishay[6]. This states that the "presence of antimony prevents "tin disease", can be used in cryogenic environments, although is quite brittle at low temperature" and refers to the alloy with 5% antimony that has a melting temperature of 232 - 238°C. Sn5%Sb solder is therefore a very poor choice for two reasons:

- Its melting range of 232 - 238°C is 21°C hotter than 60/40 SnPb and standard SAC (SnAgCu) solder that melts at 217°C. The typical soldering temperature of SAC is ~260°C which is close to the upper safe limit for some types of cryogenic sensors. 280°C would be needed for Sn5%Sb, and this would be too hot for many types of cyro-sensors, which would be damaged.
- Vishay states that Sn5%Sb is brittle at low temperatures. However in applications where there is vibration, there is a risk that Sn5%Sb would suffer from brittle failure due to this vibration.

Alternative alloys – long term reliability at low temperatures

There is very little research on the low temperature properties of lead-free solders that has been published. Alternative alloys are summarised below:

Alloy type	Melting range	Tin pest susceptibility	Suitability
Sn5Sb	232 – 240°C	Resistant	Melting point too high
Sn-25Ag-10Sb	233°C	Not known	Melting point too high.
58%Sn42%Bi	138°C	Not known	Low melting temperature but

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[5] Patent Application WO/2009/146120 "Cryogenic pump employing tin-antimony alloys and methods of use", D. Ball-Difazio, 2009

[6] Vishay "Solders and Accessories", document number 1102319th October 2004.

			is very had and brittle. Bismuth alloys have poor thermal fatigue resistance[7].
57%Sn42%Bi1%Ag	139 – 140°C	Not known	More malleable than 58Sn42Bi. Fatigue resistance concern.
SnAgBi (+others) (Sn3.3Ag4.7Bi, Sn3.5Ag1Bi, various SnAgCuBi)	Typically 208 – 213°C	Not known, but probably inferior to SnPb (based on Plumbridge's results)	Uncommon but available lead-free solders that have been used for laptop PCs (SMT only). Fatigue resistance similar to tin/lead but little data on reliability available.
SnAgIn		Test results available only for 20 months at -18°C. Subsequent behaviour not published	Very uncommon solder with little reliability data available
SnCu	227°C	Very susceptible	M.pt. 217°C. Harder and more brittle than SnPb
SnAg (+Cu)	217°C (eutectic alloy)	Susceptible	Common lead-free used for wave and SMT. Less ductile than SnPb
Sn9Zn, Sn8Zn3Bi	189 - 199	Inferior to SnPb	Requires very corrosive fluxes which can damage sensors. Zinc solders are susceptible to corrosion and so are rarely used

Solder wetting to non-magnetic terminals

Research has shown that all of the commercially available types of tin-based lead-free solder have higher substrate dissolution rates and longer wetting times. This is in part due to the higher soldering temperature needed for lead-free solders, but the absence of the lead phase also appears to have an impact. Comparative tests have been published by Asahi (a solder manufacturer)[8] in which a variety of alloys were compared by wave soldering a standard PCB using a soldering temperature of 245°C.

Alloy composition	Wetting time (seconds)
Tin / lead	0.6
Sn0.7Cu	1.0
Sn3.5Ag	1.4
Sn3.5Ag3.0Bi	1.7
Sn4Ag0.5Cu	1.9

As the temperature affects wetting times by a solder alloy, it is unrealistic to compare tests at 245°C because SnPb is typically soldered at ~235°C whereas lead-free

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[7] HP tested 58%BiSn with 63%SnPb for cyclic thermal fatigue resistance and found that SnBi bonds failed much sooner than SnPb with all of the package types tested. "Low-Temperatre Solders", Z. Mei, H. Holder and H A. Vander Plas. H. P Journal, August 1996.

[8] http://www.asahisolder.com/Publication/Comparative.pdf

alloys may be at ~255°C. At these temperatures, Asahi's test results show that SnPb has considerably shorter wetting time.

SnPb at 235°C	~0.77 seconds
SnAgCu at 255°C	~1.28 seconds

During soldering, the substrate metal dissolves in molten solder at a rate that depends on the alloy composition as well as being proportional to the temperature and the rate increases as the temperature is raised. Research by two organisations is shown below to illustrate this effect with copper as a substrate.

Solder alloy	Rate of dissolution of copper immersed in solder bath[9]	Copper dissolution rate (wave soldering) at specified temperature[10]
SnPb	1.8µm/sec at 275°C	~1.38µm/sec at 255°C (72°C above m.pt.)
SnCu	2.7µm/sec at 275°C	3.28µm/sec at 275°C (~48°C above m.pt.)
SnAg	4.4 µm/sec at 275°C	3.28µm/sec at 275°C (~54°C above m.pt.)
Sn3.7Ag0.7Cu	-	2.3µm/sec at 275°C (~58°C above solidus.) or 3.3µm/sec at 300°C (~80°C above solidus.)

These results show that the risk of complete loss of copper substrate is higher with lead-free solders than with tin/lead solder. Nickel barrier coatings react with liquid solder much more slowly, but cannot be used. Silver and gold substrates also dissolve in liquid solder as rapidly as copper. One manufacturer (Syfer) of non-magnetic passive components having silver/palladium end terminations without nickel barrier layers, advise that one type of these components can be soldered at 240˚C for at most 20 seconds. At the standard lead-free reflow temperature times, no more than 7 seconds is acceptable to avoid a too thick intermetallic layer forming between the tin, silver and palladium. Another manufacturer (Temex) states in their technical datasheet that the maximum time (for one of their components) at 260˚C with the non-magnetic versions must be less than 10 seconds, whereas components with nickel barriers can be at 260˚C for 120 seconds. Lake Shore's sensors are usually hand soldered, where temperature control is difficult and so complete dissolution and loss of the sensor's terminal coatings is likely to occur with lead-free solders on nonmagnetic sensors without a nickel barrier layer.

Resistance to vibration

Most research with lead-free solders has been carried out to simulate and accelerate the conditions experienced by consumer, household and IT products although some military-type applications have also been considered. Some of the tests involve brief excursions below 0°C (down to -40°C) but the time at low temperature in total is always relatively short and almost no research has been carried out at liquid helium

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[9] D. Di Maio, C. P. Hunt and B. Willis, "Good Practice Guide to Reduce Copper Dissolution in Lead-Free Assembly", Good Practice Guide No. 110, 2008, National Physical Laboratory, UK.

[10] C. Hunt and D. Di Maio, "A Test Methodology for Copper Dissolution in Lead-Free Alloys", National Physical Laboratory, UK

temperatures. So apart from the risk of tin pest, the long term reliability of lead-free solder joints at very low temperatures is not known. Solders become less ductile as the temperature decreases and so at very low temperature they can become very brittle. Lead-free solders are less ductile than tin lead at room temperature, examples for unannealed alloys are:

- Eutectic tin 37%lead   Vickers hardness = 12.9
- Tin 4.7%silver 0.7%copper   Vickers hardness = 21.9

Many types of equipment can experience vibration and also big temperature fluctuations and these can have detrimental effects on solder joints. Vibration and temperature cycling typical of consumer and IT equipment has been extensively studied but there has been no research carried at the low temperatures that occur in types of equipment that Lake Shore sensors are used. Research has shown that lead-free solders are more susceptible to failure than eutectic tin lead solders when exposed to vibration with high g-forces[11]. There is therefore an unquantifiable risk that lead-free solders that will be very brittle at low temperature, will have a greater risk of failure at very low temperature than ductile tin/lead solders if vibration or stress, due to temperature changes, occur.

Thermal fatigue research

Thermal fatigue is a well-known cause of failure due to cracking of solder joints. This is due to cyclic stress and is well understood for tin/lead and a lot of research has been carried out with lead-free solders but not at the very low temperatures experienced by Lake Shore sensors. R&D to simulate stresses that occur at “normal” temperatures of 10 to 40˚C may not be applicable at temperatures down to 1K. Thermal fatigue research with lead-free solders shows that at high stress levels, they are inferior to tin-lead, whereas at lower stress levels they appear to be superior. Stress levels are likely to increase as temperature drops from ambient to 1K – a range of nearly 300˚, where the solder will become very brittle. High stress and brittle solder would suggest poor reliability for lead-free solders but as yet, no research is available to determine the true behaviour.

A variety of solder alloys have been suggested for use at cryogenic temperatures but there has been only very limited research carried out and very little published. Indium solders are softer and more ductile than tin/lead and some limited researched has been carried out for it use in space applications, down to -150˚C[12]. This research showed that thermal fatigue life is affected by the type and thickness of intermetallic phase that forms. Also, fatigue life is shorter (failure after fewer cycles) at very low temperatures. For example, with soldering to 0.5µm gold metallisation, at -55˚C, under the test conditions used, there were 6500 cycles to failure, but at -150˚C, there were only 2500 cycles to failure (far fewer cycles). Lake Shore sensors are used at below -250˚C, so the number of cycles to failure are likely to be even fewer (as this solder will be less ductile), although tests at this temperature were not carried out or reported.

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[11] Various research studies, e.g. http://www.jgpp.com/projects/lead_free_soldering/April_4_Exec_Sum_Presentations/JTR%20Reliability%20Conclusions%20March%2028%202006.pdf

[12] http://drum.lib.umd.edu/bitstream/1903/8768/1/umi-umd-5787.pdf

Vishay has published a guide to soldering strain gauges for use at cryogenic temperatures[13]. The optimum alloys for long life at cryogenic temperatures are an alloy with 93.5% lead (plus tin and silver) and SnPb with a trace addition of antimony. Vishay say that tin 5% antimony can be used at cryogenic temperatures but warn that it is “quite brittle” and so will not be suitable for Lake Shore sensors as these can experience vibration and thermal cycling. Vishay do not recommend tin/silver (presumably due to tin pest).

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.

Very extensive testing will be needed to avoid using a small amount of lead. Lake Shore has already carried some research into the possibility of using alternatives, but options for R&D are very limited. All lead-free solders are unlikely to be suitable because of the risk of tin pest. A very uncommonly used solder: eutectic AuSn (gold-tin) has been tested by Lake Shore with a few types of sensor. Solder wetting is poor and the soldering process is very difficult to carry out (poor yields were achieved) as it must be carried out in a vacuum. Work with this alloy has been abandoned by Lake Shore because of the very poor wetting achieved, which is likely to result in early failures of solder bonds. AuSn is rarely used by the electronics industry for this type of soldering due to the difficulty of achieving good bonds and so there is no published research available that describes its long term reliability at cryogenic temperatures.

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

Lead-free solders need to be evaluated to establish the sensor lifetimes under the conditions of use. One of the likely causes of failure is due to tin pest, but testing for this cannot be accelerated, as explained above, and so is likely to require very long periods for testing. Lake Shore are aware that some of its customers use their sensors for at least 15 years and some for even longer. Another potential failure cause is embrittlement (cracking within solder joints). Any potential alloys attached to sensors will need to be thermally cycled at the same temperature ranges that Lake Shore’s sensors experience in use. Fatigue cracking rates depend on many variables such as the rate of change of temperature, the temperature range, etc. and it is likely that many cycles and several cycling regimes will be needed to fully assess each alloy. This type of testing can take many years, because acceleration factors for accelerated tests are not known. Although industry now has some experience with temperatures cycling between -40 and 200˚C, there are no published test results at cryogenic temperatures. Solders are much more brittle at very low temperatures so their thermal cycle behaviour is likely to be very different at -250˚C than at -40˚C. Accelerated testing, to shorten testing times, to simulate use at very low temperature is not reliable unless the acceleration factor is known and this cannot be determined until solders have been used for at least 15 years at cryogenic temperature. It will therefore require many years to carry out this research and this exemption is needed for the maximum validity period.

8. Justification according to Article 5(1)(a):
(A) Links to REACH: (substance + substitute)

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[13] http://www.vishaypg.com/docs/11023/soldacce.pdf

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

Lead and other solder constituents have been registered by EU manufacturers and importers, but Lake Shore manufacturer articles outside of the EU and so registration is not applicable.

2) Provide REACH-relevant information received through the supply chain.
Not applicable

(B) Elimination/substitution:
1. Can the substance named under 4.(A)1 be eliminated?

~~Yes. Consequences?~~

No. Justification:	Potential substitutes will be much less reliable and give inferior performance

2. Can the substance named under 4.(A)1 be substituted?

Design changes:	No, alternative types of sensor either requires a tin-pest resistant solder (with lead) for making electrical connections or the sensors give inferior or unsuitable performance
Other materials:	
Other substance:	No, All lead-free solders are more susceptible to tin pest and from embrittlement at cryogenic temperatures than lead-based solders. There is almost no research published (apart from the work described here) with lead-free solders at cryogenic temperatures for long periods.
Justification:	See section 6

3. Give details on the reliability of substitutes (technical data + information):
See answer to question 6

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to:

1) Environmental impacts:	*Use of potential substitutes (lead-free solder) will shorten the lifetime of products which will result in the*

creation of an increased quantity of waste electrical equipment. There will also be an increase in materials and energy consumption required to manufacture replacement equipment and sensors. Silver is one of the lead-free solder ingredients that has a significant detrimental environmental impact, mainly during the manufacturing and refining life cycle phases but the overall life cycle of silver cannot be directly compared with the overall lifecycle of lead to determine which will have the worse environmental life cycle impact.

2) Health impacts:	None expected unless increased quantity of waste has a health impact on workers who recycle WEEE
3) Consumer safety impacts	None expected (not a consumer application.)

Do impacts of substitution outweigh benefits thereof?
Not applicable as no suitable alternatives exist
Please provide third-party verified assessment on this: Not applicable

(C) Availability of substitutes:
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?
Yes; No;
d) What conditions need to be fulfilled to ensure the availability?
There is no limitation on lead-free solder supply but these are technically unsuitable.

(D) Socio-economic impact of substitution:
What kind of economic effects do you consider related to substitution?

Increase in direct production costs	Yields are expected to be lower so that there will be costs due to increased waste and rework.
Increase in fixed costs	Because the majority of these sensors are sold for out of scope end uses (CERN, NASA, EU Space Agency, as examples,) that specify 63%/37% PbSn solder, we would be required to set up separate production facilities to supply the EU Academic/ Commercial market, if different solders had to be used. Installing a separate additional production facility would be a significant financial burden as more space and equipment would be required. We follow IPC J-STD-001E-2010 for all of our production, which references J-STD-006, as the joint industry standard for aeronautic applications. Using any solder other than what is listed as acceptable in this standard under 3.2 will require setting up a duplicate production
Increase in overhead	Duplicate lines would require a larger facility
Possible social impacts within the EU	Cryogenic temperature devices for scientific research and discovery are vital for laboratories of EU Institutions of Higher Learning. We have (up to 80) papers from EU University Physics, Materials and

	other Laboratories published since 2009 that relied on these temperature devices for their research. Inability to purchase cryogenic temperature sensors will be a burden to these institutions
Possible social impacts external to the EU	
Other	
Provide sufficient evidence (third-party verified) to support your statement:	Not applicable to this exemption request, as it is justified by a lack of suitable alternative bonding methods that have known equivalent reliability.

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:

The answers to Q.4.5 and Q5.3 are confidential, so provided separately. This data gives information on Lake Shore’s market size so is commercially sensitive.