RoHS Exemption Extension Request
Public Statement

Lake Shore Cryotronics, Inc. concurs with and supports COCIR's findings concerning the request for an extension of Annex IV Exemption 26 for:

- Category 8 Medical Device and Equipment, and
- Category 9 Monitoring and Control Equipment

We request that the Commission renew the existing exemption (Annex IV, Exemption 26) that exempts the use of lead in solders used to make electrical connections to include use at and cycling through cryogenic temperatures for Categories 8 and 9, as it currently reads.

Cryogenic sensors are used by many types of customers in the EU, from OEMs that integrate sensors into measurement and control and medical equipment to research labs and departments large and small, who are advancing technological progress. Each use case is different, but the need for reliable measurement at cryogenic temperatures is the same.

The cryogenic sensor industry produces, and customers have come to expect, high quality, durable sensors which provide accurate and reliable measurements over long periods, ten to twenty years in many cases. The use of leaded solders has enabled this long term use and reliability for sensors including those cycled from ambient to cryogenic temperatures used by commercial enterprises and research organizations.

The quality requirements of alternative solders which will enable the cryogenic sensor industry to continue to support business and research organizations with accurate, repeatable, long life sensors requires thorough, long term testing. To date, tests show that alternative methods and materials produce an unreliable, unacceptable, short-lived device with unacceptable performance.

Denying this extension would harm researchers and businesses in the EU who require these devices in their operations and in their scientific and material research. This paper summarizes some of the findings since our original application.

Alternative Methods

Welded/Brazed Bonds and Mechanical Connections

Lake Shore's original exemption application included a detailed description of lead-free solder alloy substitutes, electrically conductive adhesives, welded or brazed bonds, and mechanical connections. This information is just as relevant and accurate today as it was 5 years ago. The underlying problems that make electrically conductive adhesives, welded or brazed bonds, and mechanical connections unreliable for use in cryogenic applications remain unchanged and are unlikely to change with future technological advancement:

- Electrically conductive adhesives are not as conductive as solder and are subject to resistance increase over time.
- Welded and brazed joints still must be conducted at too high of a temperature.
- Mechanical connections are still prone to fretting.

Alternative Materials

Since the previous application, significant research has been conducted to better understand reliability issues with lead-free solder alloy substitutes. Although this research has been ongoing, the issues associated with tin pest, maintaining non-magnetic terminals, and solder ductility described in the previous application are still applicable.

The research conducted since the previous application confirms that these issues are likely to impact reliability, and must be thoroughly investigated before transitioning to a substitute lead-free solder alloy. This is supported by recent studies into low temperature solder reliability, ductility and tin pest/tin whiskers.

Through continued literature exploration and material testing, we have not found:

1. Research on alternative solders over time periods required to evaluate tin pest development,
2. Any alternative manufacturing methods to eliminate the use of 37% lead/ 63% tin solders in these devices, or a
3. Any RoHS compliant solder that makes reliable electrical connections for cryogenic temperature sensors.

Literature Review

Lake Shore's original exemption application included a detailed description of ductility, tin pest / tin whiskers, long term reliability at low temperatures, solder wetting to non-magnetic materials, resistance to vibration, and thermal fatigue research.

This information is just as relevant and accurate today as it was 5 years ago. Lake Shore is continually investigating publications to determine promising candidate solders, which solders have been proven unsuitable, and how to most realistically test solders.

The breadth of knowledge on lead-free solders is ever expanding, but increasingly indicative that solder performance is affected by many factors. Solder alloy, solder pad composition, substrate material, solder application temperature, aging and its temperature, thermal cycling temperatures and dwell times, etc. have all been shown to affect reliability.

The possible permutations of all these factors make it unlikely that published literature will exactly replicate the conditions that Lake Shore products experience. Specific device testing is required to verify that lead-free substitute solders still provide reliable products.

A continual review of updated literature has been beneficial to determine which solders may be the most likely to survive cryogenic temperature sensor environments. Additionally, the published studies provide guidance on test methods and considerations for obtaining useful and representative results. Relevant literature reviewed since the original exemption is summarized below with regards the three of the solders currently being evaluated (SAC305, Sn96Ag4, and SN100C).

Lake Shore's original exemption application asserted that no published research included thermal cycles to very low temperatures, indicating how brittle lead-free solder alloys become in cryogenic applications. Since this application, several studies have tested the ductility of lead-free solder alloys at low temperatures and after exposure to very low temperature thermal cycles.

Low temperature ductility is critical to the solder joints in cryogenic temperature sensors as described in Lake Shore's original exemption application. While some studies have published that the strength of solders increases at low temperatures, this typically corresponds with the solder becoming more brittle, which is problematic. The solder's ability to deform without fracture is more critical to solder joint reliability. Since the original application, several studies have tested the ductility of lead-free solder alloys at low temperatures and after exposure to very low temperature thermal cycles.

Solders with Promise

SAC305:

Research published by Tian et al. at the State Key Laboratory of Advanced Welding and Joining - Harbin Institute of Technology in 2016 showed that SAC305 solder was subject to brittle fracture at temperatures of 123 K and 77 K. (Tian, Ruyu, et al. 2016) Furthermore, the solder tensile strength was halved going from 123 K to 77 K, meaning that the solder joint would survive only half as much stress while strain due to coefficient of thermal expansion (CTE) mismatch is continually increasing.

Research was continued and published with more results in 2017 by An et al., again at the State Key Laboratory of Advanced Welding and Joining - Harbin Institute of Technology. (An, Qi, et al. 2017)This study published that the ductile to brittle transition temperature (DBTT) of SAC305 is higher than that of leaded solder. Additionally, the ductile to brittle transition for leaded solders is more gradual over temperature. At some low temperatures, SAC305 might suffer brittle failure, where leaded solder would merely be subject to strain (elongation).

In 2017, Tian et al. displayed that intermetallic compounds (IMCs) grew in SAC305 joints during 250 thermal shocks from 77 K to 423 K, resulting in more brittle fractures and decreased joint pull strength. Later, in 2019, Tian et al. published that the IMCs grew faster as temperature decreased from -100°C to -196°C. (Ruyu Tian, et. Al., 2017, 2019)

SAC305 remains a viable candidate for further evaluation, with literature indicating that low temperature and thermal cycling have significant effects on its solder joint reliability.

Sn96Ag4

In 2012, R. Pfister published that Sn96Ag4 solder actually loses shear strength at the tested temperature of 77 K, when compared with room temperature. (Pfister, R., Et al. 2012) This behavior is opposite of typical solders, including 63Sn37Sb. The expected cause of this change is the formation of tin pest on Sn96Ag4. When evaluating Sn96Ag4, its strength at low temperatures will require verification after aging to allow some likelihood for tin pest development.

SN100C

When solder joints were tested on resistors by DfR Solutions, presented by Schueller et al., SnPb solder was shown to survive the most vibration cycles, followed by SN100C, and last SAC305. (Schueller, et al. 2010) These resistors are stiff components, most similar to Lake Shore's products, where solders are used to attach wires to stiff ceramic sensor packages. For -40°C to 125°C thermal cycles, SN100C was comparable or better than SAC305 and SnPb.

In 2014, J. Johansson published data comparing -55°C to 125°C thermal cycle data for 0402 and 1206 (imperial) size surface mount resistors, soldered with SnPb, SAC305, and Sn100C solders. (Johansson, et.al 2019) For both size resistors, SnPb solder had the higher number of mean cycles to failure.

George et al. published a study in 2014 on thermal cycling ball grid array (BGA) devices attached with different solders.(Elviz George, et al. 2014) Devices were cycled from -15°C to 125°C. In this study, SN100C had a longer characteristic life than SnPb solder, and SAC305 had the greatest thermal cycle life of all the solders tested.

Published by Arfaei et al. in 2015, another study of solder thermal fatigue reliability on BGA devices, but with -40°C to 125°C cycles agreed that SAC305 had the greatest life, but ranked SnPb solder as having greater life than SN100C. (Arfaei, et. al., 2015)

Varying degrees of reliability have been achieved with SN100C with performance impacted by specific applications. This solder may perform well on Lake Shore devices similar in size to the 0402 resistors tested in the literature.

Since Lake Shore's previous exemption request, many studies have been conducted on the reliability of compliant solders, but the results of these studies are often conflicting. Where one study might demonstrate that a particular alloy had superior performance, another study of the same alloys has shown that a different alloy was superior. Researchers acknowledge that the results of their studies are affected by many factors, including the substrate stiffness, bond pad composition, temperature range and dwell time at temperature extremes. Because solder performance is so application specific, Lake Shore is extensively testing different solder alloys under test conditions most representative of cryogenic temperature sensor environments and duty cycles. Due to the many and varied applications of these sensors, comprehensive testing requires considerable time to acquire informative results.

Lake Shore continues to explore alternative solutions.

Tin pest / tin whiskers

As described in Lake Shore's previous exemption request, tin pest growth is a concern for high tin content solders at low temperatures. This degradation of the material occurs over a timespan of many years. Since tin pest initiation and propagation only occur at low temperatures, typical advanced aging strategies, such as elevated temperature, will not provide meaningful test results.

Outside of Lake Shore, studies have been done to provide some indication on the likelihood of tin pest degradation on lead free solder joints. In 2013, A Lupinacci et al. published results of an accelerated tin pest study.(Lupinacci, et.al. 2013) two phases of tin pest failure exist: nucleation and propagation. Nucleation, the initial defect, can take decades to appear. Once present, the small defect grows in size during the propagation stage. One study bypassed the nucleation phase, by purposefully inserting a defect into a bulk Sn sample. With the defect in place, tin pest did not occur at room temperature, but consumed the sample in a matter of days once cooled to -25°C to -35°C. This study indicates tin pest needs to be studied at low temperature, and the nucleation phase is most critical to long term reliability since propagation can occur relatively quickly compared with the expected life of the sensors. Due to the long times required to witness tin pest nucleation, data from external studies is limited.

Studies that have attempted to characterize tin pest, do not allow for testing over decades. In addition to studies described in the original exemption application, in 2014, Du published observations of tin pest appearance in 63Sn37Pb/Cu and 62Sn36Pb2Ag/Cu solder joints after 10 days of storage. (Du, Xue, et al.

2014) After further testing, no tin pest was observed in SAC305/Cu joints and other 63Sn37Pb/Cu and 62Sn36Pb2Ag/Cu solder joints after 20 days of testing, resulting in a conclusion that “Sn whisker is random and unpredictable.” Since nucleation can take decades, long study durations are required to achieve conclusive results.

As shared in the COCIR application, tin pest testing cannot be accelerated.

Customer Equipment and Sensor Placement

Many applications of cryogenic temperature sensors require that sensors are located where they are difficult or impossible to service or replace.

Replacing sensors that are embedded in in-scope equipment (*MRIs, small scale accelerators, Material Characterization Systems, etc.*) and removing them, if even possible, would prove burdensome, requiring lengthy decommissioning and start up processes for the machine being monitored or controlled by the sensor.

There are also applications where decommissioning equipment to replace a faulty sensor would be burdensome, such as in quantum computers and superconducting turbines, currently under development.

In some cases, because of the way they are mounted, the only way to replace a sensor could be destructive to the equipment. Given this reality, Lake Shore’s products are designed with reliability in mind with expected useful lives of 20 years or more. Since SnPb solders have been in use for many decades and proven, they are trusted by customers.

Continued Development

RoHS compliant lead-free solders are continually being developed and improved. While better alloys will benefit the electronics industry, as a whole, until the industry collects long term tin pest data this phase transformation is a potential cause for future failure of cryogenic sensors.

Lead-free solder research is an active area of research interest as evidenced by the multitude of recent publications. Many studies have shown what appear to be conflicting rankings of solder alloy reliabilities, but are likely results representing unique test conditions. During a continued exemption period, Lake Shore would be able to continue its pursuit of a lead-free substitute solder, with confidence that customers would be provided with reliable products.

Lake Shore continues to test solders to find a suitable and compliant replacement. Continuing this testing during an extended exemption period will allow for longer term study of tin pest, and better prediction of which solder(s) will result in a sensor that can achieve the useful life of existing products.

Availability of Substitutes

Lake Shore does not consider availability to be an obstacle to transition to compliant products. *Reliability of the available compliant products, however, must be demonstrated to ensure product performance is maintained during the typical product life.*

Solder alloys are available off the shelf. That said, some convenient solder form factors are not as readily available that ensure manufacturability such as solder sleeves, solder balls, and solder pastes that have been developed and made commercially available for standard solder mixes.

Sensors are small devices, requiring microelectronic assembly. Lake Shore uses solder form factors to precisely apply solder to its small electronic products. Where 63Sn37Pb was a widely used product within the electronics industry with available form factors, if we were to discover lead-free solders that may work best at cryogenic temperatures, they may not have the market size to justify development of many alternate form factor products for the cryogenic sensor industry. This would be a manufacturing challenge.

Many solders are a patented or proprietary blend. The manufacturers who hold the rights to these products typically sell their products directly or through their own distributors, making sources of supply less universal than standard 63Sn37Pb solders.

Market Expectations for Reliability

While not all customers order flight qualified sensors, cryogenic sensor customers expect the sensors to meet the same long-term reliability requirements. Lake Shore produces sensors against IPC-JSTD-001, Requirements for Soldered Electrical Electronic Assemblies, and to the requirements of MIL-STD-750, Test Methods for Semiconductors and MIL-STD-883, Test Methods for Microcircuits. While not designed to a specific international standard, Lake Shore sensors are designed to withstand the extreme environment of our customers' applications. There is no reason to believe that customers expect less from competing devices.

Long-term stability of the temperature readings is critical to researchers. The sensors must withstand being cycled many times to temperatures even below-150^{o}C without degrading the solder connection. Our customers expect the sensors to perform and meet specification during the life of the sensor, which has been known to be 20 years or more.

Customers also expect repeatability and reproducibility of measurement. Repeatability is the closeness of agreement of successive measurements over a period under the same conditions. Reproducibility is the closeness of agreement of successive measurements over a period under changed conditions. The solder used is a critical component of the sensor and its ability to be repeatable and reproducible over a long period of use.

Summary

The combination of essential properties and durability requirements by customers and researchers at these temperatures and the small size of these sensors requires adhesion with leaded solders.

Lake Shore estimates that at least 11% but up to 25% of the EU research market requiring reliability of cryogenic temperature measurement is *in scope* of the Directive. This includes basic materials research in both the Academic and Government Research communities. This does not include out of scope applications.

> *Not extending the exemption for these devices would negatively affect those doing this scientific and materials research.*

In addition, there are measurement and control equipment requirements in Industrial sectors within the scope of the Directive for equipment that may or may not be used in R&D. Examples include: Dilution refrigerators and cryostats and other equipment that are used in Quantum Computing, Material Deposition and Materials Characteristic testing, as well as industrial Quality Control.

> *Not extending the exemption for these devices would negatively affect those businesses needing these technologies.*

As COCIR discussed at length, we also have found that technology has not been developed for alternative materials and methods. Those materials explored to date produce an unreliable, unacceptable, short-lived device.

Confidential support outlining Lake Shore's testing protocols supporting this statement will be sent under separate cover.

Lake Shore Cryotronics, Inc.

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