

1st Questionnaire (Clarification Questionnaire) Exemption No. 7c-I (request for renewal and change of wording)

Exemption for „Lead containing piezoelectric hard PZT for high performance ultrasonic transducers, and electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in capacitors, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound“

Acronyms and Definitions

HPZT	Hard PZT
PTC	Positive Temperature Coefficient, materials increasing their electrical resistance with increasing temperature; as PTC ceramics used in PTC resistors or PTC thermistors
PZT ceramics	Ceramics consisting of a mixture of PbZrO_3 and PbTiO_3

Background

The Oeko-Institut and Fraunhofer IZM have been appointed within a framework contract¹ for the evaluation of applications for the renewal of exemptions currently listed in Annexes III of the new RoHS Directive 2011/65/EU (RoHS 2) by the European Commission.¹

Bandelin GmbH submitted a request for the renewal and rewording of the above mentioned exemption, which has been subject to a first evaluation. The information you have referred has been reviewed and as a result we have identified that there is some information missing and have formulated a few questions to clarify some aspects concerning your request before we can start the online consultation.

Please answer the below questions until 11 August 2015 latest or otherwise let us know until when you can provide the requested information.

¹ Contract is implemented through Framework Contract No. ENV.C.2/FRA/2011/0020 led by Eunomia

Questions

- 1) Please check whether the translation of your exemption request from German to English in the above headline correctly reflects the intended scope and wording of your exemption request.

Answer:

The translation corresponds to our proposal for changes to Exemption No. 7c1 in Appendix III. However, no account seems to have been taken of our proposal regarding Exemption No. 14 in Appendix IV.

- 2) You propose adding lead in HPZT ceramics to the exemption wording. Does the exemption in the current wording not sufficiently cover your applications, or are there any other reasons for this?

Answer:

Yes, the wording of exceptions 7c1 (Annex III) and 14 (Annex IV) does not currently clearly describe the applied use, as no differentiation is made between soft PZT and hard PZT. Only hard PZT is suitable for high-performance applications. Soft PZT is used for actuators and sensors. Unfortunately the manufacturers of piezo ceramics are unable to produce parameters for high-performance applications, only parameters for small-signal application.

- 3) In the 2008/2009 review² of the Annex to Directive 2002/95/EC (predecessor of today's RoHS Directive 2011/65/EU), the following applications were identified for ceramics containing lead:
- i. PZT ceramics
 - ii. Dielectric ceramics
 - iii. PTC ceramics
 - iv. Thickfilm technology

Please allocate your application of lead in ceramics to one of the applications listed above, or, in case this is not possible, add a new application.

Answer:

Our applications are classified according to Category I, in which PZT ceramics are usually subdivided into soft and hard PZT.

- 4) You mention that lead-free piezoelectric ceramics are available for low performance applications like ultrasonic sensors. They are based on sodium-potassium-niobate (KNN) or bismuth-potassium-barium-titanate (BNT).
- a) Are the sensors you mention actually available on the market, and does Bandelin possibly use them for some applications?

Answer:

We are aware that KNN and even BNT ceramics have since become available on a laboratory basis (pilot production) for sensor applications. However, we are unable to make any detailed statement, as BANDELIN electronic does not use any sensors of this type.

² Gensch et al. 2009

b) Please indicate thresholds that demarcate low from high performance applications.

Answer:

High-performance applications with hard PZT basically employ the inverse piezoelectric effect to produce high dynamic alternating oscillations in high-frequency resonant operation, with amplitudes of up to 10 μm per ceramic element in continuous operation without cooling.

Actuators in static operation work differently, as the oscillation of individual ceramic elements is in the higher nm range, and actuators are consequently always constructed as stack actuators. The electrical alternating excitation in high-performance applications extends into the kV range for each piezo element, unlike the unipolar excitation in the actuator element. Sensors use the direct piezoelectric effect and under mechanical loads generally generate lower electrical voltages.

The known material threshold values also yield clear evidence of the unsuitability of lead-free BNT and KNN piezo ceramics for high-performance applications:

Material	$\tan\delta$ (10^{-3}) (electrical loss angle)	Q_m (mechanical Q)	T_c/T_d Curie/depolarisation temperature
Soft PZT	20	70	260 °C (T_c)
Hard PZT	4	800	320 °C (T_c)
BNT ceramic	30	200	200 °C (T_d)
KNN ceramic	30	unknown	290 °C (T_c)

The figures correspond to the usual mean values

Due to the higher internal losses in lead-free piezo ceramics, a higher proportion of the supplied electric power is converted into heat, leading to significantly lower energy efficiency in the products. For instance, high-performance ultrasonic transducers are pre-stressed by the sonication liquid by up to 80 °C in ultrasonic baths, so the remaining permitted range for the piezo ceramic operating temperature (a continuous operation temperature of only 120 °C is generally prescribed by the manufacturers) is extremely limited, and thus the piezo ceramic must have high efficiency rates or low losses.

To our knowledge, no commercial technology is available for manufacturing adequate piezoelectric components from BNT/KNN which could replace PZT material. Moreover, there is still no reliable evidence of the reliability, long-term stability or availability of piezoelectric components made from these materials.

- 5) You state that you already tested lead-free piezoelectric high performance ultrasonic transducers from an international manufacturer. Can you please provide details about the materials, the tests and the results? It is not necessary to mention the manufacturer of the lead-free ceramics.

Answer:

In our own experiments we have used lead-free BNT piezo ceramic material from HONDA ELECTRONICS, Japan, with the same geometrical dimensions as our own hard PZT ceramics. This permitted direct comparison with high-performance ultrasonic transducers of identical construction. The results showed that, due to the lower Q and higher loss factor, the necessary amplitude and performance range in the analogue HF operating voltage range for hard PZT could not be achieved.

Even in the ordinary continuous operation test, the transducers constructed with BNT discs heated up so strongly as to preclude their use in our products. Due to the low losses, cooling of our high-performance transducer with hard PZT is unnecessary, and, in fact, functionally impossible!

- 6) You say that 10 medium sized companies manufacture PZT ceramics in Germany, and around 30 in Europe. Can you give us a list of those companies?

Answer:

Unfortunately, the wording of our application to the Commission has led to a misunderstanding here. We were actually referring to the users of hard PZT who incorporate this in their high-performance ultrasonic transducers.

A list of the users of hard PZT based high-performance ultrasonic transducers is also given in the appendix, together with a list of manufacturers of piezoelectric ceramics.

Please note that answers to these questions are to be published as part of the available information relevant for the stakeholder consultation to be carried out in the course of the evaluation of this request. If your answers contain confidential information, please provide a version that can be made public along with a confidential version, in which proprietary information is clearly marked. Please take into account that any recommendation on the continuation or revocation of exemption can be based on publicly available information only.

References

(Carl-Otto Gensch, Öko-Institut e. V., et al. 19 February 2009) *Adaptation to scientific and technical progress under Directive 2002/95/EC: Final Report*. With the assistance of Stéphanie Zangl, Rita Groß, Anna Weber, Öko-Institut e. V. and Otmar Deubzer, Fraunhofer IZM. Freiburg: . Accessed July 14, 2015.

http://ec.europa.eu/environment/waste/wEEE/pdf/final_reportl_rohs1_en.pdf;

http://ec.europa.eu/environment/waste/wEEE/pdf/report_2009.pdf.

Appendix

List of manufacturers of ultrasonic devices with high-performance ultrasonic transducers

Company	Germany/Europe
BANDELIN electronic GmbH & Co. KG	Germany
Elma Schmidbauer GmbH	Germany
Herrmann Ultraschalltechnik GmbH & Co. KG	Germany
EMAG AG	Germany
Martin Walter Ultraschalltechnik AG	Germany
Weber Ultrasonics GmbH	Germany
KLN Ultraschall AG	Germany
RINCO ULTRASONICS GmbH	Germany
SONOTRONIC Nagel GmbH	Germany
Hielscher Ultrasonics GmbH	Germany
Ultrasonics Steckmann GmbH	Germany
German Sonic Ultraschallanlagen GmbH	Germany
DE SONIC GmbH	Germany
HGH GmbH & Co. KG	Germany
Hega Systems GmbH	Germany
Sonotop Ultrasonic GmbH	Germany
Gerätetechnik Brieselang GmbH	Germany
Kan-Tech GmbH	Germany
Everest Elektromechanik... Ltd.	Turkey
Ekyma Ultrasonidos s.l.u.	Spain
Protechnology Ltd.	Turkey
Novatec S.r.l.	Italy
Medisafe International Ltd.	United Kingdom
Sono Swiss AG	Switzerland
Sinap Tec	France
KKS Ultraschall AG	Switzerland
FinnSonic Oy	Finnland
TELSONIC AG	Switzerland
Grant Instruments Ltd.	United Kingdom
Langford Electronics Ltd.	United Kingdom
Ultrawave Ltd.	United Kingdom
Z-Projects	Belgium
Soltec S.r.l.	Italy
Notus-Powersonic s.r.o.	Slovenia
C.E.I.A. S.p.A.	Italy
POLSONIC Palczynski Sp. J.	Poland
Greiner Electronics AG	Switzerland
FISA S.A.	France
Liarre s.r.l.	Italy

Nickel-Electro Ltd.	United Kingdom
FALC Instruments s.r.l.	Italy
Tierra Tech S. L.	Spain
JP SELECTA S. A.	Spain
Raypa-R. Espinar S. L.	Spain
ATU Ultrasonidos	Spain
000 Capfir	Russia

List of manufacturers of PZT piezo ceramics

Company	Germany/Europe
CeramTec GmbH	Germany
PI Ceramic GmbH	Germany
Morgan Matroc Technical Ceramics	United Kingdom
NOLIAC A/S	Denmark
Noliac Ceramics s.r.o.	Czech Republic