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PIEZOCERAMICS A/S

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Stakeholder consultation on Adaptation to scientific and technical progress under Directive 2002/95/EC (RoHS) of the European Parliament and of the Council for the purpose of a possible amendment of the Annex

Comments by Ferroperm Piezoceramics A/S regarding Exemption 7(c): "lead in electronic ceramic parts (e.g. piezoelectronic devices)"

Recommendation

We recommend continuing Exemption 7(c) in the Directive.

General introduction

Ferroperm Piezoceramics A/S is a manufacturer of piezoelectric ceramics for a wide range of applications. Only a few of these applications are presently regulated by the RoHS Directive, but some of the major ones are considered for inclusion in the next revision of the directive (in the categories Medical Devices and Monitoring & Control Instruments). The latter categories of applications will be given the main emphasis in the present response. These are of course also regulated by the WEEE Directive, but apart from we are aware of no other overlapping issues with other directives.

General questions

1. For which substance(s) or compound(s) should the requested exemption be valid?
Lead-containing piezoelectric ceramics, such as lead zirconate titanate (PZT) with various dopants and lead titanate with dopants (or more generally, electroceramics as in Exemption 7(c)).

2. What is the application in which the substance/compound is used for and what is its specific technical function?
i) Ultrasonic transducers for medical applications.
ii) Acceleration and vibration measurement.
(for further details see Question 1 in the part specific to Exemption 7(c)).

3. What is the specific (technical) function of the substance/compound in this application?
(see Question 1 in the part specific to Exemption 7(c)).

4. Please justify why this application falls under the scope of the RoHS Directive (e.g. is it a finished product? is it a fixed installation? What category of the WEEE Directive does it belong to?).
i) Ultrasonic transducers for medical applications.

Category 8 of the WEEE Directive. In most cases, the ultrasonic transducer may be considered a separate, replaceable and finished product.
ii) Acceleration and vibration measurement.
Category 9 of the WEEE Directive. In most cases, the piezoelectric accelerometer may be considered a separate, replaceable and finished product.

5. What is the amount (in absolute number and in percentage by weight) of the substance/compound in: i) the homogeneous material1, ii) the application and iii) total EU annually for RoHS relevant applications?
(see Question 2 in the part specific to Exemption 7(c)).

6. Please check and justify why the application you request an exemption for does not overlap with already existing exemptions respectively does not overlap with exemption requests covered by previous consultations.
The present comment refers to an existing exemption. However, we also recommend that this exemption should cover the categories Medical Devices and Monitoring & Control Instruments if these are included in a new version of the RoHS Directive.

7. Please provide an unambiguous wording for the (requested) exemption.
See answer to Question 6.

Specific questions concerning exemption 7(c) ("lead in electronic ceramic parts (e.g. piezoelectronic devices)"):

1. What are the **different applications of lead** in electronic ceramic parts?
Lead is one of the main constituents in the most important type of piezoelectric ceramics, lead zirconate titanate (acronym: PZT; general formula: $PbZr_xTi_{1-x}O_3$), and in lead titanate ($PbTiO_3$). PZT and related lead-based compositions generally show the best combination of properties for the most commercially important applications of piezoceramics. In the following, all these compositions will be referred to as PZT for simplicity.

The main feature of the compositions addressed here is that they exhibit a very large piezoelectric effect. Piezoelectricity is defined as the formation of electric polarisation in certain materials when they are subjected to mechanical stress – or the formation of mechanical stress in such materials when an electric voltage is applied to them. It is a phenomenon closely related to the crystal symmetry and only seen in certain compositions. Although PZT has been used since the late 1950's, the basic understanding of the exceptional properties of this and other lead-based electroceramics (compared with isostructural lead-free materials) is relatively recent. According to Warren *et al*. [1996], a key feature of these materials is the lone pair of Pb^{2+}, which gives quite unique polarisation properties to the whole structure.

Since piezoelectricity is a general link between mechanical energy and electrical energy, there are a large number of applications. The ones that will be described here are i) generation and detection of ultrasound in medical devices, and ii) measurement of acceleration and vibration.
i) Ultrasonic medical devices
The best known application of ultrasound in the medico-technical field is ultrasonic imaging. Piezoceramic parts are used for generating ultrasonic signals, typically in the range 1 MHz to 50 MHz and the echoes are transformed into electrical signals (also by the piezoelectric effect), which is then electronically converted to an image. One of the first applications was foetus examination and other important fields are dermatology and ophthalmology.

A growing application is therapeutic ultrasound, where a strong ultrasonic signal (often high-intensity focused ultrasound, HIFU) is used for treating various diseases ranging from kidney stones to prostate cancer. Finally, ultrasonic monitoring of blood flow using the Doppler effect is a well-established market.

ii) Measurement of acceleration and vibration

In piezo-accelerometers the piezoelectric effect is used to produce an electric signal when the piezoceramic is subjected to vibration. This is widely used for condition monitoring in industrial, automotive and aeronautic applications.

<u>2. What is the **amount of lead** per application, the lead content in the homogeneous material, the annual production volume as well as the number of applications related to exemption 7(c) put on the EU market annually?</u>

Amount of lead per application: typically in the range 0.2 g to 3 g (for the two categories of applications described above – varies strongly with the design).

Lead content in the homogeneous material: typically in the range 60 wt% to 65 wt%.

Annual production volume for applications described above: for Ferroperm Piezoceramics A/S the annual production volume is less than 5 tonnes/yr (i.e. less than 3 tonnes/yr Pb); the total volume for the EU market is not known.

<u>3. Please explain whether and how lead can be **substituted** in the different applications in ceramics.</u>

It is not possible to substitute lead in PZT while maintaining sufficient performance for the above applications. Arguments will be given below.

The search for lead-free alternatives to PZT has been going on for many years and several materials have been proposed. It is outside the scope of the present response to review the literature in this field, but some main conclusions will be given.

a) Substitution of Pb^{2+} by other divalent cations

Other zirconates/titanates than those based on lead exist, but the only one that has been shown to function as a piezoceramic in bulk form is barium titanate ($BaTiO_3$). This material was discovered a few years before PZT, but rather quickly the latter material conquered the market for almost all applications. One of the main problems with barium titanate is the low Curie point of only 120 ºC, above which the ferroelectric polarisation is completely lost (cf. PZT: in most cases above 200 ºC and typically above 325 ºC for commercial compositions). Another very important point is the inferior piezoelectric properties of barium titanate, e.g. longitudinal coupling coefficient $k_{33} \approx 0.49$ (cf. doped PZT: typically 0.7) [Jaffe, 1971; Moulson & Herbert, 2003]. Finally, it should be mentioned that barium (like lead) is a heavy metal and is likely to be the subject of regulation in the future.

b) Layered bismuth oxides

A number of ferroelectric layered bismuth oxides (Aurivillius phases) have been known for many years, the simplest example being $Bi_4Ti_3O_{12}$. A common feature of these is a very high Curie point and a number of them also find use in specialised applications for sensors working at high temperatures. However, for applications requiring good sensitivity or high power, they cannot be used, e.g. $k_{33} \approx 0.09$ for a typical commercial composition (Pz46) [Ferroperm 2008]. Like in the case of barium, one might foresee environmental concerns for bismuth some time in the future.

c) Alkali niobates

This group of materials is probably the most interesting as a possible substitute for PZT. The prototype example is KNN, $K_xNa_{1-x}NbO_3$, with various dopants. A major advantage of this material is that all constituent elements are considered environmentally friendly. Within the last decade, KNN has been the subject of extensive research, since the piezoelectric properties are also interesting. There are some serious practical problems to overcome, however.

KNN has been known for many years to be very difficult to sinter to dense ceramics [Jaffe, 1971] and some of the recent research has examined solutions to this, including modified compositions, changes in processing and alternative ways of sintering (e.g., [LEAF, 2004; Hollenstein, 2005; IMMEDIATE, 2007]). An important publication by Japanese researchers at the companies Toyota and Denso announced the development of modified KNN ceramics with very high properties [Saito *et al.*, 2004]. These materials had a rather complex composition, e.g. $(Li,K,Na)(Nb,Ta,Sb)O_3$, and a complex processing route was used to obtain textured ceramics. The properties reported were in the same range as PZT and consequently many other groups have examined similar materials. The large commercial breakthrough has not resulted, however, since a number of problems have been seen with these materials [Hollenstein *et al.*, 2005]. For practical applications, the major one is the difficulty of obtaining reproducible properties from batch to batch, since small differences in composition or processing may have very serious effects. Furthermore, there are severe reliability issues where properties may change significantly over time, especially in the presence of humidity.

For commercial applications, the price of the materials is of course also important. In this respect it is a serious problem that the content of tantalum in the most promising compositions proposed by Saito *et al*. [2004] is in the range of 20 mol%, since this element is significantly more expensive than the main constituents of PZT (e.g., indicative prices: Ta_2O_5 1000 EUR/kg, TiO_2 100 EUR/kg [AlfaAesar, 2008]).

4. Please provide a **roadmap** or similar evidence with activities, milestones and timelines towards the replacement of lead in these applications.

Given the problems outlined above, it is estimated that a feasible alternative to the lead-based piezoelectric ceramics will not be ready for commercialisation until 2018.

5. Do you consider **thickfilm applications** to be covered by the current wording of exemption 7(c)?

Yes. Ferroperm Piezoceramics A/S are commercialising piezoceramic thick films through the spin-off company InSensor A/S, but these products are also described by the term “electronic ceramic parts”.

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