Exemption Renewal Form – Exemption 14 Annex IV

Date of submission: **02 January 2020**

1. Name and contact details

1) Name and contact details of applicant

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2) Name and contact details of responsible person for this application (if different from above):

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

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2. Reason for application:

Please indicate where relevant:

☐ Request for new exemption in:

☐ Request for amendment of existing exemption in

☒ Request for extension of existing exemption in Annex IV

☐ 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: **14 Annex IV**

Proposed or existing wording: **Lead in single crystal medical ultrasound transducers**

Duration where applicable: **Maximum validity period**

☐ Other: _____

3. Summary of the exemption request / revocation request

Single crystal piezoelectric materials that contain lead give the best imaging performance for medical ultrasound, being superior to polycrystalline lead compounds and lead-free single crystal and polycrystalline materials. Single crystal materials are considerably more expensive than lead-based polycrystalline materials and so are used only where the superior imaging performance justifies the higher cost to EU hospitals. A considerable amount of research into lead-free substitutes has been carried out and is described in the exemption renewal request. Researchers who have reviewed lead-free substitutes have concluded that none give the same performance as lead-based materials and all are inferior. One alternative design has been developed; capacitive Micromachined Ultrasonic Transducers (cMUT), which operates in a different way to ceramic transducers but research has shown that these have much shorter lifetimes and so can be used only for certain applications.

Exemption 14 of Annex IV is related to exemption 7cI of Annex III as both provide exemptions for lead in types of medical ultrasound transducers. These could be combined into one exemption.

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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: Medical ultrasound imaging

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

☐ 1	☐ 7
☐ 2	☒ 8
☐ 3	☐ 9
☐ 4	☐ 10
☐ 5	☐ 11
☐ 6	

b. Please specify if application is in use in other categories to which the exemption request does not refer: _____

c. Please specify for equipment of category 8 and 9:

   The requested exemption will be applied in

   ☐ monitoring and control instruments in industry

   ☐ in-vitro diagnostics

   ☒ other medical devices or other monitoring and control instruments than those in industry

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

   ☒ Pb ☐ Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substance: Piezoelectric material

4. Content of substance in homogeneous material (%weight): Lead content varies, typically about 40 - 65%.

5. Amount of substance entering the EU market annually through application for which the exemption is requested: Estimated amount in EU is about 500 g of lead.
   Please supply information and calculations to support stated figure.
   Calculated from mass of single crystal material used annually for transducers supplied to the EU market and assumes an average of 60% lead content. This has been estimated by one manufacturer using the amount they ship into the EU and their estimated market share.

6. Name of material/component: Most commonly used single crystal materials are: lead magnesium niobate - lead titanate (PMN-PT) e.g. $0.67Pb(Mg_{0.33}Nb_{0.67})O_3$-$0.33PbTiO_3$ and $0.9Pb(Mg_{0.33}Nb0_{.67}$-$0.1(PbTiO_3)$ and also PIN-PMN-PT where PIN = lead indium niobate, such as: $0.23Pb(In_{0.5}Nb_{0.5})O_3$-$0.5Pb(Mg_{0.33}Nb_{0.67})O_3$-$0.27PbTiO_3$.

7. Environmental Assessment: _____
   LCA: ☐ Yes
   ☒ No

(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?

Medical ultrasound imaging is used to generate images of the interior of the human body, such as to examine unborn babies, to examine internal organs to look for tumours or abnormalities, etc. muscles, tendons, blood vessels, etc. It is also used for minor surgery for example to guide hypodermic needles to the required locations.

Medical imaging uses a driver circuit to impose a broad range of AC frequencies onto the piezoelectric material which causes it to generate a broad range of frequency vibrations akin to sound waves. These waves travel from the transducer to an interface, such as the surface of an organ, within the patient where these waves are reflected back to the transducer where they are detected. The force from the reflected waves striking the piezoelectric material generates an electric field that is used to generate an image.

Different imaging frequencies are used depending on what is being viewed, for example higher frequencies give better image quality but lower frequencies are needed to view deeper inside the body (higher penetration). As a result, the transducer should generate a wide range of frequencies, referred to as a large bandwidth.

The ultrasound transducer obtains an image by using one or more piezoelectric elements (often as an array with many elements) which are connected to the control system which also has a display and digital recorder. Modern medical ultrasound imaging uses lead zirconium titanate (PZT) based ceramic materials that are covered by exemption 7c-I of Annex III of the RoHS Directive as well as single crystal materials that give superior performance, but are more difficult to fabricate and so are more expensive than ceramic PZT transducers.

Superior quality medical ultrasound imaging is carried out using single crystal piezoelectric materials rather than polycrystalline (ceramic) materials that are typically used by the electronics industry as buzzers, loudspeakers and actuators and also used for less demanding medical ultrasound applications (and are covered by exemption 7c-I of Annex III of the RoHS Directive). Single crystal materials are superior because of the lack of grain boundaries that would cause loss of signal so that the efficiency and sensitivity are superior to polycrystalline ceramic material. Single crystal technology enables an increase in bandwidth, offering enhanced signal to noise ratio and enhanced axial resolution and penetration. They have larger coupling coefficients and piezoelectric coefficients that lead to better medical diagnostics, i.e. more accurate diagnosis and ability to detect very small features earlier.

Exemption 14 of Annex IV was originally requested in 2006 during the ERA study to determine whether it was possible to include categories 8 and 9 in the scope of RoHS. There was at that time and still is an exemption for lead in glass and ceramic electronic components (7c-I of Annex III), but it is not clear that this includes single crystal materials. Ultrasound piezo single crystal materials are not glass (as they are crystalline, whereas glass is amorphous) nor are they what is normally regarded as a typical ceramic which would be a polycrystalline material and so this exemption was deemed to be necessary.

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

While there are many properties of piezoelectric materials that have a bearing on the quality of the ultrasound image that they provide, only one property continuously improves the output as it is increased, which is the coupling factor. Coupling factor is the efficiency of the material's ability to convert mechanical energy from vibrations into an output electrical charge and vice-versa. It should be noted that this is not the same as the ratio of force applied to charge generated; because the same crystal is used as the receiver and transmitter, so any change in this property would either make it easier to transmit or receive, but the overall effect cancels out.

Two main properties are desired in medical ultrasonic transducers:

- High imaging resolution
- High depth of penetration

To achieve these, the following are needed:

1. High bandwidth – this improves axial resolution and contrast resolution
2. High sensitivity - high frequency at greater depth = higher centre frequency= better lateral resolution

Both a large bandwidth and high sensitivity are required to get the best resolution of ultrasound images.

Ultrasound materials are defined by five piezoelectric parameters:

1. Coupling factor
2. Piezoelectric constants
3. Dielectric constant
4. Insertion and other losses
5. Depoling and Curie temperatures
6. Velocity

Coupling Factor

The coupling factor is the most fundamental property.

$$coupling\ factor = \sqrt{\frac{energy\ that\ can\ be\ converted}{between\ mechanical\ and\ electrical\ energy}}$$

If ultrasound energy is not efficiently converted from electrical to mechanical energy or vice versa, then there is a reduction is sensitivity. Oakley and Zipparo state in their paper that:

> "*A failure to convert a large fraction of energy in a single cycle must result in either a loss of sensitivity (if the energy is not converted in a later cycle) or a loss of bandwidth (if the energy is converted in later cycle, thus spreading the response in time). A loss of coupling cannot be compensated for by any known design strategies to maintain bandwidth and sensitivity simultaneously*".

A high coupling factor is therefore essential as it is impossible to compensate for inferior coupling factors by design change, etc[1]. It may be possible to compensate to some extent for other characteristics by design change, but this is not possible for the coupling factor. Most other properties can be altered with alterations to the circuit of the device or the way that the material is cut or produced, although these will have limitations that can affect performance. The coupling factor is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy, or converts mechanical energy into electrical energy and so is closely related to and dependent on the piezoelectric constants of the material.

Piezoelectric Constants

These define the properties of the material. Crystals are usually anisotropic and so these may be expressed as different values in the three axes. Properties include the Piezoelectric Charge Constant and the piezoelectric voltage constant, both of which define the performance of the material. The piezoelectric charge constant is the mechanical strain

[1] 'Single Crystal Piezoelectrics: A Revolutionary Development for Transducers' by CG Oakley and MJ Zipparo, Ultrasonics Symposium, 2000 IEEE.

experienced by a piezoelectric material per unit of electric field applied, and piezoelectric voltage constant is the mechanical strain experienced by a piezoelectric material per unit of electric displacement applied.

Dielectric Constant

This is a primary parameter that affects the impedance of a transducer element. It is possible to compensate to some extent for low values such as by changing the electrical control circuit design and using multilayer piezoelectric materials, but this increases circuit complexity and difficulties with fabrication. Dielectric constant therefore is important and the best single crystal materials have relatively higher values.

Losses

Insertion loss is proportional to the material's sensitivity and so can be an important parameter for image quality. Ultrasound crystals can also suffer from a loss of energy. A loss in performance can be dealt with by increasing power (applied current), but this heats the crystal, which if the temperature becomes too hot can cause loss of performance (sometimes due to a phase change) or even exceed the Curie temperature, resulting in depoling. Cooling is an option but is impractical with medical ultrasound transducers. Losses cannot be zero, but should not be greater than 10%.

Depoling/phase transition temperatures:

Piezoelectric materials undergo a series of phase transitions with increasing temperature. For example, above the Curie temperature, they lose their ferroelectric properties due to the depoling process which makes them not usable for ultrasound transducer applications. Each phase transition is accompanied by a corresponding strain within the piezoelectric material structure. This internal strain can either result in cracking the material or changing its properties. Therefore, piezoelectric materials with low phase transition temperatures show unstable performance during the operation of an ultrasound transducer which normally runs at temperatures higher than room temperatures (due to internally generated heat). In addition, low Curie temperature materials can partially depole during shipping or storage in areas with hot environment. This partial depoling will have an adverse effect on the performance of ultrasound transducer.

Velocity

Low ultrasound velocity requires a thinner transducer, but thinner materials have higher capacitance, which is good for smaller elements - but fabrication is more difficult.

Curie temperature should be sufficiently high so that use and storage and if possible also solder bonding do not degrade performance. Piezoelectric properties degrade if the material is heated to temperatures close to and above this temperature

Anisotropic properties of single crystal materials

Single crystal materials may be anisotropic with different properties along each of their three axes. Crystals need to be oriented to maximise their performance.

- Electromechanical coupling coefficient – these describe the conversion of energy by the ceramic element from electrical to mechanical form or vice versa and are ratios that should be as high as possible. Characteristics include K_{33}, K_{31} and K_{15} which refer to different crystal axes. For example, K_{33} refers to induced strain in direction 3 per unit electric field applied in direction 3. Kt is the thickness mode coupling coefficient.

The piezoelectric constant are important characteristics on which other characteristics depend. These should be as high as possible and are measured as charge in coulombs/stress in Newtons.

Typical values of commercially available PMN-PT piezoelectric single crystal used for medical ultrasound transducers are as follows:

Characteristic	Value
Electromechanical coupling coefficient K33	Up to 95%
Electromechanical coupling coefficient Kt	Up to 62%
Piezoelectric constant (d33)	Up to 2300 pC/N
Curie temperature	145 to 210°C

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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.)

Although the majority of ultrasound transducers are returned to the manufacturer, a significant proportion, due to the small size, reach disposal and recycling via other routes (i.e. the WEEE Directive) so a closed loop does not exist for this application.

Please indicate where relevant:

☒ Article is collected and sent without dismantling for recycling
☐ 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

2) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:

☐ In articles which are refurbished ______
☒ In articles which are recycled ca. 200 grams per year
☐ 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

Substitute piezoelectric materials

Research into substitute piezoelectric materials for medical ultrasound imaging has been carried out in recent years. A wide variety of dielectric materials have been produced and tested and some are commercially available. However, as shown below, none of the lead-free materials can achieve the same high performance of the best performing lead compounds, especially single crystal PMN-PT.

A fairly recent review of research in the Journal of Dielectrics compared the properties of PMN-PT with a wide variety of lead-free potential medical ultrasound substitutes[2]. This showed that no lead-free materials could achieve the performance of PMN-PT. A summary of published data of piezoelectric materials from Taghaddos et al and data from other sources are as follows:

Table 1. Published performance characteristics of piezoelectric materials[3]

Material	Dielectric constant $\varepsilon_{33}/\varepsilon_0$	Piezoelectric constant D_{33}	Coupling coefficients		Comments
			K_{33}	K_t	
PMN-PT[4]	Up to 7000	1,620	0.93	0.62	Optimal performance
Barium sodium titanate – barium potassium titanate – barium	1000	181	0.56		Typical values for barium titanate based piezo-materials

[2] Lead-free piezoelectric materials and ultrasonic transducers for medical imaging, by Elaheh Taghaddos, Mehdi Hejazi and Ahmad Safari, Journal Of Advanced Dielectrics, Vol. 5, No. 2 (2015) 1530002 (15 pages)

[3] Most data is from "Lead-free piezoelectric materials and ultrasonic transducers for medical imaging", Taghaddos et. al., Journal of Advanced Dielectrics, Vol. 5, No. 2 (2015)

[4] Data for PMN-PT is of commercially available single crystals from CTS Corporation product datasheet. https://www.ctscorp.com/wp-content/uploads/2016.12.15-Single-Crystal-Brochure.pdf

titanate BNT–BKT–BT					
Unusual Barium zirconium titanate – barium calcium titanate ceramic (BZT–BCT)	2820	Up to 560–620			Has too low a Curie temperature of ca. 93°C
Potassium sodium niobate – lithium titanate – lithium antimonite (KNN-LT-LS)	506 - 1865	175 - 315		0.39	
Potassium Sodium Niobate – Lithium Titanate (KNN-LT)	890	245		0.42	
Barium niobium titanate – barium titanate (BNT-BT) ceramic	730	125	0.55	0.52	
Barium niobium titanate – barium titanate (BNT-BT) single crystral	1000	430		0.63	
Potassium, sodium niobate antimonate – Bismuth sodium potassium zirconate KNNS-BNKZ		490			Highest D_{33} value for lead-free material listed in review by Hong[5].
Bismuth sodium titanate[6]	700	120	-	0.40	Commercially available ceramic piezoelectric material
Potassium Sodium Niobate (KNN) thick film	90			0.34	Coupling coefficient and dielectric constant are too low
Lithium niobate single		35		0.49	Very high curie temperature

[5] „Lead-free piezoceramics - Where to move on?“, C-H Hong et. al., J Materiomics 2 (2016) 1 – 24.

[6] Physik Instrumente GmbH & Co. KG. Material PIC700. http://www.piezo.ws/pdf/Piezo_Materials_Piezo_Technology_Piezo_Components.pdf

crystal					but too low D_{33} and K_t. Used for non-destructive testing of industrial equipment.

The review by Taghaddos includes many other lead-free materials as well as transducers made using various lead-free piezo materials, but all materials and devices are very inferior to PMN-PT single crystal. Other publications provide similar values of piezoelectric properties for lead-free materials. Hong et al, for example quotes a highest value for D_{33} of 490 for the complex material KNNS-BNKZ[7] and states that lead-free materials are not yet (as of 2016) equivalent to lead-based materials such as polycrystalline ceramic PZT (lead zirconium titanate), which is itself inferior to the newer single crystal piezoelectric materials such as PMN-PT.

Summary of research into lead-free piezoelectric materials for medical ultrasound transducers

In the past two decades, lead-free piezoelectric materials have been extensively studied for various applications such as electronics, sensors, actuators, capacitors, sonars, ultrasound transducers, and so forth. Promising lead-free composition have been developed for some electronics and high power device applications.

Lead-based piezoelectric ceramics and single crystals which are commercially used in fabricating ultrasound transducers for medical imaging possess a unique combination of electromechancial properties such as high dielectric constant, high piezoelectric constant, high coupling coefficient, and relatively high depolarization or Curie temperature. These properties have been optimized for specific medical imaging applications to enhance the performance of the transducers and hence the image quality. As a result, there are different grades of Lead-based piezoelectrics with wide range of electromechancial properties which cover a wide range of medical imaging applications performed at different frequencies. Lead-based single crystals, for example, offer a remarkably high dielectric constant and coupling coefficient. This resulted in a revolution in medical imaging industry by introduction of Matrix arrays for high quality 3D imaging. Lead-based piezoelectrics are also thermally stable across the working temperature range in which the ultrasound transducers operate.

Pb-free piezoelectrics, on the other hand, have much lower electromechancial properties due to their intrinsic chemistry. Despite the remarkable progress made in improvement of properties of lead-free materials in the last two decades, there is still an appreciable deficit compared to Pb-based materials used in medical imaging applications. The majority of research done on lead-free materials has been focused on so-called Morphotropic Phase Boundary (MPB) compositions where the material offers the highest electromechanical properties compared to other compositions. However, MPB compositions have very low thermal stability which is not desirable for medical imaging applications. Even in the vicinity of MPB region, lead-free material still have much lower piezoelectric and dielectric properties

[7] „Lead-free piezoceramics - Where to move on?", Hong et. al. J Materiomics Vol 2, issue 1 (March 2016) https://www.sciencedirect.com/science/article/pii/S2352847815300083

compared to lead-based materials. Pb-based piezoelectric ceramics and single crystals with rhombohedral structure offer a more stable performance compared to MPB compositions. These rhombohedral compositions are widely used in medical ultrasound market. A few lead-free compositions with rhombohedral structure have been developed recently. They all suffer from low electromechanical properties or high coercive field requiring very high voltages for operating the ultrasound transducers which would not be practical. Another prohibitive factor in using lead-free piezoelectrics in medical imaging transducers is that the manufacturing process of these material is not mature and very well understood yet. Lead-free materials have complex chemistry containing elements such as K, Na, and Li which are light and volatile therefore are difficult to control during the synthesis process. The data available in the literature mostly relate to the materials prepared on the laboratory scale as opposed to commercially available materials. There is no viable lead-free composition commercialized for medical imaging applications. Below is a brief summary of some of the mostly studied lead-free piezoelectric materials in the literature:

Barium Titanate (BT): BT ceramic has relatively high electromechanical properties, high dielectric constant, but low Curie temperature (T_C ~ 120 ^{O}C). BT-based ceramics have been mainly used for capacitor applications. Their low Curie temperature restricts the working temperature range in which these materials can be used. The highest electromechanical properties were achieved at BZT–50BCT composition around the morphotropic phase boundary (MPB). A piezoelectric coefficient d33 of 560–620 pC/N was attained for this composition which was noticeably higher than that of other BT-based ceramics. However, due to low Curie temperature of about 90 ^{o}C, this composition is thermally unstable and not suitable for medical imaging applications.

Bismuth Sodium Titanate (BNT): Pure BNT ceramics, however, suffer from high conductivity and a large coercive (73 kV/cm) field which makes the poling process difficult. Therefore they are not usable for making ultrasound transducers. In order to enhance the electromechanical properties and decrease the coercive field, binary or ternary solid solutions in the vicinity of MPB have been developed. BT, $Bi_{0.5}K_{0.5}TiO_3$ (BKT), $Bi_{0.5}Li_{0.5}TiO_3$ (BLT) are the most widely used materials which have been added to BNT ceramics to improve their electromechanical properties. As mentioned above, MPB compositions are not attractive for medical imaging application due to their thermal instability. Rhombohedral BNT based ceramics have been used in high power devices due to their high coercive field and thermal stability. However, they are not suitable for medical transducers because if their very low dielectric constant and high operating voltage.

Potassium Sodium Niobate (KNN): KNN has the most complex chemistry among the lead free piezoelectrics. This makes it difficult to process high density ceramics or single crystals with stoichiometric composition. A dielectric constant of 1255, d_{33} of 230 pC/N, and kp of 0.5 was reported for $(K_{0.5}Na_{0.5})_{0.07}Li_{0.03}(Nb_{0.8}Ta_{0.2})O_3$ ceramics reported by Saito et al. The simultaneous addition of Li and Sb via LiSbO3 decreased the tetragonal–orthorhombic phase transition temperature while not significantly affecting the Curie temperature. Shifting the transition temperature down to room temperature considerably improved the electromechanical properties. However, this results in a highly unstable thermal properties which is not acceptable for medical imaging transducers.

Figure 1 below compares the electromechancial properties of most common Lead-based and lead-free piezoelectrics. It is obvious that lead-based materials show superior properties compared to lead-free compositions and especially lead-based single crystal materials.

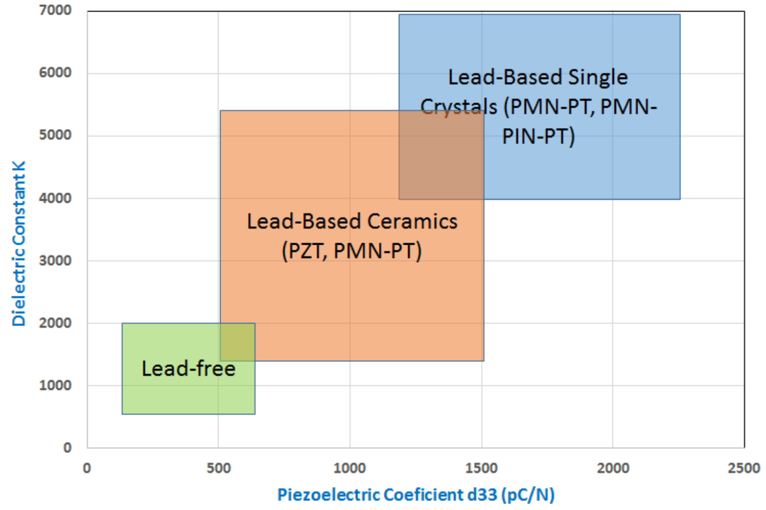

Figure 1. Electromechanical Properties of Lead-free Piezoelectrics vs their Lead-based counterparts

Summary

Lead-free piezoelectrics have lower electromechancial properties and inferior thermal stability compared to their lead-based counterparts. As a results, a medical imaging transducer made with lead-free piezoelectrics would have lower performance and image quality compared to commercially available lead-based materials. The manufacturing of lead-free materials is not mature yet and there is still great amount of work need to be done before lead-free single crystals can be commercialized. The risk of medical misdiagnosis using lead-free transducers would very high, and therefore, their use for medical applications is not possible at the present time.

Peer reviewed published research on lead-free piezoelectric materials is listed in an appendix at the end of this exemption renewal request.

Substitute transducer design

An alternative design technology that has been developed is capacitive Micromachined Ultrasonic Transducers (cMUT)[8], which do not contain lead. These function in a completely different way to piezoelectric ultrasound transducers and so it is not possible to compare the

8 https://www.innovationservices.philips.com/looking-expertise/mems-micro-devices/mems-applications/capacitive-micromachined-ultrasonic-transducers-cmut/

technical characteristics of CMUT with those of single crystal piezoelectric materials, such as piezoelectric coupling constants, piezoelectric constants, etc.

cMUTs have the potential to be a lead-free alternative for ultrasound imaging with potentially wider bandwidths and smaller feature size. However cMUT technology has yet to overcome significant technical limitations necessary to be a clinically viable alternative to lead based single crystals and PZT ceramics for medical imaging. These limitations include output pressure, reliability and linearity.

Engholm et al.[9] gives a recent comparison with PZT (ceramic transducers). They report a deficit in insertion loss (this includes both transmit and receive losses) of ~15dB compared to PZT which would result in an unacceptable loss in penetration (depth of imaging inside the patient) and flow sensitivity (e.g. ability to image and measure blood flow) for core clinical applications. This comparison did not use harmonic imaging mode which is today's standard for difficult to image patients. Harmonic imaging insertion loss would double the transmit loss since tissue generated transmit pressure is proportional to the square of the transmit pressure. Losses compared with PZT for harmonic modes would then be an additional 5dB for this transducer.

Zhao et al[10] report what is perhaps the best cMUT reliability results found in the published literature (published in 2017), but of only a 2 year lifetime achieved for low duty cycle modes (therefore even shorter for high duty cycle modes). This is well-short of the desired 5 to 10 year lifetime of a clinical transducer that may also use high duty cycle modes such as shear wave imaging[11]. Lifetimes significantly degrade as pressures are increased in an attempt to achieve pressures that are routinely achieved with PZT and single crystal materials. Some desirable configurations such as 2D arrays for 3D imaging (these use arrays of many elements) use a common bias for all elements. However, if an individual cMUT element fails in such a way as to short the bias, the whole array will no longer function.

cMUTs are fundamentally non-linear devices since their pressure (force of transmitted wave) is proportional to the square of the applied voltage (signal + bias). This presents difficulty with harmonic imaging since it is important not to transmit 2nd harmonic energy (as this will distort images or make them illegible). Solutions to this issue have been presented[12] but require the substantially added complexity of a high voltage arbitrary waveform transmit generator. This complexity presents technical and design challenges for handheld devices (the device will be

[9] Mathias Engholm, Hamed Bouzari, Thomas Lehrmann Christiansen, Christopher Beers, Jan Peter Bagge, Lars Nordahl Moesner, Søren Elmin Diederichsen, Matthias Bo Stuart, Jørgen Arendt Jensen, Erik Vilain Thomsen, "Probe development of CMUT and PZT row–column-addressed 2-D arrays", Sensors and Actuators A: Physical, Volume 273, 2018, Pages 121-133

[10] Zhao, Danhua, Simopoulos, Costas & Zhuang, Steve. (2017). Long term reliability test results of CMUT *Ultrasonics Symposium (IUS), 2017 IEEE International*, 1-3. doi:10.1109/ULTSYM.2017.8092902

[11] A relatively new technique used for detecting viscosity abnormalities, which can be caused by serious internal injuries, such as internal bleeding, brain injury, and concussive organ damage

[12] Savoia, Alessandro Stuart, Caliano, Giosue, Matrone, Giulia, Ramalli, Alessandro, Boni, Enrico & Tortoli, Piero. (2016). Nonlinear ultrasound imaging experiments using a CMUT probe *Ultrasonics Symposium (IUS), 2016 IEEE International*, 1-4. doi:10.1109/ULTSYM.2016.7728699

too large and heavy) and matrix devices which use an array of transducers, with each transducer element requiring its own control circuitry.

Recognizing these limitations, researchers have focused their investigations on applications that play to the strengths of cMUTs, namely their ability to produce small feature sizes and wide bandwidths. These applications include catheters[13], endoscopic probes[14], high frequency linear arrays[15] and probes with wide clinical coverage[16]. Transducers for these applications cannot be fabricated easily using PZT or single crystal technology and therefor accept the reduced acoustic output performance associated with cMUTs. Also, single use catheter devices can accept limited lifetimes as they are disposed of after one use.

Due to the current limitations of cMUT technology, lead base sensor technology is necessary to achieve the adequate clinical performance in core imaging modes. Given it took 20 years to mature cMUTS to their current performance, it is unlikely that sufficient performance will be obtained for at least another 5-10 years.

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

Substitutes give inferior images, but overall do not appear to be less reliable (except see comments above on cMUT lifetimes)

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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.

There has been considerable research into lead-free piezoelectric materials in the last 20 years by academics as well as by piezoelectric material manufacturers. Medical device manufacturers have investigated new materials but no lead-free substitutes come close to reaching the high performance of lead-based materials. Use of materials with lower coupling coefficient and piezoelectric constants will give inferior image quality which is unacceptable to

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[13] Pekař, Martin, Mihajlović, Nenad, Belt, Harm, Kolen, Alexander F, van Rens, Jeannet, Budzelaar, Frank, Jacobs, Bas, Bosch, Johan G, Vos, Hendrik J, Rem-Bronneberg, Debbie, van Soest, Gijs & van der Steen, Antonius F W. (2017). Quantitative imaging performance of frequency-tunable capacitive micromachined ultrasonic transducer array designed for intracardiac application: Phantom study *Ultrasonics*, *84*, 421-429. doi:10.1016/j.ultras.2017.11.021

[14] Moini, Azadeh, Nikoozadeh, Amin, Choe, Jung Woo, Chang, Chienliu, Stephens, Douglas N., Sahn, David J. & Khuri-Yakub, Pierre T.. (2016). Fully integrated 2D CMUT ring arrays for endoscopic ultrasound *Ultrasonics Symposium (IUS), 2016 IEEE International*, 1-4. doi:10.1109/ULTSYM.2016.7728542

[15] Danhua Zhao, Steve Zhuang & Lee Weng. (2016). One-probe solution in medical ultrasound imaging with CMUT technology *Ultrasonics Symposium (IUS), 2016 IEEE International*, 1-3. doi:10.1109/ULTSYM.2016.7728443

[16] Probes available form Hitachi and Kolo Medical

health professionals. High image quality is essential for accurate and early diagnosis and for treatment of patients.

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

Research into lead-free materials is likely to continue. Some industry sectors that do not need such high performance can use less efficient and sensitive piezoelectric lead-free materials, but others including medical require the highest possible sensitivity and efficiency.

There is a limit to the combinations of elements that can be tested and as shown in the recent reviews, all obvious candidates have already been assessed and even the best is very inferior to PMN-PT. It seems unlikely at present that a combination of substances will be found soon that can equal the best PMN-PT materials and so this exemption will be needed for at least the maximum validity period permitted by RoHS.

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8. Justification according to Article 5(1)(a):

(A) Links to REACH: (substance + substitute)

1) Do any of the following provisions apply to the application described under (A) and (C)?

☐ Authorisation

- ☐ SVHC – single crystal materials are not SVHCs.
- ☐ Candidate list
- ☐ Proposal inclusion Annex XIV
- ☐ Annex XIV

☐ Restriction

- ☐ Annex XVII
- ☐ Registry of intentions

☒ Registration - lead titanium oxide is registered https://echa.europa.eu/registration-dossier/-/registered-dossier/11894 and Lead titanium zirconium oxide is registered https://echa.europa.eu/registration-dossier/-/registered-dossier/14607 , but most ultrasound transducers are imported into the EU as articles. Single crystal formulations are not registered.

2) Provide REACH-relevant information received through the supply chain.
Name of document: _____

(B) Elimination/substitution:

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

   ☐ Yes. Consequences? ______

   ☒ No. Justification: Too large reduction in image quality

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

   ☐ Yes.

   ☐ Design changes:

   ☐ Other materials:

   ☐ Other substance:

   ☒ No.

   Justification: Too large reduction in image quality

3. Give details on the reliability of substitutes (technical data + information): Not applicable (except that cMUT lifetimes are shorter than single crystal transducers)

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

   1) Environmental impacts: Not applicable to this renewal request
   2) Health impacts: Not applicable to this renewal request
   3) Consumer safety impacts: Negative impact on EU citizens' health if this exemption is not renewed due to inferior image quality from lead-free substitutes.

⇨ Do impacts of substitution outweigh benefits thereof? Not applicable to this renewal request

Please provide third-party verified assessment on this: ______

(C) Availability of substitutes:

a) Describe supply sources for substitutes: None exist with equivalent performance

b) Have you encountered problems with the availability? Describe: Not applicable

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? See Q6

(D) Socio-economic impact of substitution:

⇨ What kind of economic effects do you consider related to substitution?

☐ Increase in direct production costs

☐ Increase in fixed costs

☐ Increase in overhead

☒ Possible social impacts within the EU – There would be a negative impact on EU citizens' health if this exemption is not renewed due to inferior image quality of lead-free substitutes. There were 800,000 ultrasound scans carried out in England per month in the year 2018/19[17]. There is no data on the proportion using single crystal ultrasound transducers, but this is likely to be 12% of the total (500g lead used in single crystal/4.2kg lead used in polycrystalline – see renewal request for Annex III exemption 7cI), so 96,000 scans per month. The number for the EU, based on population is likely to be 10 times as many at about 900,000 scans per month or up to 10.8 million per year. This means that eventually, if single crystal ultrasound transducers cannot be sold in the EU, about 10 million EU citizens will potentially suffer from ill health because their medical conditions are diagnosed later (or not at all) than if single crystal ultrasound was available. Later diagnosis can mean that patients require more costly treatments and these take longer than if a diagnosis was made earlier. Although this cannot be quantified, this would potentially equate to many millions of lost working days, high healthcare costs for EU hospitals and possibly some unnecessary deaths (e.g. if a small tumour were missed).

☐ Possible social impacts external to the EU – no as lead-based materials can continue to be used

☐ Other: _____

⇨ Provide sufficient evidence (third-party verified) to support your statement: _____

9. Other relevant information

Please provide additional relevant information to further establish the necessity of your request:

_____

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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:

_____

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17 https://www.england.nhs.uk/statistics/statistical-work-areas/diagnostic-imaging-dataset/diagnostic-imaging-dataset-2018-19-data/

Appendix

Peer reviewed published literature on lead-free piezoelectric materials

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