Assistance to the Commission on Technological Socio-Economic and Cost-Benefit Assessment Related to Exemptions from the Substance Restrictions in Electrical and Electronic Equipment:

Study to assess renewal requests for 29 RoHS 2 Annex III exemptions [no. l(a to e -lighting purpose), no. l(f - special purpose), no. 2(a), no. 2(b)(3), no. 2(b)(4), no. 3, no. 4(a), no. 4(b), no. 4(c), no. 4(e), no. 4(f), no. 5(b), no. 6(a), no. 6(b), no. 6(c), no. 7(a), no. 7(c) - I, no. 7(c) - II, no. 7(c) - IV, no. 8(b), no. 9, no. 15, no. 18b, no. 21, no. 24, no. 29, no. 32, no. 34, no. 37]

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Report for The European Commission

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Disclaimer:

Eunomia Research & Consulting, Oeko-Institut and Fraunhofer Institute IZM have taken due care in the preparation of this report to ensure that all facts and analysis presented are as accurate as possible within the scope of the project. However no guarantee is provided in respect of the information presented, and Eunomia Research & Consulting, Oeko-Institut and Fraunhofer Institute IZM are not responsible for decisions or actions taken on the basis of the content of this report.

22.0 Exemption 7c-I: “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”

Declaration

In the sections that precede the “Critical Review” the phrasings and wordings of stakeholders’ explanations and arguments have been adopted from the documents provided by the stakeholders as far as required and reasonable in the context of the evaluation at hand. Formulations have been altered in cases where it was necessary to maintain the readability and comprehensibility of the text. These sections are based exclusively on information provided by applicants and stakeholders, unless otherwise stated, and the views presented should not be taken to represent the views of the consultants (authors of this report).

Acronyms and Definitions

Curie temperature	Temperature at which piezoelectric ceramics lose their piezoelectric properties; *Source: Zangl et al. 2010*[967]
Electro Mechanical Coupling Coefficient (k) of piezoelectric ceramics	Coefficient to show the efficiency to transform and communicate electric alteration into the energy of mechanical alteration (or vice versa) due to the piezoelectric effect $k = \sqrt{\frac{\text{mechanical energy stored}}{\text{electrical energy applied}}}$ or

[967] Zangl, Stéphanie [Oeko-Institut e.V.] et al. 2010a “Adaptation to scientific and technical progress of Annex II to Directive Adaptation Directive2000/53/EC (ELV) and of the Annex to Directive 2002/95/EC (RoHS): Final report - revised version,” Final Report Oeko-Institut e. V. und Fraunhofer IZM, accessed August 4, 2015, http://elv.exemptions.oeko.info/fileadmin/user_upload/Consultation_2014_1/Ex_3_2010_Review_Final_report_ELV_RoHS_28_07_2010.pdf; or https://circabc.europa.eu/sd/d/a4bca0a9-b6de-401d-beff-6d15bf423915/Corr_Final%20report_ELV_RoHS_28_07_2010.pdf

	$$k = \sqrt{\frac{\text{electrical energy stored}}{\text{mechanical energy applied}}}$$ In order to gain filter characteristics, materials with high values in this category are essential; *Source: Zangl et al. 2010*[968]
Mechanical Quality Factor Coefficient of piezoelectric ceramics	Shows the extent of mechanical loss near frequencies where the piezoelectric substance resonates; in resonators and oscillators, as the value becomes higher, the oscillator becomes more efficient and the fluctuation in the resonance frequency decreases; *Source: Zangl et al. 2010*[969]
NTC	Negative Temperature Coefficient, materials decreasing their electrical resistance with increasing temperature; *Source: Zangl et al. 2010*[970]
Piezoelectric Strain Coefficient (d constant) (Piezoelectric material constant)	Indicates how efficient an electric field can generate strain of the piezoelectric material, or vice versa how efficient a strain applied on the ceramic can generate an electrical field. Higher values indicate higher efficiency. d=strain / applied electrical field If the value is high, the piezoceramic can generate displacement efficiently from a low electric field. Also, the output is larger for sensors and it can be used as a good sensor material with high sensitivity *Source: Zangl et al. 2010*[971]
PTC	Positive Temperature Coefficient, materials increasing their electrical resistance with increasing temperature *Source: Zangl et al. 2010*[972]
PTCR	Positive temperature coefficient of resistance
PZT ceramics	Ceramics consisting of a mixture of $PbZrO_3$ and $PbTiO_3$ *Source: Zangl et al. 2010*[973]
Saturation polarization	Highest practically achievable magnetic polarization of a material when exposed to a sufficiently strong magnetic field *Source: Zangl et al. 2010*[974]

[968] Ibid.
[969] Ibid.
[970] Ibid.
[971] Ibid.
[972] Ibid.
[973] Ibid.

22.1 Background and History of the Exemption

The current wording of exemption 7c-I in Annex III of Directive 2011/65/EC (RoHS 2), is:

"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"

When Directive 2002/96/EC (RoHS 1) (EuropeanUnion) was published in 2003, the above exemption did not yet exist in this form. The use of lead in glass and ceramics was covered by two different exemptions with a different wording: Exemption 5 allowed the use of lead in glass:

"Lead in glass of cathode ray tubes, electronic components and fluorescent tubes"

Exemption 7d covered the use of lead in ceramics of electronic components:

"Lead in electronic ceramic parts (e.g. piezoelectronic devices)"

In 2007, the Commission received an application for exemption of

"Lead in cermet-based trimmer potentiometer elements"

The applicant requested this exemption claiming that exemptions 5 and 7 in the annex of directive 2002/95/EC (RoHS 1) in the status of 2006/2007 did not cover the use of lead in these cermet-based trimmer potentiometers. The applicant said that this resistive layer in the cermet-based trimmer potentiometer is a homogeneous material, as it can be mechanically separated from the ceramic base. This homogeneous material, the thick-film layer containing the lead, in itself is neither a glass nor a ceramic material. The exemption request was reviewed[975] and the Commission granted the exemption as exemption 34 in the annex of RoHS 1.

Exemption 11 of Annex II in Directive 2000/53/EC (ELV Directive), the equivalent to exemption 7c-I of RoHS Annex III, was reviewed in 2007/2008[976]. The stakeholders decided that the wording in the ELV Directive covers applications like lead in cermet-based trimmer potentiometers. To avoid insecurities whether and how far similar uses of lead like in the cermet-based trimmer potentiometers are exempted, it was decided in the review of RoHS exemption 7d in 2008/2009[977] to take over the wording of ELV

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[974] Ibid.

[975] For details see report of Gensch, Carl-Otto, Stéphanie Zangl, and Otmar Deubzer 2007 "Adaptation to scientific and technical progress under Directive 2002/95/EC: Final report." Accessed August 11, 2015. http://ec.europa.eu/enviro nment/waste/weee/pdf/rohs.pdf., page 18 et sqq.

[976] Lohse, Joachim; Gensch, Carl-Otto; Groß, Rita; Zangl, Stéphanie, Oeko-Institut e.V.; Deubzer, Otmar, Fraunhofer IZM (2008): Adaptation to Scientific and Technical Progress of Annex II Directive 2000/53/EC. Final Report - Amended Final. https://circabc.europa.eu/sd/a/f5d79a51-2e5a-47eb-85d3-7b491ae6a4b3/Final_report_ELV_2008_Annex_II_revision.pdf; page 65 et sqq.

[977] Carl-Otto Gensch, Oeko-Institut e. V., et al. (2009): Adaptation to scientific and technical progress under Directive 2002/95/EC. Final Report. With the assistance of Stéphanie Zangl, Rita Groß, Anna Weber, Oeko-Institut e. V. and Otmar Deubzer, Fraunhofer IZM.

exemption 11 with further slight adaptations, resulting in the current wording of exemption 7c-I.

The exemption was transferred from the annex of RoHS 1 into annex III of RoHS 2 without changes and has become due for review as stakeholders have requested its continuation prior to its expiry in July 2016.

22.2 Description of the Requested Exemption

22.2.1 Overview of the Submitted Exemption Requests

Several stakeholders have requested the continuation of exemption 7c-I. Table 22-1 gives an overview of the submitted requests.

Pyreos' request for exemption[978] had actually been submitted as part of pack 8 of the RoHS exemption reviews[979]. Since the applicant asks for the application-specific renewal of exemption 7c-I, Pyreos[980] agreed that its exemption request will be evaluated in the broader context of exemption 7c-I in this review round.

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http://ec.europa.eu/enviro nment/waste/weee/pdf/final_reportl_rohs1_en.pdf; http://ec.europa.eu/enviro nment/waste/weee/pdf/report_2009.pdf; page 98 et sqq.

[978] Pyreos Ltd. 2015a "Document "Questionnaire-1_Clarification_Exe-Req-Pyreos_cg130415 final - publication.pdf": 1st questionnaire (clarification questionnaire)," http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_7/2015_1/Questionnaire-1_Clarification_Exe-Req-Pyreos_cg130415_final_-_publication.pdf

[979] C.f. reviews of pack 8 and 9 RoHS exemption requests, http://rohs.exemptions.oeko.info/index.php?id=221

[980] Pyreos Ltd. 2015b "Document "Pyreos_Suspension-of-Request-with-Conditions.pdf", sent via e-mail to Dr. Otmar Deubzer, Fraunhhofer IZM, by Torben Nørlem, Intertek, on 20 July 2015,"

Table 22-1: Overview of requests for the continuation of exemption 7c-I and application-specific wordings

Applicant	Requested Exemption	Requested Expiry Date/ Continuation	Remarks
Bandelin[981]	Annex III: Continuation with specification: **Piezoelectric hard PZT containing lead for high performance ultrasonic 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 Annex IV: Lead in single crystal piezoelectric materials for ultrasonic transducers and in **piezoelectric hard PZT containing lead for high performance ultrasonic transducers**	Maximum validity period (5 years)	Applicant additionally requests amendment of exemption 14 in Annex IV
Bourns[982]	Continuation of exemption without changes	Maximum validity period (5 years)	Applicant mentions lead-free glasses applied in some components
IXYS	Lead in coatings of high voltage diodes	Maximum validity period	IXYS had applied for this exemption under Exemption 37; it was agreed with the applicant that the exemption is related to glass coatings of high voltage diodes, and not to lead in the platings of such diodes. The exemption request therefore was shifted to Exemption 7c-I.

[981] Bandelin Electronic GmbH 2015a “Request for continuation of exemption 7c-I with addition, document "Ex_7c_I_Application_Bandelin.pdf: Exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/BANDELN/Ex_7c_I_Application_Bandelin.pdf
[982] Bourns Inc. 2015a “Exemption request, document "7c-I_Exemption_extension_ap_7c-I.pdf": Request for continuation of exemption 7c-I,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Bourns/7c-I_Exemption_extension_ap_7c-I.pdf

Applicant	Requested Exemption	Requested Expiry Date/ Continuation	Remarks
JEITA et al.[983]	Continuation of exemption with clarification of scope: “Electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in **discrete** capacitor **components**, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound”	Maximum validity period (5 years)	Request almost identical to that of Murata et al.
Murata et al.[984]	Continuation of exemption with clarification of scope: “Electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in **discrete** capacitor **components**, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound”	Maximum validity period (5 years)	Request almost identical to that of JEITA et al.
Ralec[985]	Continuation of exemption without changes	Maximum validity period (5 years)	Applicant did not reply timely to clarification questionnaire; application has therefore not been followed up

[983] JEITA et al. 2015a “Exemption request, document "JEITA/7c-IandII_RoHS_Exemption_Renewal_Request_7_c_I_Japan4EEEassociations.pdf": Exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/JEITA/7c-IandII_RoHS_Exemption_Renewal_Request_7_c_I_Japan4EEEassociations.pdf

[984] Murata et al. 2015a “Original exemption request, document "Exemption_7_c_-I/Murata/7c-I_RoHS_V_Application_Form_7c1_20140116_combined_final.pdf": Exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Murata/7c-I_RoHS_V_Application_Form_7c1_20140116_combined_final.pdf

[985] Ralec Technology 2015 “Exemption request, document "7c-I_RoHS_V_Application_Form_to_RoHS.pdf": Exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/RALEC/7c-I_RoHS_V_Application_Form_to_RoHS.pdf

Applicant	Requested Exemption	Requested Expiry Date/ Continuation	Remarks
Pyreos[986 987]	Add following exemption to Annex III and Annex IV: Lead in thin film electronic sensor elements such as pyroelectric sensors or piezoelectric sensors	7 years	Sensors currently used in monitoring and control instruments (category 9) for both industrial and non-industrial use, but can possibly expand to other product groups of RoHS Directive;
Schott[988]	Continuation of exemption without changes	Maximum validity period (5 years)	Schott specifies the application of lead in "solder glasses" to attach optical elements like windows or lenses into metal components for high quality hermetic package for optoelectronic devices
Sensata[989]	Continuation of exemption without changes	Not specified	Request for lead in glasses to manufacture sensors and to bond sensors to other materials like e.g. metals

[986] Pyreos Ltd. 2014 “Original exempiton request for renewal of exemption 7c-I with new wording, document "RoHS_V_Application_Form-Pyreos_final 14112014 - publication.pdf": Original exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_7/2015_1/RoHS_V_Application_Form-Pyreos_final_14112014_-_publication.pdf
[987] Op. cit. Pyreos Ltd. 2015a
[988] Schott AG 2015a “Exemption request document "20150820_Ex_7c-I_Schott_Application_Revised_A.pdf": Exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/SCHOTT/20150820_Ex_7c-I_Schott_Application_Revised_A.pdf
[989] Sensata Technologies 2015a “Request for continuation of exemption 7c-I, document "7c-I_RoHS-Exemptions_Application-Format_Ex_7cI_Pb_in_glass_20150115.pdf": Exemption request,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Sensata/7c-I_RoHS-Exemptions_Application-Format_Ex_7cI_Pb_in_glass_20150115.pdf

Applicant	Requested Exemption	Requested Expiry Date/ Continuation	Remarks
Vishay[990] [991]	Continuation of exemption without changes; provides application examples with below wordings in support of the unchanged continuation of exemption 7c-I: “Wire wound resistors with enamel coatings containing lead (Pb) as lead-oxide (Pb3O4) in glass” “Lead in glass of the Ag top and bottom electrode of NTC chips”	Maximum validity period (5 years)	Member of the consortium of Murata et al.[992] (Annexed to exemption request document)
YAGEO Corporation [993]	Continuation of exemption without changes		Applicant did not reply to clarification questionnaire; application has therefore not been followed up

[990] Vishay 2015a 2015 “Document "RoHS-Exe-7c-I_Pb-in-glass-Enamel-Coating_Wirewound_Resistors.pdf", submitted as additional reference for the exemption request of Murata et al. 2015a: Document referenced in the exemption request of Murata et al. 2015a” (January 2015) unpublished manuscript,

[991] Vishay 2015c “Document "Request for exemption 7c-I NTC chips update dec15.pdf", submitted as additional reference for the exemption request of Murata et al. 2015a: Document referenced in the exemption request of Murata et al. 2015a” unpublished manuscript,

[992] Op. cit. Murata et al. 2015a

[993] Yageo Corporation 2015 “Exemption request, document "7c-I_RoHS_V_Application_Form_YAGEO_2015-01-19.pdf",” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/YAGEA/7c-I_RoHS_V_Application_Form_YAGEO_2015-01-19.pdf

22.2.2 Technical Background of the Requests for Renewal of Exemption 7c-I (Murata/JEITA et al.)

Murata/JEITA et al.[994] [995] request the renewal of the exemption for five years, but ask for a slight modification of the exemption wording to clarify its scope without extending it:

> *"Electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in* ***discrete*** *capacitor* ***components****, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound"*

The background of this proposed change is explained in detail in the review of exemption 7c-II, see Chapter 23.0.

The technical background for the use of lead in glass[996] and in ceramics[997] under exemption 7c-I was explained in detail in the report of the 2008/2009 review. The exemption is used in all types of electrical and electronic equipment (EEE) listed in Annex I of the RoHS Directive. The description of the exemption is therefore limited to the main aspects.

Murata et al.[998] state that the applications of lead in ceramic and glass are too numerous and that it is impossible to list all of them. They provide illustrative examples, reproduced in Table 22-2, which they claim not to constitute a comprehensive list of the uses of lead in ceramics and in glass used in electronic components.

Murata et al.[999] explain that lead is used to obtain appropriate physical characteristics in glass and/or ceramic. In ceramics, lead provides particular dielectric, piezoelectric, pyroelectric, ferroelectric, semiconductor, magnetic properties over a wide use ranges in terms of temperatures, voltages and/or frequencies.

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[994] Op. cit. Murata et al. 2015a
[995] Op. cit. JEITA et al. 2015a
[996] Gensch, Carl-Otto, Oeko-Institut e. V., et al. 20 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, Oeko-Institut e. V., and Otmar Deubzer, Fraunhofer IZM http://ec.europa.eu/environment/waste/weee/pdf/final_reportl_rohs1_en.pdf, page 52 et seqq.
[997] Ibid., page 98 et seqq.
[998] Op. cit. Murata et al. 2015a
[999] Ibid.

Table 22-2: Example applications of lead in exemption 7c(I)

Application	Function	Product examples
Ceramic (including applications using thick film & thin film technology)		
PZT in piezoelectric ceramic	Piezoelectric effect	Transformer, filter, resonator, buzzer, actuator, sensors (pressure, shock)
Semiconductor ceramic (PTC)	Temperature dependent resistance	PTC resistor / thermistor, heater
Pyroelectric ceramic	Pyroelectric effect	Infrared sensor, temperature sensor
Ferroelectric /magnetic ceramic	Ferroelectric / Magnetic effect	Ferroelectric memories, ferrite core
Dielectric ceramic	Energy storage by polarization effect	Capacitive layers in electronic components (discrete capacitor components are in scope of 7c(II) and 7c(III))
Glass and glass-ceramic matrix compounds (including applications using thick film & thin film technology)		
Glass and/or glass frits for amorphous isolating solid or interconnection	Protection, Insulating	Discrete Semiconductors
		Glass passivation of semiconductor chips
		Glass sleeve diodes (various sizes)
		Thick film resistors
		Wire wound resistors
		NTC – Glass coating
		Metal pressure sensors
	Adhesives / Bonding	MEMS
		SMD Components
		Capacitive pressure sensing element
		Resistive pressure sensing element
	Hermetic sealing	Electronic components with hermetically sealed ceramic package
Glass-ceramic matrix compound	Functional glass compound, resistance	Thick film resistors coating, resistance and conductor layer
		High voltage resistors
		Outer electrode of ceramic components
Glass-ceramic material	Functional glass	Glass-ceramic cooking field

Source: Murata et al.[1000]

22.2.2.1 Electrical and Electronic Components Containing Lead in Ceramic

Murata et al.[1001] explain that ceramic constituted by oxides of tetravalent cations of Group 4 elements and divalent cations of lead (Pb) have the outstanding special characteristics of stably bringing out electrical properties (dielectric, piezoelectric,

[1000] Murata et al. 2015b “Questionnaire 1 (clarification questionnaire), document "RoHS_7c-I_Murata__1st_Questionnaire_answers_final_20Aug.pdf",” Clarification questionnaire, http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Murata/RoHS_7c-I_Murata__1st_Questionnaire_answers_final_20Aug.pdf

[1001] Op. cit. Murata et al. 2015a

pyroelectric, ferroelectric, semiconductor, magnetic properties) over a wide use range (temperature, voltage, frequency).

According to Murata et al.,[1002] these lead-containing ceramics are widely used as main constituent materials of electrical and electronic components and as important additives for controlling and enlarging the usable environment range (temperature, voltage) of other ceramic. Moreover, lead-containing ceramic has characteristics of densely sintering throughout a wide range of sintering conditions, low energy consumption in manufacturing and high electrical and mechanical durability of the product after sintering. By controlling the sintering conditions, a fine layered structure can be internally formed and the functionality of the electronic components can be largely improved.

The specific examples of various types of ceramics containing lead and the status of substitution or elimination are explained in Section 22.3.1 (General Status of Lead Substitution in Ceramics of Electrical and Electronic Components from page 444).

22.2.2.2 Electrical and Electronic Components Containing Lead in Glass or Ceramic Matrix Compounds

According to Murata et al.[1003] glass for electronic components is an amorphous isolating solid. In electrical and electronic components, together with making use of the various properties exhibited by glass, the desired function is obtained by the combination of glass with other materials such as metal, ceramic, etc. Lead as a constituent element of glass:[1004]

- Lowers the melting and softening points;
- Improves workability and machinability;
- Increases wettability with metal and ceramic and improves the bonding strength with other materials;
- Facilitates controlling electrical properties like conductivity, resistance values in combination with other materials over a wide range and thus provides excellent functionality; and
- Improves the chemical stability and mechanical strength of glass and helps to achieve excellent reliability;

Murata et al.[1005] state that lead-containing glass can be used over a wide range of applications. It is used for insulating, protection, resistance, adhesives, bonding, hermetic sealing and other uses. Table 22-3 provides examples.

[1002] Ibid.
[1003] Ibid.
[1004] Ibid.
[1005] Ibid.

Table 22-3: Example applications of glass containing lead

Example#	Functional group	Product and Parts example
# 1.1	Protection & Insulating	Discrete Semiconductors
# 1.2		Glass sleeve diodes (various sizes)
# 1.3		Thick film resistors
#1.4		Wire wound resistors
#1.5		NTC – Glass coating
#1.6		Metal pressure sensors
#2.1	Functional glass compound/Resistance	Thick film resistors coating and/or contact layer
#2.2		High ohmic / high voltage resistors materials
#2.3		NTC – Inner electrode
#3.1	Adhesives / Bonding	MEMS
#3.2		SMD Components
#3.3	Hermetic sealing	Electronic components with hermetically sealed ceramic package

Source: Murata et al.[1006]

Murata et al.[1007] [1008] highlight that in the above list neither the functional groups nor the product examples are exhaustive. The list serves to explain why lead in glass is needed and lead-free substitutes are not technically suitable. The examples for the various functional groups and the prospects to substitute or eliminate lead are explained in more detail in Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds from page 460).

[1006] Ibid.
[1007] Ibid.
[1008] Murata et al. 2016a "Answers to second questionnaire, document "Exe_7c-I_Questionnaire-2_Murata-JEITA_2015-12-30_answers_final.pdf", received by Dr. Otmar Deubzer, Fraunhofer IZM, from Wolfgang Werner, Vishay, on 29 January 2016" unpublished manuscript, Second questionnaire

22.2.3 Technical Background of the Bandelin Application-specific Exemption Request

Bandelin[1009] requests an addendum to the current exemption wording:

> ***Piezoelectric hard PZT containing lead for high-performance ultrasonic transducers and*** *electrical and electronic components containing lead in glass or ceramic materials other than dielectric ceramic in capacitors*

Bandelin[1010] claims that the wording of exemption 7c-I does not 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.

Bandelin[1011] explains that they use piezoceramic material, which is used as lead zirconium titanate (PZT) in great quantities and various forms to create high-performance piezoelectric transducers, which are a major part of equipment such as ultrasonic cleaning systems and homogenisers. Piezoceramic "hard PZT" in the form of perforated discs is the exclusive material used for these high-performance transducers worldwide. In Europe, it bears the designation PZT 4 or PZT 8, and it contains more than 0.1 % by weight of lead.

Bandelin[1012] considers itself a leading manufacturer of high-performance ultrasound equipment with a wide range of devices for cleaning technology and ultrasound technology for industrial, medical and laboratory applications. They install roughly 70,000 perforated discs made of hard PZT 4 and PZT 8 in their high-performance ultrasonic transducers every year.

The development of high-performance piezoceramic ultrasonic transducers began in the 1950s and has undergone an enormous upswing since the invention of lead zirconium titanate materials – especially in the overall field of cleaning technology. Among other things, this led to chlorinated hydrocarbons and chlorofluorocarbons being replaced by water-based ultrasonic cleaning processes.[1013]

As an equipment manufacturer, Bandelin[1014] absolutely relies on purchasing high-performance piezoelectric ceramics made of hard PZT for the construction of high-performance ultrasonic transducers.

[1009] Op. cit. Bandelin Electronic GmbH 2015a

[1010] Bandelin Electronic GmbH 2015b "Questionnaire 1 (clarification questionnaire), document "Ex_7c-I_Bandelin_1st_Questionnairie_and_Answers.pdf","
http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/BANDELN/Ex_7c-I_Bandelin_1st_Questionnairie_and_Answers.pdf

[1011] Op. cit. Bandelin Electronic GmbH 2015a

[1012] Ibid.

[1013] Ibid.

[1014] Ibid.

22.2.4 Technical Description of the Bourns Exemption Request

Bourns[1015] uses lead in thick films, which are resistive and conductive films greater than 0.0001 inches thick, resulting from firing a paste or ink that has been deposited on a ceramic substrate. These thick film inks typically contain a glass material that includes lead.

Bourns[1016] also uses lead-containing glass frits that have several applications including barrier layers for stopping the migration of silver and a sealing material for hermetic packages. Glasses are typically part of a thick film formulation. Various oxides are melted together to form a glass matrix. It is also used as a sealant in hermetic ceramic and metal electronic (semiconductor and hybrid) component packages. The lead oxide is used to lower melting temperature and viscosity for processing below 550 °C and to raise the dielectric strength. The lead oxide content of the glass can be adjusted controlling the coefficient of thermal expansion which is favourable for high sintering temperature operations.

Components using lead-glass include chip arrays, chip resistors, ESD protectors, transient voltage suppressor diodes, encoders, fuel cards, ceramic PTC resettable fuses, thick film moulded dips, panel controls, power resistors, trimming potentiometers. These electronic components are typically used on circuit boards and other internal electronics in products of all RoHS categories in Annex I by Bourns' customers.[1017]

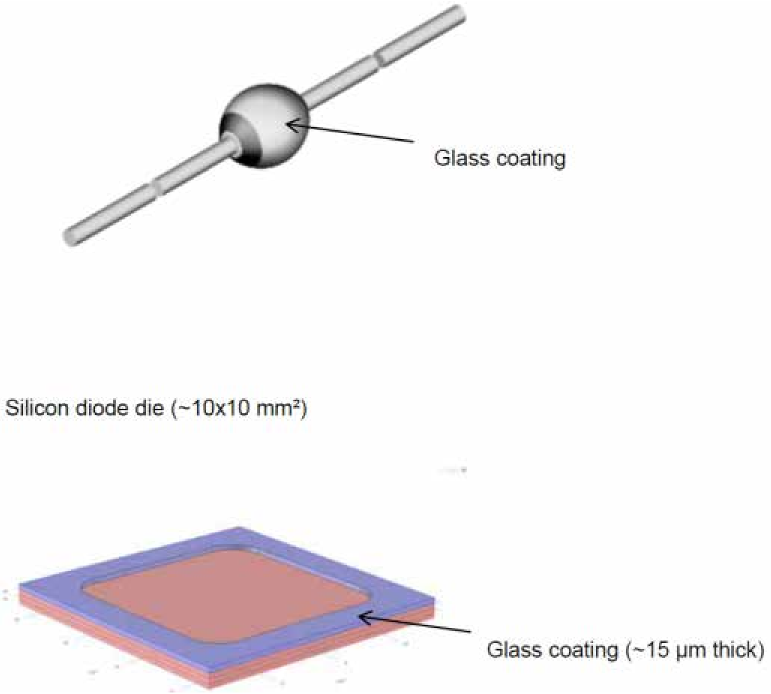
The homogeneous material is the glass included in the thick film ink or encapsulation, which is then fired on a substrate. The lead content will vary and can range from 1-75 % in the glass only. The total ink/encapsulation including the glass is generally less than 1 % of the finished part.[1018]

22.2.5 Technical Description of the IXYS Application-specific Exemption Request

IXYS[1019] request an exemption for lead in coatings of high voltage diodes. The glass coatings used for high reliability semiconductor power device passivation and packaging contain lead. Lead-based glasses are used because they have unique combinations and characteristics that cannot be achieved by other materials or methods. Zinc borosilicate glasses with lead are used to prevent degradation of high reliability semiconductor devices in applications at or above 100 V AC for rectification and other electric power converters.

1015 Op. cit. Bourns Inc. 2015a
1016 Ibid.
1017 Ibid.
1018 Ibid.
1019 IXYS Semiconductor GmbH 2014 2014 "Request for continuation of exemption 37, document "37_IXYS_RoHS_V_Application_Form_pass_glasses.pdf": Original exemption request," http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_37/IXYS/37_IXYS_RoHS_V_Application_Form_pass_glasses.pdf

Figure 22-1: Lead glass in high voltage diodes and on silicon diode dies



Source: IXYS[1020]

Examples are provided by IXYS of lead glass used in high voltage diodes and on silicon diode dies in Figure 22-1. According to IXYS,[1021] these components are used in transportation, automotive, and in high power equipment in the industry, from which only the latter is in the scope of the RoHS Directive.

IXYS[1022] explains that lead provides good physical properties in combination with pure silicon crystals and a good ability to withstand high electric fields in the range of 200,000 V/cm in alternate and direct current power semiconductor devices.

1020 Ibid.
1021 Ibid.
1022 Ibid.

22.2.6 Technical Background of the Pyreos Application-specific Exemption Request

Pyreos[1023] requested to add an exemption with the following wording to both RoHS Annex III and Annex IV with a maximum validity of seven years:

> *"Lead in thin film electronic sensor elements such as pyroelectric sensors or piezoelectric sensors"*

Pyreos[1024] explains the request to relate to lead in thin film $PbZrTiO_3$ (PZT) sensors for pyroelectric or piezoelectric applications. The sensors are currently used in monitoring and control instruments but the future use could expand to other product groups under RoHS.

According to Pyreos[1025], lead in the sensing elements of thin film PZT sensors is used for pyroelectric applications such as:

- low power gesture / proximity detection;
- gas detection;
- safety and security applications such as gas detection and intruder alarms;
- Infrared spectroscopy for industrial and consumer applications; or
- piezoelectric applications such as piezo actuators or transducers.

Pyreos[1026] states the lead atoms are fundamental to the unique properties of the PZT material system and it is the special electronic structure of lead together with its weight that gives the PZT material system its unique properties. Present lead-free alternatives are not commercially viable and the substitution of lead may potentially adversely impact the performance of monitoring and control equipment relying on the PZT thin film sensors whereby consumer and worker safety may be impaired.

Pyreos[1027] explain that there are a total of 32 crystal configurations of which 10 are polar showing a pyroelectric effect. Ferroelectric materials form a sub-class of the polar materials, and some ferroelectric materials are characterised by a very high pyroelectric effect. Figure 22-2 shows the technically most relevant material groups including some key performance parameters.

[1023] Op. cit. Pyreos Ltd. 2015a
[1024] Op. cit. Pyreos Ltd. 2014
[1025] Ibid.
[1026] Ibid.
[1027] Ibid.

Figure 22-2: Ferrocelectric materials and pyroelectric effects

Material	Example	$\varepsilon/\varepsilon_o$	$\tan\delta$	p $10^{-4} C/m^2K$	F_D $10^{-5}/\sqrt{Pa}$
Ferroelectric single crystals	$LiTaO_3$	45	0.005	2.0	4.4
Modified ferroelectric ceramics	$PbTiO_3$	250	0.007	4.2	4.3
Ferroelectric thin films on silicon	PZT	250	0.006	2.2	2.4
Ferroelectric polymers	PVDF	12	0.015	0.3	0.9

Source: Pyreos[1028]

Pyreos[1029] states that for most applications it is not only important to have a large pyroelectric effect, but other factors, such as temperature dependence of the pyroelectric material, its Curie temperature and the manufacturing costs are also important factors that will ultimately determine the commercial success of a sensor material.

Pyreos[1030] claim that they can realise all of the above mentioned requirements with thin-film, ferroelectric lead zircon titanate (PZT) layers on silicon (line 4 in the above table). This is compared to the most commonly used ceramic pyroelectric infrared sensors based on PZT and lead titanate ($PbTi0_3$, line 2 of the table above), for which a RoHS exemption is required. The sensors with thin-film PZT layers on silicon contain only about 1/3000 of lead.

The PZT layers, which are the homogeneous material, contain around 80 % of lead resulting in only around 1 g of lead annually that would be used in the EU under this requested exemption.

[1028] Ibid.
[1029] Ibid.
[1030] Ibid.

Pyreos[1031] concludes that it requests the new exemption as the quantity of lead and the technology used for thin film sensors is fundamentally different from the conventional technology covered by the existing exemption 7c-I.

22.2.7 Technical Background of the Schott Exemption Request

Schott[1032, 1033] supports the continuation of exemption 7c-I in its current wording and scope, but specifically lead-oxide-based glasses, so called “solder glasses”, to attach optical elements like windows or lenses into metal components to achieve a glass-to-metal sealing for the hermetic packaging of electronic devices. This assembly is part of a hermetic package (“Cap”) for optoelectronic devices like laser diodes, photo detectors etc.

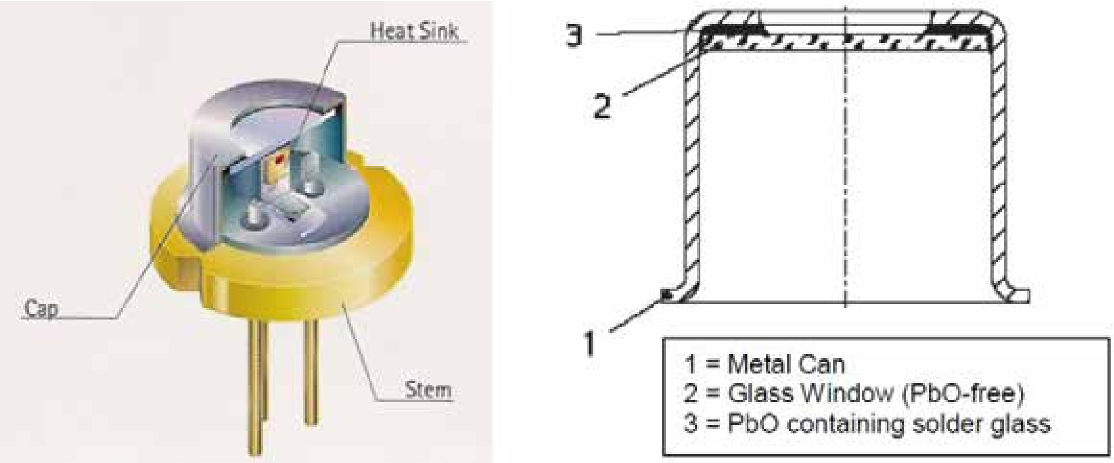
SCHOTT AG produces components for many types of EEE. Applications of these components are[1034]:

- Fibre Optic Data Communication Components:
  - Laser Diodes for Transmit Modules; and
  - Photodiodes and Avalanche Photo Diodes for Receive Components;
- Laser Packaging;
- Optical Sensor Devices:
  - Laser Diode-based Gas Sensors;
  - Infrared Sensors;
  - Photodiodes and photoresistors;
- Optical micro-electromechanical systems (MEMS) Packaging;
- High Power light emitting diode (LED) Packaging;

The “solder” glass contains around 75 % of lead to achieve a sufficiently low working temperature.

[1031] Op. cit. Pyreos Ltd. 2015a
[1032] Op. cit. Schott AG 2015a
[1033] Schott AG 2015b “Questionnaire 1 (clarification questionnaire), document "20150820_Ex_7c-I_Schott_Ans_Questionnaire-1_Schott_2015-07-30.pdf": Questionnaire 1 (clarification questionnaire,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/SCHOTT/20150820_Ex_7c-I_Schott_Ans_Questionnaire-1_Schott_2015-07-30.pdf
[1034] Op. cit. Schott AG 2015a

Figure 22-3: Laser diode package (left) and cross section of its window cap (right)



Source: Schott[1035]

22.2.8 Technical Background of the Sensata Exemption Request

Sensata applies for the renewal of exemption 7c-I in its current scope and wording. Sensata[1036] uses lead in glass to obtain good bonding, sealing and encapsulation properties in for example: [1037]

- Bonding ceramic to ceramic to form a pressure sensing element;
- Bonding diverse sensing elements on steel including sealing; or
- Encapsulating electronic components, like thick film paste for hybrid integrated circuits, resistors, capacitors, etc..

The use of lead in bonding glasses results in lowering the softening point, lowering the viscosity, matching the coefficient of thermal expansion (CTE), improving affinity and strengthening environmental resistance of parts to be bonded, sealed and/or encapsulated.[1038]

The lead glass is used in sensors for measuring for example pressure and temperature to improve safety, increase energy efficiency, reduce emissions etc.[1039] The lead in the glass helps to achieve the following glass properties:

- Lead in the glass lowers the softening point. The glass is used to bond for example silicon strain gages with aluminium bond pads on stainless steel

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[1035] Ibid.
[1036] Op. cit. Sensata Technologies 2015a
[1037] Ibid.
[1038] Ibid.
[1039] Ibid.

diaphragm. The firing temperature (at which the silicon is bonded to the stainless steel) must not exceed the (eutectic) temperature of the aluminium, potentially causing junction spiking and other reliability issues in the aluminium on silicon. Firing temperature is normally in the 850 °C range.[1040]

- Lead glass also has a low viscosity needed to flow well during the bonding process. Bad flow potentially causes pin holes and other (surface) imperfections which makes the glass sensitive to cracks and other mechanical damages when subjected to mechanical stresses which will occur during normal operation (= pressure exerted on steel and ceramic diaphragm). Cracks cause unacceptable sensor drift and potential sensor failure. Lead-free glasses have much higher viscosity (in the order of 100).[1041]
- Match the coefficient of thermal expansion of parts to be bonded. The coefficient of thermal expansion (CTE) of the glass should be within a specific range and compatible with stainless steel and alumina. Too low values cause a too high compressive stress in the glass, too high values can cause tensile stress. Both may result in glass cracks and, consequently, sensor failure.
- Improve affinity - to guarantee a sufficient adhesion between ceramic element and metal electrode or between semiconductor device and glass.
- Increase the resistance against adverse environmental conditions.

There is a growing need in for example household and industrial applications for mission critical sensors as made by Sensata, to make applications safer, more energy efficient and less emissive.[1042]

22.2.9 Amount of Lead Used Under the Exemption

Murata/JEITA et al.[1043, 1044] quantify the amount of lead used under the exemption in the EU with around 350 tonnes annually.

Murata/JEITA et al.[1045, 1046] base their estimate on 2013 data from the below companies, which represent the major players on the EU market:

- Ceram Tec;
- Emerson;
- EPCOS;
- Freescale;

[1040] Ibid.
[1041] Ibid.
[1042] Ibid.
[1043] Op. cit. Murata et al. 2015a
[1044] Op. cit. JEITA et al. 2015a
[1045] Op. cit. Murata et al. 2015a
[1046] Op. cit. JEITA et al. 2015a

- Johnson Matthey Piezo ProductsMeggitt DK;
- Morgan Advanced Materials;
- Murata;
- PI Ceramic.

Murata/JEITA et al.[1047, 1048] state that electrical and electronic components are used in a wide range of final products and markets, it is impossible to provide a precise figure of the amount of lead included in glass and ceramic components in the EU for EEE. The electronic equipment industry is engaged in the reduction of lead and environmental burdens within its powers, although it is impossible to completely cease the use of lead under the scope of 7(c)-I. They present the above estimate based on company figures. It should be noticed that there may be components with lead-containing ceramic and companies which are not included in this estimation. For this reason, the values presented here are given for reference purposes only.

22.3 Applicants' Justifications for the Exemption

Murata et al.[1049] state that our society requires the best health care and safety technology. Many components containing lead in a glass and/or ceramic matrix compound provide high security performance in EEE or save lives like, for example, overcurrent or over-temperature protection.

Murata et al.[1050] investigated the substitution of lead in glass and/or ceramic used in electrical and electronic components prior to the last review and have continued the investigation after 2009 as well; however, they have not found any substitution technology up to the present day, and extensive research has shown that there are no prospects of finding substitutes in the next five years. Consequently, they claim that it is necessary to extend exemption 7(c)-I for an additional validity period of 5 years for categories 1 – 7 and 10 equipment.

22.3.1 General Status of Lead Substitution in Ceramics of Electrical and Electronic Components

According to Murata et al.[1051] numerous potential compositions have been investigated for ceramic in the last 10 years and the main task is still the development of reliable technical solutions on an industrial scale. However up to the present moment, substitution technology has not been found and there is no prospect of finding it at least until the maximum validity period. No lead-free substitute with equivalent electrical properties, environmental adaptability range, reliability, workability and productivity has been found. Consequently, lead-containing glass and/or ceramic are indispensable for

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[1047] Op. cit. Murata et al. 2015a
[1048] Op. cit. JEITA et al. 2015a
[1049] Op. cit. Murata et al. 2015a
[1050] Ibid.
[1051] Ibid.

bringing out the required functionality and properties of the electrical and electronic components applicable to exemption 7(c)-I.

For piezoelectric ceramics, according to Murata et al.,[1052] niobium, tantalum, antimony, lithium, rare earth elements etc. have been investigated as elements for substituting lead as a constituent element of ceramic. However, the electrical (piezoelectric) properties are inferior when compared with lead-containing ceramic and cannot be stably achieved throughout a wide temperature range. Moreover, the properties described in research papers were obtained in the laboratory and experience has shown that these cannot generally be achieved stably at a mass production scale. There are still many remaining technical issues needing to be solved in order to achieve mass production of practical products. Adding to that, even in the case that mass production technology is achieved; the research has shown that the required properties for substituting almost all of the applications cannot be obtained.

Murata et al.[1053] claim that replacing PTC even in a certain resistance-Tc range only at the moment would need an overall change in powders conception used in the production of PTC. This is because not just one powder is used in production of a certain product but usually a mixture of two or more powders. With the alternative materials examined up until now, because of the strong limitations in regard to certain properties, only ceramic for applications with low Curie temperatures might be meaningful to undergo further investigation and development. Also for these low Tc applications, several constraints still exist.

22.3.1.1 Principle Elements for Lead Substitution in Ceramics

Murata et al.[1054] state that electrical properties of ceramic strongly depend on their crystal structure. According to Pauling's rule, in order to form the same crystal structure, constituent elements of ceramic, which can substitute lead are restricted to ions with a divalent valence and an ionic radius of 0.93-1.81 Å. On a purely scientific basis the elements which meet these conditions are limited to the following four:

- Cadmium;
- Calcium;
- Strontium; and
- Barium.

Cadmium is much more toxic than lead and is already restricted by the RoHS Directive, and thus is not appropriate even for consideration as a substitute material. "Lead-free" ceramics formed from alkaline-earth metals and titanium and zirconium, etc. have electrical properties strongly dependent on the operating environment temperature and voltage, and as they lack stability throughout a wide use environment range, i.e.

[1052] Ibid.
[1053] Ibid.
[1054] Ibid.

temperatures, voltages, frequencies, the alkaline-earth metals cannot be used as substitute materials of lead.

22.3.1.2 New Ceramics

Murata et al.[1055] report about the alternative approach of ceramics having a completely different composition than those using lead, as a substitute material for lead-containing ceramics. In spite of that, up to the present moment it has not been possible to achieve mass production of electrical and electronic components using substitute materials and having the same level of functionality. The electrical properties (piezoelectric properties) of (K, Na)NbO_3-type ceramics constituted of potassium, sodium and niobium are inferior when compared with lead-containing ceramic and cannot be stably achieved throughout a wide temperature range. [1056] Moreover, the properties obtained in the laboratory cannot generally be stably achieved at a mass production scale. There are still many remaining issues needing to be solved in order to achieve mass production of practical products. Adding to that, even in the case that mass production technology is achieved; the required properties for substituting almost all of the applications cannot be obtained.

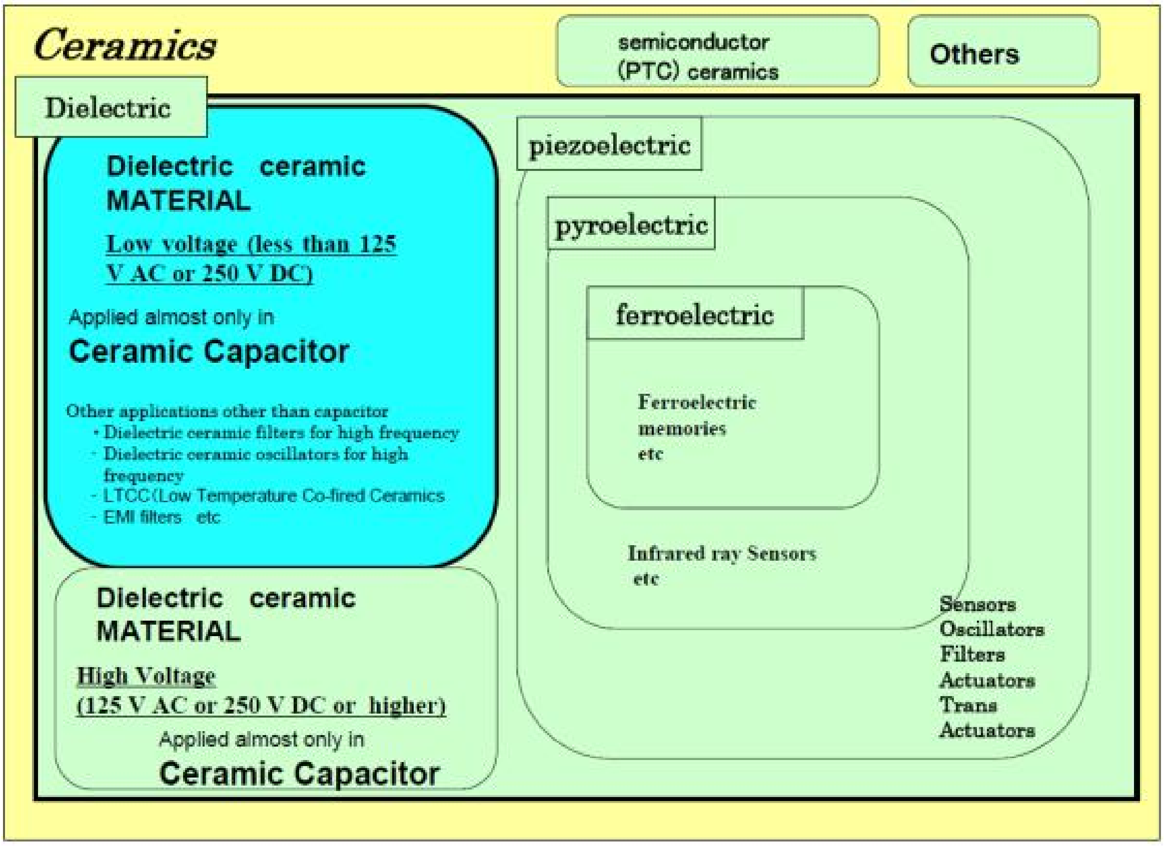
22.3.1.3 General Conclusion for Substitution or Elimination of Lead in Ceramics

Murata et al.[1057] conclude that for lead-containing ceramic falling into the technical scope of exemption 7(c)-I it is not possible to substitute lead by simply replacing it by another element. Moreover, attempts to obtain equivalent electrical properties from a completely different perspective have not progressed beyond ultimately obtaining similar results at best for a small part of the properties at laboratory level, and there are absolutely no technical perspectives to comprehensively eliminate lead from ceramic as of now.

Figure 22-4 gives an overview on the main types of ceramics in the scope of exemption 7c-I.

[1055] Ibid.
[1056] Jing-Feng Li, Ke Wang, Fang-Yuan Zhu, Li-Qian Cheng and Fang-Zhou Yao. "(K, Na) NbO3-Based Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies and Remaining Challenges", J. Am. Ceram. Soc., 1-20 (2013); source referenced in Murata et al. 2015a
[1057] Ibid.

Figure 22-4: Classification of ceramic materials and their main uses



Source: JEITA et al. in Zangl et al. (2010 [1058])

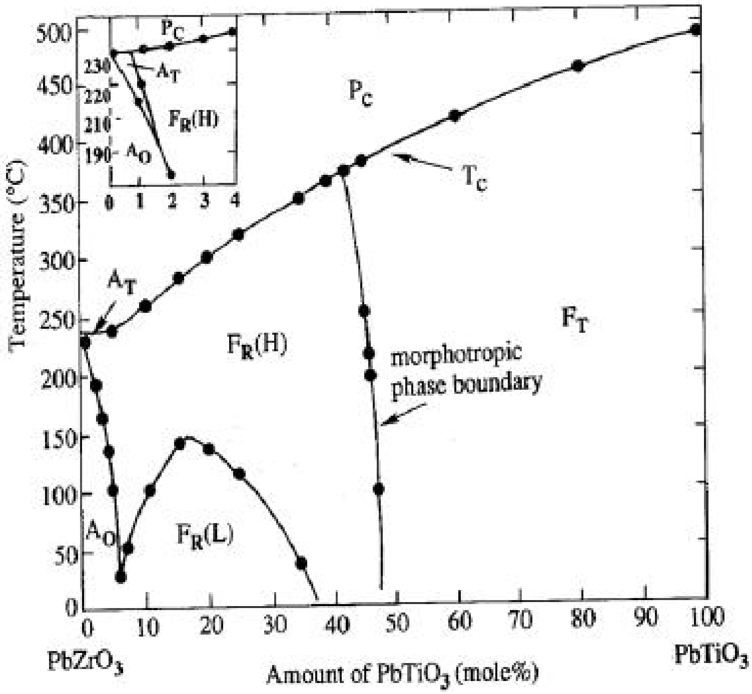
The following applicants present justifications for the continued use of lead in piezoelectric and PTC ceramics. The use of lead in dielectric ceramics in ceramic capacitors is covered by exemptions 7c-II, 7c-III and 7c-IV.

22.3.2 Substitution of Lead in PZT Ceramics

Murata e al.[1059] explain that Lead Titanium Zirconium Oxide abbreviated as PZT is the main material for piezoelectric devices. Lead (Pb^{2+}) is the main constituent in the solid solution of Lead Titanium Oxide with a tetragonal crystal structure and lead zirconium oxide with a rhombohedral crystal structure. Lead titanium oxide and lead zirconium oxide form a unique morphotropic phase boundary which is vertical above temperature as shown in the following phase diagram.

[1058] Op. cit. Zangl, Stéphanie [Oeko-Institut e.V.] et al. 2010a
[1059] Op. cit. Murata et al. 2015a

Figure 22-5: Phase diagram with morphotropic phase boundary of PZT



Source: Jaffe, Cook Jaffe: Piezoelectric ceramics, referenced by Murata et al.[1060]

According to Murata et al.[1061], this special perovskite structure in combination with the unique electron structure of Pb brings out the unique combination of piezoelectric properties over a wide temperature range, like:

- High Curie temperatures;
- High piezoelectric charge constants;
- High electromechanical coupling factors;
- High quality factors and low losses for ultrasonic devices;
- High stability under different driving and environmental conditions, especially temperature;
- High reliability.

Murata et al.[1062] put forward that those properties are required for the applications. To aid the understanding of the applicant's justification, Table 22-4 explains essential parameters of PZT ceramics.

[1060] Ibid.
[1061] Ibid.
[1062] Ibid.

Table 22-4: Essential characteristics of PZT ceramics

Curie temperature	Temperature at which piezoelectric ceramics lose their piezoelectric properties.
Electro Mechanical Coupling Coefficient (k) of piezoelectric ceramics	Coefficient to show the efficiency to transform and communicate electric alteration into the energy of mechanical alteration (or vice versa) due to the piezoelectric effect: $k = \sqrt{\frac{\text{mechanical energy stored}}{\text{electrical energy applied}}}$ or $k = \sqrt{\frac{\text{electrical energy stored}}{\text{mechanical energy applied}}}$ In order to gain filter characteristics, materials with high values in this category are essential.
Mechanical Quality Factor Coefficient of piezoelectric ceramics	Shows the extent of mechanical loss near frequencies where the piezoelectric substance resonates. In resonators and oscillators, as the value becomes higher, the oscillator becomes more efficient and the fluctuation in the resonance frequency decreases.
Piezoelectric Strain Coefficient (d constant) (Piezoelectric material constant)	Indicates how efficient an electric field can generate strain of the piezoelectric material, or vice versa how efficient a strain applied on the ceramic can generate an electrical field. Higher values indicate higher efficiency. d=strain / applied electrical field If the value is high, the piezoceramic can generate displacement efficiently from a low electric field. Also, the output is larger for sensors and it can be used as good sensor material with high sensitivity.
PZT ceramics	Ceramics consisting of a mixture of $PbZrO_3$ and $PbTiO_3$.
Saturation polarization	Highest practically achievable magnetic polarization of a material when exposed to a sufficiently strong magnetic field.

Source: Zangl et al. 2010[1063]

Murata et al.[1064] inform that intensive work has been done in the past to identify alternatives for PZT resulting in more than 2,500 patent publications[1065]. Most of them go back to the known base compositions and indicate the development effort to improve the piezoelectric properties related to the base lead-free compositions. Murata et al.[1066] claim to continuously review the possibility of using alternative lead-free piezoelectric materials and have done internal and external developments towards lead-

[1063] Op. cit. Zangl, Stéphanie [Oeko-Institut e.V.] et al. 2010a
[1064] Op. cit. Murata et al. 2015a
[1065] C.f. http://www.geocities.jp/kusumotokeiji/wadi.htm, source as referenced by Murata et al.
[1066] Ibid.

free materials, e.g. in the REALMAK[1067] and DELLEAD[1068] projects funded by the German Government, and in the sfb 595 at TU Darmstadt[1069], Germany.

Based on the state of the art in the development of lead-free alternatives for PZT, Murata et al.[1070] list three main groups of compositions as potential lead-free piezoceramic candidates:

- Barium titanate-based;
- Bismuth sodium titanate (BNT)-based; and
- Potassium sodium niobate (KNN)-based.

According to Murata et al.[1071], none of the above materials can be considered as a suitable overall lead-free substitute for PZT applications in the scope of the RoHS Directive. Figure 22-6 presents a comparison of basic physical properties of PZT and lead-free ceramics.

[1067] RealMAK - Technische Informationsbibliothek (TIB); Link: https://www.tib.eu/de/suchen/?id=198&tx_tibsearch_search%5Bquery%5D=RealMAK&tx_tibsearch_search%5Bsearchspace%5D=portal&tx_tibsearch_search%5Bsrt%5D=rk&tx_tibsearch_search%5Bcnt%5D=20; source as referenced by Murata et al./JEITA et al. 2016b

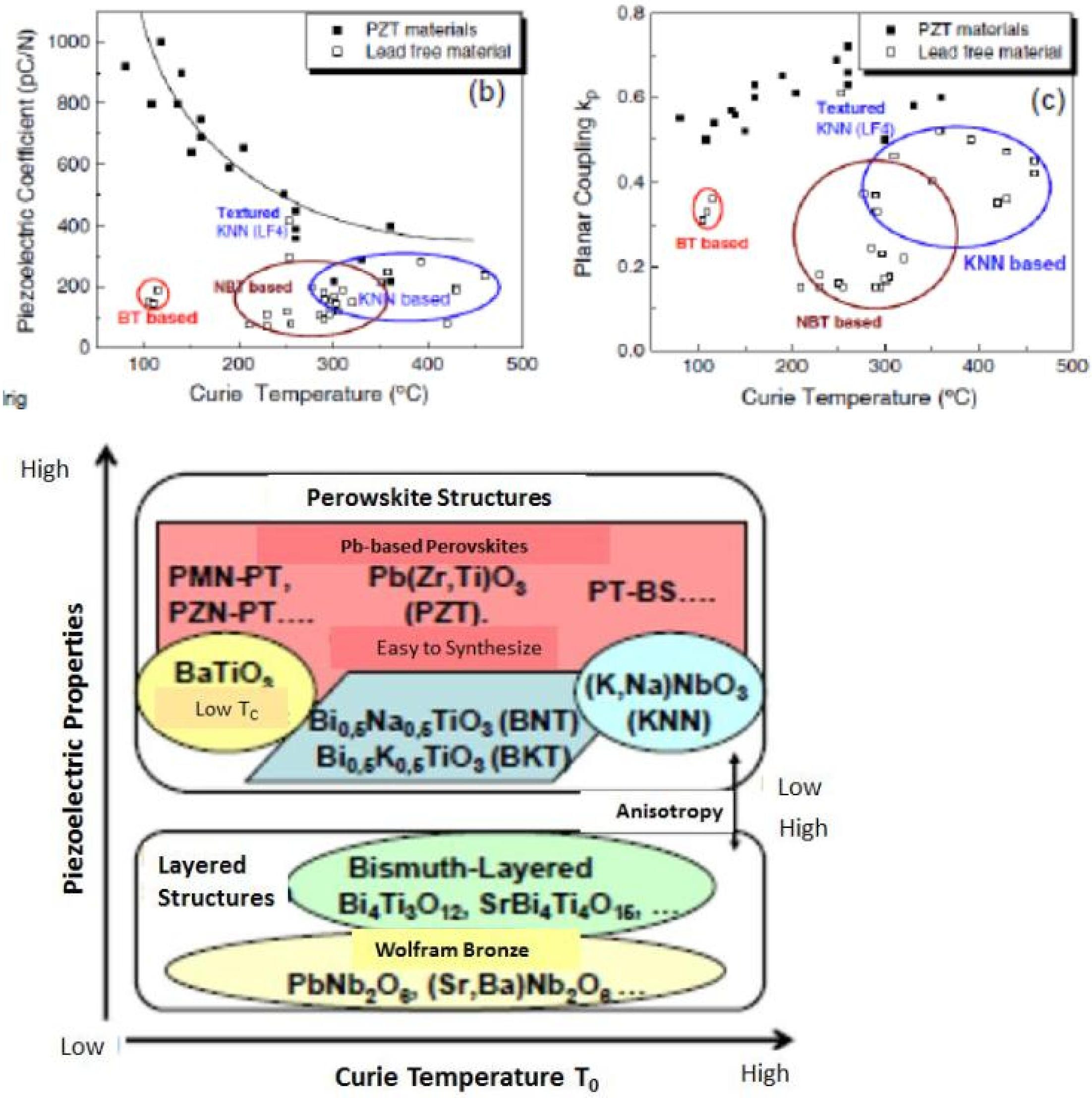
[1068] DelLead Bleifreie Piezokeramik für die Aktorik DelLead - Technische Informationsbibliothek (TIB); Link: https://www.tib.eu/en/search/id/TIBKAT%3A577111779/; source as referenced by Murata et al./JEITA et al. 2016b

[1069] Sfb595 – Technische Universität Darmstadt; Link: http://www.sfb595.tu-darmstadt.de/sfb595/sfb595_1.de.jsp; source as referenced by Murata et al./JEITA et al. 2016b

[1070] Ibid.

[1071] Ibid.

Figure 22-6: Performance comparison of lead-free and PZT ceramics



Source: M. Matsubara[1072]*, T.R. Shrout et al.*[1073]*, referenced in Murata et al.*[1074]

According to Murata/JEITA et al.[1075], the two top figures in Figure 22-6 show that the piezoelectric characteristics of piezoelectric ceramics largely fluctuate in a domain close

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[1072] M. Matsubara 2005: Processing and piezoelectric properties of lead-free (K, Na)NbO³; dissertation department of applied chemistry, Graduate School of Engineering, Nagoya University

[1073] T.R. Shrout, S.J.Zhang: Lead-free piezoelectric ceramics: Alternatives for PZT?, in: Journal of Electroceramics 19, 2007, page 113 - 126

[1074] Murata et al. 2015c "Addendum to original exemption request, document "Leadfree_PZT_comparison.pdf","

[1075] Murata et al./Jeita et al. 2016b "Answers to third questionnaire (ceramics), document "Exe_7c-I_Questionnaire-3_Murata-JEITA_2016-03-03_ceramics.pdf", received via e-mail by Dr. Otmar Deubzer, to the Curie temperature, and when exceeding the Curie temperature the functionality of the ceramics is lost through depolarization. In order to use piezoelectric ceramics in practice, it is necessary that the piezoelectric characteristics be stable, therefore when considering the use environment and manufacturing conditions of general EEE, the Curie temperature needs to be 200 °C or more as a minimum, and preferably 250 °C or more.

22.3.2.1 Barium Titanate-Based Ceramics as PZT Substitute

Murata et al.[1076] [1077] state that lead-free barium titanate ($BaTiO_3$), the first piezoceramic ever, to their best knowledge for historic reasons is still used for niche military applications, specifically for naval underwater acoustics, which are outside the scope of the RoHS Directive. In the lead-free versions the working temperature is limited to the low Curie temperature of about 120 °C.

According to Murata et al.[1078] [1079], all other $BaTiO_3$ materials are modified with up to 10 % lead titanate to increase the Curie temperature. These materials are not used as a replacement for PZT, but are used due to other properties, e.g. density, where PZT cannot be used. Murata/JEITA et al.[1080] to the best of their knowledge, however, do not know applications for which such $BaTiO_3$ can be used, but PZT cannot. Upon further request, Murata/JEITA[1081] reaffirm that they do not know other properties besides density that would qualify the use of the $BaTiO_3$-based ceramics with up to 10 % of lead and that they do not know applications where they could be used where PZT cannot be used.

In principle, the $BaTiO_3$ materials with up to 10 % of lead titanate could be used to replace PZT ceramics, which contain 50 % of lead and more, in order to reduce the total amount of lead where its material properties are sufficient. Murata/JEITA et al.[1082] explain that the modification of $BaTiO_3$ with up to 10 % $PbTiO_3$ is a compromise to increase T_c from ~120 °C to ~150 °C. But with increasing lead content, the piezoelectric properties decrease. Therefore, $BaTiO_3$ with a lower lead content still have piezoelectric properties which are inferior compared to PZT. It is actually inferior even compared to other lead-free compounds.[1083] Moreover, in almost all applications, heat is applied in manufacturing processes or use environments, therefore higher Curie temperatures (200 °C or more, preferably 250 °C or more) are required. Even by partially substituting $BaTiO_3$

Fraunhofer IZM, from Klaus Kelm, Murata, on 22 March 2016” unpublished manuscript,

[1076] Op. cit. Murata et al. 2015a

[1077] Op. cit. (Murata et al. 2016a)

[1078] Op. cit. Murata et al. 2015a

[1079] Op. cit. (Murata et al. 2016a)

[1080] Op. cit. (Murata et al./Jeita et al. 2016b)

[1081] Murata et al./JEITA et al. 2016d “Answers to questionnaire 5a, document "Exe_7c-I_Questionnaire-5a_Murata-JEITA_2016-03-28_Ceramics_final.pdf", received via e-mail from Klaus Kelm, Murata, by Dr. Otmar Deubzer, Fraunhofer IZM, on 1 April 2016” unpublished manuscript,

[1082] Op. cit. (Murata et al./Jeita et al. 2016b)

[1083] Jaffe, Cook, Jaffe; Piezoelectric Ceramics; Academic Press Ltd.; 1971; source as referenced by Murata/JEITA et al. 2016b by lead titanate, the Curie temperatures will increase to levels of not more than 20-30 °C, which is insufficient.

22.3.2.2 Bismuth Sodium Titanate (BNT) as PZT Substitute

BNT-based compositions are characterized by so called depolarization temperatures, at which the macroscopic piezoelectric properties are lost within a very narrow temperature range, which is much lower than the Curie temperature. Therefore, the usable working temperature range is limited to about 200 °C. BNT-based compositions show a strong anisotropic behaviour, which means that these materials have a low planar mode but a high thickness mode piezoelectric coupling with low piezoelectric charge coefficients, a low dielectric permittivity and moderate dielectric losses. Sometimes a high normalized charge coefficient d_{33}, i.e. induced strain / applied electric field strength, is mentioned in the literature suggesting a strong piezoelectric effect. At this point it must be clarified that this so called “giant piezoelectric effect” is caused by a field induced phase transition and it is not a linear piezoelectric effect. For PZT or similar components field induced phase transitions or domain switching processes lead to reliability issues due to crack propagation in the grains. Nonetheless, no reliability study is currently available according to Murata et al.[1084]

22.3.2.3 Potassium Sodium Niobate (KNN) as PZT Substitute

KNN-based compositions, textured or non-textured, have the highest potential to be an alternative to PZT because the Curie-temperatures are comparable to the PZT family and piezoelectric coefficients are between the BNT-based materials and PZT. But it must be pointed out that this strong piezoelectric coupling is found around polymorphic phase transitions and therefore shows a remarkable temperature dependence.

Murata et al.[1085] state that besides the dielectric and piezoelectric properties for the possible alternatives for PZT, the technological requirements for production on an industrial scale must be considered. The safe mass production of PZT materials based on conventional ceramic processes, including water-based mixing and milling processes as well as sintering in normal atmosphere, is well established. In contrast, for BNT-based materials as well as for KNN-based materials, different processes must be developed to bring out the properties obtained in the laboratory to mass production. In particular the KNN-based materials are the most challenging with respect to the synthesis. It is well known that the properties are strongly dependent on real stoichiometric composition, which can hardly be controlled because of the volatility of the alkaline metals. For both KNN and BNT materials, especially the mixing and milling play a crucial role. Because of the water solubility of most of the raw materials, processes must be switched from water- to solvent-based ones, with a high impact on health and environment protection.

[1084] Op. cit. Murata et al. 2015a
[1085] Ibid.

Murata/JEITA et al.[1086] state that new technological routes for a stable mass production must be developed. At the moment this is not yet achieved, and it is not foreseeable when a breakthrough can be achieved. In summary, Murata et al.[1087] conclude, none of the known lead-free piezoelectric materials is a suitable overall substitute for PZT.

22.3.2.4 Bandelin's Application-specific Exemption Request for use of PZT Ceramics in High Power Transducers

Bandelin[1088] claims they are in constant contact with the manufacturers Ceram Tec and Pi Ceramic in Germany in order to develop potential alternatives to substitute lead in high-performance piezoelectric ceramics, especially for the early testing of lead-free perforated discs in high-performance ultrasonic transducers. Bandelin has already conducted such tests with samples from Honda/JP, but the results were quite negative. It is not possible to substitute PZT by changing the construction of high-performance ultrasonic transducers and substituting the material with a lead-free ceramic has not been conceivable to date.

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.[1089]

The known material threshold values also yield clear evidence of the unsuitability of lead-free BNT and KNN piezo ceramics for high-performance applications. Table 22-7 compares the mean values for core performance parameters of various ceramics.[1090]

Table 22-7: Comparison of material properties of ceramics

Material	tanδ (10^{-3}) (electrical loss angle)	Qm (mechanical Q)	Tc/Td Curie/depolarisation temperature
Soft PZT	20	70	260 °C (Tc)
Hard PZT	4	800	320 °C (Tc)
BNT ceramic	30	200	200 °C (Td)
KNN ceramic	30	unknown	290 °C (Tc)

Source: Bandelin[1091]

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

[1086] Op. cit. (Murata et al./Jeita et al. 2016b)
[1087] Op. cit. Murata et al. 2015a
[1088] Op. cit. Bandelin Electronic GmbH 2015a
[1089] Op. cit. Bandelin Electronic GmbH 2015b
[1090] Ibid.
[1091] Ibid.

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 is extremely limited (a continuous operation temperature of only 120 °C is generally prescribed by the manufacturers), and thus the piezo ceramic must have high efficiency rates or low losses.[1092]

To Bandelin's 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.

Bandelin[1093] used lead-free BNT piezo ceramic material from HONDA ELECTRONICS, Japan, with the same geometrical dimensions as their 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 Bandelin's products. Due to the low losses, cooling of their high-performance transducers with hard PZT is unnecessary, and, in fact, functionally impossible.

Bandelin[1094] does not expect any alternative materials to substitute the PZT ceramics in the next 10 years. PZT is the only material that can be used in high-performance ultrasonic transducers. PZT in a finished component is said by Bandelin to be neither harmful to the health nor hazardous to the environment and can be disposed of properly.

Bandelin[1095] fulfil their duties in the disposal of electronic waste (including piezo materials) in the scope of their electronic waste registration and annual verification thereof. In light of these facts, they apply for the amendment of exemption 7c-I.

22.3.2.5 Pyreos'Application-specific Exemption Request for Lead in Ceramics

Pyreos[1096] claims it has spent considerable resources to reduce the content of lead in the sensors resulting in a lead reduction compared to the incumbent pyroelectric sensor technology by about a factor 1,000. As a result, the amount of lead in the sensors already implemented by Pyreos today is extremely low. In order to reduce the amount of lead in the sensors, Pyreos[1097] used PZT materials with the same lead-content like other

[1092] Ibid.
[1093] Ibid.
[1094] Op. cit. Bandelin Electronic GmbH 2015a
[1095] Ibid.
[1096] Op. cit. Pyreos Ltd. 2014
[1097] Pyreos Ltd. 2016a "Answers to questionnaire 2, document "Questionnaire-2_Pyreos_2016-03-06.pdf",

manufacturers, but the PZT thinfilm on the silicon decreases the total amount of PZT in the sensors and as a consequence the amount of lead.

In a next step, Pyreos[1098] wants to develop an infrared absorption layer that will allow to further reduce the thickness and the pixel area of the pyroelectric sensor by a factor of 10-100 within an intended timescale until 2018, and a lead-free infrared absorption layer until 2020. Pyreos[1099] recently located a new partner for the absorption layer implementation with superior performance and is evaluating manufacturability. With the lead-free infrared sensor they have just started as partners of a government funded project to further investigate and establish the production of useful lead-free pyroelectric thin films. If successful, it would in principle enable lead-free thin film sensors, but it will take considerable time for it to mature to be industrially accepted at a cost effective price.

22.3.3 Substitution of Lead in PTC Semiconductor Ceramics

Murata et al.[1100] explain that PTC ceramics (Positive Temperature Coefficient) increase their electrical resistance with increasing temperature. Examples of material compositions are doped barium (BT) and lead titanate (PT) mixtures. The basic PTC material barium-strontium-lead-titanate is a perovskite which undergoes a phase transition from ferro- to paraelectric at the Curie temperature. If properly processed and slightly donor doped (< 1 mol%) such materials are PTCR active so to speak, i.e. semiconductive at low temperatures and quite highly resistive at temperatures above the Curie temperature. It is possible with dopants and some changes in proportions of components and additives to tune the properties of a composition to a specific targeted application.

22.3.3.1 Classification of PTC Ceramics

Murata et al.[1101] divide the active PTCR materials into four sections based on resistivity and Curie temperature, in which each individual section contains hundreds of material recipes based on BT and PT:

- **Materials with Curie temperatures below 120 °C and resistivity values below 1,000 ohm.cm:**
  These materials serve applications like overload protection, inrush current limitation, heating, telecom line protection, motor protection, motor start and temperature sensing. Lead titanate is added to the recipes to decrease the resistivity and increase performance because lead increases the ferroelectricity in the ceramic material.

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received via e-mail by Dr. Otmar Deubzer, Fraunhofer IZM, from Torben Norlem, Intertek, on 23 March 2016: Second questionnaire" unpublished manuscript,

1098 Op. cit. Pyreos Ltd. 2014

1099 Op. cit. (Pyreos Ltd. 2016a)

1100 Op. cit. Murata et al. 2015a

1101 Ibid.

Lead-free materials are available for this region but the performance and durability that can be achieved is significantly lower and for most applications, such materials can therefore not be used. Based on the current state of the art, breakdown voltages are lower by approximately 30 % for lead-free ceramics. As a result, the present situation is that no lead replacement with sufficient performance has been found yet to produce a PTC with a Curie temperature below 120 °C and low resistance values.

- **Materials with high Curie temperatures above 120 °C and resistivity values below 1,000 ohm.cm:**
  This is the most commonly used material type. It serves applications like overload protection, inrush current limitation, telecom line protection, motor protection, motor start, temperature sensing and heating. Lead is added to the recipes to achieve both higher Curie temperatures and lower resistance.
  A lead-free bismuth-based perovskite material was the main material investigated as a substitute in the literature. It exhibits higher Curie temperatures and can therefore be used to increase the Curie temperature of a solid solution with barium titanate. However, it has been demonstrated that such components as BNT (bismuth sodium titanate) have limited solubility in barium titanate and can increase the Curie temperature only to regions around 160 °C. At the same time electrical parameters including important ones like steepness of resistance change and breakdown voltage strength deteriorate dramatically. Especially the energy efficiency for switching applications like motor starters will be influenced strongly. The break down voltage for typical motor start elements would be reduced by approximately 30 % and the resistance stability during application would decrease as well. The performance in terms of reliability is affected most. Tests according to the industry standard IEC 60738-1 like electrical endurance, electrical cycling, temperature storage, show higher resistance changes by an order of magnitude, compared to the current standard. In the IEC 60738-1 test procedure for humidity even higher changes of up to two orders of magnitudes are observed.
- **Materials with low Curie temperature and resistivity values of 1,000 ohm.cm and more:**
  This section is one of the most critical ones in regard to material development. It mainly serves applications like overload protection, inrush current limitation, temperature sensing and heating. Nevertheless, Industry has started some further investigations in this direction. The reduction of lead would reduce the breakdown voltage performance by approximately 30 %. Additionally, materials with reduced or no lead are especially problematic in terms of reproducibility of the resistance and resistance spread.
- **Materials with high Curie temperature and resistivity values of 1,000 ohm.cm and more**:
  They serve applications like overload protection, inrush current limitation and especially heating. These materials require lead titanate compounds in the

ceramic because of the high Curie temperature of up to 300 °C. So far no material system beside BT and PT has been developed that achieves Curie temperatures above 200 °C. Adding lead to the barium titanate matrix of the PTC ceramic is the only known procedure to raise the Curie temperature of the basic barium titanate without loss of important properties and functionality.

22.3.3.2 Substitution of Lead in Ceramic Materials with Curie Temperatures below 120 °C

Murata et al.[1102] explain that adapting strontium titanate generally may achieve certain temperature ranges for applications with Curie temperatures Tc < 120 °C.

In the low ohmic section at Tc<120°C, Murata et al.[1103] report that the reduction of lead reduces the ferroelectricity (permittivity, polarization) of the material involved. BNT and BKT are reported to have a relative permittivity of less than 5,000 where lead titanate shows a relative permittivity of around 10,000. The effectiveness of the charge compensation, which appears at temperatures below Tc, is due to the magnitude of the ferroelectric material involved. According to Heywang[1104], the mechanism which causes the PTC effect decreases if relative permittivity at the grain boundary is reduced.

According to Murata et al.[1105], the replacement of lead will decrease the lifespan of the product as well as its voltage breakdown strength for around 30 % depending on the material type in question. Even if PTC materials are produced without lead for Tc lower than 120°C, it will come at the cost of reduced performance.[1106] Hence, increased dimensions, more material and energy need to be used to produce the individual product. Furthermore, lead-free materials cannot serve all applications and functions. This demonstrates the still many problems need to be solved before a "lead-free" material can be produced in practice.

Murata et al.[1107] see a major challenge in substituting lead in ceramic materials with low Tc and high resistance because of the difficulties with reproducibility and resistance spread.

[1102] Ibid.
[1103] Ibid.
[1104] W.Heywang. Semiconducting Barium Titanate. J Mater Sci 1971; 6:1214-1226; source as referenced by Murata et al.
[1105] Ibid.
[1106] H. Takeda et.al.: Fabrication and operation limit of Lead -Free PTCR ceramics using BT-BNT; Journal of Electroceramics (2009) 22, 263-269; source as referenced by Murata et al.
[1107] Ibid.

22.3.3.3 Substitution of Pb in Ceramics with Curie Temperatures of 120 °C and Higher

For high temperature sections, Murata et al.[1108] consider BNT (bismuth sodium titanate) and BKT (bismuth potassium titanate) to be the most promising materials to push the lead-free limit. Those materials work best at higher resistances above 1,000 ohm-cm. In this high ohmic section above 120°C, a Tc could be reached up to 200°C according to Takeda et al.[1109]. This limitation is mainly caused by the volatility of Bi which changes the composition and incorporation mechanism and thereby the sintering characteristics and achievable resistance, respectively. Wei et al.[1110] suggest a limit at 160 °C because above that temperature the ceramic becomes highly resistive. The best performances were reported at Curie temperatures below 150 °C, which are, however, still distinctly inferior to the traditional materials containing lead titanate.

Murata et al.[1111] expect the breakthrough voltage to be rather low due to the fact that the PTCR steepness α [%/C] around Tc is below 10 %/C, which influences the maximum resistance that is directly related to the break down voltage. For comparison, values of 60 %/C can be achieved with the standard lead titanate material. At the moment it is not possible to make a reliable statement about the Tc reproducibility. However, due to the volatility of Bi a poor Tc reproducibility and predictability is expected.

Murata et al.[1112] point out that the results obtained so far are at laboratory (research) level, and reliability and mass production technology have not been ensured. Consequently, there are no prospects for actual mass production supply being provided, and the current situation does not allow the substitution in the next few years.

According to Murata et al.[1113], the low ohmic section above 120°C, which is the economically most important section, is even more challenging. Naturally, the PTC effect is weaker than for higher resistances due to the very basic principles involved. The drawback of the new BNT- and BKT-based materials in terms of steepness; break down voltage and so on, becomes even more dominant than at high ohmic quarters. B.Y. Wu et.al.[1114] assessed the limit at Tc=160°C for BT PTC materials doped with BNT. Higher additions of BNT to BT in order to increase the Tc to higher temperatures would lead to high resistivity well above 1,000 ohm-cm in the PTCs, which Murata et al.[1115] deem

[1108] Ibid.
[1109] H. Takeda et.al.: BaTiO 3–(Bi 1/2 Na 1/2) TiO 3 Solid-Solution Semiconducting Ceramics with Tc> 130 C; Appl. Phys. Lett. 87 (2005) 102104; source as referenced by Murata et al.
[1110] J. Wei et.al.: Effects of BNT Addition on the Microstructure and PTC Properties of La-Doped $BaTiO_3$-Based PTCR Ceramics; Ferroelectrics, 403; 91-96, (2010); source as referenced by Murata et al.
[1111] Ibid.
[1112] Ibid.
[1113] Ibid.
[1114] B.Y. Wu et.al.: A Study of PTC Ceramics Based on (V1-x, Crx)2 O3 Electroceramics; British Ceramic Proceedings No.41 Stoke-on-Trent, 1989, p.195-203 Institute of Ceramics; referenced by Murata et al.
[1115] Ibid.

unacceptable. According to Wei et al.[1116], the limited solubility of BNT in BT causes the effect due to which Bi^{3+} as an acceptor would occupy Ti^{4+} positions, which would lead to a reduction of free charge carriers.

According to Leng et al.[1117], the use of BKT-doped BT induces a similar limitation. Although there are reports of BNT and BKT-containing materials as an additive to BT replacing lead titanate in the range up to 160 °C for low voltage applications, Murata et al.[1118] explain that it is most important that the lowest resistance that is achievable is in the range of 100 Ohm-cm. This is still well above the limit of 2 Ohm-cm for lead-containing materials (traditional technique).

Murata et al.[1119] conclude that material studies on BNT reveal the lower performance and lower reliability of these lead-free PTC materials compared to the standard lead-containing materials. Actual results show 30 % lower breakdown voltage, 30 % lower steepness of the RT-curve and more than 1,000 % less stability at temperatures above 160 °C.

22.3.4 Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds

Murata et al.[1120] claim manufacturers have investigated boron, phosphorus, zinc, tin, bismuth, etc. as potential elements for substitution of lead as a constituent element of glass. “Lead-free” glasses using these elements can partially promote machining efficiency (ability to minimize energy consumed to apply heat, mechanical pressure, etc. in manufacturing processes) and affinity (ability for mutually wetting and bonding different materials such as metal and ceramic) which are necessary properties for achieving the required functionality of electrical and electronic components. However, when compared with lead-containing glasses, chemical stability and mechanical strength of the glasses are insufficient and do not meet the required functionality.

Murata et al.[1121] state that boron, phosphorus, zinc, bismuth, etc. are, in a general manner, inadequate for substituting lead as constituent elements of glass and as of now there are absolutely no technical perspectives for comprehensively eliminating lead from glass of electrical and electronic components.

[1116] J. Wei et.al.: Effects of BNT Addition on the Microstructure and PTC Properties of La-Doped BaTiO3-Based PTCR Ceramics; Ferroelectrics, 403; 91-96, (2010); source as referenced by Murata et al.

[1116] Ibid.

[1117] [2] S. Leng et.al.: Synthesis of Y doped BT-BKT Lead-Free Positive Temperature Coefficient of resistivity ceramic and their PTC effects; Journal of American Ceramic Soc. (2009) 92 [11], 2772-2775; source as referenced by Murata et al.

[1118] Ibid.

[1119] Ibid.

[1120] Ibid.

[1121] Ibid.

Murata et al.[1122] conclude that no substitution technology is available that can provide the high functionality required for electrical and electronic components. Only lead glass can bring out the necessary characteristics such as integrity of the layer, step coverage, delamination resistance, hermetic sealing, charge balance etc. and reliability to ensure public safety and avoid additional waste from premature failure, simultaneously satisfying high reliability requirements and usability over a wide range of applications. Lead glass is used for insulating, protection, resistance, adhesives, bonding, hermetic sealing and other uses.

Murata et al.[1123] state they cannot set a technical goal for a comprehensive substitution of lead glass concerning the technical scope of exemption 7(c)-I, and there are no perspectives for such in the foreseeable future. Therefore Murata et al. request the renewal of the exemption at least until the maximum validity period. Otherwise, Murata et al.[1124] fear accidents originating from crucial failures in EEE incorporating electrical and electronic components composed of glass with lead substituted by these elements due to their insufficient reliability and quick deterioration.

Bourns[1125], Murata et al.[1126], Schott[1127], Sensata[1128] and Vishay[1129] present specific and exemplary applications where lead in glass and glass ceramic matrices cannot be fully replaced. The below presentation of the application examples follows the system of Murata et al.[1130] presented in Table 22-3 on page 435.

22.3.4.1 Lead Glass for Protection and Insulation

Example 1.1 – Lead Glass Frits to Hermetically Seal Semiconductor Devices

Murata et al.[1131] explain that semiconductor device circuitries are susceptible to corrosion. They are protected by depositing a thin layer of glass to form a hermetic seal. This passivation glass layer must not impose stresses to the silicon or circuitry so its physical characteristics must be precisely controlled and its chemical composition is

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1122 Ibid.
1123 Ibid.
1124 Ibid.
1125 Bourns Inc. 2015b “Request for continuation of exemption 7c-I, document "20150818_Ex_7c-I_Bourns_Questionnaire-1_2015-07-28.pdf", clarification questionnaire: Clarification questionnaire,” http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/20150818_Ex_7c-I_Bourns_Questionnaire-1_2015-07-28.pdf
1126 Op. cit. Murata et al. 2015a
1127 Op. cit. Schott AG 2015a
1128 Op. cit. Sensata Technologies 2015a
1129 Op. cit. (Vishay 2015a January 2015)
1130 Op. cit. Murata et al. 2015a
1131 Ibid.

important to avoid interactions with dopants or with subsequent process step chemicals. The glass must have the following properties and processability:[1132]

- Temperature of the annealing process > 800 °C to better flow glass into the silicon groove / step coverage integrity of the layer (to avoid cracks);
- Chemical compatibility with the further steps of the process, and the back end: dicing and assembly integrity of the layer (holes);
- Compatibility of the thermal expansion coefficient with the silicon for mechanical behaviour to control stress resistance (delamination); and
- Electric charges in the glass balanced with the dopants in the junctions, for electrical stability in temperature and electrical stress (leakage current drift under high voltage stress).

According to Murata et al.[1133], the glass passivation is needed to protect the junction and to guarantee the proper behaviour of the semiconductor under high reverse voltage and the reliability of the component. The glass layer must not impose stresses on the silicon and must be compatible with the chemical process integration. The electrical insulation capability of glass is very high: it helps to achieve high voltage devices with a limited periphery area.

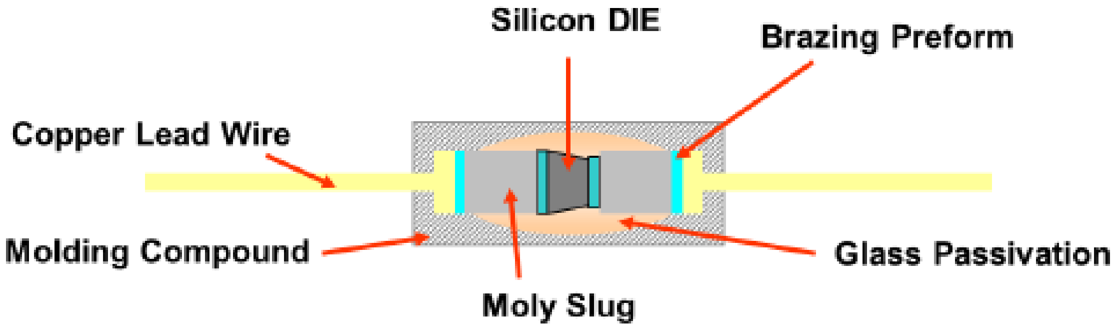
Murata et al.[1134] do not mention any specific research or efforts to substitute or eliminate lead in this application besides the general justification directly under Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds, page 460).

Example 1.2 – Glass for Hermetical Sealings of Diode Chips

According to Murata et al.,[1135] glass sleeve diodes in various sizes like in DO-35, DO-41, SOD-80 MELF (Metal Electrode Leadless[1136] Faces) packages, glass bead diodes, super-rectifiers etc., use glass to hermetically seal the diode chip. The advantage of packages with glass as the body or part of the body is the ability to hermetically seal the chip. This has technological advantages like better reliability, moisture-resistance, etc. over non-glass packages. Lead is needed in the glass to lower the melting point and reduce the viscosity, which together provides good hermetic sealing and adhesion to the adjacent metal plugs. Figure 22-8 shows an example.

[1132] Ibid.
[1133] Ibid.
[1134] Ibid.
[1135] Ibid.
[1136] “Lead” does not stand for the chemical element Pb, but for the carrying structure of the component

Figure 22-8: Schematic view of a high voltage "Superectifier ®" diode with glass as part of the package



Source: Murata et al.[1137]

Murata et al.[1138] do not mention any specific research or other efforts to substitute or eliminate lead in this application besides the general justification directly under Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds, from page 460).

Example 1.3 – Lead Glass for Insulation and Protection in Thick Film Resistors

Glass passivation layers block or help to block the sulfur, e.g. from traces of atmospheric hydrogen sulphide, from reaching the silver in the inner electrodes of thick film resistors, which might cause open circuit failures. The lead makes the glass pliable in the manufacturing process of the chip resistor to form a hermetic seal. The lead addition allows for lower oven temperatures, better quality and higher yields.

Murata et al.[1139] do not mention any specific research or efforts to substitute or eliminate lead in this application besides the general justification directly under Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds, from page 460).

Example 1.4 – Lead in Enamel Coatings of Wire Wound Resistors

Vishay[1140] requests an exemption for wire wound resistors with enamel coatings containing lead (Pb) as lead-oxide (Pb_3O_4) in glass. In order to limit thermal stresses and gain long term stability and high reliability, the applicant claims that exemption 7(c)-I is needed to reach:

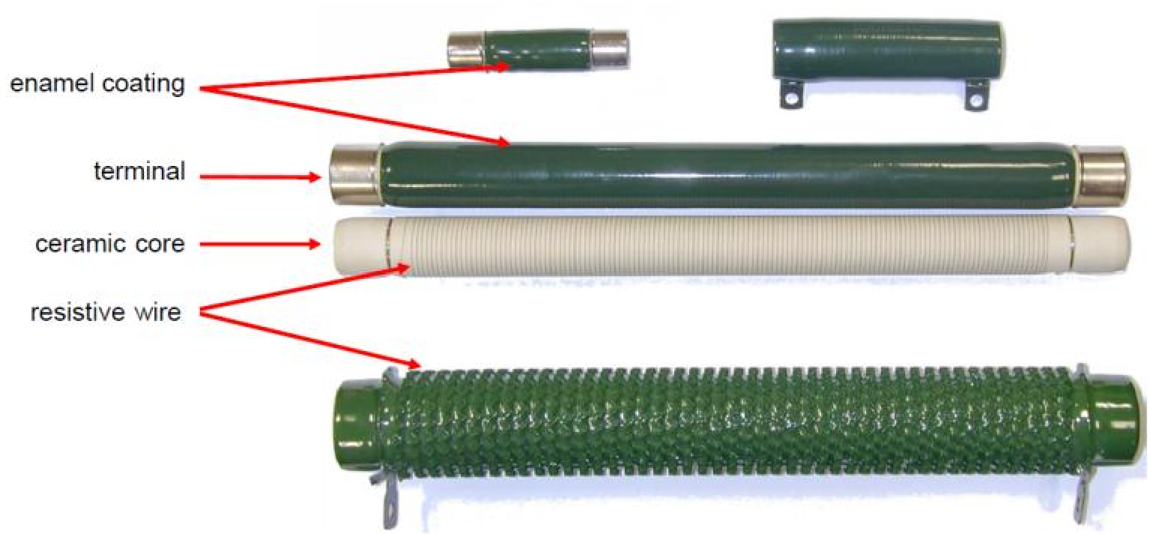
- Good flow conditions of the molten glass during production;

[1137] Ibid.
[1138] Ibid.
[1139] Ibid.
[1140] Op. cit. (Vishay 2015a January 2015)

- Virtually void free coverage of resistive metal wire and ceramic core; and
- Thermal expansion well matched to the resistive metal wire and ceramic core.

Vishay [1141] explains that wire wound resistors are made long-lasting and reliable by protecting the resistive wire from detrimental ambient conditions such as high humidity by virtually impenetrable enamel coatings (glass) that contain lead. Examples provided are shown in Figure 22-9.

Figure 22-9: Wire wound resistors



Source: Vishay[1142]

Vishay[1143] states that the thermal expansion of the different materials (ceramic, metal and glass) must match each other in order to limit destructive thermal stresses. The enamel coating (glass) otherwise cracks and can delaminate from the ceramic core and/or the metal wire, as Figure 22-10 illustrates.

[1141] Ibid.
[1142] Ibid.
[1143] Ibid.

Figure 22-10: Cracks (left) and delamination (right) in enamel wire wound resistor coatings

Source: Vishay [1144]

Vishay[1145] describes that cracks allow humidity to penetrate and reach the metal wire. This can lead to detrimental corrosion of the wire. Delamination reduces the effectiveness of heat transport away from the resistive wire. This can lead to hot spots and over-heating. Both effects can destroy the resistor within a fraction of the usual lifetime even under standard operating conditions.

According to Vishay[1146], wire wound resistors are used in many applications in the industry and transportation sector because of their unrivalled high pulse load capability. The load, continuous or pulse, leads to an excess temperature of the resistor of up to 600 °C. Therefore, the thermal expansion of the different materials (ceramic, metal and glass) must match each other in order to limit destructive thermal stresses. The enamel coating is non-flammable too, making the durable wire wound resistors an excellent choice for relevant “safety” applications.

Vishay[1147] takes significant effort to eliminate lead (Pb) in the enamel coating of wire wound resistors, but so far no technically equivalent solution is available to allow for the present quality standard under usual operating conditions. Vishay[1148] had carried out a first project to use lead-free enamel coating on wire wound power resistors from 1999 to 2002, and was not successful. A following project has been started in December 2014. An enamel coating has to comply with the following requirements like, to name some:[1149]

- Melting temperature;

[1144] Ibid.
[1145] Ibid.
[1146] Ibid.
[1147] Ibid.
[1148] Op. cit. Murata et al. 2015b
[1149] Ibid.

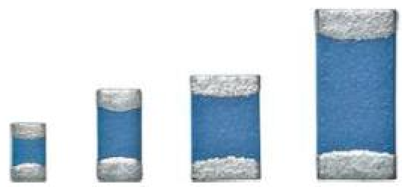
- Viscosity;
- Surface tension;
- Coefficient of thermal expansion; and
- Alkaline ions.

According to Vishay[1150], typical lead (Pb) free enamel coatings usually have too high melting temperatures, and the viscosity, surface tension, and the coefficient of thermal expansion do not meet specifications for suitable processing. From today's viewpoint the most likely replacement of lead is bismuth (Bi).The melting temperature of the lead-free enamel coating can be lowered to some extent by adding considerable amounts of bismuth. However, this may pose unforeseeable health risks due to the lack of knowledge about the level of toxicity of bismuth. Other materials than lead containing glass, such as cement or epoxy, do furthermore not fulfil the specifications of long term stability or non-flammability, respectively. Only the present mix of glass frits with special additives fulfils all of the technical/physical requirements to meet customers' specifications concerning reliability and long term stability.

Example 1.5 – Glass Coatings for Insulation in Negative Temperature Coefficient (NTC) SMD Resistors

Vishay[1151] uses lead-containing glass in two series of NTC surface mount device (SMD) thermistors illustrated in Figure 22-11. The thermistors cover a size range of 0402 to 1206 and a large resistance range from 2 kΩ to 470 kΩ.

Figure 22-11: NTCS and NTHS SMD thermistors

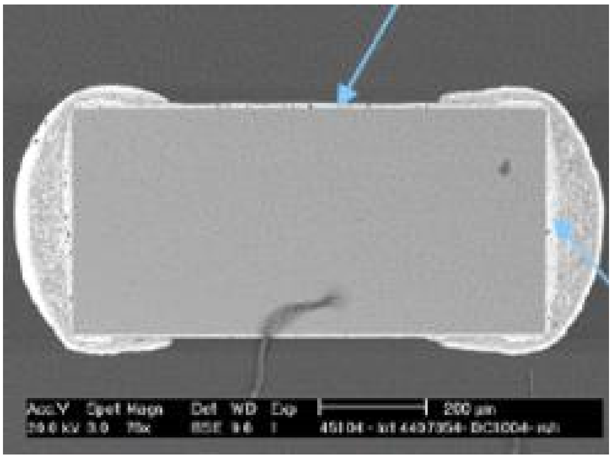



Source: Vishay[1152]

As shown in Figure 22-12, the thermistors contain lead silicate glass on four sides (upper arrow) and a lead silicate glass frit in Ag wrapped around the termination (lower / right hand arrow).

[1150] Ibid.
[1151] Vishay 2015b 2015 "Document "NTC – Glass coating for insulation.pdf", submitted as additional reference for the exemption request of Murata et al. 2015a: Document referenced in the exemption request of Murata et al. 2015a" (January 2015) unpublished manuscript,
[1152] Ibid.

Figure 22-12: Lead-silicate class in thermistors



Source: Vishay[1153]

Vishay [1154] reports that NTC SMD (Surface Mounted Devices) resistors need lead-containing glass coatings for several reasons:

- **High accuracy:**
  The distance between the two terminations does not influence the R value as the glass layer insulates the ceramic body.
- **Insulation of the ceramic body during the plating process**:
  Without the glass coating, Sn and Ni metals are deposited as well on the ceramic body modifying the electrical properties.
- **Variety of ceramics compositions:**
  Each resistance value has a specific ceramic composition. More than 60 different ceramic compositions are used with thermal expansion coefficient going from 6 ppm/K to 14 ppm/K. So it is very difficult to find one glass that can be used for the complete resistance range.
- **Firing temperature:**
  The firing temperature of the glass must be high enough to sustain the firing of the silver termination in the subsequent process.
- **Purity and stability of the glass**:
  The glass is deposited onto the ceramic body by electrophoretic deposition. Therefore a stable glass suspension must be achieved. Very pure glass (free of alkali) and a narrow particle size distribution are needed.
- **Adhesion of the silver layer (Ag) to the ceramic:**
  Glass frits with Ag paste are used to achieve good adherence of the Ag layer

1153 Ibid.
1154 Op. cit. (Vishay 2015a January 2015)

onto the ceramic. During firing, the glass diffuses into the ceramic and reacts with it creating an interface between ceramic material, glass and silver. Again here, it is very difficult to find a lead-free glass reacting properly with the complete ceramic range keeping all the performances: ohmic contact, no cracks, good adherence, good reliability in thermal cycling, damp heat, endurance tests. Furthermore, the interface must be resistant to the acidic plating bath solutions entering the porous terminations during plating. It is known that Pb free glasses are not well resistant to those solutions. The chemical attack of the interface by plating solutions has a dramatic effect on the reliability of the parts as the termination is coming lose from the ceramic body.

Vishay[1155] claims to undertake significant efforts to eliminate lead in the glass coating and silver termination of the NTC SMD but so far, no technical mature solution is available. As each resistance value has a specific ceramic composition, more than 60 different ceramic compositions are used with thermal expansion coefficient going from 6 ppm/K to 14 ppm/K. So Vishay[1156] states that it is very difficult to find one glass that can be used for the complete resistance range.

Example 1.6 - Metal Pressure Sensors

Murata et al.[1157] report the use of lead oxide glass in glass metal pressure sensors. The glass provides a seal and an electrically insulating surface for a capacitor plate.

Murata et al.[1158] do not mention any specific research or other efforts to substitute or eliminate lead in this application besides the general justification directly under Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds, from page 460).

22.3.4.2 Lead in Functional Glass Compounds/Resistance

Example 2.1 - Pastes with Lead in Glass

According to Murata et al.[1159], pastes with lead in glass are generally used as functional (resistive) material, glass coating and/or contact layer.

Murata et al.[1160] claim that substitutes are unreliable as current product specifications or stability requirements cannot be fulfilled. In substitutes, lead is replaced by bismuth (Bi) with possible environmental concerns, c.f. Section 22.3.5 from page 478.

[1155] Op. cit. (Vishay 2015b January 2015)
[1156] Ibid.
[1157] Op. cit. Murata et al. 2015a
[1158] Ibid.
[1159] Ibid.
[1160] Ibid.

Example 2.2 - Pastes With Lead In Glass And Lead Containing Functional Complex Oxides For High Ohmic Resistive Materials

According to Murata et al.[1161], pastes for high ohmic resistive layers require lead in glass and lead containing functional complex oxides in order to meet required specifications:

- No reaction with the glass matrix and no decomposition;
- Sufficiently high sheet resistivity;
- Low TCRs (Temperature Coefficient of Resistance);
- Low temperature sensitivity;
- Low moisture sensitivity – this alters resistance;
- Low humidity sensitivity – this changes the resistance value;
- Low process sensitivity;
- High resistance deviation after soldering processes used in surface mount processes.

Murata et al.[1162] claim lead-free resistor pigments in combination with the lead-free glasses showed:

- A reaction with the glass matrix and decomposition;
- Too low sheet resistivity;
- Too high TCRs (Temperature Coefficient of Resistance);
- Too high temperature sensitivity;
- Too high moisture sensitivity – this alters resistance;
- Too high humidity sensitivity – this changes the resistance value;
- Too high process sensitivity;
- Too high resistance deviation after soldering processes used in surface mount processes.

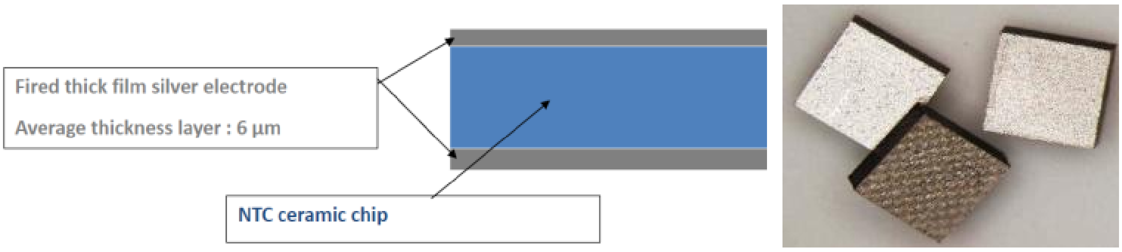
Murata et al.[1163] conclude that substitutes are technically impracticable and/or unreliable so that these materials cannot yet replace lead-containing glasses in this function.

Example 2.3 - Lead in Glass of the Silver Top and Bottom Electrode of NTC Chips

Vishay[1164] requests an exemption for NTC (negative temperature coefficient) chips with a silver top and bottom electrode that contains 4.5 ± 0.3% lead silicate glass as illustrated in Figure 22-13.

[1161] Ibid.
[1162] Ibid.
[1163] Ibid.
[1164] Op. cit. (Vishay 2015c)

Figure 22-13: NTC ceramic chips with thick film silver electrodes



Source: Vishay[1165]

Vishay[1166] applies the thick film silver paste electrode, a low firing Ag paste with lead containing glass frit, by screen printing and firing. The lead glass serves as interface for good adherence properties, electrical characteristics and reliability of the electrode, for which the lead in the glass is indispensable. The whole product range of NTC chips is produced with more than 60 different ceramic compositions. The actual silver electrode is compatible with all ceramic compositions and excellent in reliability tests and electrical behaviour.

According to Vishay[1167], these NTC chips are mainly used for accurate temperature sensing or compensation mainly in automotive, medical, and domestic applications. The total number of manufactured NTC chips accounts for 60,000,000 pieces per year.

Vishay[1168] mentions that Ag pastes with lead-free glass frits are available on the market, but claims there is no single one fitting to Vishay's wide variety of ceramics. Since one product series requires this many ceramics, it is impossible to change to a lead-free Ag paste for practical purposes.

Vishay[1169] claims to undertake significant efforts to eliminate lead in glass frit of the Ag electrode of the NTC chip, but so far no technical mature solution is available. A study is being started up to develop an NTC chip with a Pb free glass frit.

22.3.4.3 Lead Glass Used as Adhesive/Bonding Material

Example 3.1 - Micro Electro Mechanical Systems (MEMS)

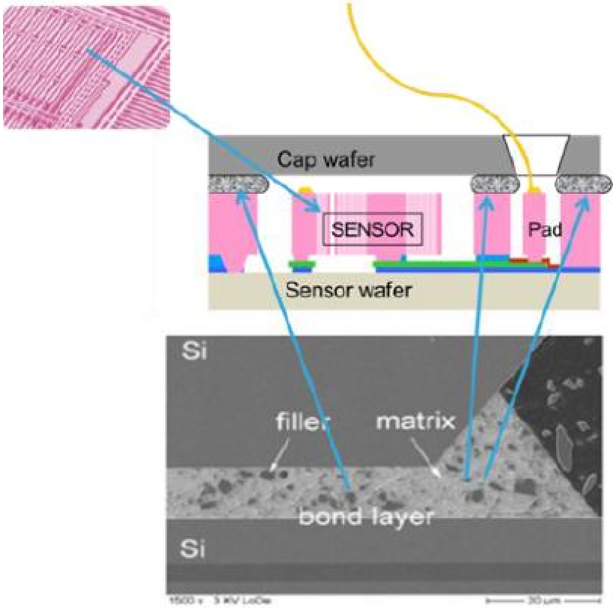
According to Murata et al.[1170], lead-based glasses are used in MEMS devices for low temperature compatibility with aluminium pads in a glass frit wafer-to-wafer bonding process. Such devices are used in e.g. accelerometers, gyroscopes, etc.

According to Murata et al.[1171], only lead glass can achieve the low process temperature of less than 450 °C. Moreover, the lead glass frit is compatible with a wide variety of

[1165] Ibid.
[1166] Ibid.
[1167] Ibid.
[1168] Ibid.
[1169] Ibid.
[1170] Op. cit. Murata et al. 2015a

substrates, not only silicon, and can adapt to different types of surfaces and topology (rough, smooth, with steps), which are typical of MEMS devices. Lead-glass frit bonding ensures a strong bond between different substrates, and ensures a stable and hermetic sealing of the device, unlike with lead-free glass frits.

Figure 22-14: MEMS device with lead-containing glass (Arrows)



Source: Murata et al.[1172]

According to Murata et al.[1173] glass frit wafer bonding is the most commonly used process for MEMS devices, where fully processed wafers have to be bonded at wafer level. This end-of-line wafer level bonding process must fulfil stringent requirements, and must not affect the final yield of bonded wafers. Specifically, the process temperature (i.e. the bonding temperature) must be below 450 °C in order to be compatible with the aluminium pads of the device and to avoid thermal stress on the wafer. This low melting temperature can be obtained only by adding lead to the glass. Moreover, the glass frit is compatible with a wide variety of substrates, not only silicon, and can adapt to different types of surfaces and topology (rough, smooth, with steps), which are typical of MEMS devices. Lead-glass frit bonding ensures a strong bond between different substrates, and ensures a stable and hermetic sealing of the device, unlike with lead-free glass frits.

Murata et al.[1174] do not mention any specific research or other efforts to substitute or eliminate lead in this application besides the general justification directly under

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[1171] Ibid.
[1172] Ibid.
[1173] Ibid.
[1174] Ibid.

Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds, from page 460).

Example 3.2 – Lead Glass in SMD Components

Murata et al. report that SMD components are being used to control operating conditions in power semiconductor modules. To achieve a useful temperature signal, the SMD temperature sensors should be placed as close as possible to the silicon dies. To guarantee customers' reliability conditions the assembly processes - usually soldering processes - are being operated by temperature profiles that are far away from JEDEC profiles for standard SMD dies. SMD components, which are available on the global market, and which ride out increased process temperatures are MELF dies (Metal Electrode Leadless Faces) whose glass insulator contains lead oxide (PbO) in addition to quartz.

Murata et al.[1175] report that no lead-free dies are available on the global market that provide a comparable (or better) reliability and which are approved for the required or even higher process temperatures than those assembled with lead-containing glass. Lead-free dies would not ride out the high temperatures of the soldering process.

Murata et al.[1176] do not mention any specific research or other efforts to substitute or eliminate lead in this application besides the general justification directly under Section 22.3.4 (Substitution of Lead in Glass and Glass/Ceramic Matrix Compounds, from page 460).

Example 3.3 - Electronic Components with Hermetically Sealed Ceramic Package

According to Murata et al.[1177], electronic component packages with hermetic sealings using a ceramic body with a ceramic or glass lid require lead glass as sealing material between the two parts of the package. The lead in the glass reduces the melting temperature enough to not harm the functional element itself. At the same time, the temperature is still sufficiently high to withstand the reflow soldering temperatures without losing its strength and sealing properties. Even a temporary loss of the sealing properties would be fatal as in many cases the inside of the hermetically sealed package is under vacuum.

Murata et al.[1178] state that many materials have been tested to replace the Pb in glass in this function, but failed either due to a too high melting point (i.e. $Bi2O_3$-100 °C or higher and V_2O_5-50 °C or higher) or extreme sensitivity to moisture and humidity (i.e. P_2O_5-based materials), which destroys the vacuum and causes corrosion of the internal circuitry. The use of Au-Sn-based sealings leads to failures, especially in applications which need to cover wide operating temperature ranges. This is because the thermal expansion coefficient of ceramic ($7.1*10^{-6}$/°C) is vastly different to that of Au-Sn

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[1175] Ibid.
[1176] Ibid.
[1177] Ibid.
[1178] Ibid.

(17.5*10^{-6}/°C), thus generating extensive mechanical stress inside the sealing, resulting in reliability problems and finally yielding in component failures (cracks).

22.3.4.4 Bourns Exemption Request for Lead in Glass

Bourns[1179] have developed lead-free glasses internally. These glass formulations are proprietary. These limited solutions do not solve the lead-glass issue in all applications. Obviously, any successful substitution will be used to eliminate lead in glass when possible. The majority of applications are still in the research stage. It is a lengthy process to identify potential solutions, test on a small scale basis, test on a larger scale, and qualify with reliability checks. The test phase is trial and error taking an unspecified amount of time. To date, Bourns' internal analysis as well as published information clarifies that more time is needed to find suitable substitutes.[1180]

There is no drop-in solution or a one-size-fits-all solution. Any change will take research, testing, final qualification, process changes, etc. for each specific application. Potential substitutes in these articles do not yet meet all the positive characteristics of lead-based glasses that are also cost-effective. There may be one or more alternatives to address each individual application. It appears that at this time there may be solutions; however, most likely the solutions will not be identified, tested, qualified and adapted to the process in the mid-2016 time frame when the exemption is set to expire.[1181]

Bourns[1182] references the below research papers:

- *Review of High-Lead Solder and Lead-Glass RoHS Exemptions,* http://rohs.exemptions.oeko.info/fileadmin/user_upload/Stakeholder_comments/Exemption-7a_5_Pecht_Uni_Maryland_25_March_2008.pdf
- *REACH Dossier: Exemption from registration for glass under REACH regulation n. 1907/2006/EC.,* http://www.glassallianceeurope.eu/images/cont/dossier-glass-alliance-europe-on-glass-exemption-under-reach_1_file.pdf
- *Position paper concerning the status of the raw materials for the production of glass, as intermediates, under the EU REACH regulation,* http://www.glassallianceeurope.eu/images/cont/glass-alliance-europe-statement-for-intermediates-revision-may-2012_1_file.pdf

1179 Op. cit. Bourns Inc. 2015a
1180 Ibid.
1181 Ibid.
1182 Ibid.

22.3.4.5 IXYS' Application-Specific Exemption Request for Lead in Coatings of High Voltage Diodes

IXYS[1183] requests the renewal of the exemption for the use of lead in **coatings of high voltage diodes.** Lead-based glasses are used because they have unique combinations and characteristics that cannot be achieved by other materials or methods. Lead is required in combination with pure silicon crystals for good withstandability against high electric fields in the range of 200,000 V/cm in alternate and direct current power semiconductor devices. The justification follows the same rationale like that of Murata/JEITA et al.

IXYS[1184] mentions, however, new passivation systems under development, i.e. diamond-like carbon coatings or amorphous silicon-oxide layers (SIPOS, semi-insulating polycrystalline silicon). Their long term stability in various environments, workability, and the fabrication equipment are still under research and development. These developments could replace the use of lead glass in the high voltage components.

IXYS[1185,1186] states that the diamond like carbon coating method very much depends on equipment design and manufacture – where IXYS has minimum influence. SIPOS (semi-insulating polycrystalline silicon) is under development at IXYS in several lower voltage applications.

As mostly with new developments and technologies, IXYS[1187] states that there is no guarantee on when there will be a breakthrough on the whole front of this kind of power semiconductors.

22.3.4.6 Schott Request for Renewal of the Exemption

To ensure the production of high quality hermetic packages for opt-electronic devices it is crucial to use lead-oxide-based glasses. These so called "solder glasses" are necessary to attach optical elements like windows or lenses into metal components.[1188]

SCHOTT[1189] started a PbO substitution project for solder glasses in the year 2000. New glass systems have been developed for replacement of PbO containing solder glasses. These new glasses were based on the following substitutes:

[1183] Op. cit. IXYS Semiconductor GmbH 2014
[1184] IXYS Semiconductor GmbH 2014 "Request for continuation of exemption 37, document "37_IXYS_RoHS_V_Application_Form_pass_glasses.pdf": Original exemption request," http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_37/IXYS/37_IXYS_RoHS_V_Application_Form_pass_glasses.pdf
[1185] IXYS Semiconductor GmbH 2016a "Answers to questionnaire 1 (clarification questionnaire), sent via e-mail to Dr. Otmar Deubzer, Fraunhofer IZM, by Markus Bickel, Ixys Semiconductor GmbH, on 27 January 2016,"
[1186] Ibid.
[1187] Ibid.
[1188] Op. cit. Schott AG 2015a
[1189] Ibid.

- Bismuth-oxide, Bi_2O_3;
- Phosphate glasses P_2O_5.

The development for these glasses was mainly done for glass to glass or glass to ceramic joints. In a separate project, which was launched 2004, Schott tested all these new systems for usability for metal to glass joints.[1190]

The substitute glass has to meet the following requirements:

- Gas tight seal: hermeticity better than 1x10-8 mbar*l/s; must remain unchanged after 15 cycles of thermal shock liquid to liquid (-65°C <> 150°C);
- No outgassing;
- Mechanically strong bond: the assembly has to pass stringent shock, typically 1500 g gravitational acceleration and vibration testing;
- Chemical resistance: No performance change after 1000 h at 85°C and 85 % relative humidity;
- Low cost, which excludes the usage of metalized windows and metal solder;
- Working temperature less than 500 °C;
- Mechanically stable up to 260 °C.

Table 22-5 shows the test results. The metal solders used with the metalized windows were gold/tin solders with 80 % (weight) of gold (AuSn 80/20) to achieve a melting point of more than 260 °C, which is higher than the conventional lead-free and lead-solders. This solution is only applicable to window caps. Moreover, these products will not fit Schott's customers´ requirements because they have to accept that the counterpart is gold-plated. [1191]

[1190] Ibid.
[1191] Op. cit. Schott AG 2015b

Table 22-5: Test results of lead-free alternatives to leaded solder glass

Glass System	Weaknesses	Positive Findings	Further conclusion
Bi_2O_3	• Sealing Temperature 550-570°C (dependant on Cap geometry) • Optical elements damaged by high sealing temperature • Metal surface requirement cannot be met (Damp Heat, Bellcore Spec GR468)	• Mechanically good bonding to metal and glass • Chemical resistance of solder glass improved compared to PbO	• Launch of new project for improved Bi_2O_3 glass with lower sealing temp (see next line)
Bi_2O_3 Next Gen. Glasses	• Sealing Temperature only reduced to 530-550°C No glass composition identified with lower seal temp. (appr. 50 new glass compositions tested)	• See above	• No Solution found with Bi_2O_3 system
P_2O_5	• No bond to suitable metal surfaces • Chemical resistance no adequate for Cap application	• None	• No further activities
SnO_2-P_2O_5	• Environmental Stability not adequate	• Sealing Temperature requirement <500°C met • Bond between Solder glass and metal achieved	• No further activities
Metalized Windows & Metal Solder	• Metallization process is too costly for this application (costs are about 5-10x too high) • Not applicable to all products (i.e. ball lenses)		• No further activities

Source: Schott[1192]

Lead oxide as a glass constituent is responsible for the low working temperature of the glass, yet maintaining an acceptable level of environmental resistance. Higher working temperatures will damage the optical elements of the components. Without using lead containing solder glasses Schott will no longer be able to produce their huge variety of high level electronic components.[1193]

Regarding the small amount of lead containing solder glass needed for Schott's purposes and the fact that glass is an inert and stable material, which does not pose any danger to human health and environment along the lifecycle, Schott applies for the extension of the existing exemption in Annex III, no. 7(c)-I.[1194]

[1192] Ibid.
[1193] Op. cit. Schott AG 2015a
[1194] Ibid.

As no substitutes are available or foreseeable in the near future, Schott[1195] requests the continuation of Exemption 7(c)-I for the maximum five year period.

22.3.4.7 Sensata's Request for the Renewal of the Exemption

Alternative lead-free glasses meeting the requirement of matching coefficient of thermal expansion of parts to be bonded are available, but these materials do not fulfil other requirements as shown in Table 22-6. Experiments on alternative materials are conducted but with marginal results. The material match and process profiles are not fulfilling the requirements. Lead glasses are superior in the combination of characteristics versus for example Zn, P-S and Na-Al-P-B glasses.

Table 22-6: Test results of lead-free glasses

Characteristics	Pb glass	Zn glass	P-Sn glass	Na-Al-P-B
Affinity	Good	Not good	Not good	Good
Low melting point	Yes	No	Yes	Yes
Coefficient to thermal expansion	Good	Good	Good	Not good
Weather resistance	Good	Good	Not good	Not good

Source: Sensata[1196]

Sensata[1197] claims there are no applications where not all of the characteristics listed in Table 22-6 are required, so that neither lead-free glasses nor alternative technologies like lead-free solders can be applied.

Sensata[1198] states that beyond the above arguments, the rationale of its exemption request is based on the justifications of Murata/JEITA et al. [1199] [1200]

[1195] Ibid.
[1196] Sensata Technologies 2015b "Questionnaire 1 (clarification questionnaire), document "7c-I_Questionnaire_Sensata_20150901.pdf": Questionnaire 1 (clarification questionnaire)," http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Sensata/7c-I_Questionnaire_Sensata_20150901.pdf
[1197] Ibid.
[1198] Ibid.
[1199] Op. cit. JEITA et al. 2015a
[1200] Op. cit. Murata et al. 2015a

22.3.5 Impacts on Environment, Health and Resources

Murata et al.[1201] claim that so far no substitution technology has been found, but many potential compositions have been investigated in order to develop reliable technical solutions on industrial scale, however below are further examples of environmental and health and production impacts of major candidates:[1202]

- Potential future candidates under investigation are expected to have more difficult raw materials and processes, even under mass production considerations;
- Niobium and bismuth-based substitutes have a higher impact on environment during extraction and purification than lead, as lead is already recycled with high recovery and is relatively abundant in nature (10 to 70 times more than Bi and 3 times more than niobium).

The environmental impact of lead in ceramic and glass is low, because of the low water solubility of lead contained in ceramic and glass, therefore, leakages into the environment are very low. Current PZT production is based on water; potential substitutes would require alternative technology based on organic solvents (e.g. isopropyl alcohol, ethanol, acetone). Such solvent-based technologies and the requirement to meet ATEX regulations would result in higher efforts and risks in health and environment protection, e.g. to avoid emission of solvents (Isopropyl alcohol, Ethanol, Acetone) that are VOCs (volatile organic carbon) which also need to be minimized in the EU due to the Industrial Emissions Directive 2010/75/EU.

PZT is used in industry for processing of ceramic for many years under controlled worker conditions. Health impacts have been well investigated.

Murata et al.[1203] provide the following references to support their environmental statements:

- Worker Exposure to Lead Titanate Zirconate in an Ontario Company M.L. Roy, MD, PhD; S.Siu, Md; W.Waddell, MD; P.Kennedy, BSc, J Occup Med. 1989 Dec;31(12):986-9.

- Comments on an Annex XV Dossier for Identification of a Substance as SVHC and Responses to these Comments, http://echa.europa.eu/documents/10162/25b4427f-1c53-4497-8ca2-29d24a55f4b5

Murata et al.[1204] also present the EU critical raw materials from the 2013 list (reproduced in Figure 22-15).

[1201] Ibid.
[1202] Ibid.
[1203] Ibid.
[1204] Ibid.

Figure 22-15: EU critical raw materials 2013

Antimony	Beryllium	Borates	Chromium	Cobalt	Coking coal	Fluorspar
Gallium	Germanium	Indium	Magnesite	Magnesium	Natural Graphite	Niobium
PGMs	Phosphate Rock	REEs (Heavy)	REEs (Light)	Silicon Metal	Tungsten	

Niobium, one of the potential candidates used in lead-free ceramics, is listed as a critical raw material. Additionally, Murata et al.[1205] state that tantalum was on the EU's critical material list prior to the 2013 one.

22.4 Roadmap for Substitution or Elimination of Lead

22.4.1 Substitution and Elimination of Lead in Piezoelectric and PTC Ceramics

According to Murata et al.,[1206] there are still many remaining technical issues to be solved in order to achieve mass production of practical products. Adding to that, even in the case that mass production technology is achieved, the research has shown that the required properties for substitutes in the various applications of ceramics cannot be obtained.

For ceramics, Murata et al. indicate the following steps towards the substitution or elimination of lead:

- Achievable material properties are known;
- First demonstrations of applications published;
- Technologies for industrial production must be developed;
- Simple replacement of PZT components have already been shown not to be possible;
- Adaption or new development of EEE, reliability investigations;
- Certain replacements: time frame >5 years, overall replacement not foreseeable;

Murata et al.[1207] states that introducing new chemical compounds and materials in order to replace PTC ceramics even in a certain resistance-Tc range would need an overall change in powders conception used in the production of PTC at the moment. This is because not just one powder is used in production of a certain product but usually a mixture of two or more powders is used. With the alternative materials examined up to now, only ceramic for applications with low Curie temperatures might be meaningful to

1205 Ibid.
1206 Ibid.
1207 Ibid.

undergo further investigation and development because of the strong limitations in regard to certain properties as mentioned above. Furthermore, for these low Tc applications there still exist several constraints as explained in the justification of the exemption for PTC ceramics.

Overall, Murata et al.[1208] do not see any perspectives for a comprehensive transition to ceramic in the next five years and therefore claim they cannot set a technical goal.

Murata/JEITA et al.[1209] were asked again about their plans and the steps they want to undertake in the next five years towards the substitution and/or elimination of lead for the various types of ceramics (roadmap) described in their exemption request. They replied they will continue developing, requesting development and/or applying possible alternatives taking into account the practicability, reliability or environmental, health and consumer safety impacts of substitution. However, as this involves individual company policies, unpredictable technical and scientific findings and market and consumer developments it is impossible to draw any serious roadmap under the present circumstances.

22.4.2 Substitution and Elimination of Lead in Glass and Glass or Ceramic Matrix Compounds

Murata/JEITA et al.[1210] [1211] claim that there are no prospects concerning the technical scope of exemption 7(c)-I for a comprehensive substitution to "lead-free" glass and/or ceramic at least until the next revision (21 July, 2021)

Murata et al.[1212] report that boron, phosphorus, zinc, tin, bismuth, etc. as elements for substituting lead as a constituent element of glass, have been investigated. However, when compared with lead-containing glasses, chemical stability and mechanical strength of the glasses are insufficient (to meet the required functionality). As a result, there are concerns of accidents originating from crucial failures in EEE incorporating electrical and electronic components composed of glass with lead substituted by these elements due to their insufficient reliability and quick deterioration.

Murata/JEITA et al.[1213] remain committed to supporting the procedure for the adaptation to scientific and technical progress, and will continue developing, requesting the development and/or applying possible alternatives taking into account the practicability, reliability or environmental, health and consumer safety impacts of substitution.

[1208] Ibid.
[1209] Op. cit. (Murata et al./JEITA et al. 2016d)
[1210] Op. cit. Murata et al. 2015a
[1211] Op. cit. JEITA et al. 2015a
[1212] Op. cit. Murata et al. 2015a
[1213] Murataet al./JEITA et al. 2016e "Answers to questionnaire 6a, document"Exe_7c-I_Questionnaire-6a_Murata-JEITA_2016-03-2.pdf", received from Klaus Kelm, Murata, by Dr. Otmar Deubzer, Fraunhofer IZM, on 1 April 2016" unpublished manuscript,

However as this involves individual company policies, unpredictable technical and scientific findings and market and consumer developments it is impossible to draw any serious roadmap under the present circumstances.

Schott[1214] states that after spending 5.5 person years of research, and thorough testing of substitute systems, Schott sees no adequate replacement for PbO to attach optical elements like windows or lenses into metal components. Therefore, no substitutes are likely to be developed in the foreseeable future and so the maximum validity period is required for this exemption.

IXYS[1215] wants to continue with the development of new passivation systems, i.e. diamond-like carbon coatings or amorphous silicon-oxide layers (SIPOS, semi-insulating polycrystalline silicon). As mostly with new developments and technologies, IXYS[1216] states that there is no guarantee on when there will be a breakthrough on the whole front of this kind of power semiconductors.

Bourns[1217] will continue to work with their suppliers, explore possible solutions, and experiment with possible alternatives. It is a slow process with research, experimentation, testing, scale-up, qualification & reliability testing. If there is a failure along the way, the process starts over.

22.5 Critical Review

22.5.1 REACH Compliance - Relation to the REACH Regulation

Lead is used in glass in the scope of Exemption 7c-I. Barium titanate (BT), lead titanate (PT), lead zirconium titanate (PZT) as well as barium strontium lead titanate are used in the ceramics in the scope of this exemption according to the applicants. These ceramics and their constituents therefore need to be evaluated whether their use weakens the environmental and health protection afforded by Regulation (EC) No 1907/2006 (REACH Regulation). There are, however, hundreds of material recipes for each of the ceramics, which could not be addressed and mentioned in this review and which may be even proprietary knowledge. They cannot be taken into account.

Since no substitutes have been identified in the review process that would result in the restriction of the exemption scope, the various substances used in lead-free ceramics were not specifically taken into account. As, however, lead-free lithium tantalate sensors have been identified as a potential future alternative to PZT-based sensors, lithium tantalate will be evaluated as well.

[1214] Op. cit. Schott AG 2015a
[1215] Op. cit. IXYS Semiconductor GmbH 2014
[1216] Op. cit. IXYS Semiconductor GmbH 2016a
[1217] Bourns Inc. 2016a “Request for continuation of exemption 7c-I, document "20150818_Ex_7c-I_Bourns_Questionnaire-1_2015-07-28.pdf": Answers to second questionnaire” unpublished manuscript,

Appendix A.1.0 of this report lists various entries in the REACH Regulation annexes that restrict the use of lead in various articles and uses.

Annex XIV contains several entries for lead compounds, whose use requires authorization:

- 10. Lead chromate
- 11. Lead sulfochromate
- 12. Lead chromate molybdate sulphate red

In the applications in the scope of the reviewed exemption, lead is used in electronic components that become parts of articles. None of the above listed substances is relevant for this case, neither as directly added substances nor as substances that can reasonably be assumed to be generated in the course of the manufacturing process.

Annex XVII bans the use of the following lead compounds:

- 16. Lead carbonates in paints
- 17. Lead sulphate in paints

Neither the substances nor the application are, however, relevant for the exemption in the scope of this review.

Appendix A.1.0 of this report of this report lists Entry 28 and Entry 30 in Annex XVII of the REACH Regulation, stipulating that lead and its compounds shall not be placed on the market, or used, as substances, constituents of other substances, or in mixtures for supply to the general public. A prerequisite to granting the requested exemption would therefore be to establish whether the intended use of lead in this exemption request might weaken the environmental and health protection afforded by the REACH regulation.

In the consultants' understanding, the restrictions for substances under Entry 28 and Entry 30 of Annex XVII do not apply. The use of lead in this RoHS exemption in the consultants' point of view is not a supply of lead and its compounds as a substance, mixture or constituent of other mixtures to the general public. Lead is part of an article and as such, Entry 28 and 30 of Annex XVII of the REACH Regulation would not apply.

Entry 63 of Annex XVII stipulates that lead and its compounds

- *"shall not be placed on the market or used in any individual part of jewellery articles if the concentration of lead (expressed as metal) in such a part is equal to or greater than 0.05 % by weight."*
  This restriction does not apply to internal components of watch timepieces inaccessible to consumers;
- *"shall not be placed on the market or used in articles supplied to the general public, if the concentration of lead (expressed as metal) in those articles or accessible parts thereof is equal to or greater than 0.05 % by weight, and those articles or accessible parts thereof may, during normal or reasonably foreseeable conditions of use, be placed in the mouth by children."*
  This restriction, however, does not apply to articles within the scope of Directive 2011/65/EU (RoHS 2).

The restrictions of lead and its compounds listed under entry 63 thus do not apply to the applications in the scope of this RoHS exemption. Should the ceramics in the scope of the exemption actually be used in watch timepieces, this use of lead would be allowed.

Various entries in the REACH Regulation annexes restrict the use of barium and strontium compounds in several articles and uses. Nickel barium titanium primrose priderite and strontium chromate are specified for Annex XVII entry 28. These compounds are, however, not relevant for the ceramics in the scope of Exemption 7c-I. The same applies to strontium chromate, which is also listed in Annex XIV under Entry 29.

No other entries for the above mentioned ceramics and their compounds relevant for the requested exemption could be identified in Annex XIV and Annex XVII (status February 2016). Based on the current status of Annexes XIV and XVII of the REACH Regulation, the requested exemption would not weaken the environmental and health protection afforded by the REACH Regulation. An exemption could therefore be granted if other criteria of Art. 5(1)(a) apply.

Lithium nickel dioxide, cobalt lithium nickel oxide, lithium perfluorooctane sulfonate and lithium heptadecafluorooctanesulfonate are also listed under Entry 28 and Entry 30 in Annex XVII of the REACH Regulation so that the same conditions apply to these substances like for lead and its compounds. These substances and compounds are not relevant for the use of lithium tantalate in sensors, which may be a potential and commercially available alternative to PZT-based sensors. No other entries relevant for the use of lithium tantalate in these sensors could be identified in Annex XIV and Annex XVII (status February 2016). Based on the current status of Annexes XIV and XVII of the REACH Regulation, the use of lithium tantalate to substitute or eliminate lead would not weaken the environmental and health protection afforded by the REACH Regulation.

22.5.2 Substitution and Elimination of Lead in Ceramics

The applicants argue that none of the known lead-free piezoelectric materials is a suitable overall substitute for PZT. Art. 5(1)(a) would, however, require to apply lead-free solutions if they were available for specific application fields. Not all applications of PZT-containing components may require the all properties of PZT to the highest level at the same time, these being:

- High Curie temperatures;
- High piezoelectric charge constants;
- High electromechanical coupling factors;
- High quality factors and low losses for ultrasonic devices;
- High stability under different driving and environmental conditions, especially temperature; and
- High reliability.

22.5.2.1 Use of Lower Performing Ceramics in Less Demanding Applications

Murata et al.[1218] explain that the functions and properties (e.g. Curie temperature, breakdown voltage, etc.) required for ceramic of electrical and electronic components and the usage environment are not only diverse but also change during use due to changes in the usage environment. For example, a high voltage of a few tens of thousands of volts may be instantly applied over electrical/electronic equipment, or temperature loads exceeding the expectations may occur, etc. In order to use these items with safety it is necessary that they can withstand such conditions. Since lead-containing ceramics, which are stable and show excellent functionality over a wide range of usage environments, are essential for compatibility with the required functionality and usage environment, the decision on whether substitution by "lead-free" ceramics is possible or not will vary with the equipment type and subpart on a case-by-case basis and it is not possible to identify applications, which can be substituted.

Murata et al.[1219] furthermore state that electrical and electronic components have to withstand conditions in manufacturing that are different from those during use so that it is impossible to decide on the use of lead-free PTC only by application. For example, in the manufacturing of electrical and electronic equipment the components can be heated to 150 °C so that ceramic that breaks down or deteriorates at this temperature cannot be used. $BaTiO_3$ with a T_C of 120 °C would, for instance, simply depole during such processes.

Murata et al.[1220] also point out that piezoelectric materials are selected based on a combination of properties. Even if a given lead-free composition fits the sensitivity criteria, it does not necessarily mean that it will be stable over a given temperature range or have the required dielectric or mechanical properties. In addition to this, lead-free materials are known to have different and generally more complex temperature characteristics such as additional phase transitions within the operating temperature range. Moreover, the reproducibility of lead-free piezoceramics' properties is significantly lower due to the fact that their production is considerably more sensitive to process parameters.

Overall, the information provided by the applicants explains that currently the substitution of lead in the ceramics in the scope of exemption 7c-I is scientifically and technically still impracticable. The available information suggests that lead-free ceramics are still inferior in performance, and their manufacturing in industrial scale is not yet achieved. The submitted information also suggests that such lead-free ceramics cannot be used in components that could be applied where not all of the properties of lead-containing ceramics are required.

[1218] Op. cit. (Murata et al. 2016a)
[1219] Ibid.
[1220] Ibid.

The applicants' exemption requests and the answers to the clarification questionnaire were made available through the online consultation to the public, i.e. to industry, governments, NGOs and other stakeholders, and a consultation questionnaire had been prepared for the public online consultation with specific questions to stakeholders. No further information supporting or discrediting the technical application in question was received, and there were no hints that lead-free solutions would be foreseeable for the near future.

22.5.2.2 Commercial Availability of Lead-free Sensors

In the last questionnaire received on 1 April 2016, Pyreos [1221] mentions that Panasonic commercially offers lead-free lithium tantalate sensors for specific applications. A short internet investigation actually showed that there are scientific publications on lithium tantalate sensors[1222] and examples of commercial sensor products[1223] where it is explicitly stated that these pyroelectric elements "*[...] contain lithium tantalate and are lead-free. Typical PIR sensing elements are ferroelectric ceramic (PZT) containing lead*."

According to Pyreos,[1224] lithium tantalate can substitute thick film PZT-based sensors in applications, which have lower performance requirements and are not so robust, such as low operating temperatures (-20 to +85 °C). Lithium tantalate cannot so easily substitute thin film PZT as there are even more different performance requirements such as temperature shock response etc. In general, litihium tantalate cannot substitute thin film PZT in applications where higher cost, reproducibility and superior performance are a consideration.

The Panasonic data sheet[1223] lists commercial / residential equipment (including lighting fixtures, sensor switches, video intercoms, vending machines, home automation control panels) and home appliances (including television and PC monitors, air conditioners and air purifiers) as applications for the lead-free pyroelectric sensors.

Thus, the substitution or elimination of lead is viable at least in pyroelectric sensors even though they might not have the properties that would allow covering the whole range of applications where PZT ceramics are used. In the consultants' understanding, the results of the internet investigation are at least an indication that contrary to the statements in particular of Murata et al., substitution or elimination of lead may be scientifically and technically practicable to a certain degree. The considerable efforts already spent on the

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[1221] Pyreos Ltd. 2016b "Answers to third questionnaire, document "Exe_7c-I_Questionnaire-3_Pyreos_2016-03-30_final.pdf", received via e-mail from Torben Norlem, Intertek, by Dr. Otmar Deubzer, Fraunhofer IZM, on 31 March 2016" unpublished manuscript,

[1222] Vincent Stenger, Michael Shnider and Sri Sriram, SRICO, Inc.; Donald Dooley and Mark Stout, Gentec-EO USA, Inc.: Thin Film Lithium Tantalate (TFLT™) Pyroelectric Detectors; SPIE Photonics West 2012, Optoelectronic Materials and Devices THz Technology and Applications V – OE107, Paper Number 8261-27 http://www.srico.com/files/PW2012_TFLT%20Pyro%20Detectors.pdf

[1223] Panasonic: PaPIRS Passive Infrared Motion Sensor, http://datasheet.octopart.com/EKMC1601111-Panasonic-datasheet-43724067.pdf

[1224] Ibid.

review of exemption 7c-I and the time restrictions did not allow a further clarification with Murata et al.

Adding to the above, Murata et al. provide only very general and unspecific information on their future efforts to substitute or eliminate lead in ceramics. They justify this with confidentiality, but the consultants believe that even though the members of the industry consortium are competitors, there should be possibilities to describe in more details future steps, which should also be related to the various types of ceramics and their application-specific requirements to find specific solutions where general drop-in alternatives are not viable.

22.5.2.3 Bandelin

Bandelin requests to add a specific application (identified by the bold addition) to the current wording of exemption 7c-I, and to add this exemption to Annex IV as well:

> ***"Piezoelectric hard PZT containing lead for high-performance ultrasonic transducers and*** *electrical and electronic components containing lead in glass or ceramic materials other than dielectric ceramic in capacitors"*

The principle rationale of the exemption request follows the arguments of the other stakeholders that the substitution or elimination of lead is currently scientifically and technically not possible, and Bandelin explains this plausibly for the PZT used in high performance ultrasonic transducers.

Based on this information and in the absence of contrary information, granting the exemption would be in line with the requirements of Art. 5(1)(a).

Technically, the use of lead in the applicant's transducers is fully covered by the current exemption 7c-I, and it shall be decided in the context of the future wording of this exemption 7c-I whether and how to take into account this specific exemption in RoHS Annex III.

The applicant applies to adopt the same exemption wording to RoHS Annex IV. It is the consultants' understanding that, to avoid the proliferation and overlapping of exemptions, Annex IV should only list exemptions that are exclusively required for EEE in categories 8 and 9 of RoHS Annex I, which according to Bandelin[1225] is not the case for their high power transducers. The consultants therefore recommend not to adopt this exemption to Annex IV as long as an exemption in Annex III covers the use of lead in this application and consequently allows the uses of lead in the scope of the exemption for all categories of EEE.

[1225] Op. cit. Bandelin Electronic GmbH 2015a

22.5.2.4 Pyreos

Pyreos asks to add the following exemption to Annexes III and IV of the RoHS Directive:

> *“Lead in thin film electronic sensor elements such as pyroelectric sensors or piezoelectric sensors”*

The information submitted by Pyreos suggests that the company uses lead zirconium titanate (PZT) as thin films instead of thicker films and thus has successfully reduced the amount of lead in its sensors. They are not lead-free at the current state of development, and despite further investigation[1226], it could not be clarified whether they would actually become lead-free in the next development step in the sense of the RoHS Directive, i.e. containing less than 0.1 % of lead in any homogeneous material applied.

Pyreos[1227] explains its motivation for its request that a specific exemption focused on lead in thin film PZT sensors will significantly reduce the quantity of lead used in PZT sensors sold on the market today when compared to conventional technology using other types of PZT sensors not falling within the scope of the specific exemption.

This effect will, however, not be achieved if the proposed exemption is adopted as a specific exemption, or if the current wording is amended accordingly. It would then allow the use of lead in thin film PZT sensors – which is already the case in the current exemption 7c-I – but it would not restrict the use of lead in any other sensors.

It was pointed out to the applicant[1228] that the only way to achieve their intention would be to exclude other types of sensors than PZT thin film sensors from the scope of the future exemption 7c-I allowing the use of lead in ceramics. This would require a detailed technical specification, where other sensors can be replaced, and it will also require feedback and discussions from other stakeholders, and it would best have been discussed in the online stakeholder consultation. Such an intention of Pyreos’ exemption request was not obvious based on the documents submitted.

Pyreos[1229] stated thereupon that in line with the purpose of the RoHS legislation as far as possible, they would like to seek support for this specific exemption by:

- Specifically exempting the use of lead in thin PZT film (e.g. total thickness cannot exceed 10 microns) in applications where thin PZT film can replace other PZT (e.g. thickness greater than 10 microns) sensors with an equivalent or superior cost effectiveness, performance and reliability.
- Specifically allowing the use of lead in thin film PZT sensors until a lead-free thin film pyroelectric (or sensor) material with an equivalent or superior cost effectiveness, performance and reliability, is available.

[1226] Op. cit. (Pyreos Ltd. 2016b)
[1227] Op. cit. (Pyreos Ltd. 2016a)
[1228] Op. cit. (Pyreos Ltd. 2016b)
[1229] Ibid.

The consultants agree that the reduction of lead is an important contribution to the objectives of the RoHS Directive and as such the applicant's approach is worthy of support. The approach the applicant chose does not allow to actually restrict the use of lead in the sensors in the scope of Pyreos' request for the reasons explained above. It actually required some time and discussion[1230, 1231, 1232] with the applicant to fully understand the intention. Restriction criteria in the applicant's answer to the last questionnaire[1233] are examples, and there was no further time to discuss whether these criteria are sufficient and clear with the applicant and other stakeholders.

Technically, the use of lead in the applicant's sensors is fully covered by the current exemption 7c-I, and it remains to be seen in the total context of the future wording of this exemption whether it makes sense to add an explicit exemption to Annex III as the applicant requested. In any case, the applicant can explicitly apply for the restriction of the scope of the future exemption 7c-I, and the request can then undergo the public online stakeholder consultation and subsequent review of the stakeholder information to find out how the scope of the exemption could actually be narrowed. It will then also have to be clarified whether and how far lead-free pyroelectric sensors[1223] can actually replace PZT-based pyroelectric sensors.

The applicant applies to adopt the same exemption wording to RoHS Annex IV. According to Pyreos,[1234] the exemption would be relevant for all categories of EEE. For the same reasons like explained for Bandelin's request, the consultants recommend not to follow the applicant's request.

22.5.3 Substitution and Elimination of Lead in Glass and Glass or Ceramic Matrix Compounds

22.5.3.1 Bourns and IXYS

Bourns' and IXYS' arguments for the use of lead glass and lead in glass/ceramic matrix compounds are plausible, and no information has been received during the stakeholder consultation or later discrediting the applicant's arguments. They follow the rationale of the justification of Murata/JEITA et al. for the use of lead in glass.

Bourns have developed some proprietary lead-free solutions. These, however, are not drop-in solutions and are said to only work on a case by case basis for certain components. Consequently, no rule can be accordingly deduced to demarcate applications where lead-free glass can be used to specify the exemption. Some of these components are trimmer potentiometers. The situation is therefore described in more

[1230] Op. cit. Pyreos Ltd. 2015b
[1231] Op. cit. (Pyreos Ltd. 2016a)
[1232] Op. cit. (Pyreos Ltd. 2016b)
[1233] Ibid.
[1234] Op. cit. Pyreos Ltd. 2014

detail in the review of exemption 34 (trimmer potentiometers), but also applies to other Bourns components.

IXYS is working on passivation systems that would allow substituting lead in the glass of high voltage diodes. The development still requires time and, according to the applicant, it is not foreseeable that lead can be replaced in the near future.

The situation shows, however, that the elimination or substitution of lead in glass and glass/ceramic matrix compounds is obviously scientifically and technically practicable in some cases. As such it may be possible to restrict the scope of the exemption at a future time, and hence setting a short expiry on a renewed exemption 7c-I may bring forward the potential for this to occur in the next exemption review.

22.5.3.2 Schott

Schott present research on lead-free alternatives to the lead-containing glass they use to attach optical components into metal components. The results show that there is currently no lead-free glass that can replace the lead-containing glass. The tested gold-tin metal solder seems to be viable in principle for some window caps, but Schott says it is too expensive and requires gold contacts on the customers' side as well so that their customers cannot accept this solution. Thus, technically, the substitution and elimination of lead is not yet practicale and granting an exemptin for this application would be in line with the requirements of Art. 5(1)(a).

The cost argument as raised by the applicant cannot justify an exemption in accordance with the stipulations of RoHS Art. 5(1)(a) unless the availability of the substitutes or the socioeconomic impacts would make the manufacturing of such components impossible so that the products depending on these components could no longer be produced, or similarly severe impacts. The applicant does not provide substantiated information that would suggest such severe impacts.

Schott also justifies its exemption request with the small amounts of lead used and the fact that the glass is inert and thus not hazardous along the life cycle. This is, however, only partially true as the lead has to be mined and refined, where it is not inert but emissions into the environment do occur, and the same applies to processing and disposal at end of life. Furthermore, RoHS Art. 5(1)(a) would only justify an exemption if the negative impacts from the use of lead-free alternatives are likely to outweigh the positive effects of lead substitution. The applicant does not provide information showing that this might be the case. The small amount of lead used cannot be accepted as a justification for an exemption either, as RoHS Art. 5(1)(a) does not set a threshold for minimum amounts of restricted substances that would justify granting an exemption.

Technically, the applicant's information suggests that, currently and in the foreseeable future, the substitution of lead is scientifically and technically not yet practical and granting an exemption for five years would thus be justified in line with Art. 5(1)(a).

22.5.3.3 Sensata

Sensata[1235] shows test results suggesting that there have been tests of lead-free glass, which showed that they are not a viable substitute. They claim that all properties of lead glass are required in all their applications so that lead-free glasses, which do not exhibit this combination of materials, cannot be used. There is no information available to the consultants that disproves this statement.

Beyond this specific information, Sensata's justification follows the rationale of Murata/JEITA et al. and is therefore not further discussed separately, the more as Sensata's information does not allow to deduce a specific wording for their uses of lead in glass.

22.5.4 Specification of the 7c-series Exemptions

Exemption 7(c) is related to lead in glass and ceramic type materials which may be used in electrical and electronic components. Given the broad range of ceramic and glass materials, and their multiple uses and functionalities in components, the scope of this exemption is wide so that it may hinder the gradual phase-out of lead. Following the same rationale like for exemption 7(a), it was tried to specifiy the scope of exemption 7(c)-I.

Based on information provided by the applicants in this review and in previous exemption reviews, the consultants formulated a wording targeting a scope which is as narrow as possible to exclude the abuse of the exemption and promotes specific research into lead-free solutions. In parallel, the same proposed wording is as wide as necessary to ensure all applications are covered where substitution and elimination of lead is still impracticable.

A specification of Exemption 7(c)-I in the current numbering and wording is not viable. The exemption was therefore split into two specific wordings for ceramics on the one hand, and glass and glass ceramic matrix compounds on the other hand.

22.5.4.1 Lead in Ceramics of Electrical and Electronic Components

The consultants proposed the below wording for the ceramic-part of exemption 7(c)-I. Exemptions 7(c)-II, 7(c)-III and 7(c)-IV were integrated into this wording proposal:

Lead in

i) *piezoelectric ceramics in electrical and electronic components, i.e.*
   - *ferroelectric ceramics*
   - *pyroelectric ceramics*
   - *other piezoelectric ceramics*

[1235] Op. cit. Sensata Technologies 2015b *ii) positive temperature coefficient (PTC) ceramics in electrical and electronic components*

- *with T_C < 120 °C (T_C: Curie temperature) and resistivity of less than < 1000 Ωcm*
- *with T_C < 120 °C and resistivity of 1,000 Ωcm and more*
- *with $T_C \geq$ 120 °C and resistivity of less than 1,000 Ωcm*
- *with $T_C \geq$ 120 °C and resistivity of 1,000 Ωcm and more*

iii) dielectric ceramics in discrete capacitor components for a rated voltage of 125 V AC or higher, or for a rated voltage of 250 V DC or higher

iv) dielectric ceramic in discrete capacitor components for a rated voltage of less than 125 V AC, or for a rated voltage of less than 250 V DC; for use in spare parts of EEE placed on the market before 1 January 2013

v) PZT-based dielectric ceramic materials for capacitors which are part of integrated circuits or discrete semiconductors

vi) other ceramics

Murata/JEITA et al.[1236] [1237] recommend keeping the current wording with slight modifications (see review of exemption 7c-II). They claim that the exemption scope cannot be correctly understood in the above proposed wording and fear that the effectiveness of the legal enforcement will be damaged. They strongly assert that a wording to be adopted should summarize a wide knowledge of Industry, and be carefully examined in order to not cause any misinterpretation of the legal text to avoid any unnecessary misunderstanding, misinterpretation and/or wrong usage of lead in the supply chain. Therefore, they strongly insist a wording should remain as proposed in the original application form of Murata/JEITA et al.[1238] [1239]

[1236] Murata et al./Jeita et al. 2016b "Answers to third questionnaire (ceramics), document "Exe_7c-I_Questionnaire-3_Murata-JEITA_2016-03-03_ceramics.pdf", received via e-mail by Dr. Otmar Deubzer, Fraunhofer IZM, from Klaus Kelm, Murata, on 22 March 2016" unpublished manuscript,

[1237] Murataet al./JEITA et al. 2016f "Answers to questionnaire 5b, document "Exe_7c-I_Questionnaire-5b_Murata-JEITA_2016-03-2.pdf", received via e-mail from Klaus Kelm, Murata, by Dr. Otmar Deubzer, Fraunhofer IZM, on 5 April 2016" unpublished manuscript,

[1238] Murata et al. 2015a "Original exemption request, document "Exemption_7_c_-I/Murata/7c-I_RoHS_V_Application_Form_7c1_20140116_combined_final.pdf": Exemption request," http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Murata/7c-I_RoHS_V_Application_Form_7c1_20140116_combined_final.pdf

[1239] JEITA et al. 2015a "Exemption request, document "JEITA/7c-IandII_RoHS_Exemption_Renewal_Request_7_c_I_Japan4EEEassociations.pdf": Exemption request," http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/JEITA/7c-IandII_RoHS_Exemption_Renewal_Request_7_c_I_Japan4EEEassociations.pdf

Murata/JEITA et al.[1240] put forward the following more specific justifications for their position:

- Splitting further the exemption will not eliminate existing functional requirements for lead in glass and ceramic, nor will it improve the availability for Pb-free alternatives because different functions are combined for each individual product application.
- Part i) and part ii) of the wording proposal are not based on physical laws, being simply a classification for convenience based on end-use applications in EEE. For this reason they consider that unless they prepare an application list of end-uses for all OEM/EEEs identifying the scope, it is impossible to define the exemption scope from the wording proposal.
- It is believed that a comprehensive application list of OEM EEE end-uses for lead in glass and ceramic is not currently feasible because the applications are extremely numerous and thus impossible to quantify, requiring different and complex parameters for their specification (definition).
- It is believed that the division of RoHS Ex. 7(c) into eleven applications, intended uses or components is not necessary and would be confusing.
- The proposed wording would misalign with the ELV exemption 10(a) wording included in ELV's Annex II.
- If the wording is so deeply changed, how would customers interpret this complex definition to determine how it applies?
- The application-specific wording proposals are too ambiguous, which may result in interpretation issues. It is impossible to define all end-use applications. Many of these component devices have unique characteristics, which may be excluded with the current application-based proposals. Trying to develop categories under the 7(c) exemptions that will cover all current components/devices is extremely difficult. Some products will ultimately be left out creating a compliance and economic issue for those component companies affected.
- Additionally from a technical point of view the categorization proposed above by Oeko-Institut and Fraunhofer IZM has some technical problems as well. From the point of view of properties, ferroelectric materials are a subgroup of pyroelectric materials that are a subgroup of piezoelectric materials and all should be considered as dielectrics etc. However, when this categorization is used to distinguish between applications as it seems to be the case here, it leads to ambiguity, since all piezoelectric ceramics need to be ferroelectric and thus also pyroelectric. This also leads to undesired side effects for many

[1240] Op. cit. (Murata et al./Jeita et al. 2016b) piezoelectric applications: the ferroelectric character may lead to depoling (loss of polarisation) due to an external electric field in actuators and transducers, and the pyroelectric character may give rise to pyroelectric charges in sensors due to a temperature change. It will be extremely difficult to make exhaustive lists of applications of piezoelectric ceramics covering all present and future uses, and Murata/JEITA et al. foresee that in practice it will not be possible for customers to clearly identify a category in cases where their application relies on a number of properties.

The discussion related to the consultants' rewording proposal for exemption 7(c)-I shows that a consensus on the technical details of such a rewording proposal requires further exchange with the various stakeholders to agree on the architecture and the definitions of terms. The limited time and resources available for the review of this exemption did not allow further discussions with the applicants and other stakeholders. The consultants therefore recommend to continue the exemption as proposed in the review of Exemption 7(c)-I. The above proposals and discussions can, however, be a basis to a further specification of Exemption 7(a) in a future review taking into account the new status of elimination and substitution of lead.

22.5.4.2 Lead in Glass and Glass or Ceramic Matrix Compounds in Electrical and Electronic Components

The consultants proposed the below wording related to lead in glass and glass/ceramic matrix compounds in exemption 7c-I. Exemption 34 (Lead in cermet-based trimmer potentiometers) was integrated into this wording as well as the glass beads of high voltage diodes where the use of lead glass is the root cause for contaminations in the plating, which is in the scope of exemption 37).

Lead in glass or in a glass or ceramic matrix compound

- *used for protection and electrical insulation*
  - *in glass beads of high voltage diodes on the basis of a zinc-borate glass body*
  - *in other electrical and electronic components*
- *used as resistance material*
  - *in cermet-based trimmer potentiometers*
  - *other electrical and electronic components*
- *used for bonding purposes in electrical and electronic components*
- *for hermetic sealings between ceramic packages and glass or ceramic lids in electrical and electronic components*
- *used for any other purposes in electrical and electronic components*

Murata/JEITA et al.[1241] state that the time available was not enough to allow a cross-industry association discussion. They principally disagree with the splitting of the exemption for the same reasons as mentioned above in the ceramic part of the proposed rewording.

More specifically, Murata/JEITA et al. [1242] [1243] put forward that attempting to develop categories under the 7(c) exemptions that will cover all current components/devices is extremely difficult. Some products will ultimately be left out creating a compliance and economic issue for those component companies affected.

The consultants do not share this argument. The last clause of the proposed wording should cover all those cases, which are out of the scope of the previous clauses. It is, however, crucial that the other clauses actually address specific uses of glass and glass and ceramic matrix compounds containing lead as otherwise the specification of the exemption would not make sense. The replies of Murata/JEITA et al. are not detailed enough to allow clear insights on the viability of the proposed specific uses.

Murata/JEITA et al.[1244] state that there is not just one type of lead glass but there are different glasses for different functions/applications. Even though lead in glass material used today might be rather similar in their chemical composition, potential alternative materials will not likely be the same for the different applications. Based on previous investigations and studies it does not seem likely that one material compound could be found which fulfills the specific requirements for all the variety of applications.

This statement supports in principle the specification of the exemption to gradually phase out the use of lead, as stated in recital 19 of the RoHS Directive. [1245]

In the consultants' understanding, a clear consensus should be achieved with the applicants that the exemption technically covers all applications of glass and glass ceramic materials correctly, so as to avoid that misunderstandings and misinterpretations, which had occurred in the discussion process, result in an inappropriate wording. The limited time and resources available for the review of this exemption did not allow more time for further discussion. The above wording proposal should, however, be a good basis for a specification of the exemption in the next review.

[1241] Murata et al./Jeita et al. 2016c "Answer to questionnaire 4 (glass), document "Exe_7c-I_Questionnaire-4_Murata-JEITA_2016-03-09_glass.pdf", received via e-mail by Dr. Otmar Deubzer, Fraunhofer IZM, from Wolfgang Werner, Vishay, on 22 March 2016" unpublished manuscript,

[1242] Ibid.

[1243] Murataet al./JEITA et al. 2016g "Answers to questionnaire 6b, document "Exe_7c-I_Questionnaire-6b_Murata-JEITA_2016-03-3.pdf", received via e-mail from Wolfgang Werner, Vishay, on 5 April 2016" unpublished manuscript,

[1244] Ibid.

[1245] *Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (recast)*, recital clause (19)

22.5.5 Conclusions

22.5.5.1 Lead in Ceramics of Electrical and Electronic Components

The accessible information suggests that the substitution of lead in ceramics is scientifically and technically still impractical in the majority of applications. Contrary to the statements in particular of Murata et al., substitution or elimination of lead may be scientifically and technically practical to a certain degree even though it could not be clarified whether this would justify and enable narrowing the scope of the exemption.

Appraising the overall situation, Art. 5(1)(a) would justify renewing the exemption for lead in ceramics, taking into account the fact that the substitution or elimination of lead scientifically and technically is still impractical at least in the majority of cases. It can, however, not be excluded that lead-free solutions are or shall become available in the nearer future. Granting the exemption for five years would thus not be justifiable according to Art. 5(1)(a). The consultants hence recommend a validity period of three years, which would allow restricting the scope of the exemption, while still leaving enough time to for the stakeholders to apply for the renewal of the exemption 18 months prior to its expiry, should it still be required at that time. The applicants would then also have to show dedicated efforts to achieve the substitution and elimination of lead.

22.5.5.2 Lead in Glass or in Glass or Ceramic Matrix Compounds in Electrical and Electronic Components

The information provided by the applicants suggests that currently the substitution of lead in glass and in glass/ceramic matrix compounds in the scope of exemption 7c-I is scientifically and technically still impracticable. Bourns and IXYS are both continuing to work on lead-free solutions, though at present, these are understood not to be sufficiently mature to allow narrowing the scope of Exemption 7c-I in the foreseeable future.

The applicants' exemption requests and the answers to the clarification questionnaire were made available through the online consultation to the public, i.e. to industry, governments, NGOs and other stakeholders, and a consultation questionnaire had been prepared for the public online consultation with specific questions to stakeholders. No further information supporting or discrediting the technical application in question was received, and there were no hints that lead-free solutions would be foreseeable for the near future.

Murata et al. provide only very general and unspecific information on their future efforts to substitute or eliminate lead in ceramics. They justify this with confidentiality, but the consultants believe that even though the members of the industry consortium are competitors, there should be possibilities to describe in more detail the future steps to be taken. These efforts should also be related to the various types of glass and glass/ceramic matrix compounds and their application-specific requirements to find specific solutions where general drop-in alternatives are not viable.

Taking into account the overall situation, the consultants recommend granting the exemption given the fact that lead is still required in glass and glass and ceramics matrix compounds. As no substitutes are foreseeable in the near future, Art. 5(1)(a) would justify renewing the exemption for the maximum validity period of five years. It will, however, be essential that the applicants will have undertaken dedicated efforts in the coming five years to find application-specific solutions for the various types of glass applications should they apply for another renewal of this exemption.

22.5.5.3 Specification of Exemption 7(c)-I

The discussion related to the consultants' rewording proposal for exemption 7(c)-I shows that a consensus on the technical details of such a rewording proposal requires further exchange with the various stakeholders to agree on the architecture and the definitions of terms. The above wording proposal should, however, be a good basis for further efforts to specificy the exemption in the next review.

22.6 Recommendation

The applicants' information suggests that the substitution and elimination of lead generally is still scientifically and technically impracticable in the applications in the scope of Exemption 7c-I. Art. 5(1)(a) thus would allow renewing the exemption. While for lead in glass and glass or ceramic matrix compounds no possibilities for substitution or elimination of lead are foreseeable, the information available does not allow excluding that lead-free solutions for ceramics are or will become available within less than five years.

The consultants therefore recommend renewing the exemption for five years for lead in glass or glass or ceramic matrix compounds, and for three years only for lead in ceramics of electrical and electronic components.

It should also be noted here that the exemption for lead in glass or glass or ceramic matrix compounds of electrical and electronic components technically covers the use of lead in cermet-based trimmer potentiometers, which is in the scope of Exemption 34. To avoid overlapping scopes of exemptions, Exemption 34 should be excluded from this part of the exemption.

Exemption 7(c)-I	**Expires on**
Electrical and electronic components containing lead in a ceramic other than dielectric ceramic in discrete capacitor components, e.g. piezoelectronic devices	*21 July 2019 for categories 1-7 and 10*
Exemption 7(c)-V	**Expires on**
Electrical and electronic components containing lead in a glass or in a glass or ceramic matrix compound. *This exemption does not cover the use of lead in the scope of exemption 34 (cermet-based trimmer potentiometers).*	*21 July 2021 for categories 1-7 and 10*

Exemption 7(d)	Expires on
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	*21 July 2021 for medical equipment in category 8 monitoring and control instruments in category 9* *21 July 2023 for in vitro diagnostic medical devices in category 8*
	21 July 2024 for industrial monitoring and control instruments in category 9

Exemptions 7(c)-II, 7(c)-III and 7(c)-IV can be integrated into the above table.

In order to keep the purely ceramic-related exemptions together, it is recommended above to give the exemption valid for cat. 8 and 9 a new number and to list all ceramic-related exemptions under 7c-I. This numbering would also prevent that exemptions 7(c)-II, 7(c)-III and 7(c)-IV have to be renumbered, which overall reduces the administrative burden.

If the Commission decides not to change the numbering of the part of the exemption that covers Cat. 8 and 9, the consultants recommend the below wording and numbering for Exemption 7c-I.

Exemption 7(c)-I	Expires on
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	*21 July 2021 for medical equipment in category 8 monitoring and control instruments in category 9* *21 July 2023 for in vitro diagnostic medical devices in category 8* *21 July 2024 for industrial monitoring and control instruments in category 9*
Exemption 7(c)-V	**Expires on**
Electrical and electronic components containing lead in a glass or in a glass or ceramic matrix compound. *This exemption does not cover the use of lead in the scope of exemption 34 (cermet-based trimmer potentiometers).*	*21 July 2021 for categories 1-7 and 10*
Exemption 7(d)	**Expires on**
Electrical and electronic components containing lead in a ceramic other than dielectric ceramic in discrete capacitor components, e.g. piezoelectronic devices	*21 July 2019 for categories 1-7 and 10*

Exemptions 7(c)-II, 7(c)-III and 7(c)-IV can be integrated into the above table.

22.7 References Exemption 7c-I

Bandelin Electronic GmbH 2015a Request for continuation of exemption 7c-I with addition, document "Ex_7c_I_Application_Bandelin.pdf. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/BANDELN/Ex_7c_I_Application_Bandelin.pdf.

Bandelin Electronic GmbH 2015b Questionnaire 1 (clarification questionnaire), document "Ex_7c-I_Bandelin_1st_Questionnairie_and_Answers.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/BANDELN/Ex_7c-I_Bandelin_1st_Questionnairie_and_Answers.pdf.

Bourns Inc. 2015a Exemption request, document "7c-I_Exemption_extension_ap_7c-I.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Bourns/7c-I_Exemption_extension_ap_7c-I.pdf.

Bourns Inc. 2015b Request for continuation of exemption 7c-I, document "20150818_Ex_7c-I_Bourns_Questionnaire-1_2015-07-28.pdf", clarification questionnaire. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/20150818_Ex_7c-I_Bourns_Questionnaire-1_2015-07-28.pdf.

Bourns Inc. 2016a Request for continuation of exemption 7c-I, document "20150818_Ex_7c-I_Bourns_Questionnaire-1_2015-07-28.pdf".

Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. RoHS 1European Union. February 13, 2003.

Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (recast). RoHS 2European Union. July 1, 2011.

Gensch, Carl-Otto, Oeko-Institut e. V., et al. 20 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, Oeko-Institut e. V. and Otmar Deubzer, Fraunhofer IZM. http://ec.europa.eu/environment/waste/weee/pdf/final_reportl_rohs1_en.pdf.

IXYS Semiconductor GmbH 2014 Request for continuation of exemption 37, document "37_IXYS_RoHS_V_Application_Form_pass_glasses.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_37/IXYS/37_IXYS_RoHS_V_Application_Form_pass_glasses.pdf.

IXYS Semiconductor GmbH 2016a Answers to questionnaire 1 (clarification questionnaire), sent via e-mail to Dr. Otmar Deubzer, Fraunhofer IZM, by Markus Bickel, Ixys Semiconductor GmbH, on 27 January 2016.

JEITA et al. 2015a Exemption request, document "JEITA/7c-IandII_RoHS_Exemption_Renewal_Request_7_c_I_Japan4EEEassociations.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7 _c_-I/JEITA/7c-IandII_RoHS_Exemption_Renewal_Request_7_c_I_Japan4EEEassociations.pdf.

Murata et al. 2015a Original exemption request, document "Exemption_7_c_-I/Murata/7c-I_RoHS_V_Application_Form_7c1_20140116_combined_final.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Murata/7c-I_RoHS_V_Application_Form_7c1_20140116_combined_final.pdf.

Murata et al. 2015b Questionnaire 1 (clarification questionnaire), document "RoHS_7c-I_Murata__1st_Questionnaire_answers_final_20Aug.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Murata/RoHS_7c-I_Murata__1st_Questionnaire_answers_final_20Aug.pdf.

Murata et al. 2015c Addendum to original exemption request, document "Leadfree_PZT_comparison.pdf".

Murata et al. 2016a Answers to second questionnaire, document "Exe_7c-I_Questionnaire-2_Murata-JEITA_2015-12-30_answers_final.pdf", received by Dr. Otmar Deubzer, Fraunhofer IZM, from Wolfgang Werner, Vishay, on 29 January 2016.

Murata et al./Jeita et al. 2016b Answers to third questionnaire (ceramics), document "Exe_7c-I_Questionnaire-3_Murata-JEITA_2016-03-03_ceramics.pdf", received via e-mail by Dr. Otmar Deubzer, Fraunhofer IZM, from Klaus Kelm, Murata, on 22 March 2016.

Murata et al./Jeita et al. 2016c Answer to questionnaire 4 (glass), document "Exe_7c-I_Questionnaire-4_Murata-JEITA_2016-03-09_glass.pdf", received via e-mail by Dr. Otmar Deubzer, Fraunhofer IZM, from Wolfgang Werner, Vishay, on 22 March 2016.

Murata et al./JEITA et al. 2016d Answers to questionnaire 5a, document "Exe_7c-I_Questionnaire-5a_Murata-JEITA_2016-03-28_Ceramics_final.pdf", received via e-mail from Klaus Kelm, Murata, by Dr. Otmar Deubzer, Fraunhofer IZM, on 1 April 2016.

Murataet al./JEITA et al. 2016e Answers to questionnaire 6a, document"Exe_7c-I_Questionnaire-6a_Murata-JEITA_2016-03-2.pdf", received from Klaus Kelm, Murata, by Dr. Otmar Deubzer, Fraunhofer IZM, on 1 April 2016.

Murataet al./JEITA et al. 2016f Answers to questionnaire 5b, document "Exe_7c-I_Questionnaire-5b_Murata-JEITA_2016-03-2.pdf", received via e-mail from Klaus Kelm, Murata, by Dr. Otmar Deubzer, Fraunhofer IZM, on 5 April 2016.

Murataet al./JEITA et al. 2016g Answers to questionnaire 6b, document "Exe_7c-I_Questionnaire-6b_Murata-JEITA_2016-03-3.pdf", received via e-mail from Wolfgang Werner, Vishay, on 5 April 2016.

Pyreos Ltd. 2014 Original exempiton request for renewal of exemption 7c-I with new wording, document "RoHS_V_Application_Form-Pyreos_final 14112014 - publication.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_7/2015_1/RoHS_V_Application_Form-Pyreos_final_14112014_-_publication.pdf.

Pyreos Ltd. 2015a Document "Questionnaire-1_Clarification_Exe-Req-Pyreos_cg130415 final - publication.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_7/2015_1/Questionnaire-1_Clarification_Exe-Req-Pyreos_cg130415_final_-_publication.pdf.

Pyreos Ltd. 2015b Document "Pyreos_Suspension-of-Request-with-Conditions.pdf", sent via e-mail to Dr. Otmar Deubzer, Fraunhhofer IZM, by Torben Nørlem, Intertek, on 20 July 2015.

Pyreos Ltd. 2016a Answers to questionnaire 2, document "Questionnaire-2_Pyreos_2016-03-06.pdf", received via e-mail by Dr. Otmar Deubzer, Fraunhofer IZM, from Torben Norlem, Intertek, on 23 March 2016.

Pyreos Ltd. 2016b Answers to third questionnaire, document "Exe_7c-I_Questionnaire-3_Pyreos_2016-03-30_final.pdf", received via e-mail from Torben Norlem, Intertek, by Dr. Otmar Deubzer, Fraunhofer IZM, on 31 March 2016.

Ralec Technology 2015 Exemption request, document "7c-I_RoHS_V_Application_Form_to_RoHS.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/RALEC/7c-I_RoHS_V_Application_Form_to_RoHS.pdf.

Schott AG 2015a Exemption request document "20150820_Ex_7c-I_Schott_Application_Revised_A.pdf" 2015a. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/SCHOTT/20150820_Ex_7c-I_Schott_Application_Revised_A.pdf.

Schott AG 2015b Questionnaire 1 (clarification questionnaire), document "20150820_Ex_7c-I_Schott_Ans_Questionnaire-1_Schott_2015-07-30.pdf" 2015b. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/SCHOTT/20150820_Ex_7c-I_Schott_Ans_Questionnaire-1_Schott_2015-07-30.pdf.

Sensata Technologies 2015a Request for continuation of exemption 7c-I, document "7c-I_RoHS-Exemptions_Application-Format_Ex_7cI_Pb_in_glass_20150115.pdf" 2015a. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Sensata/7c-I_RoHS-Exemptions_Application-Format_Ex_7cI_Pb_in_glass_20150115.pdf.

Sensata Technologies 2015b Questionnaire 1 (clarification questionnaire), document "7c-I_Questionnaire_Sensata_20150901.pdf" 2015b. http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/Sensata/7c-I_Questionnaire_Sensata_20150901.pdf.

Vishay 2015a Document "RoHS-Exe-7c-I_Pb-in-glass-Enamel-Coating_Wirewound_Resistors.pdf", submitted as additional reference for the exemption request of Murata et al. 2015a 2015.

Vishay 2015b Document "NTC – Glass coating for insulation.pdf", submitted as additional reference for the exemption request of Murata et al. 2015a 2015.

Vishay 2015c Document "Request for exemption 7c-I NTC chips update dec15.pdf", submitted as additional reference for the exemption request of Murata et al. 2015a.

Yageo Corporation 2015 Exemption request, document "7c-I_RoHS_V_Application_Form_YAGEO_2015-01-19.pdf". http://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_9/Exemption_7_c_-I/YAGEA/7c-I_RoHS_V_Application_Form_YAGEO_2015-01-19.pdf.

Zangl, Stéphanie [Oeko-Institut e.V.] et al. Adaptation to scientific and technical progress of Annex II to Directive Adaptation Directive2000/53/EC (ELV) and of the Annex to Directive 2002/95/EC (RoHS) 2010. http://elv.exemptions.oeko.info/fileadmin/user_upload/Consultation_2014_1/Ex_3_2010_Review_Final_report_ELV_RoHS_28_07_2010.pdf; or https://circabc.europa.eu/sd/d/a4bca0a9-b6de-401d-beff-6d15bf423915/Corr_Final%20report_ELV_RoHS_28_07_2010.pdf.