

Application for Extension of Exemption 7(C)-I in Annex III of the RoHS Directive

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1. Contact Information

Name and contact details of applicant:

Company: Photonis Scientific, Inc.

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[REDACTED]

2. Reason for Application

Please indicate where relevant:

☐ Request for new exemption in:

☐ Request for amendment of existing exemption in

☒ Request for extension of existing exemption in

☐ Request for deletion of existing exemption in:

☒ Provision of information referring to an existing specific exemption in:

☒ Annex III

☐ Annex IV

X No. of exemption in Annex III or IV where applicable: **7(C)-I**

Proposed or existing wording:

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 III).

Duration where applicable: 5 years

3. Summary of Exemption Request

To ensure the continued production and use of high quality electro-optic devices, it is crucial to use lead-oxide based glasses. These so called “electronic glasses” are necessary to provide the electrical characteristics necessary for electron multiplication to occur.

Lead oxide, as a glass constituent, is responsible for providing crucially necessary current flow within signal multiplying detection devices to accomplish electron multiplication. Removing lead from our product will result in complete operational failure of our many products.

Regarding the amount of lead containing glass needed for our purposes, and the fact that glass is an inert and stable material which does not pose any danger to human health or the environment in the product lifecycle, we apply for the extension of the existing exemption in Annex III, no. 7(c)-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.”.

4. Technical Description of Exemption Request

4.1. Channel Electron Multipliers and Microchannel Plates

Channel electron multipliers (CEMs) are non-magnetic point detectors of charged particles and electro-magnetic radiation. They are the most widely used detectors mass spectrometer based analytical instrumentation. These devices are in effect very high gain low noise amplifiers. The output signals from these devices provide both qualitative and quantitative information about the material being analyzed. Eliminating these detectors from these analytical instruments would reduce the sensitivity by a factor of 100,000 times. Figure 1 illustrates some typical CEM formats.



Figure 1: Various Channel Electron Multiplier formats

Microchannel Plates (MCPs) are two dimensional arrays of miniature single channel electron multipliers (referred to as channels) fused together in a solid device with up to 10 million channels per cm². MCP channel diameters range from 2µm to 25µm.

Microchannel plates not only detect charged particles and photons, but also provide position and timing information about the detected event. In essence, MCPs can not only provide qualitative and quantitative information, but also an image. Figure 2 illustrates some common MCP formats.

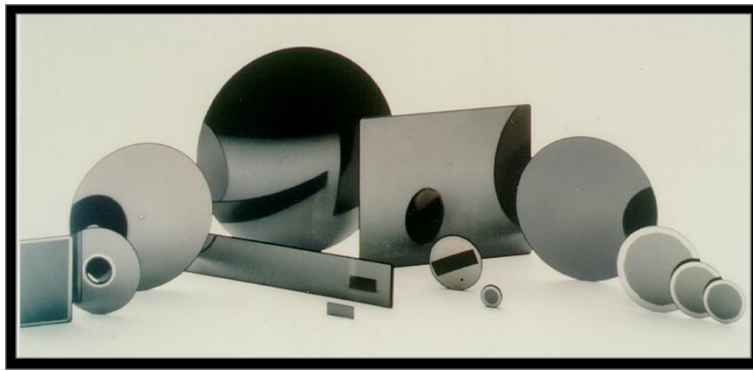


Figure 2: Various microchannel plate configurations

4.1.1. Functional Principle

Channel electron multipliers and microchannel plates are fabricated from a special alkali doped lead silicate glass which can produce 10^4 - 10^8 electrons in response to single charged particle or photon event.

In operation a high voltage is placed across the device. When a charged particle such as an ion or an electron, or energetic photon impinges on the input surface of the multiplier, several secondary electrons will be ejected from the secondary emissive layer into the vacuum space. Alkali dopants within the emissive layer lower the work function of the surface leading to increased secondary emission. A direct current flowing in the conductive layer is made possible by the lead oxide in the glass matrix and ensures a constant replenishment of secondary electrons.

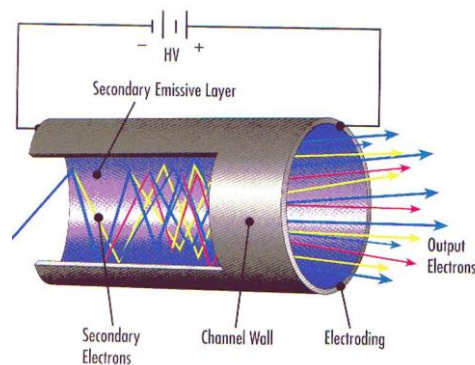


Figure 3: Cross section of a single channel showing the electron multiplication that produces the amplification.

As is shown in Figure 3, the secondary electrons travel down the channel, accelerated by the electric field. They will repeatedly collide with the channel wall, producing still more secondary electrons. The electrons are accelerated towards the anode end of the channel by the ever-increasing positive potential within the channel produced by the resistive lead oxide glass layer beneath the emissive layer. This process will be repeated until the resulting cloud of electrons exits the channel and is collected by the anode.

Microchannel plates operate in a similar fashion. Each channel in the array operates as an independent single channel electron multiplier. Each channel is connected to a common high voltage supply by a metallization layer composed typically of nichrome, Inconel, or gold. The independent nature of each channel enables the device to create a two-dimensional image of the incoming events. Figure 4 illustrates the MCP cross section in operation.

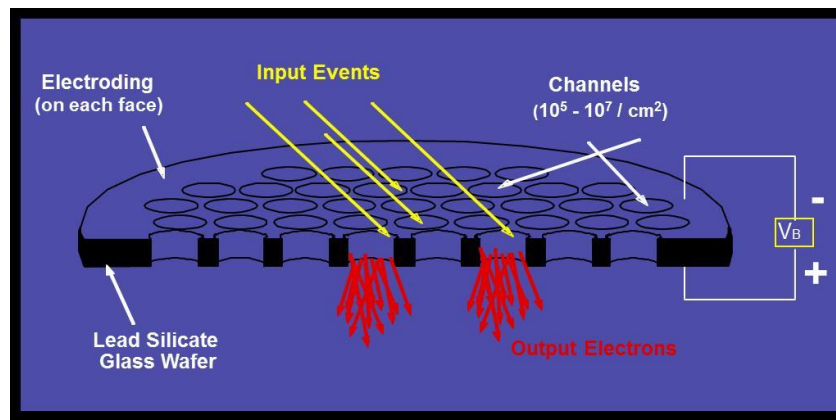


Figure 4: Cross-section of a microchannel plate in operation

Varying the high voltage across the device will both alter the electron trajectory and the number of secondary electrons produced per strike. In this manner, the gain of the device can be widely varied. Proper biasing of the device can result in a single event, impinging on the input side of the device, producing up to 100,000,000 electrons at the anode.

4.1.2. Applications

Channel electron multipliers and microchannel plates are used in a large variety of applications. CEMs are the most widely used detector in mass spectrometry. Mass Spectrometers are machines which can identify unknown materials by their molecular composition. Typically, the unknown material will be ionized. The resultant ions are then separated by mass and directed to the detector where arrival time and signal intensity is used to produce a mass spectrum, from which the unknown material can be reliably identified. The sensitivity of these machines are typically in the parts per billion range when looking for trace materials in complex mixtures.

Mass spectrometers are critical instruments used in drug discovery, food safety, forensics, cancer research, life sciences, pharmaceutical quality control, energy research, semiconductor manufacturing, personalized medicine, environmental remediation, homeland security and space exploration.

In addition, the two-dimensional aspects of microchannel plates enable their use as the primary amplification element in image intensifier tube, used in night vision applications. Without microchannel plates, no intensified night vision would be possible. Micro-channel plates are also used in intensified cameras, neutron imaging, LIDAR and high energy physics experiments such as those conducted at CERN, high performance time of flight and Secondary Ion Mass Spectrometers, and in Ion beam profiling

4.2. Resistive Glass Tubes

Resistive glass devices are monolithic glass structures used to create stable electric fields needed for efficient charge particle transport. These devices rely on the reduced lead oxide bound up in the lead glass matrix to carry the current in the conductive layer in order to produce the electric field when a voltage is applied. Figure 5 illustrate some typical resistive glass tube designs.



Figure 5: Typical resistive glass structures.

4.2.1. Resistive Glass Tube Functional Principles

In operation, the device would be connected to a DC high voltage power supply. When the voltage is raised, a current will begin to flow in the resistive, reduced lead silicate layer. When the current begins to flow, an electric field is produced, the shape of which is defined by the shape of the glass and the field intensity is defined by the voltage across the structure. The device can be operated in either a vacuum or in air depending on the application.

The resultant electric is typically used to direct charged particles to or through an analyzer. This efficient transport of charged particles significantly enhances the sensitivity of the analysis enabling lower concentrations to be detected.

4.2.2. Resistive Glass Tube Applications

Capillary inlet tubes used in mass spectrometers are the largest use of resistive glass tubes. In a mass spectrometer, the unknown material exists at atmospheric pressure but can only be analyzed in a vacuum environment. Efficient transport of the unknown material into the analyzer is key for detection of low-level constituents.

Resistive glass tubes are also used in Ion Mobility Spectrometers (IMS). These devices operate at atmospheric pressure and are most often used in homeland security applications. Using air sampling from a cargo container, or looking at the outgassing of a swab pad taken from luggage or a hand wipe down, an IMS is capable of identifying explosives or contraband drug residue down to parts per trillion sensitivity.

4.3. Characteristics and function of RoHS-regulated substance that require its use

The presence of lead oxide (PbO) in Microchannel Plates (MCPs), Single Channel Electron Multipliers (CEMs) and Resistive Glass Products (RGPs) is critical to both their forming and for their operation. The glasses used to make these products are lead silicate glasses containing from 47.5 to 58% by weight (26.5 to 31.5% by mol) of lead oxide (PbO). The presence of lead in the glass melt decreases the viscosity of the glass at high temperatures, making it suitable for the complex forming operations required to make these products. While there are other non-lead glass compositions which could be suitable for the required forming techniques, the lead oxide (PbO) plays a critical role in imparting the necessary electrical properties to the glass. When lead silicate glasses are reduced in hydrogen at elevated temperatures, a semi-conducting surface is formed through the reaction of lead oxide (PbO) with hydrogen to form positive lead ions and water vapor. This reduction of PbO leads to blackening of the glass due to lead agglomeration. While this agglomerated reduced lead makes no contribution to the conductivity

of the glass, there remains in the glass approximately $1 \text{ in } 10^6 \text{ Pb}^+$ ions isolated in the glass. These ions act as electron donors leading to conduction via a hopping mechanism. The extent of conductivity in the glass can be controlled by the glass formulation as well as by the reduction conditions. For example, the addition of bismuth to the melt increases the conductivity of the glass. This semi-conductive layer is integral to the glass after formation and can only be removed mechanically by surface abrasion. The layer only forms on the uppermost surface of the glass due to the limitation of the chemical reaction by the diffusion of OH from the reduction reaction of the glass. This semi-conductive layer can only be developed in lead containing glasses.

A CEM is a typically curved glass tube used for the detection and amplification of charged particles. Under vacuum a voltage is applied across the tube. An influx of electrons, ions, UV light, or x-rays strike the inner wall of the tube where they induce the emission of secondary electrons. These are accelerated down the tube by the voltage potential. With each impact, more secondary electrons are generated, causing an avalanche of free electrons that exit the tube at the high potential end. A microchannel plate is a planar array of channels that provide the same function as a CEM with the additional benefit of providing spatial resolution. For MCP and CEM applications, in addition to the overall electrical properties of the glass, the secondary electron yield of the surface is critical. This is controlled by the work function of the surface and the mean free path of the electrons. In MCPs the conducting layer is protected by a thin layer of silica rich glass that is formed by a chemical leaching process prior to reduction. The silica rich layer controls the secondary emissive characteristics while the reduced layer controls the electrical properties of the MCP. For CEMs there is no silica rich layer and both the secondary emissive characteristics and the electrical properties are controlled by the conducting surface. Resistances in the range of 10^6 to $10^{16} \Omega \cdot \text{cm}$ are required for the amplification process to be successful. It is not feasible to achieve this with ceramics or thin films of metal. The lead glass has the additional advantage of being easy to shape. For MCPs in particular the high length to diameter ratios and the small channel size (2.5 to 25 microns) required cannot be achieved with non-glass material. Additionally, the lead silicate glass allows for the formation of round pores that cannot be achieved with most other non-lead glasses.

Resistive glass products (RGPs) are typically larger scale reduced glass tubes. They are primarily used as inlet capillary tubes in mass spectroscopy applications. For RGPs the lead in the glass has a two-fold effect. The presence of the lead in the glass allows for formability of very high length to diameter ratio parts (300 to 500). Once the formed glass is reduced, the semi-conductive surface allows a continuous current flow under the application of voltage across the tube. This results in the formation of an electric field that improves the transfer of ions into the mass spectrometer. Improvements in ion transfer of a factor of 100 over conventional quartz tubes, and over 600X improvement for the hexabore model, have been reported.

Once the glass has been melted and formed into a glass, the lead is chemically bound and is not exposed to the environment unless the glass is completely crushed into fine powder or if the exposed surface of the glass is chemically leached to remove the lead.

Amount of Lead Used in Requested Exemption

Product Type	Est. Total wt Pb shipped for 2019 (kg)	Est. Total wt Pb shipped for 2019 to EU (kg)

Channeltron (CEM)	26	*
Resistive Glass Product (RGP)	106	*
Microchannel Plate (MCP)	1	*
Total	133	*

* Because we sell our products to customers who install them in their equipment and that equipment gets shipped all over the world, it isn't possible for us to determine from our own records how much of our lead production ends up in Europe. Industry research estimates that overall roughly 25% enters the EU market or ~36kg 1

(A) Description of the concerned application:

1. To which EEE is the exemption request/information relevant?

Name of applications or products: See above

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

- | | |
|----------------------------|---------------------------------------|
| <input type="checkbox"/> 1 | <input type="checkbox"/> 7 |
| <input type="checkbox"/> 2 | <input checked="" type="checkbox"/> 8 |
| <input type="checkbox"/> 3 | <input checked="" type="checkbox"/> 9 |
| <input type="checkbox"/> 4 | <input type="checkbox"/> 10 |
| <input type="checkbox"/> 5 | <input type="checkbox"/> 11 |
| <input type="checkbox"/> 6 | |

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

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

1. The requested exemption will be applied in
2. ☒ monitoring and control instruments in industry
3. ☐ in-vitro diagnostics
- ☒ ~~other medical devices~~ or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?

(Indicate more than one where applicable)

☒ Pb ☐ Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substance: See above

4. Content of substance in homogeneous material (%weight): 44%-54%

5. Amount of substance entering the EU market annually through application for which the exemption is requested: See table above

The total amount of lead shipped in 2019 from Photonis Scientific is ~145kg. We cannot precisely determine the amount that eventually enters the EU market but previous industry research has estimated it as 25% of the total or ~36kg.¹

6. Name of material/component: See table above

7. Environmental Assessment:

LCA: ☐ Yes

☒ No

- (B) In which material and/or component is the RoHS-regulated substance used, for which you request the exemption or its revocation? What is the function of this material or component?

See above

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

See above

5. Waste Reuse and Recycling

Information on possible preparation for reuse or recycling of waste from EEE and on provisions for appropriate treatment of waste –

1) Please indicate if a closed loop system exist for EEE waste of application exists and provide information of its characteristics (method of collection to ensure closed loop, method of treatment, etc.)

The waste material generated by the Photonis production process is mixed with other wastes then treated, stabilized, and bound with treated material and cementing agents before being placed in a secure monitored cell. The cells are poly-lined and in a naturally clay lined area near the great lakes in Canada. Since the material is stabilized and mixed in with cementing agents there is very little chance for leachate from the lined cells. The cells and leachate are monitored.

Due to the various heavy metals and the relatively low quantity of leaded glass that Photonis ships, this waste is not a candidate for recycling options. However, internally Photonis has taken a number of steps to reduce the lead waste that is generated. For example, up to 15% by weight leaded glass remelt is introduced back into each glass melt to reduce the required amount of lead containing powder required to form the glass. Additionally, the lead glass tubes used in the fusion process are salvaged and fused together in order to be used twice, again reducing the amount of lead consumed and generated at Photonis.

2) Please indicate where relevant:

- ☐ Article is collected and sent without dismantling for recycling
- ☐ Article is collected and completely refurbished for reuse
- ☐ Article is collected and dismantled:
- ☐ The following parts are refurbished for use as spare parts: _____
- ☐ The following parts are subsequently recycled: _____
- ☒ Article cannot be recycled and is therefore:
- ☐ Sent for energy return
- ☒ Landfilled

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

- | | |
|-----------------------------------------------------------------------|-------------|
| <input type="checkbox"/> In articles which are refurbished | _____ |
| <input type="checkbox"/> In articles which are recycled | _____ |
| <input type="checkbox"/> In articles which are sent for energy return | _____ |
| <input checked="" type="checkbox"/> In articles which are landfilled | <u>100%</u> |

6. Analysis of Proposed Alternative Substances

6.1. Microchannel Plates and Channel Electron Multipliers

6.1.1. Alternatives to Lead Glass for MCP Substrates

Current lead glass MCP substrates include the following characteristics:

- Round channels with pore diameters of 5µm diameter or less
- uniform spacing of channels with no distortion at boundary layers
- high open area ratio (OAR)
- high channel length to pore diameter ratio
- large input areas
- mechanically stable over a wide temperature range and not prone to cracking,

The glass used to make microchannel plates is comprised of a lead silicate glass doped with alkali metals to enhance the secondary electron yield of the glass surface.

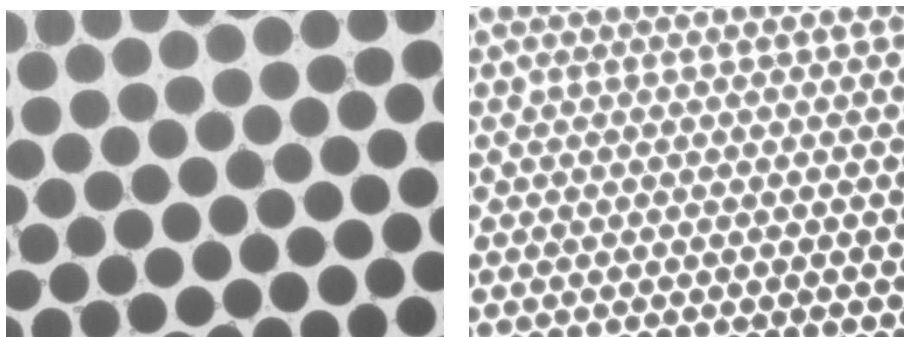


Figure 6: Detail of round 5 μ m lead glass MCP channels (left). Boundaries of adjacent hexagonal multi-fibers are visible in the channel structure shown on the right, but the channels largely have maintained their size and shape.

Using an alternate glass to form the microchannel plate structure is the most straightforward approach to removing the lead from MCPs.

Photonis and other manufacturers can make MCP-like substrates using soda-lime glass, which contains no lead. There are, however, significant limitations to these structures. Due to the mechanical and thermal viscosity properties of the many forms of soda-lime glass, the round fibers compress to a hexagonal shape when the fibers are pressed together (See Figure 7). The substrates also display more deformation at the boundaries than lead glass substrates. Soda-lime glass is less forgiving to rapid changes in temperature than lead-glass, leading to increased problems with cracking and stress fractures in the billets and blocks. These problems can appear at the time of manufacture but can also appear later with exposure to the atmosphere. Billet and edge-cracking of soda-lime substrates over long periods of time is a significant problem that is likely to take many years to fully address.

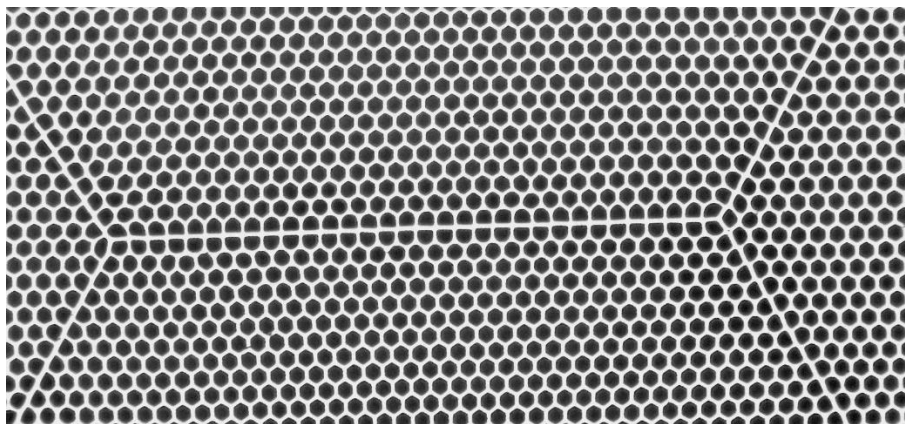


Figure 7: Hexagonal deformation of individual 10 μ m microchannel plate channels on soda-lime substrates. There is also clearly visible channel deformation at the multi-fiber boundaries that produces larger channels in those areas

Incom and others have made MCP structures out of borosilicate glass. Borosilicate glass has a much higher working temperature than lead glass. Most of the work published on borosilicate substrates describe substrates made with a hollow-draw process, where hollow fibers are pressed together. This process leads to hexagonal channel shapes and significant channel deformation at the boundaries of the multifibers² Distortion at the boundaries results in an effect known as “fixed pattern noise” in images~~Error! Bookmark not defined.~~ where there are visible geometric patterns in the image due to the channel structure. The hollow draw process has been shown to be effective for producing large area MCP structures, but large area MCPs are a very small fraction of the total existing MCP usage, most of which is focused on 25mm

diameter small channel MCPs for image intensifier tubes. The borosilicate substrates that appear in the available literature are incapable of producing an image that would be acceptable for a present-day image intensifier.

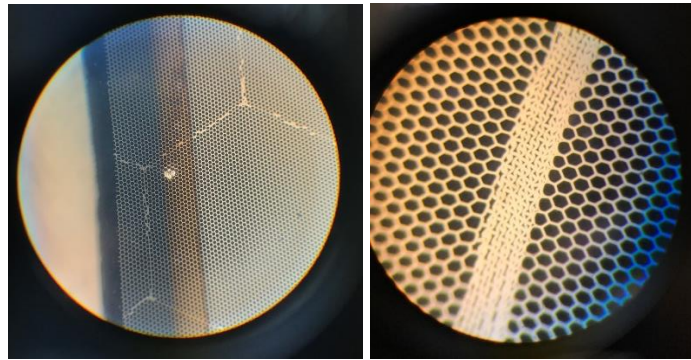


Figure 8: Deformation and collapse of hexagonal channels at multi-fiber boundaries on 20μm channel borosilicate ALD MCPs produced by Incom.

Microchannel plate substrates can be fabricated using crystalline³ or amorphous silicon^{4,5}. In the case of amorphous silicon, the silicon itself can be used to provide the resistive and emissive material whereas for polycrystalline material the resistive and emissive layers must be provided by alternate coating processes. A significant limitation of forming substrates in this way is the limited aspect ratios (the depth of the channel compared to the channel diameter). Channel depths are typically only a few hundred microns and the channel sizes are much larger than the ~10μm channels that would be required to make the optimal length to diameter ratio MCPs. Also, due to the methods used to make the holes in the silicon, the channels are not angled with respect to the input surface. This results in a significantly higher probability of ion feedback, which will destroy the photocathodes of MCP-PMT and image intensifier tubes prematurely.

Another technique for making MCP substrates is the use of ceramics. These ceramics can be given channel-like structure through a variety of techniques including semiconductor processing (similar to silicon) or the use of anodic alumina structures⁶. The channels formed by anodic alumina are irregular in shape and not capable of imaging.

Researchers at Arradiance LLC have published results for ALD MCPs made using MCP-like membranes of Polymethyl methacrylate (PMMA)⁷ but these had very low length to diameter ratios (27:1) and very large channels (~50μm) with an irregular geometry. The primary aim of this type of MCP was to enhance the measurement of fast neutrons, which is a very specialized application.

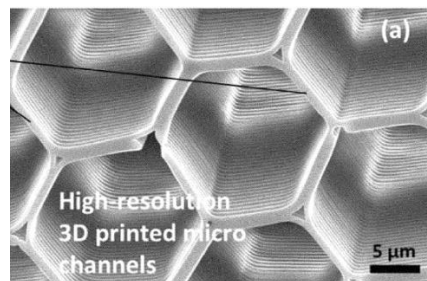


Figure 9: Hexagonal MCP structure produced by additive manufacturing / 3D printing from US patent #20190096623⁸.

US Patent #20190096623 presents details of a process for the additive manufacturing (3D printing) of MCP substrates⁸. It includes development methods to reduce the manufacture time,

which historically been a problem for this method of fabrication. An example of the structure created using this process is shown in Figure 9. These substrates offer advantages for specific applications of neutron detection and low-cost large-area detection but have visible structural deficiencies and cannot match the performance of lead-glass substrates.

Overall, while alternate methods of substrate fabrication offer advantages in specific applications, none of the alternate substrate fabrication processes addresses the full breadth of existing MCP applications. Further, it is not presently possible to provide a combination of the alternate technologies to eliminate the current need for lead glass substrates.

6.1.2. Atomic Layer Deposition as a Potential Alternate Technology for Resistive and Emissive Coatings

Atomic layer deposition (ALD) is a process by which a series of independent, self-terminating gas reactions of alternating precursor gases are used to build up a film with a desired chemistry one atomic layer at a time. The composition of the film is determined by the chemical components of the precursor gases, and these precursors must be carefully selected to produce films with the desired final chemistry. For lead glass MCPs, the manufacturing steps for producing the resistive and emissive layers are inter-dependent processes. One benefit of using ALD to produce resistive and emissive layers is that these two layers can be selected and their properties adjusted independently.

6.1.3. Alternate Technology Detectors

There are a number of technologies that can be used to perform some of the functions of MCPs and CEMs that do not require lead.

Table 1: Comparison of capabilities of alternate detector technologies as replacements for MCPs and CEMs. Performance levels are detailed in Section 7.2.

	MCP	CEM	Discrete Dynode Multiplier	Photodiode†	Photo- Multiplier tube	Electron- bombarded CCD
High Amplification	•	•	•		•	
Single-particle sensitivity	•	•	•	•	•	
Fast response	•		•‡	•		
High res. Imaging	•					•
Large input areas	•				•	•
Can measure Ions	•	•	•			
Can measure electrons	•	•	•	•		•
Can measure UV light	•			•	•	•
Can measure X-rays	•	•	•	•	•	•
Low background noise	•	•	•			
Long operating life	•	•	•	•	•	•
Compact size	•	•		•		•
Radiation hardness	•	•	•		•	
High magnetic field tolerance	•	•		•		•
Wide T range	•	•	•			

†Requires electrons with energy >5eV

‡Most discrete dynode multipliers **cannot** produce fast response times, but there are magnetic-field based DDMs that can. These DDMs produce stray magnetic fields which are not suitable for all applications

6.2. Resistive Glass Tubes

There are three main alternatives to resistive glass capillary inlet tubes; non-conducting glass tubes, metal tubes, and orifices.

Non-conducting glass tubes transport ions in a similar fashion to resistive glass tubes, but the fact that they do not conduct electricity limits their performance in two key areas. The first is that the buildup of charge on the inside of the tube leads to decreased ions transmission compared to resistive glass capillary inlet tubes.⁹ The second is the speed at which the inlet can be electrically switched between positive and negative ion modes.

Metal tubes and orifices do not have the switching time limitations of the glass tubes, but cannot support a voltage drop, which means the two sides must be at the same potential. This can complicate the post capillary ion-neutral atom separation process.

7. Proposed Actions to Develop Possible Substitutes

7.1. Technologies for Lead Substitution

The lead in the lead silicate glass is the unique component that allows the glass to be made conducting. There is no other known formulation of glass that can be made to have a conducting surface layer using the glass itself as the conductor.

7.2. Atomic Layer Deposition as an Alternative to Reduced Lead Glass

Photonis has been pursuing the evaluation and development of ALD-coated MCP technology since 2010, both on its own and in collaboration with other organizations who are focused on ALD MCP technology such as Arradance LLC, Beneq Inc., and Incom Inc. This work is continuing in these organizations and at other locations. While there are many examples of successful production of functioning devices being made using ALD, they are still in the process of being fully characterized, and their behavior in the many applications where MCPs and CEMs are used is not fully known.

The unique properties of MCPs include:

- High amplification (10,000 – 10,000,000)
- Low noise (<5 counts/s·cm²)
- Output waveforms with fast time response (full width at half maximum <1ns)
- Large area detection (~100cm² or larger)
- Compact profile (<1cm)
- Low power (<1mW/cm²)
- Uniform two-dimensional imaging with high spatial resolution (<10μm)

Alternate detectors do not possess all these properties, but alternate technologies for creating MCPs have the potential to eventually replace the need for lead-glass MCPs.

The use of ALD technology to make sufficiently uniform electron emissive layers is reasonably well characterized due in part to the compatibility of Al₂O₃ process with the technique. The deposition of uniform resistive layers over the entire surface of millions of high-aspect ratio channels is still under development. Based on the progress made in the last ten years of

published results and the projected future of ALD development¹⁷ we estimate that it will likely be at least an additional 5 years before this process is sufficiently reliable for commercial manufacturing of MCPs as particle detectors.

The use of ALD MCPs suitable for imaging applications (including image intensifier tubes used in night vision equipment) could take significantly longer to develop, since small defects in the channel shapes can produce features that make the image produced by the MCP unusable and the uniformity of the coating will also impact image quality.

The widespread implementation of ALD for manufacturing MCPs may be slowed by active patents that broadly restrict ALD MCPs¹⁰.Error! Bookmark not defined.

8. Justification According to Article 4(1)(a)

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

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

☒ Authorisation

☒ SVHC

☐ Candidate list

☐ Proposal inclusion Annex XIV

☐ Annex XIV

☐ Restriction

☐ Annex XVII

☐ Registry of intentions

☐ Registration

- 2) Provide REACH-relevant information received through the supply chain.

Name of document: NONE

(B) Elimination/substitution:

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

☐ Yes. Consequences? _____

☒ No. Justification: No substitutes that meet all requirements exist.

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

☐ Yes.

☐ Design changes: _____

☐ Other materials: _____

☐ Other substance: _____

☒ No.

Justification: No substitutes that meet all requirements exist.

3. Give details on the reliability of substitutes (technical data + information): see above
 4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
 - 1) Environmental impacts: N/A
 - 2) Health impacts: N/A
 - 3) Consumer safety impacts: N/A
- ⇒ Do impacts of substitution outweigh benefits thereof?
Please provide third-party verified assessment on this: N/A

(C) Availability of substitutes:

- a) ~~Describe supply sources for substitutes: _____~~
- b) ~~Have you encountered problems with the availability? Describe: _____~~
- c) ~~Do you consider the price of the substitute to be a problem for the availability?~~
☐ Yes ☐ No
- d) ~~What conditions need to be fulfilled to ensure the availability? _____~~

(D) Socio-economic impact of substitution:

- ⇒ What kind of economic effects do you consider related to substitution?
- ☐ ~~Increase in direct production costs~~
- ☐ ~~Increase in fixed costs~~
- ☐ ~~Increase in overhead~~
- ☐ ~~Possible social impacts within the EU~~
- ☐ ~~Possible social impacts external to the EU~~
- ☐ ~~Other: _____~~
- ⇒ ~~Provide sufficient evidence (third-party verified) to support your statement: _____~~

8.1. Reliability of Alternate Resistive and Emissive Films

8.1.1. Atomic Layer Deposition MCPs

It is standard practice in ALD coatings to use inert barrier coating layers to isolate the coatings from the substrate. Research at Photonis and elsewhere has shown however that the performance of the resistive and emissive films varies considerably between substrate materials despite the presence of relatively thick (30nm) barrier layers. More sophisticated barrier layers composed of multiple types of barrier materials (called nano-laminate barriers) have also been explored but not significantly in the context of microchannel plates. The observed substrate dependence of final microchannel plate properties is not consistent with patent claims of substrate independence for ALD films Error! Bookmark not defined.

The overwhelming majority of the ALD films currently used for making microchannel plates have a negative temperature coefficient of resistivity (TCR), which results in the resistance of the films decreasing with increasing temperature. A high negative TCR limits the temperature range over which the conductive film can safely operate by lowering the temperature at which the film will

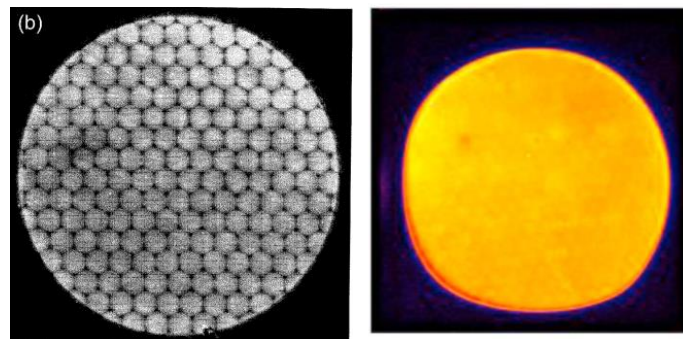
go into thermal runaway. The TCR values of the ALD coating reported in the literature are significantly higher ($1-4 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$)² than those of the conducting layer of lead glasses ($0.6-1 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$). In some cases this has forced the use of cryogenic cooling to produce functional devices². In US patent 8969823B2⁸ the authors cite positive temperature coefficients for films that are made from a stack of alternating layers of insulating and conducting forms of a metal oxide which may be a method of controlling this issue

While ALD demonstrates remarkable thickness uniformity for some films, resistance uniformity, particularly uniformity down long channels and uniformity across millions or tens of millions of parallel channels is more difficult to achieve. This can result in current instabilities¹¹. ALD-coated conductive and emissive films are not always stable to further thermal processing which is necessary for a large number of MCP applications.



Figure 10: Typical MCP gain uniformity. There is no visible fixed pattern noise in the image.

The demonstrated gain uniformity of ALD-coated MCPs is not as good as a lead glass MCP (see Figure 10 and Figure 11) and could not be used as part of the image intensifier that is the enabling technology in most night vision technology.



*Figure 11: Gain uniformity from ALD-coated borosilicate glass MCPs. The image on the left is for a 20 μm channel MCP from patent# **Error! Bookmark not defined.** The image on the right is from a 33mm diameter 6 μm channel microchannel plate that was considered the state of the art for ALD-coated MCPs at the time of it was published² The boundaries of the hexagonal multifibre boundaries are visible in both of the images indicating image distortion in these areas. While the image from the later material is much improved it is not of sufficient quality to be used for imaging.*

While there are many researchers who have successfully made functional ALD-coated MCPs, currently the only company that Photonis is aware of having ALD-coated MCPs as a commercial offering is Incom¹². The Incom technology is derived from work performed at Incom and in collaborations with Benec¹³ and Argonne National Lab**Error! Bookmark not defined.** Hamamatsu Inc. and Photech, who have licensed the technology from Arradance since 2015¹⁴ do not currently offer ALD MCPs on their corporate web sites. Photonis is planning to license the Arradance technology in 2020, but views the technology as still being in the research and

development phase and incapable of displacing the production requirements of present day MCPs.

8.1.2. Atomic Layer Deposition on Channel Electron Multipliers

Hamamatsu has presented performance data for an ALD coated ceramic CEM that they have given the name CERARION¹⁵. Photonis has also used ALD to create functional CEMs¹⁶ as part of its research and development programs. These detectors demonstrate that ALD can be used to make CEMs, but the full range of characteristics for this type of CEM have not yet been studied.

8.1.3. Atomic Layer Deposition on Resistive Glass Tubes

Photonis has ongoing development projects focused on the use of ALD coating to provide the resistive film for resistive glass capillary inlet tubes. This work was done both using resources within Photonis and in collaboration with other researchers at Arradiance LLC. The ALD coating of resistive glass capillaries inlet tubes has produced tubes with poor resistance uniformity along the length of the inlet tube (See Figure 12). The films produced by ALD deposition on capillary inlet tubes were not stable over the broad temperature range (350°C-450°C) and eventually failed and became non-conducting after a few hours at temperatures >200°C.

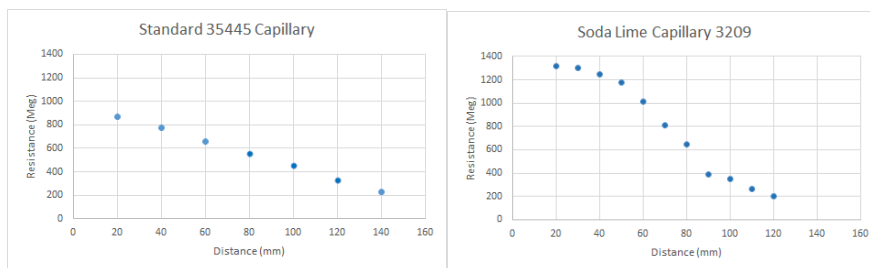


Figure 12: Measured resistance uniformity in lead-glass capillary inlet tube (left) and ALD-coated soda lime glass capillary inlet tube (right) measured as a function of the distance down the capillary tube. The lead glass capillary has uniform resistance down its length which is indicated by the curve being a straight line. The ALD coated glass has non-uniform resistance which appears on this graph as a curved line.

Presently there is no established ALD process for successfully applying a uniform resistive coating on the inner surface of any of the most common capillary inlet tube geometries.

8.2. Reliability of Alternate Detector Technologies

Discrete dynode electron multipliers are widely used as alternatives to channel electron multipliers and can be used to replace microchannel plates when two-dimensional imaging is not required and the input area is not too large. The drawback of this type of detector is typically its size. The larger size precludes the use of DDMs in all applications particularly ones where high magnetic fields are present.

Solid state detectors such as photodiodes, PIN diodes, and CCD-style detectors do not have the high gain of MCPs thus affecting the sensitivity of the devices that they would be used in. They are damaged when measuring ions, which is a very typical application for MCPs and CEMs. They are also susceptible to radiation damage, which is a critical factor in space applications.

8.3. Environmental Impact of Substitutes

One of the key environmental impacts of ALD is the large quantity of ALD precursor waste produced for each atomic layer of material and the large volume of wasted exhaust gases. A

principal emission of the ALD processes used for the making ALD MCPs is methane, which is a greenhouse gas. The smaller batch size of the typical ALD process as compared to the hydrogen reduction process used for lead glass would require many more tools operating to produce the same number of MCPs further compounding these effects

The waste stream of these ALD processes will also produce nanoparticles of Al_2O_3 . The fact that these nanoparticles would be airborne increases the likelihood of broader environmental impact when compared to solid or liquid waste streams. The effects of nanoparticles of human health have not been studied sufficiently to estimate human risk at this time¹⁷.

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