Polyurethane products

Information to support the review of Annex A to the Minamata Convention

1. Category of mercury-added product[1]	☐ Batteries ☐ Switches and relays ☐ Lamps ☐ Cosmetics	☐ Pesticides, biocides and topical antiseptics ☐ Non-electronic measuring devices ☒ **Others *(polyurethane products)***
2. Further description of the product (if any)	The primary use of mercury catalysts has been in the production of polyurethane coatings, adhesives, sealants and elastomers (referred to as CASE applications). With regard to the latter, mercury-catalyzed polyurethane elastomers consist basically of cast PU elastomers and PU elastomer coatings. According to "Mercury use in products and applications and the fate of mercury already circulating in society" (Cowi/Concorde, 2008): Page 113: *Nowadays organic mercury compounds remain a very important catalyst in one particular niche, which is the production of polyurethane elastomers, in particular for PU elastomers that are cast (poured or injected into a mould) into sometimes complex shapes, or sprayed onto a surface as insulation, corrosion protection, etc.*	

[1] Dental amalgam is subject to a separate intersessional process as specified in Decision MC-3/2.

3. Information on the use of the product	According to "Mercury use in products and applications and the fate of mercury already circulating in society" (Cowi/Concorde, 2008): Page 115: *Like any catalyst used in PU elastomer systems,* ***the mercury catalyst is incorporated into the polymer structure and remains in the final product.*** *Over time – and accelerated by exposure to harsh environments, UV, abrasion, etc. – the polymer structure breaks down and mercury is released.* *Mercury in PU products already attracted attention some years ago. According to an investigation by the Minnesota (USA) Department of Health, some PU elastomer flooring manufactured from about 1960 through at least 1980 contained up to 0.1% mercury in phenylmercuric acetate or other organo-mercuric salts that were used as catalysts. Ambient mercury concentrations in school gyms ranged from 0.13 to 2.9 µg/m3, and in 5 of 6 gyms was above the RfC level of 0.3 µg/m3 established by US EPA as the exposure level below which no adverse health effect is expected. A separate investigation in Ohio (USA) showed that PU elastomer floors in schools also emitted mercury is excess of the 0.3 µg/m3 RfC level.* Page 117: A brochure published in 2006 by a leading provider of mercury-free catalysts for PU elastomer production summarised the situation – even partly exaggerated – as follows: *"Over recent years, growing concern over the prospective toxicity of catalysts currently used, has led to renewed interest in alternative, and safer products. Noxious substances are becoming a growing issue worldwide and a total ban on mercury is expected in Europe in the near future.* ***The presence of heavy metals in the final product*** *has a big impact on its recyclability, preventing polyurethane based elastomers being used in certain market segments."*
4. Information on the availability of mercury-free (or less-mercury) alternatives	According to "Mercury use in products and applications and the fate of mercury already circulating in society" (Cowi/Concorde, 2008): Page 117: *Tin and amine catalysts are alternatives to Hg catalysts for some PU elastomer applications, titanium and zirconium compounds have been introduced for others, while bismuth, zinc, platinum, palladium, hafnium, etc., compounds are marketed for still others.* *… perfectly viable substitutes to mercury catalysts are already in use for over 95% of PU elastomer systems, and have been in use for many years.*

5.(i) Information on the technical feasibility of alternatives	According to "Mercury use in products and applications and the fate of mercury already circulating in society" (Cowi/Concorde, 2008): Page 117: *… known mercury-free catalysts could be used for nearly all elastomer applications, but some reduction in the key performance characteristics of activity, selectivity, catalyst lifetime, etc., may have to be accommodated until the best system is identified for a given application.* *As suggested, a large number of Hg-free catalysts for PU elastomers have been developed as alternatives to mercury – the large number reflecting the fact that there does not appear to be a "drop-in" substitute for mercury catalysts that can be used in so many different systems, that confers similarly desirable curing properties, and that is so forgiving and easy to adjust to the needs of the user. Although titanium alkoxide catalysts, for example, provide a rapid polyurethane cure reaction, they may not provide the desirable gel time and cure profile. In many cases the system may have only a short gel time so that the polyurethane mixture tends to gel before it can be cast into its final shape. In other cases where a short gel time is acceptable, the polyurethane system may not achieve a satisfactory degree of cure within a reasonable time, resulting in finished articles that lack the necessary strength or other physical properties. A lot of research into mercury-free catalysts is going on in this sector, which is well known for frequent innovations.*
5.(ii) Information on the economic feasibility of alternatives	According to "Mercury use in products and applications and the fate of mercury already circulating in society" (Cowi/Concorde, 2008): Page 117: *The cost of most mercury-free catalysts is quite competitive with the typical mercury catalyst cost, and even more so if one takes account of waste disposal costs, environmental and other customer concerns.*
6. Information on environmental and health risks and benefits of alternatives	
7. If any, additional information being submitted on mercury-added products pursuant to Article 4.4 of the Convention not addressed above (e.g. manufacture, general trade information, etc.)	According to "Mercury use in products and applications and the fate of mercury already circulating in society" (Cowi/Concorde, 2008): Page 9: *In particular, the large consumption of mercury catalysts for production of polyurethane elastomers,* ***where the catalysts end up in the final product in concentrations of about 0.2% mercury****, is a new finding that calls for attention.* Page 10: *…dental amalgams and mercury compounds in polyurethane account for more than 80% of the total [mercury]* ***accumulated in products*** *in the EU.*

8. Other relevant information pursuant to Decision MC-3/1	According to https://en.wikipedia.org/wiki/Polyurethane#Catalysts: The methods of manufacturing polyurethane finished goods range from small, hand pour piece-part operations to large, high-volume bunstock and boardstock production lines. Regardless of the end-product, the manufacturing principle is the same: to meter the liquid isocyanate and resin blend at a specified stoichiometric ratio, mix them together until **a homogeneous blend** is obtained, dispense the reacting liquid into a mold or on to a surface, wait until it cures, then demold the finished part. In the formation of polyurethane, mercury catalysts are used in the reaction between a polyol and an isocyanate component. During the reaction, mercury catalysts enable a long induction period, followed by a rapid reaction for curing the product. The catalyst tends to be present in the polyol component. **The mercury catalyst is integrated into the polymer and remains present in the final polyurethane product** (Norwegian Climate and Policy Agency, 2010). **In light of the information presented here, polyurethane products should be listed in Annex A as mercury-added products that should be phased out according to a specific timetable.**
9. References	ChemEurope, 2019. *Polyurethane.* Available at: https://www.chemeurope.com/en/encyclopedia/Polyurethane.html. COWI/Concorde 2008. *Options for reducing mercury use in products and applications, and the fate of mercury already circulating in society.* Available at: http://ec.europa.eu/environment/chemicals/mercury/pdf/EU_Mercury_Study2008.pdf Norwegian Climate and Policy Agency, 2010. *Annex XV Restriction Report: Proposal for a Restriction*. Available at: https://echa.europa.eu/documents/10162/13641/annex_xv_restriction_report_phenylmercury_compounds_en.pdf. https://en.wikipedia.org/wiki/Polyurethane#Catalysts

Information to support the review of Annex B to the Minamata Convention

1. Category of manufacturing process in which mercury or mercury compounds are used	☐ Chlor-alkali production ☐ Acetaldehyde production in which mercury or mercury compounds are used as a catalyst ☐ Vinyl chloride monomer production ☐ Sodium or Potassium Methylate or Ethylate ☒ **Production of polyurethane using mercury containing catalysts** ☐ Others *(Please specify:_____)*
2. Further description of the process (if any)	Polyurethanes are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives. Polyurethanes exist in a variety of forms, including flexible foams, rigid foams, chemical-resistant coatings, specialty adhesives and sealants, and elastomers. In the formation of polyurethane, mercury catalysts are used in the reaction between a polyol and an isocyanate component. During the reaction, mercury catalysts enable a long induction period, followed by a rapid reaction for curing the product. The catalyst tends to be present in the polyol component. **The mercury catalyst is integrated into the polymer and remains present in the final polyurethane product** (Norwegian Climate and Policy Agency, 2010).
3. Information on the manufacturing activities using the process (incl. amount of mercury or mercury compounds used, production amount, etc.)	According to https://en.wikipedia.org/wiki/Polyurethane#Catalysts: The methods of manufacturing polyurethane finished goods range from small, hand pour piece-part operations to large, high-volume bunstock and boardstock production lines. Regardless of the end-product, the manufacturing principle is the same: to meter the liquid isocyanate and resin blend at a specified stoichiometric ratio, mix them together until **a homogeneous blend is obtained, dispense the reacting liquid into a mold or on to a surface, wait until it cures, then demold the finished part**.
4. Information on the availability of mercury-free (or less-mercury) alternatives	
5.(i) Information on the technical feasibility of alternatives	

5.(ii) Information on the economic feasibility of alternatives	
6. Information on the environmental and health risks and benefits of alternatives	
7. Other relevant information pursuant to Decision MC-3/1	Based on the information provided in this document concerning both Annexes A and B, "polyurethane production with mercury catalysts" has been mistakenly listed as a manufacturing process in which mercury compounds are used. While mercury compounds are in fact used in manufacturing some polyurethane products, Annex B assumes that the mercury or compounds do not remain in the finished product. In fact, if and when mercury compounds are used as a catalyst in polyurethane products, these compounds remain in the final polyurethane product, which for this reason **polyurethane products should not be listed in Annex B, but instead be listed in Annex A as mercury-added products**.
8. References	ChemEurope, 2019. *Polyurethane.* Available at: https://www.chemeurope.com/en/encyclopedia/Polyurethane.html. COWI/Concorde 2008. *Options for reducing mercury use in products and applications, and the fate of mercury already circulating in society.* Available at: http://ec.europa.eu/environment/chemicals/mercury/pdf/EU_Mercury_Study2008.pdf Norwegian Climate and Policy Agency, 2010. *Annex XV Restriction Report: Proposal for a Restriction*. Available at: https://echa.europa.eu/documents/10162/13641/annex_xv_restriction_report_phenylmercury_compounds_en.pdf. https://en.wikipedia.org/wiki/Polyurethane#Catalysts