1st Stakeholder Consultation – Questionnaire for Indium Phosphide

1. Applications in which indium phosphide is in use

In the display industry, indium phosphide is currently in use within the colour converting component of liquid crystal display (LCD) backlit devices, including televisions and monitors. This technology, which utilises semiconductor quantum dots (QDs) as a colour converting material, has previously been discussed in relation to RoHS Exemption Requests 2013-2 and 2013-5.

We believe that the use of InP in QDs for displays is currently one of the largest areas of use for this material in the EU. However, we believe that it is also used in a number of other specialised electronics applications. We also anticipate that the use of QDs in specialised LED lighting products will increase in the next few years.

There are three potential strategies to integrate QDs into conventional LCD backlights: “on-chip”, “on-edge” and “on-surface”, as defined by Coe-Sullivan *et al.* (**Figure 1**).[1]

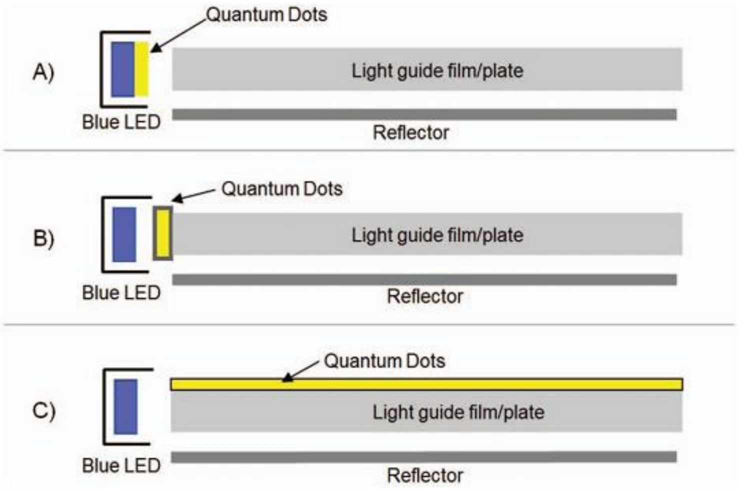

Figure 1: Integration strategies for QD-BLUs for LCD TV: A) on-chip, B) on-edge, and C) on-surface.

With on-chip geometry, the QDs are deposited directly onto the LED surface and are encapsulated within the LED package. The on-edge configuration has the QDs incorporated into a remote component, such as a capillary, that is situated in close proximity to the LED chips. Finally, on-surface configuration incorporates QDs into a remote film that covers the entire screen area. The on-chip design uses the least amount of QD material but is difficult to achieve in practice due to the thermal degradation of the QDs that are in direct contact with the LED source. In contrast, the on-surface design would have the highest QD usage but would operate near to room temperature. The on-edge design is a compromise between temperature (on-chip) and quantity (on-surface) conformations. Current QD display devices on the market utilise the on-surface configuration.

The first QD display devices to reach the market used cadmium-based QDs, such as those based on CdSe. InP QDs are currently used as a safer alternative to Cd-based QDs. The InP QDs are typically over-coated with one or more “shell” layers of another semiconductor material, such as ZnS (as shown in **Figure 2**), then integrated into a resin matrix to form a film.

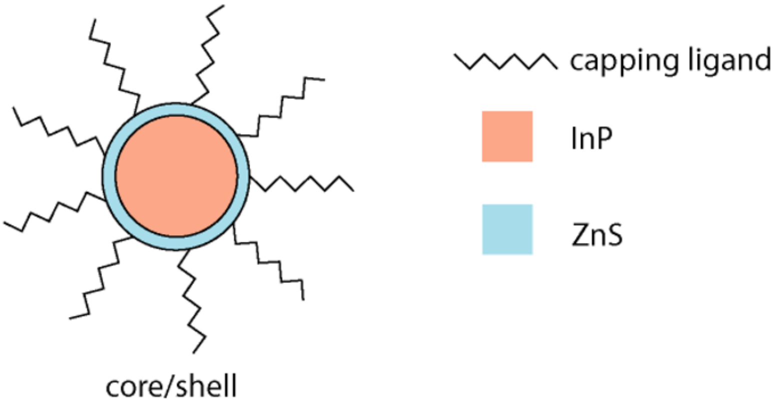

Figure 2: Structure of a quantum dot comprising an InP core, a ZnS shell, and capping ligands.

We understand that product lines utilising InP-based QDs include Samsung's QLED range of TVs and monitors. In addition we understand that the Vizio P Series and Hisense U9A and NU9700 ranges of TVs include InP QDs in combination with Cd-based QDs.

Substitution of InP is currently possible with semiconductor alloys containing indium and other elements, such as Nanoco's unique CFQD® quantum dot materials. Alternative materials are being investigated (according to published papers and public statements), such as $CuInS_2$ and halide perovskite QDs, but these materials do not currently provide the required performance for commercial applications (as discussed below). Alternatively, display technologies utilizing InP QDs could replace existing technologies such as organic-light-emitting-diode (OLED) display technology. InP QDs could also be included in display technologies such as QDEL (structure similar to OLED), QD colour conversion layers (similar to colour filter) and as colour conversion material in uLED and mLED displays. However these are all still in the development phase and have not yet been launched as commercial products. Technologies newly utilising QDs still face competitive market forces and must offer sufficient optical performance to meet and exceed industry standards.

Based on Article 6(1) RoHS, when amending Annex II RoHS by adding a new substance, the Commission should take "special account" of, among others, *"whether a substance could be replaced by substitutes or alternative technologies which have less negative impacts".* As elaborated in more details below, no substitutes are currently in commercial use – except for Cd-based QDs which have far greater negative impacts. Thus, a potential InP restriction would appear to be premature.

2. Quantities and ranges in which indium phosphide is in use

According to an IHS market research report,[2] 11.6 million Cd-free displays are expected to be sold in 2018, worldwide. The same market research predicts that 10.9 Mm^2 of display area of QD displays will be sold in 2018.[3] Based on Nanoco analysis of commercially available InP-based display products, the amount of InP per m^2 of display area is estimated to be up to 0.03 g. Thus, assuming that 100 % of QD displays sold are made with InP QDs, approximately 0.3 tonnes per year of InP would be required for this application, worldwide. Forecasts predict that around 20 % of global 4K TV sales in 2018 will be in Europe,[4] equating to a requirement of around 0.06 tonnes per year of InP for this application in Europe.

As the technology becomes more mature and applicable to a number of different display formats (*e.g.* mobile phones, *etc.*), the number of display units being sold employing the technology is set to increase (predicted to reach 23.7 million units in 2021),[2] yet at the same time technology is being developed to decrease material usage. For example, micro-LED technology, wherein QDs would be used "on-chip", could potentially reduce the amount of QDs required per display by an order of magnitude. Overall, expectations are that material usage will increase in the short-term (3 – 5 years), but then decrease thereafter as new technologies with lower material consumption are introduced.

3. Potential emissions in the waste stream

Displays screens containing InP QDs could be collected as consumer equipment (for TVs) or as IT and telecommunications equipment (for monitors). The plastic components, including the QD film, would most likely either be shredded and incinerated, or taken to landfill. When InP-based QDs are burned or dissolved, the indium and phosphorus are separated and form different compounds, such as indium oxide and phosphates, which are not classified as carcinogenic. Therefore the hazard is already neutralised before exposure can occur. If it became commercially viable to do so, recycling schemes could be set up to recover the indium content. It is worth noting that such schemes would be made much more difficult to establish if the use of CdSe QDs in film continues, as these films are visually very similar and are not clearly marked to indicate their hazardous content.

4. Substitution

InP QD technology has been investigated and developed over a number of years as a safer alternative to Cd-based QDs. To achieve sufficient optical performance, it would be difficult to substitute InP for another material that does not contain far more hazardous cadmium. One alternative is Nanoco's CFQD® quantum dot material, which is an alloy of indium and other elements. The use of this material by other manufacturers would be possible based on a licence that would be granted by Nanoco by commercial agreement. Other materials that have been investigated as substitutes include I-III-VI$_2$ nanoparticles, such as $CuInS_2$, and halide perovskite QDs, in particular $CH_3NH_3PbX_3$ and $CsPbX_3$ (X = Cl, Br, I). However, $CuInS_2$ nanoparticles typically have a broad emission full-width at half-maximum (FWHM; typically 80 – 120 nm), which is not suitable for display applications. While halide perovskite QDs have a narrow FWHM (typically 20 – 40 nm) and high photoluminescence quantum yield, there are issues relating to the stability of these materials. Further, the perovskite materials that have been investigated to date typically utilise toxic lead. Thus, it is uncertain whether halide perovskite materials will ever be suitable to replace InP QDs in display applications. Gallium arsenide (GaAs) has a similar band gap to InP and has been developed as a possible substitute for some applications where the material is formed in a layer using CVD or similar processes. However, the formation of colloidal QDs using GaAs has proved to be more difficult than using InP and the optical performance characteristics have been significantly inferior. It might be possible to develop GaAs QDs in future, but it would take many years of research and this is currently not a significant area of focus for either academic or commercial research teams.

Alternative display technologies may also be adopted. Most LCDs already use inorganic phosphors. Inorganic phosphors are cheap and relatively efficient, but are not able to give the enhanced colour reproduction increasingly demanded by consumers and using increased colour filtration to improve their colour performance leads to significantly greater energy consumption. OLED displays are well established, but they are much more expensive to manufacture in large sizes, tend to have higher power consumption and cannot achieve the same brightness as LCD displays.

Despite the fact that InP is a safer alternative to Cd-based QDs (Cd being a restricted substance in Annex II RoHS), Cd continues to be used in display technology based on the perpetuated Annex III RoHS 39(a) exemption for *“Cadmium selenide in downshifting cadmium-based semiconductor nanocrystal quantum dots for use in display and projection lighting applications (< 0,2 µg Cd per mm2 of display screen area)”* that remains valid until the end of October 2019.

Furthermore, two applications for further extension of this RoHS Cd exemption have been submitted in April 2018 by two companies. The main argument of the applicants is that Cd-free QD technology that would meet the current colour quality and energy consumption performance of cadmium QDs is still not available and that *“the performance of Cd-free quantum dots (based in InP) is expected to reach by 2020”*.[5]

This confirms that InP is indeed increasingly considered by the display industry as a substitute for Cd. Thus, if InP is included in Annex II RoHS and hence restricted in display technology, the Cd Industry would have a good case that the Cd exemption must continue as the main alternative has been restricted. This would lead to an absurd situation where InP would be replaced by Cd which is a more toxic substance for both human health and the environment. This would be against the objective set out in Article 1 RoHS, *i.e.* “*contributing to the protection of human health and the environment, including the environmentally sound recovery and disposal of waste EEE”.*

5. Socio-economic impact of possible restriction

As QD display technology matures, it is expected to become more affordable to the consumer. However, if QD manufacturers are no longer able to use InP, there is a risk that there will be a market gap until new materials or technologies are developed, during which display technology would not deliver expected performance. These delayed benefits would be passed on to the consumer.

Further, if InP is to be replaced with alternative materials according to the current state of art, this could lead to reduced performance, which may require higher operating costs if the device efficiency is reduced. If InP QDs were substituted with CdSe QDs then device performance and efficiency could be maintained, but at the expense of a massive increase in harm to the environment and risks to workers and consumers. This would be in direct opposition to the principles of the RoHS regulations.

6. Further information and comments

InP QDs were originally developed as an alternative to toxic Cd-containing QDs for display devices. Considerable investment, in terms of both time and money, has gone into the development of InP QDs to make them a commercially viable substitute for Cd-based QDs for display applications. Studies into the toxicity of InP-based QDs have concluded the material to be a safer alternative to Cd-based QDs.

Brunetti *et al.* compared the cytotoxicity of CdSe/ZnS and InP/ZnS QDs *in vitro* and *in vivo* (Drosophila).[6] It was concluded that InP/ZnS core/shell QDs provided a “safer alternative” to CdSe/ZnS QDs for biological applications. Cd^{2+} ions were shown to leach from the core of the QDs, despite a two-monolayer ZnS shell. Since an almost identical amount of In^{3+} ions leached from the InP/ZnS QDs, the results suggest that In-based QDs have a much lower intrinsic toxicity than Cd-based QDs.

Soenen *et al.* studied the cytotoxicity of InP/ZnS QDs,[7] using the Alamer Blue assay. No increase in cytotoxicity was observed up to at least 7 days, suggesting the high chemical stability of InP-based QDs. This was contrasted to Cd-based QDs, which have previously been reported to degrade under endosomal pH conditions, suggesting that the differences between the crystal structures of Cd-free and Cd-based QDs may influence their cytotoxicity, with some Cd-free QDs being very robust against environmental factors such as oxidation.

Looking specifically at InP-based QDs, the *in vivo* toxicity of InP/ZnS QDs was studied over an 84-day period in BALB/c mice.[8] During the evaluation period, there was no observable change between the body weight of the QD-treated mice and that of control mice. Histological analysis showed no damage to the major organs, while haematology and biochemical analysis showed no changes compared to the control mice. Overall, it was concluded that the QD formulation did not result in *in vivo* toxicity over the evaluation period.

Summary

In summary, we feel that the substitution of InP QDs in display applications is not currently scientifically or technically practicable and therefore InP should not become a restricted substance under RoHS. Further, we believe that restricting the use of InP in display and lighting applications would have an overall detrimental effect on the environment by encouraging the use of alternative materials based on toxic cadmium.

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[1] S. Coe-Sullivan, W. Liu, P. Allen and J.S. Steckel, *ECS J. Solid State Sci. Technol.*, 2013, **2**, R3026

[2] IHS Wide Color Gamut & Quantum Dot Display Market Tracker – H1 2017

[3] IHS

[4] IHS Markit, 2017

[5] Application by Najing Technology Co. Ltd., page 8

[6] V. Brunetti, H. Chibli, R. Fiammengo, A. Galcone, M.A. Malvindi, G. Vecchio, R. Cingolani, J.N. Nadeau and P.P. Pompa, *Nanoscale*, 2013, **5**, 307.

[7] S.J. Soenen, B.B. Manshian, T. Aubert, U. Himmelreich, J. Demeester, S.C. De Smedt, Z. Hens and K. Braeckmans, *Chem. Res. Toxicol.*, 2014, **27**, 1050

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