

This is the clarification response from 3M Optical Systems Division (OSD) for Exemption Request No. 2013-5. Exemption for “Cadmium in LCD Quantum Dot Light Control Films and Components”

### **Questions sent to 3M OSD for clarification:**

1. 3M explains that quantum dots are semiconductors whose electronic characteristics are closely related to the size and shape of the individual crystal. The exemption request refers to cadmium in quantum dots films which are components of liquid crystal display (LCD) systems.
  - a. Please describe more precisely how the cadmium is used in semiconductors (e.g. II-VI semiconductor) and bound in the quantum dot technology, regarding various areas of application for instance, in control films<sup>1</sup>, glass tube, polymer matrix, core, shell or different quantum dot sizes etc. Please provide some detailed figures for each technology for a better understanding.

### **3M OSD Response:**

The Öko-Institut together with Fraunhofer IZM has requested clarification on cadmium bound in the quantum dot technology in various applications, including in glass tube technology. Glass tubes are commonly known as quantum rails; however that type of technology is different from Quantum Dot (QD) light control films. Quantum rail technology has not been developed by, and is not manufactured by 3M. So no definitive description on where the cadmium resides and exactly how the dots are deployed can be provided for the quantum rails. 3M OSD will describe the quantum dot light control film technology.

Question 1(a) also asks about "areas of application" including "polymer matrix, core, shell or different quantum dot sizes etc." The polymer matrix, core, shell and different quantum dot sizes are all aspects of the quantum dot-enabled control film for LCD applications. 3M manufactures a Quantum Dot Enhancement Film (QDEF). The film utilizes the polymer matrix, core shell, and different quantum dot sizes. The cadmium is bound within this polymer matrix. The sections i to iv answer the questions in 1a:

- i. How the cadmium is used in semiconductors (e.g. II-VI semiconductor): These quantum dots(QDs) are II-VI semiconductor particles that down convert blue light

---

<sup>1</sup> This technology is already well described.

from an LED to green or red. These color converting materials contain cadmium-selenide.

- ii. How the cadmium is used in Quantum Dots: The cadmium containing quantum dots (QDs) used for LCD applications are typically CdSe/ZnS<sup>2</sup> core/shell crystals, as stated in Section 3.3 of the exemption dossier and as shown in Figure 1. These quantum dots are the semiconductors particles, and the cadmium is bound in the core structure of the dot (in the form of CdSe particles). The quantum dots have the same core/shell form regardless of size, with the core/shell structure scaling proportionally with size.

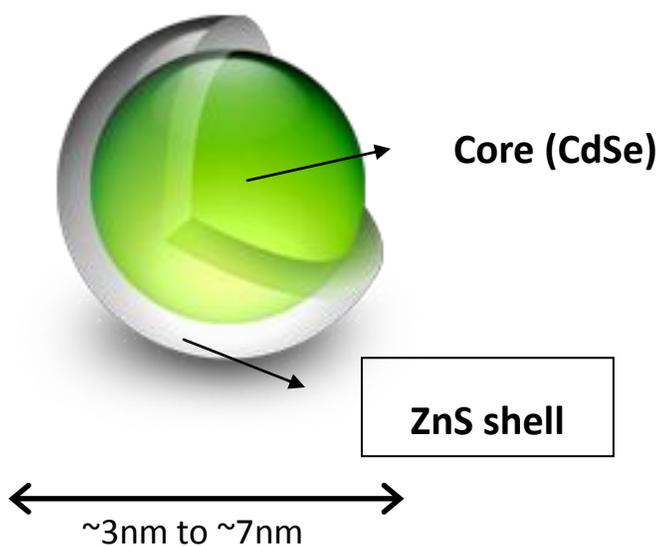
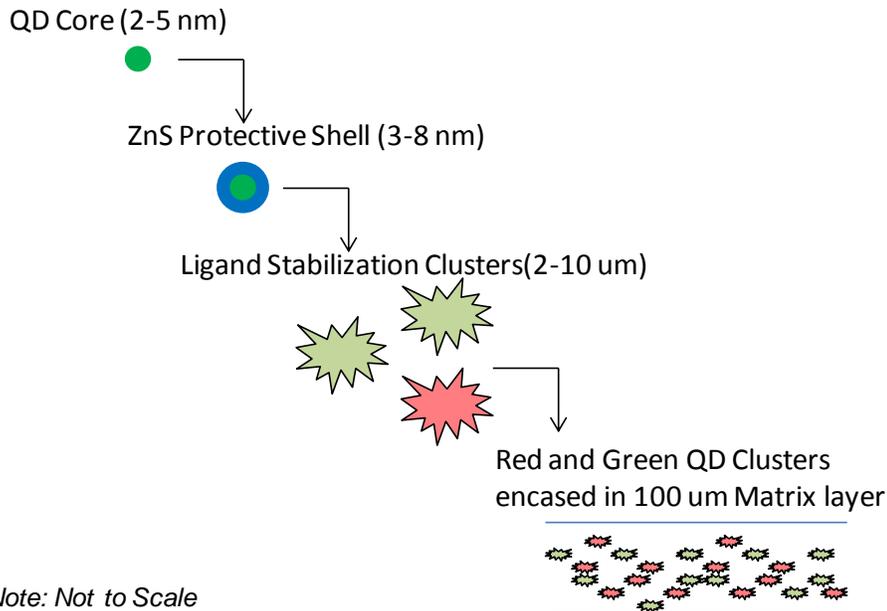


Figure 1 - CdSe/ZnS core/shell crystal structure of quantum dots

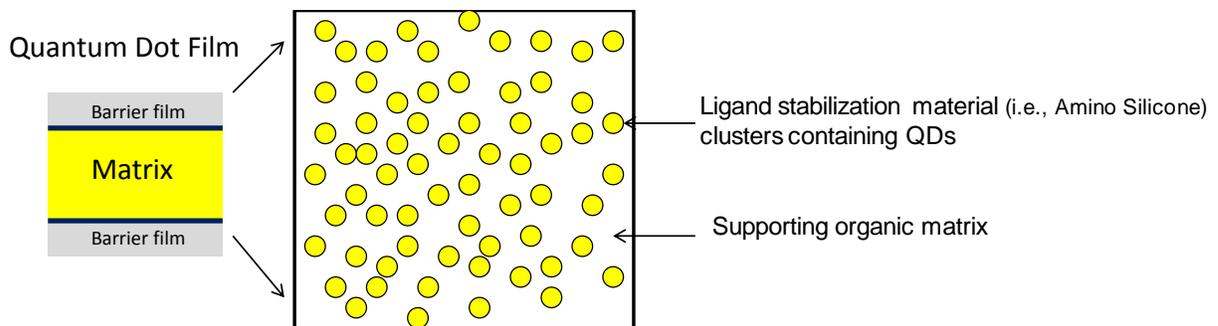
- iii. How the Cadmium is used in the Polymer Matrix: The polymer matrix is the supporting organic matrices for the cadmium containing semiconductor crystals (the QD explained in ii above) for films used in an LCD Display as shown in Figure 2. First the QDs are placed into a ligand stabilization material and then this is mixed, to form an emulsion into a supporting organic matrix to form QD clusters. Figure 3 illustrates the QD cluster geometry. It should be noted that the cadmium still resides only in the quantum dots, and nowhere else in the construction. Response b directly below also addresses the use of cadmium. This explanation is provided in Section 3.3 of the

<sup>2</sup> CdSe = cadmium selenide, ZnS = zinc sulphide

exemption dossier .



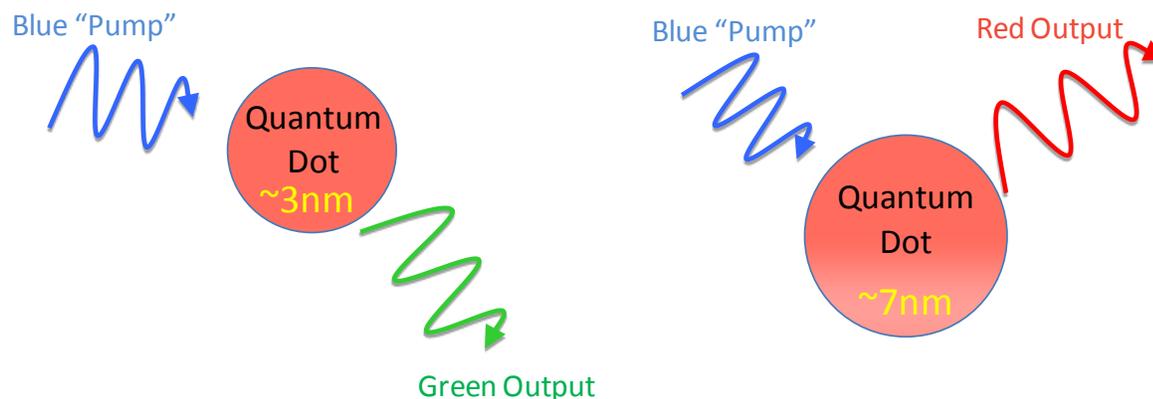
**Figure 2** - CdSe/ZnS core/shell crystal structure QDs are put into ligand stabilization materials and mixed as an emulsion into supporting organic matrices, forming QD clusters.



**Figure 3.** QD cluster geometry for control films.

- iv. How the Cadmium is used in Quantum Dot Size: The size of the quantum dot used determines the color of the down converted light emitted. The larger the QD the longer wavelength the down converted emission. In the application of QDEF, blue light from the

LED is down (color) converted to either red or green light depending on the size of the quantum dot. As stated above, the quantum dots have the same core/shell form regardless of size, with the core/shell structure scaling proportionally with size. Refer to Figure 4.



**Figure 4.** Effects of quantum dots size on spectral output. Smaller QDs emit shorter wavelength light when exposed to a blue source.

- b. Could you please indicate the relation between your request for exemption on the one side and the existing exemptions (39) of Directive 2011/65/EU in Annex III on the other side?

### 3M OSD Response:

3M's currently available technology for Quantum Dot Enhancement Film (QDEF) fits the definition of exemption 39 because the film is used for color converting and is an integral part of an LED used in solid state illumination or in display systems (see figure 5).

To utilize exemption 39, 3M OSD would request revision to the existing exemption and that the expiration date to be extended 5 years to 2019. See additional details in the response to c below.

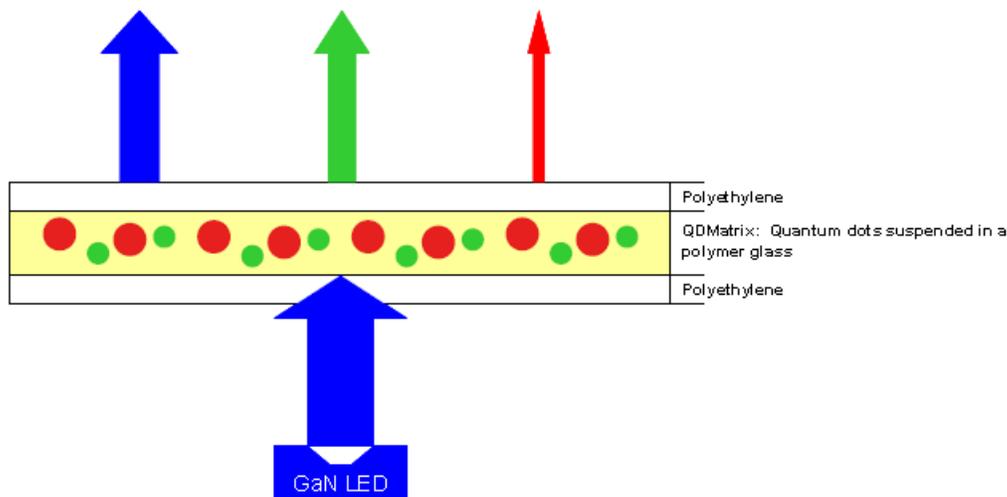


Figure 5 – Construction and functionality of the Nanosys material (Source Nanosys)<sup>3</sup>

However, the new exemption that 3M OSD is requesting will be for the QD film to be used as a color converter that is separate from the LED device. 3M desires the exemption specific to the quantum dots (QDs) used for LCD enhancement film not connected to LEDs. The new exemption would provide clarity that QDEF is in compliance with the RoHS directive. In addition, 3M would like the cadmium concentration of exemption 39 to be changed to  $<20 \mu\text{g}/\text{cm}^2$  of screen area to account for the new film technology.

- c. Would the application range and the existing exemption 39 lead to any difference for the wording of an exemption or would it be possible to formulate a general exemption for cadmium in quantum dots for LCD devices and/or light illumination applications respectively?

### 3M OSD Response:

Yes, 3M OSD would be open to continue to use exemption 39 if the wording was changed, and the expiration date was extended for 5 years to 2019. 3M OSD proposes the wording change to include film products used for color converting.

**Proposed 39 Exemption:** Cadmium in colour converting II-VI LEDs ( $<10 \mu\text{g Cd per mm}^2$  of light-emitting area) *and in light control films ( $<20 \mu\text{g of Cadmium /cm}^2$  of screen area)* for use in solid state illumination or display systems.

<sup>3</sup> (Dr. Otmar Deubzer, 2011) APPLICABILITY OF EXEMPTIONS 13 B AND 39 IN ANNEX III OF DIRECTIVE 2011/65/EU FOR THE USE OF CADMIUM IN NANOSYS MATERIAL, Fraunhofer IZM

- d. Are there other manufacturers, besides 3M, producing this application?

### 3M OSD Response:

3M OSD is the only company to offer a QD film for sale. 3M OSD is aware of one other company that currently makes, and is offering for sale, quantum rail technology that also uses quantum dots to improve LCD color performance. As discussed in response 1(a) above, glass tube/quantum rail is different from the QD film application.

2. Please describe the emissions in all the life stages of Cadmium in LCD through the production, use, and disposal or recycling of the LCD?

### 3M OSD Response:

The following provides an overview of the life stages of cadmium emissions through the production, use, and disposal. Section a is the Mining and Refining, Section b is the Manufacturing of both the quantum dots and the film, section c is the use of the QDEF film, and section d is the Disposal of the film.

- a. Cadmium emissions from Mining and Refining: Cadmium does not occur as a primary mineral and so all cadmium is produced as a by-product from zinc and lead mining and refining. Due to the quality requirements for zinc and lead as well as the EU restrictions of cadmium in materials, it is usually necessary to remove cadmium from crude zinc and lead, even if there is no demand for the cadmium. Any emissions of cadmium from zinc and lead refining are not therefore due to cadmium production, but due to the necessary purification of zinc and lead.

The conversion of cadmium extracted from zinc or lead and production of the cadmium compounds that are used for making the QD may cause some emissions, but very little data is published on the amounts. Fthenakis<sup>4</sup> has published a life cycle analysis for manufacture of cadmium telluride (CdTe) which is used for photovoltaic panels. Cadmium telluride is made by a process that has some similarities to the method used for the cadmium compounds used for QD. Once zinc and lead are refined, this gives crude cadmium from which pure cadmium is produced. Cadmium is recovered from crude zinc as a metallic sponge which is first oxidised and the oxide dissolved in acid to produce an electrolyte suitable for electrowinning. After lead production, the

---

<sup>4</sup> "Life cycle impact analysis of cadmium in CdTe PV production", V. M. Fthenakis, Renewable and Sustainable Energy Reviews 8(2004) 303 – 334

cadmium-containing dust is dissolved in acid and pure cadmium metal is recovered also by electrowinning. Fthenakis indicates that the zinc refining process results in emissions of cadmium which is equivalent to 0.2 grams Cd/tonne of zinc, but these emissions occur irrespective of whether the cadmium is wanted or not. Fthenakis describes the CdTe precipitation process and states that losses are only as waste water which is treated by the waste water plant. Firstly, only a very small proportion of input cadmium used is present in waste water. After treatment, only about 0.001% of cadmium in the waste water is not recovered for reuse.

- b. **Cadmium emissions from Manufacturing** (Quantum dots and the film associated with 3M QDEF are manufactured in the United States):

i. Manufacturing the Quantum Dots: Nanosys (A US Based Company) manufactures the quantum dots. 3M OSD purchases the quantum dots from Nanosys to use in the manufacturing of the QDEF film.

Nanosys is manufacturing the Quantum Dots under a low release and exposure (LoREX) exemption for the United States Toxic Substance Control Act (TSCA). A LoREX exemption is only granted to manufacturers that have developed manufacturing, processing, use and disposal techniques which minimize exposures to humans (workers, consumers, and the general public) and the environment. Pursuant to the LoREX (40 CFR 723.50(c)(2)) exemption the following criteria must be met:

- a) With regard to consumers and the general population: There must be no dermal exposure. Also, there must be no inhalation exposure (except by specified low levels from incineration), and there must be no exposure in drinking water greater than 1 milligram per year. The WHO report<sup>5</sup> found that most Cd is ingested from food at 10 - 35 micrograms per day (up to 12.8mg/year). From drinking water up to 2 micrograms Cd per day = 0.73mg/year.
- b) With regard to workers: There must be no dermal or inhalation exposure (these criteria may be met through the use of adequate dermal and inhalation exposure controls in accordance with applicable EPA guidance).
- c) With regard to ambient surface water: There must be no releases resulting in surface water concentrations above 1 part per billion, calculated using the methods prescribed in §721.90 and 721.91.

---

<sup>5</sup> [http://www.who.int/water\\_sanitation\\_health/dwg/chemicals/cadmium.pdf](http://www.who.int/water_sanitation_health/dwg/chemicals/cadmium.pdf)

d) With regard to incineration: There must be no releases of the new chemical substance above 1 microgram per cubic meter (maximum annual average concentration).

e) With regard to land or groundwater: There must be no releases to groundwater, to land, or to a landfill unless the manufacturer or importer has demonstrated to EPA's satisfaction in the exemption notice that the new substance has negligible groundwater migration potential.

The regulation requires that manufacturers and importers notify processors and industrial users that the substance can be used only for the uses specified in the exemption notice, and of any controls specified in the exemption notice. Also, manufacturers and importers of a new chemical substance that is subject to the LoREX exemption may distribute the chemical substance only to persons who agree in writing to not further distribute the substance until it has been reacted, incorporated into an article, or otherwise rendered into a physical form or state in which environmental releases and human exposures above the eligibility criteria are not likely to occur.

According to Nanosys's Safety Data Sheet, the Quantum dot concentrate is classified as D006 RCRA Waste and disposed of as hazardous waste according to federal regulations (40 CFR 261, California Hazardous Waste Codes 141). Cd-containing materials (both solid debris and solvent wastes generated from Nanosys) are all incinerated at an off-site waste disposal facility with a 99.9999% DRE (destruction removal efficiency) and is sent to a landfill. The type of landfill used for the ashes has a liner system to prevent any aqueous phase migration. To prevent migration, the current operating landfill cell was constructed using a state-of-the-art design, utilizing double synthetic liners with leak detection and leachate collection systems. The cell is capped utilizing a design that will eliminate infiltration of precipitation. The cap consists of a clay/HDPE composite system. By preventing infiltration, while continuing the removal of leachate, the landfill cell eventually becomes void of liquid. The thickness of the liner system is about 13 feet, with 9 feet of recompacted clay at its base.

## ii. Manufacturing of the Film:

3M OSD is the manufacture of the film. 3M obtains the Quantum Dot Concentrate from Nanosys and combines the concentrate with an epoxy resin which is coated onto the film. 3M sites processing the quantum dot concentrate for film production are operating under the LoREX conditions. Excess concentrate and uncured film are

collected and managed as hazardous waste. The excess concentrate and uncured film are sent to a licensed TDF (treatment disposal facility) incinerator.

At the TDF, the cadmium is electrostatically precipitated out from the emissions stack (e.g. preventing the cadmium air emissions). The precipitator dust and bottom ash are collected and sent to a classified landfill that is fully lined and prevents leaching into the environment. EPA's incineration emission regulations control the combined emissions of Cd+Pb as a category of semi-volatile metal hazardous air pollutants. The TDF handling the waste of the concentrate and uncured film underwent a performance test in 2009 to comply with these regulations. The EPA requires the test be repeated every 5 years, so the next evaluation is scheduled for 2014. During the performance test, the feed is spiked with Pb and then the Pb concentration is measured from the emission's stack to calculate the systems removal efficiency (SRE). This SRE is used to set the effective removal efficiency of Pb+Cd. During the 2009 test, the TDF measured the SRE during two separate test conditions and ran three replicate runs at each test condition. The lowest single run demonstrated an SRE of 98.85%, which is considered a worse case SRE estimate. Based on this estimate, the set feed rate limit for Pb+Cd is 2.48 lb/hr, which allows the TDF to meet the regulatory emissions concentration limit of 230 ug/dscm (dry standard cubic meter).

To put in perspective and to provide comparison, it is estimated that 25,000 tonnes of cadmium are released each year by weathering of rocks, volcanoes and from forest fires (wood contains small amounts of cadmium).

Film waste (fully cured) is land filled. 3M has conducted an United States Environmental Pollution Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) study to confirm that no cadmium leaches from the film.

c. **Cadmium emissions from the Use of the Film:**

i. **Display Makers**

The QDEF film (an article) is purchased by display makers for use in their display device (smart phone, TV, Monitor, etc.). The display maker would dispose of any film waste in accordance with local laws and regulations. The sections above would provide a description if the films was incinerated. If the film is landfilled it is fully cured. 3M conducted a TCLP study to confirm no cadmium leaches.

ii. **Consumer**

The final consumer who disposes of the display device would dispose of the device according to local laws and regulations. The display device (containing the QDEF film) would likely be collected and recycled with other WEEE.

d. **Disposal:**

The sections above provide disposal information for each stage in the life cycle. Below is a brief recap of the disposal.

- i. **Solution Waste:** Excess concentrate and uncured film is collected and managed as hazardous waste. It is then sent to a licensed TDF (treatment disposal facility).
- ii. **Film Product Waste:** Film waste (fully cured) is landfilled. 3M conducted a TCLP study to confirm no cadmium leaches.
- iii. The final consumer who disposes of the display device would likely to be collected and recycled with other WEEE.  
(Please refer to section 8 of the exemption dossier. The re-use and recycling is described in more detail)

3. You stated that OLED are the only foreseeable substitute in the near future that can achieve 100% NTSC colour gamut. Whereas the RoHS Directive bans the use of cadmium since 2006 and there are no comparative products on the EU market.

- a. Do you agree that Cadmium in quantum dot LED enables a reduction of the total cadmium amount used in traditional LCD? If yes please provide supporting information.

**3M OSD Response:**

3M OSD does not reduce the amount of cadmium used in each traditional LCD, however, it does reduce the amount of cadmium released to the environment for each LCD.

3M OSD film manufactured with quantum dots enables the reduction of total cadmium introduced into the environment over film that does not use QD technology. As described in section 3.7 of the exemption dossier, a case study of 55" LCD TVs has concluded that QD films result in an average power savings of 46% over existing LCD technologies.<sup>6</sup> This study also concluded that while the QD film itself contains approximately 39.7 mg of Cadmium per 55" display, the power savings from the QD film results in 149 mg of avoided Cadmium emissions from power plants, which in turn results in 110 mg of net environmental Cadmium avoided per 55" display during a 5.7 year operating lifetime (50,000 hours in use) or 35 mg avoided during a 2.9 year operating lifetime (25,000 hours in use).

---

<sup>6</sup> Quantum Dot Enhancement Film Cadmium Emissions Analysis, SourceOne, Inc., <http://www.sourceone-energy.com/>

- b. Please explain in more detail, why OLED in comparison to QLED currently do not provide the same performance or energy efficiency.

### **3M OSD Response:**

This proposed exemption is concerned with quantum dot enabled film (QDEF). QDEF is not the same as QLED. QLED is different theoretical method of quantum dot enabled LEDs to improve color performance. 3M OSD assumes in your question above that QLED is meant to be QDEF.

The relatively lower energy efficiency of OLED could be explained with the low light extraction efficiency and OLED material development status as described below.

Due to their inherent multilayer planar device structure, the light extraction, or out-coupling efficiencies of OLEDs are about 20% or less.<sup>7 8</sup> Even though there have been active developments in light extraction technologies of OLEDs, no successful adoption to manufacturing have been reported, yet. In spite of recent rapid advances in OLED efficiencies (OLED material), blue OLED material development is way behind compared to green and red OLED materials. According to Displaymate's report, Green OLEDs are 12 times more power efficient than Blue OLEDs and 1.8 times more efficient than Red OLEDs at producing visible light (Luminance) for a given amount of display power (Watts).<sup>9</sup> This tremendous imbalance results in overall low energy efficiency, too.

- c. What display sizes cannot yet be manufactured with OLED? Is it possible to use OLED and QLED in the same applications, for instance in the small-size displays.

### **3M OSD Response:**

The exemption is concerned with quantum dot enabled film (QDEF). This is different from the theoretical method of quantum dot enabled LEDs (QLEDs) to improve color performance. QDEF is a different technology than QLED. 3M OSD assumes in your question above that QLED is meant to be QDEF.

---

<sup>7</sup> Rico Meerheim, *et al.*, Appl. Phys. Lett. 97(2010), 253305

<sup>8</sup> Kihyon Hong, *et.al.*, Electron. Mater. Lett.

<sup>9</sup> [http://www.displaymate.com/OLED\\_Galaxy\\_S123\\_ShootOut\\_1.htm](http://www.displaymate.com/OLED_Galaxy_S123_ShootOut_1.htm)

The only commercially viable OLED-display products are in the cell phone and small tablets. Larger sizes are not yet economically viable. Current OLEDs are not suitable for all applications (e.g., IT applications with fixed images such as computers). Images will burn similar to plasma. Despite some success, OLED is still currently limited to one dominant supplier with less than 1% of the area of the LCD industry<sup>10</sup>. QDEF can be used in all sized devices.

Most of the OLED products in the market these days are for the mobile applications, which are 7.7" diagonal or less. Introduced recently are 55" OLED TV in the market. However, it costs about \$15,000 USD and is considered as a pre-product with limited volume only.<sup>11</sup> The main reason for this limited OLED manufacturing capability and capacity is the current cost of manufacturing.<sup>12 13</sup> In order to reduce the production cost and take advantage of economies of scale, scaling up to larger substrate size with high yield will be required. Most existing AMOLED-display (active-matrix organic light-emitting diode) fabrication facilities (fabs) are Gen 4 or smaller, which is suitable for small size display manufacturing. This is due to limitations in scaling both the TFT (Low Temperature Poly Silicon-Thin Film Transistor) backplane array and OLED materials deposition to larger substrate sizes. Up to today, LTPS TFT and thermal evaporation with a fine metal mask are considered as the most prevalent method for the TFT backplane array and OLED materials deposition, respectively. To scale up to very large substrate sizes, however, it is likely that new approaches will be needed. Several upcoming fabs are planning to adopt both oxide-TFT backplanes and white OLEDs, as these new technologies appear to be most easily scaled to larger substrate sizes. It should be noted that both of these techniques are new to mass production, and so it is likely that there will be unforeseen barriers to mass production that could impact schedules and output.

4. The OLED production is relatively new, however in the consultants view already established on the market, whereas QLED is not currently available on the EU market.
  - a. Please elaborate what stages are necessary and which efforts will be made to develop QLED based displays with sufficient reliability.

---

<sup>10</sup> (iSuppli)

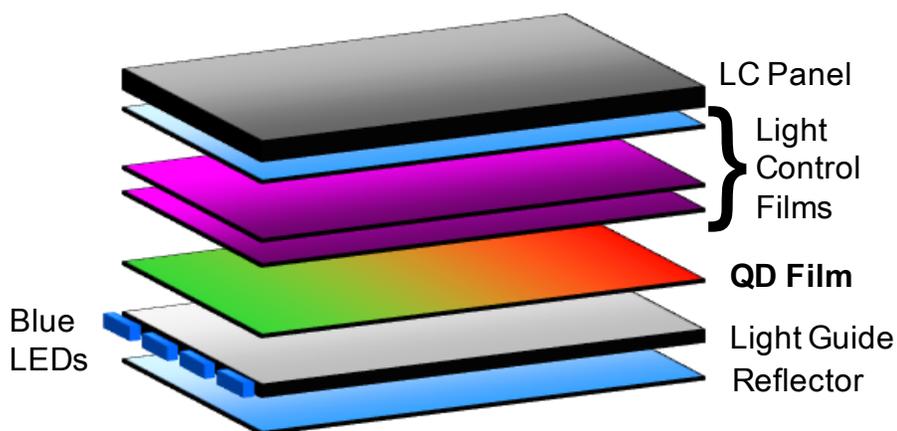
<sup>11</sup> <http://www.oled-info.com/lgs-and-samsungs-curved-oled-tvs-land-us-15000> and <http://www.oled-info.com/lg-launches-55ea9800-curved-oled-tv-korea-13500>

<sup>12</sup> Ho-Kyoon Chung, Information Display 2 (2013), 4

<sup>13</sup> Paul Semenza, Information Display 2 (2013), 26-29.)

### 3M OSD Response

Again, this exemption is primarily concerned with quantum dot enabled films (QDEF) for LCD applications, not QLED technology. The use of QD films in LCD applications only requires the addition of the film into the already existing light control film stack and the replacement of white LEDs with blue LEDs (see Figure 6). The blue LEDs are the same technology as the white LEDs with the phosphor removed. Therefore, the reliability of the blue LEDs are similar to that of the white LEDs they replace. Additionally, 3M has performed numerous accelerated aging lifetime studies on QD film, and found lifetimes of 30,000 - 50,000 hours of operating use until the luminance of the display drops to 85% of its initial luminance. This measured lifetime is more than sufficient for most LCD applications. Therefore, as it currently exists, no efforts are needed to improve QD film based display reliability, as it already meets industry requirements. 3M has recently completed development of the QD film.



**Figure 6** - Schematic example of QD film used in an LCD system.

- b. Why do you think that this target shall be achieved earlier than the OLED technology?

### 3M OSD Response:

As mentioned above (3c), larger-size OLED technology is relatively new to mass production. Despite active development toward mass production, the reality has been that developing the equipment, materials, and manufacturing process to make OLED displays at high yield rates has been very difficult. Even the

dominant firms have struggled to scale the technology to make TV panels in real mass production scale. In addition, it is likely that there are unforeseen barriers to mass production that could impact schedules and output, because OLED technology is relatively new to mass production.

3M OSD is an established leader in backlight films for LCD displays. 3M OSD has proven the ability to develop and scale multiple new to the world enhancement films to supply the entire LCD industry. 3M OSD is a recognized leader in large format precision coating of optical quality films. Refer to the response in c below for additional information.

- c. Aren't there products / applications with shorter periods for re-design?

**3M OSD Response:**

There are no other new technologies on the horizon with similar energy efficiency. QD enabled films can integrate immediately into the existing LCD supply chain. QD films can be introduced into the next LCD design cycle.

5. Even if WEEE (Waste Electrical and Electronic Equipment Directive 2002/96/EC) were collected separately and submitted to recycling processes, its content of cadmium would be likely to pose risks to health or the environment especially when treated in less than optimal conditions.

**3M OSD Response:**

It would be difficult for 3M OSD to speculate on "less than optimum conditions". This hypothetical question could be posed to any product within the RoHS scope. 3M OSD believes this is an agency enforcement policy and interpretation issue and but existing laws and regulations have been introduced to mitigate the situation of "less than optimum conditions".

The EU waste export legislation is Regulation 1013/2006 for the shipment of wastes. This prohibits export of waste to non-OECD countries unless the country has formally stated that it is able to safely treat the type of waste. This Regulation is designed to prevent EU waste being recycled by less than optimal conditions. Recycling processes that are less than optimal are also illegal in the EU due to the Industrial Emissions

Directive 2010/75/EU which regulates most recycling processes including all WEEE recycling. 3M cannot speculate on hypothetical questions, in which the situation described should be controlled by EU enforcement agencies.

- a. Could you please elaborate more in detail the (existing) efforts which have been made for a closed-loop business-to business return system? Please provide evidence in more detail.

### 3M OSD Response:

Business to business returns were established for final products. The film that uses the quantum dots is a component not a finished product. Films sold to display manufacturers are fully cured and are incorporated in the manufacturers' final products. 3M has conducted a Toxicity Characteristic Leaching Procedure (TCLP) study to confirm that no cadmium leaches from the film. 3M does not have a return system for its film. 3M recommends that display manufacturers dispose of any film wastes according to local laws and regulations.

- b. Please explain what happens to the cadmium which cannot be recycled.

### 3M OSD Response:

The film which contains the cadmium that is not recycled would be sent to a landfill and 3M has conducted the TCLP study to confirm the cadmium does not leach.